CHEMISTRY
MODULE-IV

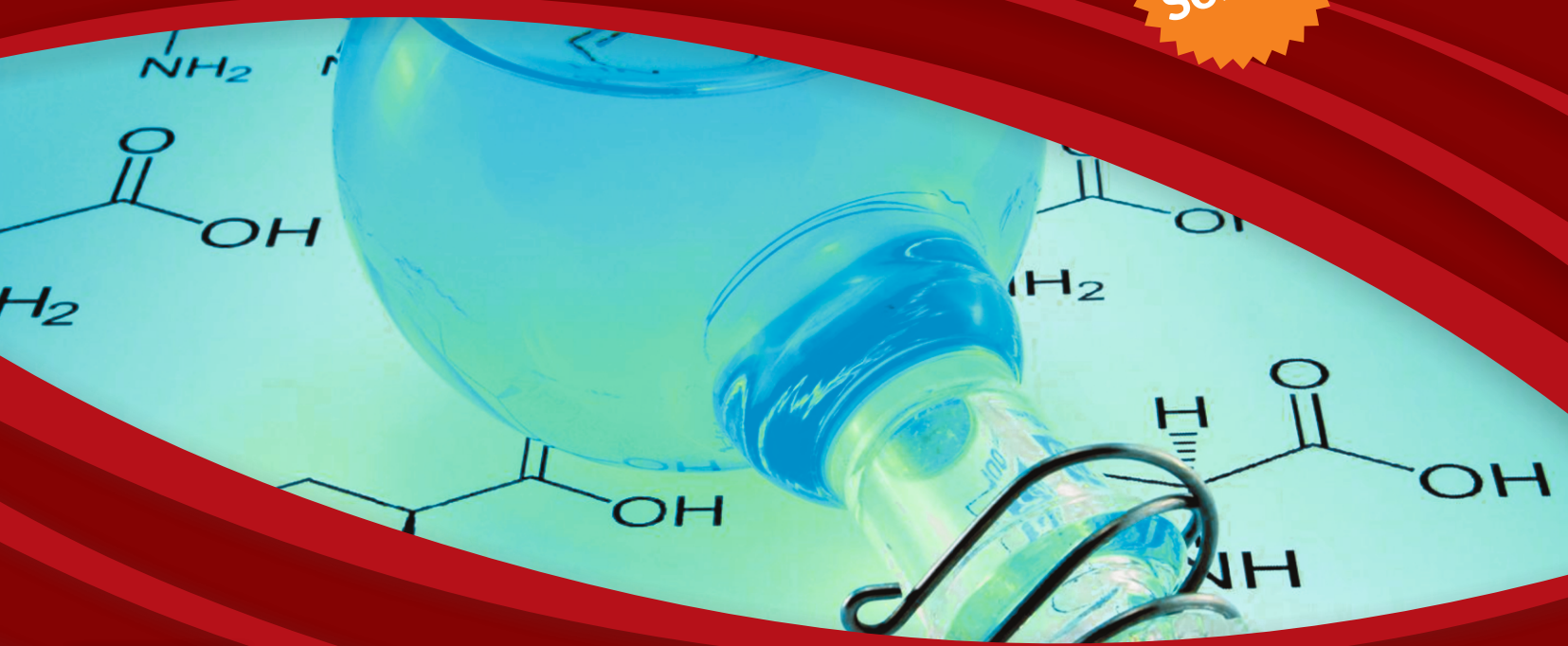
ORGANIC CHEMISTRY-I

for

JEE

(MAIN & ADVANCED)

Fully Solved



Rajesh Agarwal

Mc Graw Hill Education

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About the Author

The author is a key member of the founding team of CollegeDoors.com (an online Test Prep and Test Analytics Platform). A lot of thought behind the composition of this book has taken shape because of the challenging experience of leading the academics vertical of CollegeDoors.com.

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Dedicated to a great Chemistry teacher,
my father,
Late Shri J. P. Agarwal

Preface

Organic Chemistry-I has been written for students who want to undertake well-rounded preparations for JEE (Main as well as Advanced). It is imbued with the essence of 20+ years' experience of coaching and mentoring IIT aspirants. It has been written in a manner that students may learn the concepts from a basic level. It will also sharpen the concepts of learners who have already prepared well.

This book has nine chapters with all the important concepts and multiple choice questions with solutions for clear understanding of concepts. The chapters have been classified into sections such as key points, solved examples, exercises and solutions.

Exercises given at the end of every chapter are further categorised into three difficulty levels of questions and their patterns as asked in the JEE along with the previous years' questions with solutions.

- Level-1 has the questions mainly suitable for JEE-Main exam
- Level-2 contains slightly difficult questions suitable for JEE-Advanced
- Level-3 has the toughest questions of various patterns asked in JEE-Advanced (such as more than one correct answer, comprehension, match the column and single-digit integer)

The content of this book has been laid in a manner that will engage students meaningfully and in turn help them to acquire deep knowledge of concepts. This book stands out in terms of satisfying the need of students for a focussed study material for specific competitive exams like JEE-Main and Advanced.

I have put my best effort towards making the book error free. Nevertheless, constructive suggestions and feedback from readers are welcome as it is important for the continuous improvement of the same.

Acknowledgements

This work would not have been possible without the support of my colleagues, friends and family.

I express my gratitude to the publisher for providing this opportunity and the editorial team for the immensely painstaking task of copyediting and typesetting. My thanks also go to the scores of students who have helped me in learning for more than 20 years. I also thank my wife, Sunita, for allowing me to spend time on this work despite an already hectic coaching schedule.

Contents

CHAPTER 1

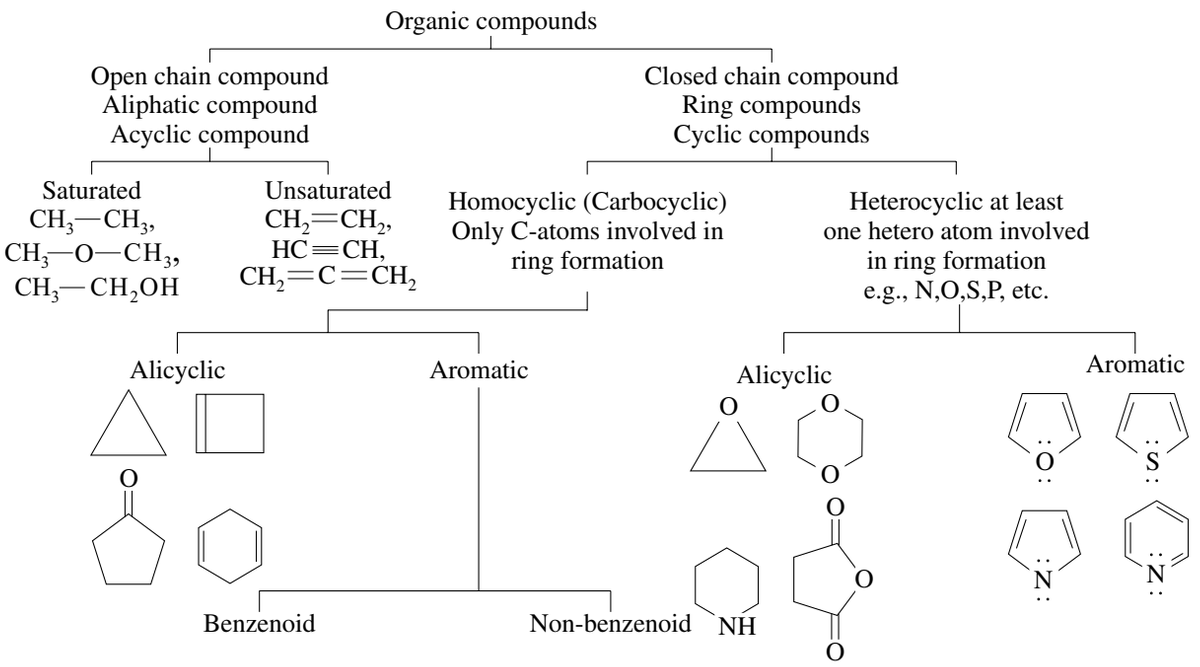
Classification and Nomenclature

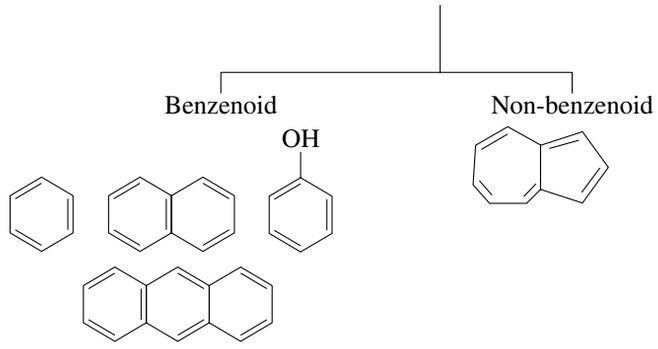
INTRODUCTION

- Organic substances are mainly found in living organisms like animals and plants.
- The first synthesised organic substance is urea discovered by Whölar.
- Organic substances mainly contain C and H and one or more additional elements like oxygen, nitrogen, sulfur, phosphorous, halogens.
- **Catenation:** The self-linking tendency by covalent bond in non-metals whose co-valency is 2 or more than 2, known as catenation.
- Carbon shows to maximum catenation property.
- Maximum covalency of carbon is 4.
- Carbon atoms join together by single, double or triple bond that gives carbon Skeleton.

CLASSIFICATION OF ORGANIC COMPOUNDS

All the known organic compounds have been divided in the following manner:





The four valencies of carbon atom can be represented by the following way:

Structure	σ bonds	π bonds	Hybridisation	Shape	Bond Angle	No. of Bond angles
$-\overset{\vert}{C}-$	4	0	sp^3	Tetrahedral (Non planar)	109°28′	6
$-\overset{\vert}{C}=$	3	1	sp^2	Planar (Trigonal)	120°	3
$-C\equiv$	2	2	sp	Linear	180°	1
$=C=$	2	2	sp	Linear	180°	1

Determination of Hybridisation

- It is based upon 'electron pair' (ep) of hybrid atom.

e.p. = σ bond + ℓp + (–ve) charge

No. of ep.	2	3	4
Hybridisation	sp	sp^2	Sp^3

Identification of Carbon

1. *Primary, Secondary, Tertiary, and Quaternary carbon*

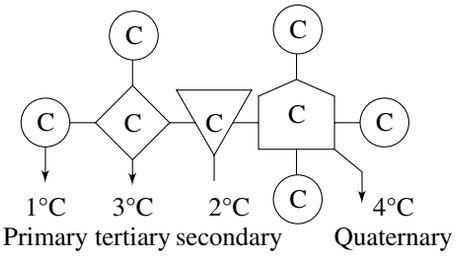
There are four types of carbons in the carbon chain.

(i) **Primary carbon:** A carbon atom attached to one (or no) other carbon atom is termed primary carbon or 1° carbon atom.

(ii) **Secondary carbon:** A carbon atom attached to two other carbon atoms is termed secondary carbon or 2° carbon atom.

(iii) **Tertiary carbon:** A carbon atom attached to three other carbon atoms is termed tertiary carbon or 3° carbon atom.

(iv) **Quaternary carbon:** A carbon atom attached to four other carbon atoms is termed quaternary carbon or 4° carbon atom.



Identification of Hydrogen

- Nature of H, just same as the nature C through which it is joined

  The hydrogen atoms attached to primary, secondary and tertiary carbon atoms are correspondingly termed as primary, secondary and tertiary hydrogen atoms respectively.

Type of Structure

1. Normal structure – prefix "n" is used for unbranched carbon chain
2. Iso structure – prefix "iso" is used when one methyl group is attached on 2^{nd} carbon from either terminal.
3. Neo structure – prefix "neo" is used when two methyl group is attached on 2^{nd} carbon from either terminal.

Homologous Series

Series of such compounds in which the various members have similar structural features and similar chemical properties but the successive members differ in their molecular formula by CH_2 known as homologous series.

General Characterstics

(i) All compounds in the series composed of some element
(ii) All compounds have same general formula.
(iii) Molor mars of adjacent member differ by 14.
(iv) All compounds in the series have similar chemical properties however different physical properties.

Naming of Organic Substance

(1) Common name or Trivial name
(2) Derived name
(3) I.U.P.A.C Name and Jeneva Names system

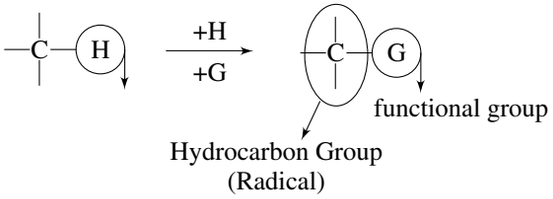
[1] Common name or Trivial name system

Type 1 *Common name based on source:*

- This type of nomenclature is based on their source of origin known as trivial name.

Substance	Source of origin	Trivial Name
CH_4	Marsh places	Marsh gas
$CH_3–OH$	Destructive Distillation of wood	Wood spirit
H–C(=O)–OH	Red ant (Formica)	Formic acid
$CH_3—COOH$	Acetum (Vinegar)	Vinegar
$CH_3—CH_2—CH_2—COOH$	Butter	Butyric acid
$NH_2–C(=O)–NH_2$	Urine	Urea (Carbamide)
$CH_3–CH(OH)–COOH$	Lactum (Milk)	Lactic acid

Type 2 *Common name radicals*

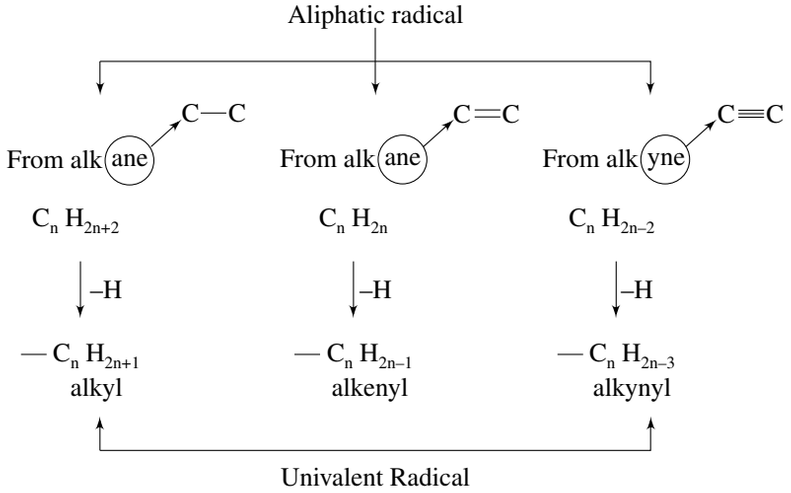


Radical (– R)

- It is framework of only C and H
- It is formed by the removal of at least one H from hydrocarbon
- It influences physical property of substance.

Type of Radical

(1) **Aliphatic Radical:** Those radical which are formed by aliphatic hydrocarbon.



1. Alkyl Radical

- Common name = Alk + yl

Alk	meth	eth	prop	but	pent	hex	hept	oct	non	dec
No of carbon	1C	2C	3C	4C	5C	6C	7C	8C	9C	10C

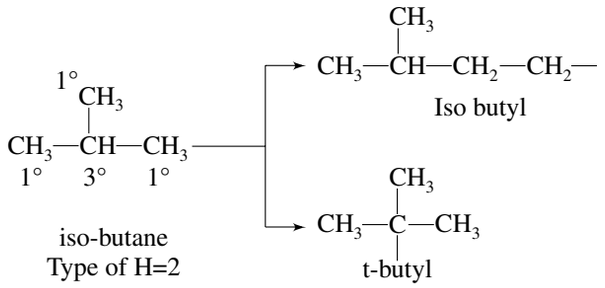
(i) $CH_4 \xrightarrow{-H} —CH_3$
Methane — Methyl (me)

(ii) $CH_3—CH_3 \xrightarrow{-H} CH_3—CH_2—$
ethane — ethyl (et)

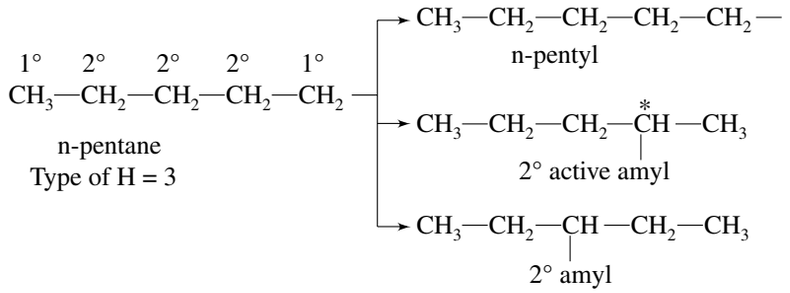
(iii) $CH_3—CH_2—CH_3$
1° 2° 1°
2° Prop ane 2°
Type of H = 2
→ $CH_3—CH_2—CH_2—$ n-propyl
→ $CH_3—\underset{|}{CH}—CH_3$ Iso-propyl

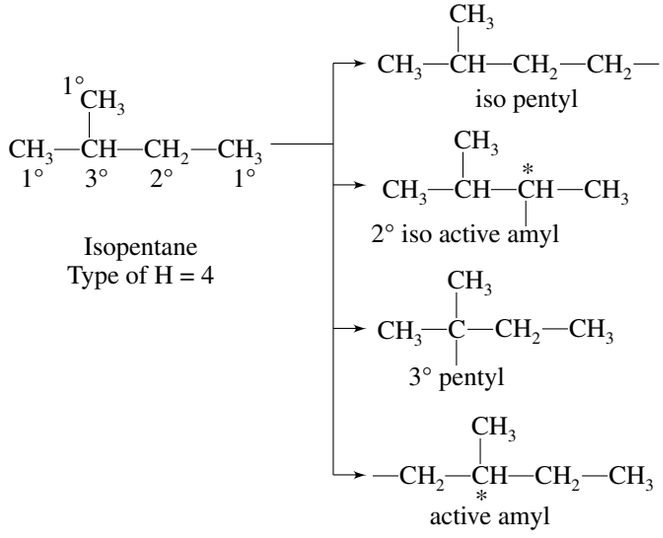
(iv) $C_4H_{10} \xrightarrow{-H} —C_4H_9$
butane — butyl = 4

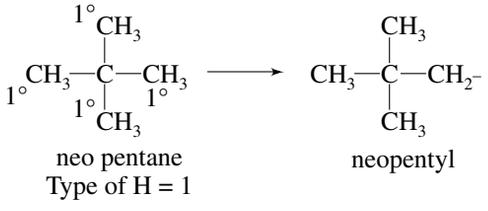
1° 2° 2° 1°
$CH_3—CH_2—CH_2—CH_3$
n-butane
Type of H = 2
→ $CH_3—CH_2—CH_2—CH_2—$ n-butyl
→ $CH_3—\underset{|}{CH}—CH_2—CH_3$ s-butyl



(v) $C_5H_{12} \xrightarrow{-H} -C_5H_{11}$
Pentane — Pentyl (8)



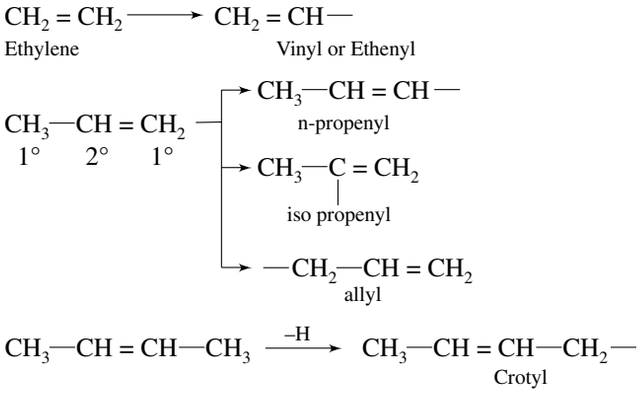




Note: Chiral C(*) containing 5C alkyl always named as active amyl

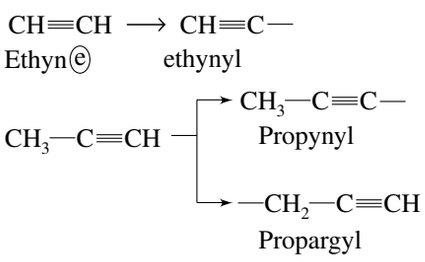
2. Alkenyl Radical

Common name = alk + en + yl



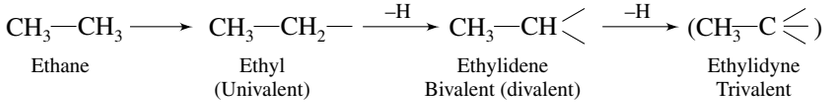
3. Alkynyl Radical

Common name = alk + yn + yl

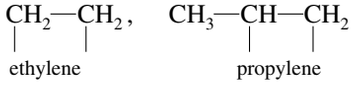


• Polyvalent Radical

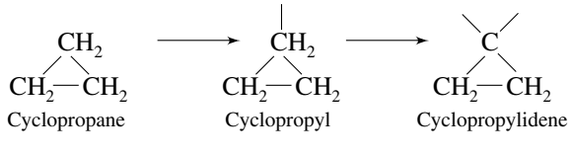
Case-I: Removal of more than one H from same carbon.



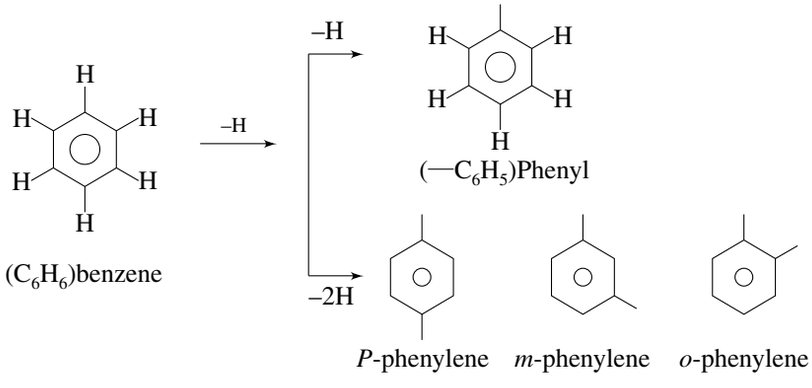
Case-II: Removal of more than one H from adjacent carbon.

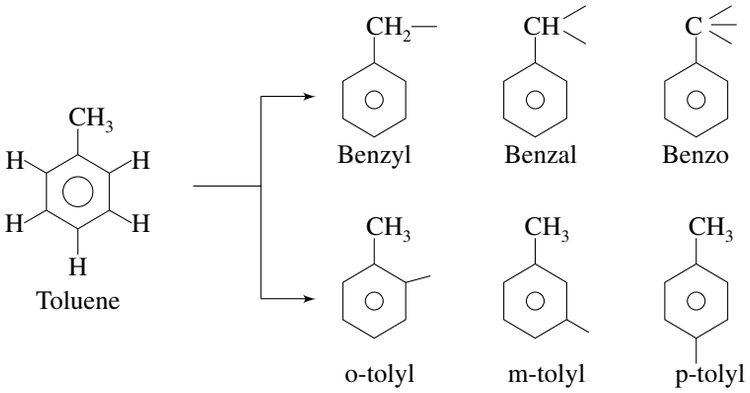


(2) Alicyclic Radical



(3) Aromatic Radical





Type 3 *Common name of alkane:*

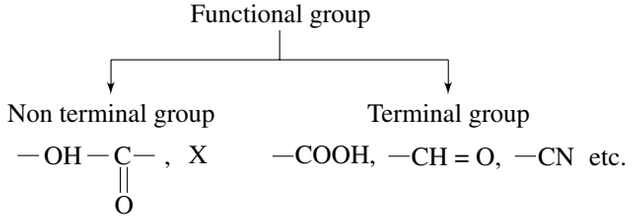
- It is given by using prefix n, iso, neo.

Type 4 *Common name of alkene:*

- Common name = Alkylene

- In more than 3 carbon containing alkene
  (i) For straight chain-prefix α, β, γ, δ, etc. is used to locate the position of double bond at 1, 2, 3, 4. carbon, respectively from nearest terminal.
  (ii) For branched alkene- iso, neo prefix used but only when double bond at terminal carbon.

Type 5 *Common name for functional group containing substance.*



Case-I: Substance containing non terminal functional group

- Common name → Name of radical + Name of functional group.

S.No.	Functional group	Group name
1	$-SO_3H$	Sulphonic acid
2	–X (–F, –Cl, Br, –I)	halide
3	–OH	alcohol
4	–SH	thio alcohol
5	–O–	ether
6	–S–	thio ether
7	—C— O	ketone
8	$-NH_2-NH-, -\underset{\vert}{N}-$	amine

- In polyvalent group, more than one radical present.
  (i) More than one same radical, expressed by numerical prefix
  2 – di, 3 – tri, 4 – tetra, etc.
  (ii) Different radical always write in alphabet manner.

Case-II: Substance containing terminal functional group

- Common name = prefix + suffix

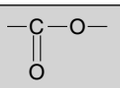
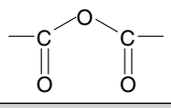
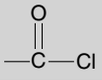
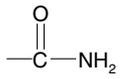
  Prefix–It is based on of total number of carbon present

Number of carbon	1C	2C	3C	4C	5C
Prefix	Form	Acet	propion	Butyr	Valer

Special Prefix

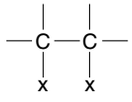
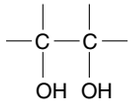
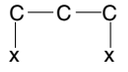
$C=C-C_{fn}$	$C-C=C-C_{fn}$	$Ph-C=C-C_{fn}$	$CH_3-CO-Cgr$
Acryl	Croton	Cinnam	Pyruv

Suffix → It is based on of terminal functional group.

S.No.	Terminal functional group	Suffix
1.	—COOH	ic Acid
2.		ate
3.		ic anhydride
4.		yl chloride
5.		Amide
6.	—CH=O	Aldehyde
7.	—C≡N	O-nitrile/Cyanide
8.	—N≡C	O-isonitrile/isocyanide

Note: –CN and –NC are considered in both systems (Case I & Case II)

Type 6 *Geminal/vicinal/ α-ω type substance*

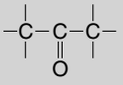
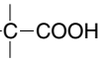
Geminal compound	Vicinal compound	α-ω type compound
 Gem dihalide	 vicinal dihalide  vicinal dialohol Glycol	 α-ω type
Common name Alkylidene + functional group	Common name alkylene + functional group	Common name poly methylene + functional group

Note: Poly word expressed number of CH_2–groups.

No of CH_2–	3	4	5
Poly	Tri	Tetra	Penta

[2] Derived name system:

According to this system name of any compound is given according to the representative compound of the homologous series. This system is reserved for following homologous series.

Series	Name of Homologous series	Name of Representative compound	Structure of group
1	Alkane	Methane	
2	Alkene	Ethylene	>C=C<
3	Alkyne	Acetylene	–C≡C–
4	Alcohol	Carbinol	
5	Aldehyde	Acetaldehyde	
6	Ketone	Acetone	
7	Carboxylic acid	Acetic acid	

[3] IUPAC name system or Geneva name system:

1. A given compound can be assigned only one name.
2. A given name can clearly direct in writing of one and only one molecular structure.
3. The system can be applied in naming complex organic compounds.
4. The system can be applied in naming multifunctional organic compounds.
5. This is a simple, systematic and scientific method for nomenclature of organic compound.

IUPAC Nomenclature of Aliphatic Compounds:

The name of an organic compound consists of three parts:

- Word root
- Prefix
- Suffix

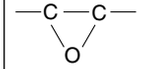
Word root: It is given on the basis of number of C in parent chain.

No of C	1C	2C	3C	4C	5C	6C	7C	8C	9C	10C	11C	12C	20C
Word root	meth	eth	prop	but	pent	hex	hept	oct	non	dec	undec	dodec	Eicos

Prefix: It is given on the basis of the side chain in parent chain

(i) All alkyl radical works as side chain

(ii) Some of the given functional group always behave as side chain

S.No.	Functional group	Side chain (prefix)
1.	–X	Halo
2.	–OR	Alkoxy
3.		Epoxy
4.	$-NO_2$	Nitro
5.	–N=O	Nitroso
6.	–N=N–	Azo

(iii) Rest functional group (except above) may be work as side chain according to their priority with respect to other functional group.

Suffix

Primary suffix: If is given by the bonding nature between C–C in selected parent chain.

S.No.	Bonding nature (PC)	1° Suffx
1.	–C–C– (All single bond)	ANE
2.	–C=C– (Al least one)	ENE
3.	–C≡C– (Al least one)	YNE
4.	–C=C–C≡C– (Both (=) bond and (≡) bond	(ENYNE)

Secondary suffix: It is given on the basis of principal functional group present in parent chain.

- 2° Suffx always written after 1° Sufix as follows.

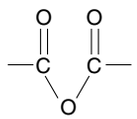
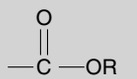
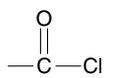
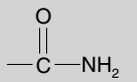
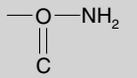
AN E
EN E
YN E
ENYN E) 2° suffix

Note: 'e'cancelled only when 1st alphabet of 2° suffix is vowel (a,i,e,o,u)

Arrangement of prefixes, Root word and Suffixes:

IUPAC Name = prefix (es) + word root + Primary suffix + Secondary suffix

Priority table of functional group (selection of Principal functional group)

Functional group	Prefix	2° Suffix
—COOH	carboxy	Oic Acid
—SO_3H	sulpho	Sulphonic Acid
	–	Oic anhydride
	alkoxy carbonyl or carbo alkoxy	Oate
	chloro formyl or Chloro carbonyl	Oyl chloride
	carbamoyl	Amide
—C≡N	cyano	Nitrile
—N≡C	isocyano	Iso carbonitrile
—CH=O	formyl / oxo	AL
	keto or oxo	ONE
—OH	hydroxy	OL
—SH	mercapto	Thiol
—NH_2	amino	Amine

Salient features of priority table:

(1) Above given table shows decreasing priority of functional group.

(2) When only one of above functional group is present in parent chain, then this functional group behave as 2° suffix, known as Principal Functional group.

(3) When more than one of above functional groups is present then higher priority functional group is the principal functional group (2° suffix) and rest are least priority functional groups will be represented by prefix.

(4) Mostly 2° Suffix C will be included in word root.

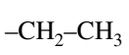
(5) Prefix, C never included in word root except only ketone.

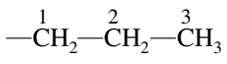
IUPAC Naming of Side Chain (Radical)

- Numbering always start from free valency containing carbon
- Ending always with 'yl'

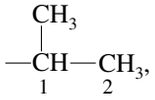
Simple radicals

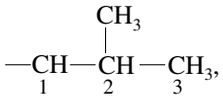

Methyl

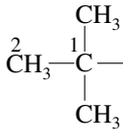

Ethyl

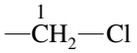

Propyl

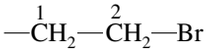
Complex radicals

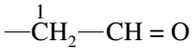

Methyl ethyl (isopropyl)

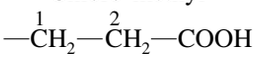

2-Methyl propyl

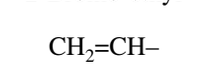

1,1-di methyl ethyl

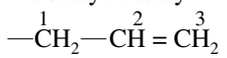

Chloro methyl

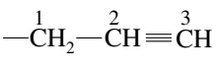

2-Bromo ethyl

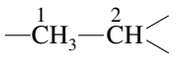

Formyl Methyl

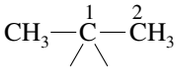

2-Carboxy ethyl


ethenyl (vinyl)


2-propenyl (Allyl)


2-propynyl (propargyl)


Ethylidene


1-Methyl ethylidene

Important Points

1. Repetition of side chain expressed by numerical prefix 2-di, 3-tri, 4-tetra etc.
2. Repetition of complicated side chain expressed by numerical prefix 2-bis, 3-tris, etc.
3. Different side chain is always written in alphabet manner
4. If alphabet order is same then least locant number side chain written at Ist place
5. If di, tri prefix included in complicated side chain then these prefixes include in alphabet comparison.

Rules of I.U.P.A.C Naming

Rule 1: Selection of parent chain (PC)

Parent chain must be contain following in given order of priority:

Maximum number of Principal functional group	>	Maximum number of multiple bond	>	Maximum number of carbon	>	Maximum number of side chain	>	Lowest set of locant number

Note: For open chain substance selection always start and end at terminal carbon.

Rule 2: Least locant number rule

Numbering of parent chain start from the terminal that has through which functional group, multiple bond, side chain must have least locant number or lowest set of locant number in given order.

Principal functional group > Multiple bond > side chain

Rule 3: Alphabet rule

This rule comes into existence only when least locant number rule does not apply.

When different member of similar category like functional group, multiple bond, side chain are present at equivalent position from either of terminal, then alphabetically preferred member of same category gets least locant number.

Special Case

1. *Use of some special suffix:*

   When more than two similar terminal functional groups are directly attached with Parent chain or directly attached with ring then according to latest IUPAC convention carbon atom of these functional group is not included in the parent chain even that they work as a Principal functional group (2° suffix)

   • Latest 2° suffix of terminal functional group are given below:

Functional group	2° suffix
COOH	Carboxylic acid
COOR	Carboxylate
COCl	Carbonyl chloride
$CONH_2$	Carboxamide
C≡N	Carbo nitrile
CH=O	Carbaldehyde

2. *Use of some special prefix:*

   In IUPAC naming O, S, N, Se atom can also be included in parent chain like carbon. The presence of these atom is expressed with special prefix given below with suitable locant no.

Atom	Prefix
O	Oxa
S	Thia
N	Aza
Se	Selena

IUPAC Nomenclature of Alicylic Compounds

(1) Rules 1,2,3 apply as usual like in open chain.
(2) Additional prefix cyclo is used just before word root.
(3) Numbering of cyclic parent chain starts at any C of ring according to rule-2 and 3
(4) We never count number of C of ring and outside ring simultaneously
(5) When both open and closed chain have same feature than closed chain will be selected as a parent chain.

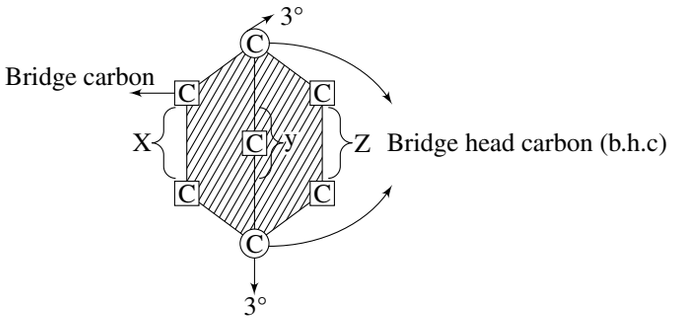
IUPAC Nomenclature Aromatic Compounds:

1. The common name of aromatic substance is also recognised as their I.U.P.A.C. name.
2. When benzene ring selected as parent chain

Word root +1° suffix ⇒ Benzene

IUPAC Nomenclature of Bicyclo Compounds:

Such cyclic substance two lines are fused together in such a way that they have two common tertiary carbon with ring or one side is common, known as bicyclo substance.



General rules of naming:

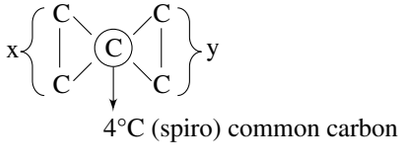
1. Additional prefix bicyclo is used
2. In big bracket write number of bridge carbon of all three direction individually in decreasing order separated by commas.
3. Word root is given on the basis of total number of carbon present in a bicyclic part

Number of C in bicycle ring = x + y + z + 2

4. Numbering of Bicyclo ring.
   (i) Numbering always starts from one of the b.h.c (Bridge head carbon).
   (ii) It is proceed along higher number of bridge carbon site to next b.h.c.
   (iii) Again proceed along second higher bridge, carbon site.
   (iv) Finally terminate along least bridge carbon site.

IUPAC Nomenclature of Spiro compounds:

Such cyclic substance in which two rings are fused together in such a ways that they have only one common carbon, is known as spiro substance.



General rule of naming:

1. Additional prefix spiro is used
2. In big bracket write number of carbon of two rings individually except common carbon in increasing order.
3. Word root is given on the basis of total number of carbon present in a spiro ring.

Number of C in spiro ring = x + y + 1

4. Numbering of spiro ring.
   (i) Numbering always starts from adjacent common carbon in smaller ring.
   (ii) Proceed along smaller ring to spiro carbon.
   (iii) Finally terminate along bigger ring.

SOLVED EXAMPLE

1. Ethyl methyl vinyl amine has the structure–

(1) $CH_3CH_2—\underset{\displaystyle CH_3}{\overset{|}{N}}—CH_2CH=CH_2$

(2) $CH_3CH_2—\underset{\displaystyle CH_3}{\overset{|}{N}}—CH=CH_2$

(3) $CH_2=CH—\underset{\displaystyle CH_3}{\overset{|}{N}}—CH=CH_2$

(4) $CH_3—\underset{\displaystyle CH_3}{\overset{|}{N}}—CH=CH_2$

Sol. **[2]**

Ethyl $\rightarrow -C_2H_5$

Methyl $\rightarrow -CH_3$

Vinyl $\rightarrow -CH = CH_2$

3-alkyl containing amine must be 3° amine

$CH_3CH_2—\underset{\displaystyle CH_3}{\overset{|}{N}}—CH=CH_2$

2. Derived name of $CH_2=CH–CH_2CO–CH_3$ is

(1) 1-Pentene-1-one (2) Allyl methyl ketone

(3) 4-Pentene-2-one (4) Vinyl acetone

Sol. **[4]**

$CH_2= CH—CH_2—\underset{\displaystyle O}{\overset{||}{C}}—CH_3$

(Sidechain) Vinyl acetone

(representative compound)

3. The hybrid state C-atoms which are attached to single bond with each other in the following structure are– $CH_2 = CH—C\equiv CH$

(1) sp^2, sp (2) sp^3, sp

(3) sp^2, sp^2 (4) sp^2, sp^3

Sol. **[1]**

$CH_2 = \underset{\displaystyle ep=3+0+0}{\underset{\displaystyle sp^2}{CH}}—\underset{\displaystyle ep=2+0+0}{\underset{\displaystyle sp}{C}}\equiv CH$

4. The third member of the family of alkenynes has molecular formula-

(1) C_6H_6 (2) C_5H_6

(3) C_6H_8 (4) C_4H_4

Sol. **[3]**

General formula of alkenyne $\rightarrow C_n H_{2n–4}$

For 1^{st} member n = 4

2^{nd} member n = 5

3^{rd} member n = 6

$\because$ Molecular formula = $C_6H_{2\times6–4} = C_6H_8$

5. Which of the following is not correctly matched?

(1) Acetonitrile $CH_2 = CHCN$

(2) Allyl chloride $CH_2 = CH – CH_2Cl$

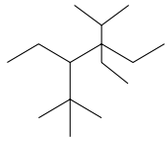
(3) s-Butyl group $CH_3—\underset{\displaystyle CH_3}{\overset{|}{CH}}—C_2H_5$

(4) Ethylidene chloride $CH_3—CH\begin{matrix}Cl\\Cl\end{matrix}$

Sol. **[1]**

Aceto nitrile $\rightarrow CH_3–C \equiv N$ but given $CH_2 = CHCN$ so it is incorrectly matched.

6. The correct IUPAC name of the following compound is



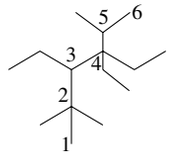
(1) 3-ethtyl-3-isopropyl-4-tertiarybutyl hexane

(2) 3, 3, 4-triethyl-2, 5, 5-trimethyl hexane

(3) 3, 4-diethyl-4-isopropyl-2, 2-dimethyl hexane

(4) 3, 4, 4triethyl-2, 2, 5-trimethyl hexane

Sol. **[4]**



Parent chain must be contain maximum number of side chain.

7. What is the IUPAC name of the following compound?

$CH_3—C\equiv C—CH_2—\underset{\displaystyle CH_3}{\overset{\displaystyle C\equiv N}{\overset{|}{\underset{|}{C}}}}—CH_2—OH$

(1) 2-cyano-2-methyl hex-4-yne--ol

(2) 2-hydroxy methyl-2-methyl-hex-4-yne-nitrile

(3) 2-methyl-2-hydroxy methyl hex-5-yne-nitrile

(4) 1-cyano-2-hydroxymethyl-2-methyl-4-hexyne

Sol. **[3]**

$\overset{\displaystyle 6}{CH_3}—\overset{\displaystyle 5}{C}\equiv\overset{\displaystyle 4}{C}—\overset{\displaystyle 3}{CH_2}—\underset{\displaystyle CH_3}{\overset{\displaystyle 1\ C\equiv N}{\overset{\displaystyle 2}{\overset{|}{\underset{|}{C}}}}}—CH_2—OH$

2-methyl-2-hydroxy methyl hex-5-yne-nitrile

Word root = 6C (Hex)

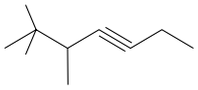
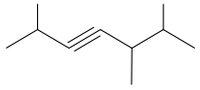
Side chain = $-CH_3$ (methyl) and $-CH_2-OH$ (Hydroxymethyl)

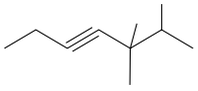
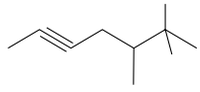
1° suffix → yne

2° suffix → –CN (Nitrile)

Principal functional group must have least locant number.

8. Which is the correct structure 5, 6, 6-trimethyl-3-heptyne?

(1)  (2) 

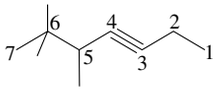
(3)  (4) 

Sol. **[1]**

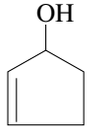
Parent chain must have 7C

1 suffix → yne at 3[ed] C

Three methyl side chain at 5, 6, 6



9. The correct IUPAC name of the compound is



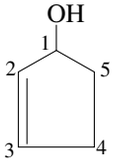
(1) Cyclo pent-1-en-3-ol

(2) Cyclo pent-2-en-1-ol

(3) 3-hydroxy cyclo pentene

(4) None of these

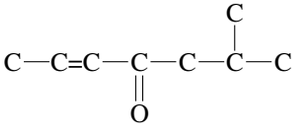
Sol. **[2]**



Principal functional group have proirity than multiple bond (rule-2)

Cyclo pent-2-en-1-ol

10. The correct IUPAC name of the compound is



(1) 2-methyl hept-5-en-4-one

(2) 6-methyl-4-oxo-2-heptene

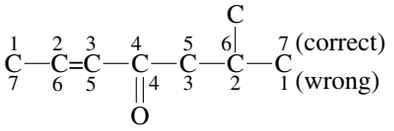
(3) 6-methyl hept-2-en-4-one

(4) None of these

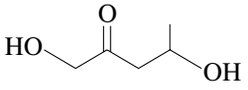
Sol. **[3]**

- Numbering of parent chain according to least locant number rule.
- Priority order →

  functional group > Multiple bond > side chain.



6-methyl hept -2-en-4-one

11. The IUPAC name of  is–

(1) 3-hydroxybutanoic acid

(2) 4-methyl-2-oxo-1, 4-butanediol

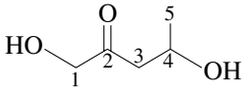
(3) 1, 4-dihydroxy-4-methyl-2-butanone

(4) 1, 4-dihydroxy-2-pentanone

Sol. **[4]**

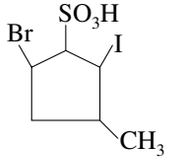
Principal functional group ketone must have least locant number.

–OH group works as side chain.



1, 4-dihydroxy-2-pentanone

12. The correct IUPAC name of the compound is



(1) 2-iodo-3-methyl-5-bromocyclo pentane sulphonic acid

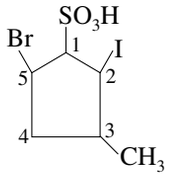
(2) 5-Bromo-4-methyl-5-iodocyclo pentane sulphonic acid

(3) 5-Bromo-3-iodo-2-methylcyclo pentane sulphonic acid

(4) 5-Bromo-2-iodo-3-methylcyclopentane sulphonic acid

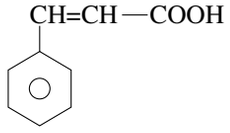
Sol. **[4]**

- Cyclic chain selected as parent chain.
- $-SO_3H$ is principal functional group.
- Br, –I, $-CH_3$ are side chain.
- Apply least locant number rule.



5-Bromo-2-iodo-3-methylcyclopentane sulphonic acid

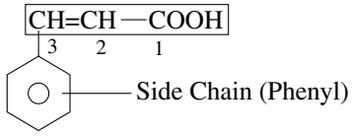
13. The correct IUPAC name of the compound is



(1) Cinamic acid
(2) 3-phenyl-2-propenoic acid
(3) β-phenyl acrylic acid
(4) 1-phenyl-2-propenoic acid

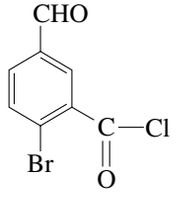
Sol. **[2]**

- Open chain contains –COOH group so it is selected as parent chain.



3-phenyl-2-propenoic acid

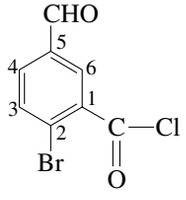
14. The IUPAC name of the following compound is



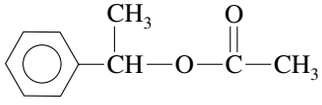
(1) 4-bromo-3-chlroformyl benzaldehyde
(2) 2-bromo-5-formyl benzene carbochloride
(3) 2-chloro carbonyl bromobenzene
(4) 6-bromo-3-formylbenzo-3-yl chloride

Sol. **[2]**

- Benzene ring must be selected as parent chain.
- —C(=O)—Cl group is principal functional group.
- –CH=O, –Br, are side chain.
- Numbering of benzene ring according to least locant number rule.



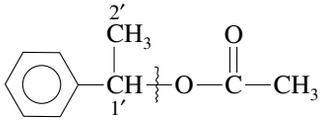
2-bromo-5-formyl benzene carbochloride

15. The IUPAC name of  is

(1) 1-phenyl ethyl ethanoate
(2) 1-acetoxyethylbenzene
(3) ethoxycyclohexyl ketone
(4) ethyl cyclohexanecarboxylate

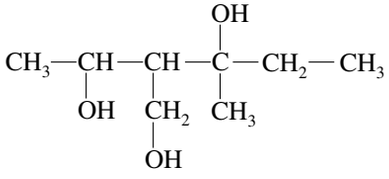
Sol. **[1]**

- Principal functional group is ester
- Open chain selected as parent chain.



1-phenyl ethyl ethanoate

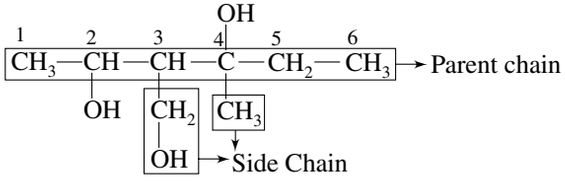
16. The correct IUPAC name of the compound is



(1) 3-hydroxy methyl-4-methyl hexane-2,4-diol
(2) 2-(1-hydroxy ethyl)-4-methyl pentane-1,3-diol
(3) 4-hydroxy methyl-3-methyl hexane-2,4-diol
(4) None of these

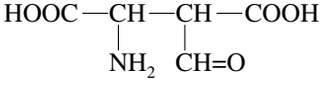
Sol. **[1]**

- Parent chain must have maximum number of principal functional group (–OH) with maximum number of carbon.
- Numbering of parent chain according to least locant number rule.



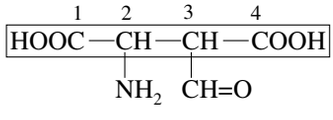
3-hydroxy methyl-4-methyl hexane-2,4-diol

17. The correct IUPAC name of the compound is



(1) 3-amino-2-formyl butane-1, 4-dioic acid
(2) 3-amino-2, 3-dicarboxy propanal
(3) 2-amino-3-formyl butane-1, 4-dioic acid
(4) 1-amino-2-formyl succinic acid

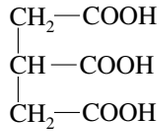
Sol. **[3]**

 alphabet rule NH_2—amine

Although CHO group is before NH_2 but after deciding top most in order group (COOH) next groups are arranged alphabetically. So numbering is done from left to right.

Prefix for NH_2– group is amino and for CHO– group is formyl.

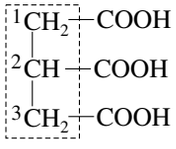
18. The correct IUPAC name of the compound is



(1) 1, 2, 3-tricarboxy-propane
(2) 3-carboxy-1, 5-pentane dioic acid
(3) propane-1, 2, 3-tri carboxylic acid
(4) none of these

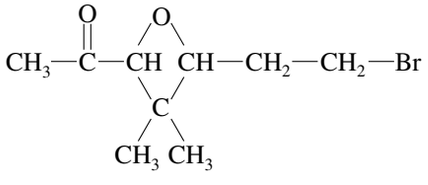
Sol. **[3]**

When more than two terminal functional groups are directly attached with parent chain then no such group carbon included in word root; according to the latest IUPAC convention 2° suffix is carboxylic acid (–COOH)



Propane-1, 2, 3-tri carboxylic acid (1st Choice)
3-carboxy-1, 5-pentane dioic acid (2nd Choice)
1, 2, 3-tricarboxy-propane (3rd Choice)

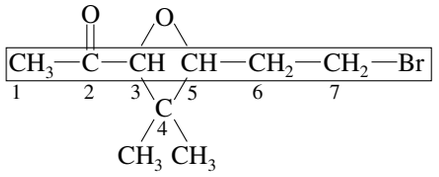
19. The correct IUPAC name of the compound is



(1) 7-bromo-3, 5-epoxy-4,4-dimethyl-2-heptanone
(2) 7-bromo-3, 5-epoxy-4, 4-dimethyl-2-oxo heptane
(3) 1-bromo-3, 5-epoxy-4,4-dimethyl-6-heptanone
(4) 1-bromo-4, 4-dimethyl-5-oxo-heptane

Sol. **[1]**

- Numbering of parent chain according to the least locant number rule.
- Priority order →
  functional group > Multiple bond > side chain.

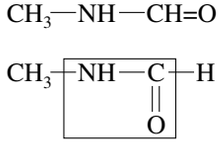


7-bromo-3, 5-epoxy-4,4-dimethyl-2-heptanone

20. The correct IUPAC name of the compound is CH_3–NH–CH=O

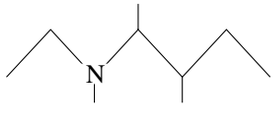
(1) N-formyl methanamine
(2) N-methyl methanamide
(3) Methylanino methanal
(4) N-methy–N–formyl amino methane

Sol. **[2]**



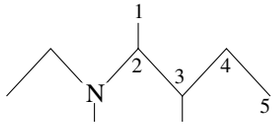
- Principal functional group is amide (–CONH–)

21. The correct IUPAC name of the compound is



(1) N-Ethyl-N, 3-dimethyl-2-amino pentane
(2) N-ethyl-N, 3-dimethyl-2-pentanamine
(3) N-Ethyl-N, 3-Dimethyl-4-pentanamine
(4) 2-(Ethylmethyamino)-3-methyl pentane

Sol. **[2]**



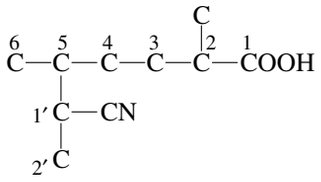
N-ethyl-N, 3-dimethyl-2-pentanamine

22. A compound named 5-(1-cyanoethy)-2-methyl hexanoic acid has something wrong according to IUPAC. What is its correct IUPAC name?

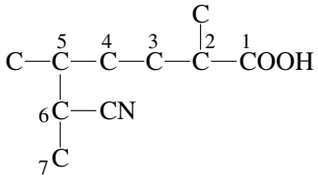
(1) 5-ethyl cyanide-2-methyl hexanoic acid
(2) 6-cyano-2, 5-dimethyl heptanoic acid
(3) 6-cyano-5-methyl-2-heptanoic acid
(4) 6-carboxy-2, 3-dimethyl heptanenitrile

Sol. **[2]**

- Parent chain must have 6C with COOH group.
- Side chain —CH(CN)—CH_3 and —CH_3
- So that possible structure is

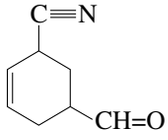


• Correct numbering of parent chain is



6-cyano-2, 5-dimethyl heptanoic acid

23. The correct IUPAC name of the compound is

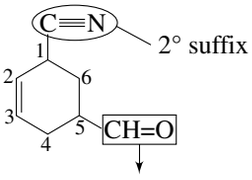


5-formyl cyclo hex-2-en-carbonitrile

(1) 3-cyano cyclo hex-5-en-carbaldehyde
(2) 5-cyano cyclo hex-3-en-carbaldehyde
(3) 5-formyl cyclo hex-2-en-carbonitrile
(4) 3-formyl cyclo hex-5-en-carbonitrile

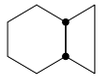
Sol. **[3]**

• Numbering of parent chain according to least locant number rule.
• Priority order →
functional group > Multiple bond > side chain.



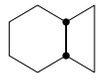
5-formyl cyclo hex-2-en-carbonitrile

24. The correct IUPAC name of the compound is



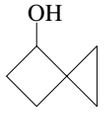
(1) Bicyclo [4, 2, 0] octane
(2) Bicyclo [2, 4, 0] octane
(3) Bicyclo [4, 2, 0] hexane
(4) None of these

Sol. **[1]**



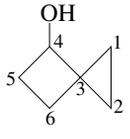
Bicyclo [4, 2, 0] octane

25. The correct IUPAC name of the compound is



(1) Spiro [3,2] hexan-4-ol
(2) Spiro [2,3] hexan-2-ol
(3) Spiro [2,3] hexan-4-ol
(4) Spiro [3,2] hexan-2-ol

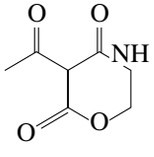
Sol. **[3]**



Spiro [2,3] hexan-4-ol

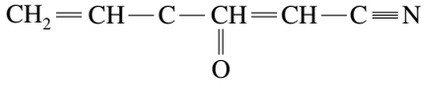
EXERCISE 1

1. Identify which functional group is **Not** present in the following compound?



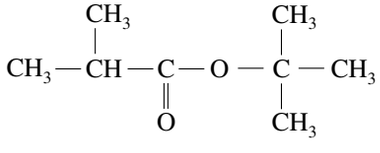
(1) Ketone (2) Ester
(3) Amide (4) Ether

2. The number of olefinic bonds in the given compound is–

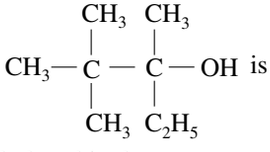


(1) 2 (2) 3
(3) 1 (4) 4

3. The common name of given ester is–

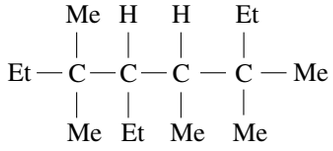


(1) Neo butyl isobutyrate (2) t-Butyl n-butyrate
(3) t-Butyl isobutyrate (4) Iso butyl isobutyrate

4. The derived name of  is

(1) t-Butyl ethyl methyl carbinol
(2) t-Butyl ethyl methyl methanol
(3) t-Butyl methyl ethyl carbinol
(4) t-Butyl methyl ethyl methanol

5. Numbers of 3° carbon and 2° hydrogen respectively in the following structure are:

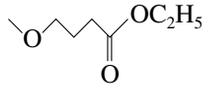


(1) 3, 6 (2) 2, 4
(3) 2, 6 (4) 1, 6

6. Which is true regarding cinnamaldehyde?
(1) All carbon have same hybridisation
(2) It is non-polar
(3) IUPAC name is phenyl propenal
(4) It is an aromatic aldehyde

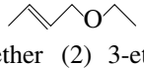
7. Give the IUPAC name of an alkane with the formula C_8H_{18} that has only primary hydrogen atom
(1) 2, 2, 4, 4-tetra methyl butane
(2) 2, 2, 3, 3-tetra methyl butane
(3) 2, 3-dimethyl hexane
(4) octane

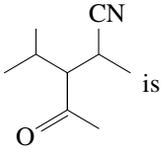
8. The IUPAC name of the following compound is:



(1) 3-methoxy ethylpropanoate
(2) ethyl4-methoxybutanoate
(3) 1,4-diethoxybutane
(4) 4-methoxy-ethylbutanoate

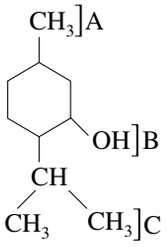
9. The correct decreasing order of priority for the functional groups of organic compounds in the IUPAC system of nomenclature is
(1) $-SO_3H$, –COCl, $-CONH_2$, –CHO
(2) –CHO, –COCl, $-SO_3H$, $-CONH_2$
(3) $-CONH_2$, –CHO, $-SO_3H$, –COCl
(4) –COCl, $-SO_3H$, $-CONH_2$, –CHO

10. The IUPAC name of  is
(1) 2-butenyl ethyl ether (2) 3-ethoxy-2-butene
(3) 3-oxa-5-heptene (4) 1-ethoxy-2-butene

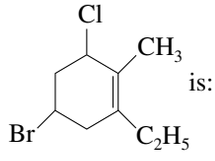
11. The IUPAC name of  is

(1) 2-methyl-3-(1-methylethyl)-4-oxopentanenitrile
(2) 4-cyano-3-(1-methylethyl)-2-pentanone
(3) 3-Acetyl-2-cyano-4 -methylpentane
(4) 3-ethanoyl-2-methyl-3-(1-methylethyl) pentane nitrile

12. In the following compound, group designated as A, B, C will be numbered as:

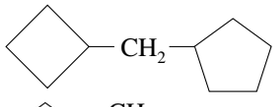


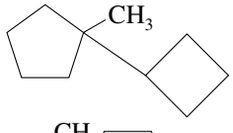
(1) 1, 2, 4 (2) 4, 2, 1
(3) 5, 1, 2 (4) 3, 1, 6

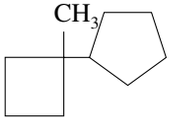
13. IUPAC Name of  is:

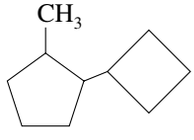
(1) 4-Bromo-6-chloro-2-ethyl-1-methylcyclohex-1-ene
(2) 5-Bromo-1-chloro-3-ethyl-2-methylcyclohex-2-ene
(3) 5-Bromo-3-chloro-1-ethyl-2-methylcyclohex-1-ene
(4) 1-Bromo-5-chloro-3-ethyl-4-methylcyclohex-3-ene

14. The correct structure of cyclobutylmethyl cyclopentane is

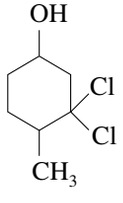
(1) 

(2) 

(3) 

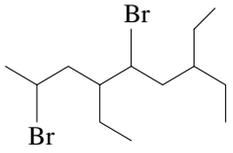
(4) 

15. What is IUPAC name of the compound shown below?



(1) 3, 3-dichloro-4-methyl cyclohexanol
(2) 1, 1-dichloro-6-methyl-3-cyclohexanol
(3) 1, 1-dichloro-2-methyl-5-cyclohexanol
(4) 2, 2-dichloro-1-methyl-4-cyclohexanol

16. The systematic name of the given structure is



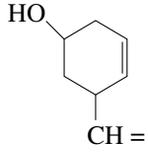
(1) 2, 5-dibromo-4, 7-diethyl octane
(2) 4, 7-dibromo-2, 5-diethyl octane
(3) 5, 8-dibromo-6-methyl-3-methyl nonane
(4) 2, 5-dibromo-4-ethyl-7-methyl nonane

17. One of the names given below violates an important IUPAC convention. Which is that name?
(1) 2-cyclopropyl-2-methyl propane
(2) 2-bromo-4-chlorobutane
(3) Ethyl pentane
(4) 3-bromo-1, 1-dichlorocyclohexane

18. A hydrocarbon X has molar mass 84 but contains no double or triple bonds. Also X has no methyl locant. How many different IUPAC name can be assigned to X?
(1) 2 (2) 3
(3) 4 (4) 6

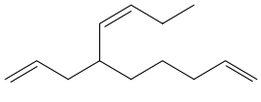
19. Which of the following is an incorrect name according to the IUPAC?
(1) 2-cyclopropyl butane
(2) 1-bromo-2, 2-dichloro cyclobutane
(3) Cyclohexyl cyclohexane
(4) 1-cyclobutyl cyclobutane

20. What is the correct IUPAC name of the compound?



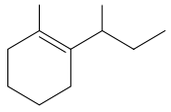
(1) 3-hydroxy cyclo hex-2-ene-1-carbaldehyde
(2) 5-hydroxy cyclo hex-2-ene-1-al
(3) 3-formyl-Cyclo hex-4-ene-1-ol
(4) 5-hydroxy cyclo hex-2-ene-carbaldehyde

21. What is the correct IUPAC name of the following compound?



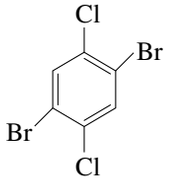
(1) 4-(1-propenyl)-1, 8-nonadiene
(2) 5-(2-propenyl)-3, 9-decadiene
(3) 6-(2-propenyl)-1, 7-decadiene
(4) 4-(1-butenyl)-1, 8-nonadiene

22. IUPAC name of the given compound is



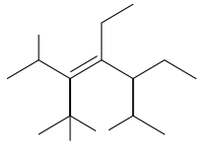
(1) 2-methyl-1-(1′-methyl propyl) cyclohexene
(2) 1-(1′-methyl propyl)-2-methyl cyclohexene
(3) 2-Methyl-1-(1′-methyl ethyl) cyclohexene
(4) None of these

23. What is the correct IUPAC name of the following compound?



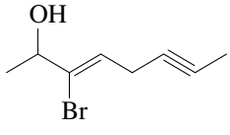
(1) 2, 5-dibromo-1-4-dichlorobenzene
(2) 1, 4-dibromo-3, 5-dichlorobenzene
(3) 3, 5-dibromo-1, 4-dichlorobenzene
(4) 1, 4-dibromo-2, 5-dichlorobenzene

24. The IUPAC name of the structure



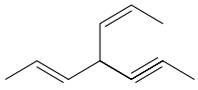
is
(1) 3-t-butyl-4-ethyl-5-isopropyl-2-methyl-3-heptene
(2) 4, 5-diethyl-2, 2, 6-trimethyl-3-(1-methylethyl)-3-heptene
(3) 3-(1, 1-dimethyl ethyl)-4, 5-diethyl-2, 6-dimethyl-3-heptene
(4) 4-ethyl-2, 2-dimethyl-3, 5-bis (1-methylethyl)-3-heptene

25. What is the correct IUPAC name of the compound shown below?



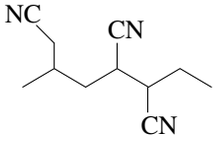
(1) 3-bromo-3-octen-5-yne-2-ol
(2) 3-bromo-3-octen-6-yne-2-ol
(3) 6-bromo-5-octen-2-yne-7-ol
(4) None of these

26. What is correct IUPAC name of the following compound?



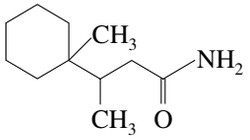
(1) 4-(2-propynyl)-hepta-2, 5-diene
(2) 4-(1′-propynyl) hepta-2, 5-diene
(3) 4-(1-propenyl)-2-heptene-5-yne
(4) 4-(1-propenyl)-5-heptene-2-yne

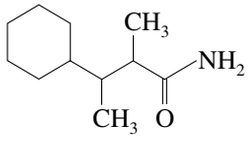
27. What is the correct IUPAC name of the compound?

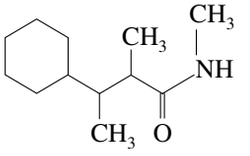


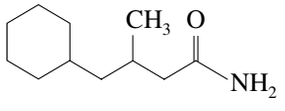
(1) 3-cyano-2, 5-dimethyl heptanedinitrile
(2) 5-cyano-3, 6-dimethyl heptanedinitrile
(3) 2, 5-dimethyl-1, 3, 7-heptanedinitrile
(4) 2-methyl hexane-1, 4, 5 tricarbonitrile

28. Which is the correct structure of 3-cyclohexylmethyl butanamide?

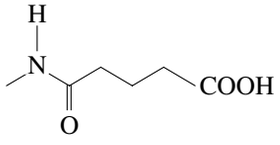
(1) 

(2) 

(3) 

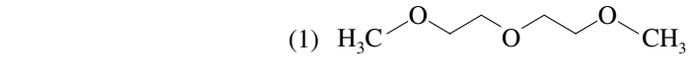
(4) 

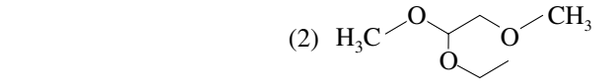
29. What is the correct IUPAC name of the following compound?

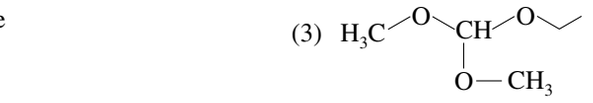


(1) 3-(N-methyl amino) carbonyl propanoic acid
(2) 3-carboxy (N-methyl) propanamide
(3) 4-(N-methyl amino)-4-oxobutanoic acid
(4) 3-(N-methyl carbamoyl) propanoic acid

30. Which is the correct structure of compound 1-methoxy-2-(2-methoxy ethoxy) ethane?

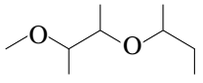
(1) 

(2) 

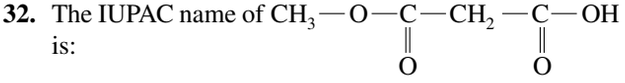
(3) 

(4) 

31. What is the correct IUPAC name of



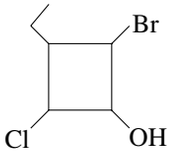
(1) 2-methoxy-3-(methyl propoxy) butane
(2) 2, 3-dioxy-2, 4-dimethyl butane
(3) 3, 4, 6-trimethyl-2, 5-dioxa octane
(4) both (1) and (3)

32. The IUPAC name of 

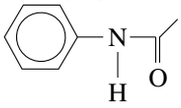
is:

(1) 2-carbomethoxy ethanoic acid
(2) 2-Acetoxy ethanoic acid
(3) 2-Ethanoyloxy acetic acid
(4) 2-Ethanoyloxyethanoic acid

33. Correct IUPAC name of the given compound is:



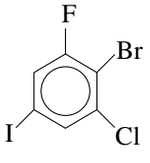
(1) 2-bromo-3-ethyl-4-chlorocyclobutanol
(2) 4-bromo-1-chloro-3-ethylcyclobutanol
(3) 3-bromo-4-chloro-3-ethyl cyclohydroxybutane
(4) 2-bromo-4-chloro-3-ethylcyclobutanol

34. The IUPAC name of 

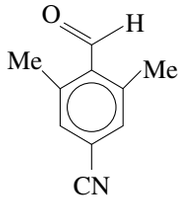
compound is

(1) N-phenylaminoethanone
(2) N-phenylethanamide
(3) N-phenylmethanamide
(4) N-phenylaminomethane

35. The correct IUPAC name of

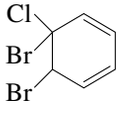


(1) 1-bromo-2-chloro-6-fluoro-4-iodobenzene
(2) 1-bromo-6-chloro-2-fluoro-4-iodobenzene
(3) 2-bromo-1-chloro-3-fluoro-5-iodobenzene
(4) 2-bromo-3-chloro-1-fluoro-5-iodobenzene

36. IUPAC Name of  is:

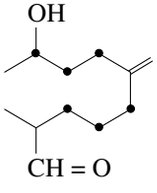
(1) 4-oxo-2, 6-dimethyl benzene carbonitrile
(2) 4-Cyano-2, 6-dimethyl benzaldehyde
(3) 4-formyl 3,5-dimethyl benzonitrile
(4) None of these

37. What is correct IUPAC name of the compound shown below?



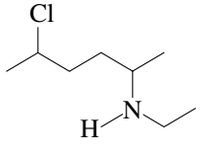
(1) 5, 6-dibromo-6-chloro-1, 3-cyclohexadiene
(2) 2, 3-dibromo-2-chloro-1, 4-cyclohexadiene
(3) 1, 2-dibromo-1-chloro-3, 5-cyclohexadiene
(4) 5, 6-dibromo-5-chloro-1, 3-cyclohexadiene

38. Write the IUPAC name given



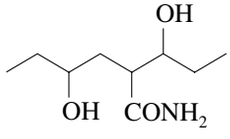
(1) 2-methyl-1-(3′-hydroxy butyl)-6-heptenal
(2) 9-hydroxy-2-methyl-5-decene
(3) 1-(3′-hydroxy butyl)-2-methyl- 6-heptenal
(4) None of these

39. What is the correct IUPAC name of the compound?



(1) 4-chloro-N-ethyl-1-methyl-1-pentanamine
(2) 5-chloro-N-ethyl-2-hexanamine
(3) 5-chloro-N-ethyl-1-hexanamine
(4) 2-chloro-N-ethyl-5-hexanamine

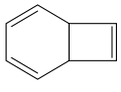
40. What is the correct IUPAC name of the compound shown below?



(1) 3, 6-dihydroxy-4-octanamide
(2) 3, 6-dihydroxy-5-octanenamide
(3) 4-hydroxy-2-(1-hydroxy propyl) hexanamide
(4) 3-hydroxy-2-(2-hydroxy butyl) pentanamide

EXERCISE 2

1. The number of sp^2–sp^2 sigma bonds in the compound given molecule below is:

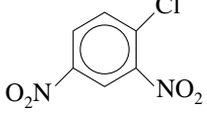


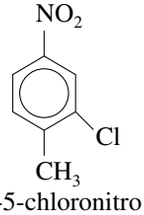
(1) 1 (2) 3
(3) 4 (4) 5

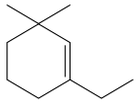
2. In compound $HC{\equiv}C–CH_2–CH{=}CH–CH_3$ the C_2–C_3 bond is the type of–

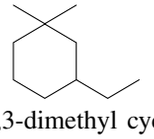
(1) sp–sp^2 (2) sp^3–sp^3
(3) sp–sp^3 (4) sp^2–sp^2

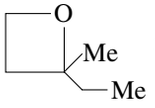
3. Which of the following is correctly named?

(1) 
4-Chloro-1,3-dinitro benzene

(2) 
4-Methyl-5-chloronitro benzene

(3) 
1-Ethyl-3,3-dimethyl cyclohexene

(4) 
1-Ethyl-3,3-dimethyl cyclohexene

4. IUPAC name of  is:

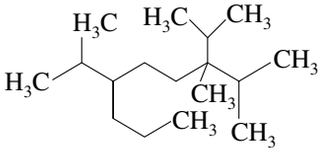
(1) 2-Ethyl-3-methyl epoxy butane

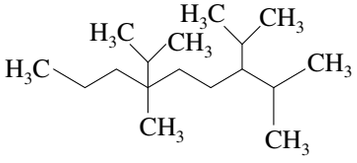
(2) 4-Ethyl-4-methyl oxetane

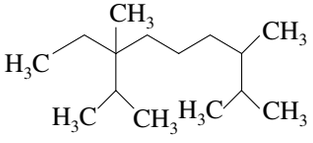
(3) 2-Ethyl-2-methyl oxetane

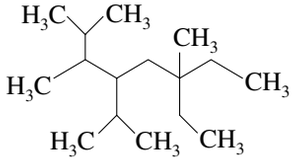
(4) 2-methyl-2-ethyl oxetane

5. The correct structure of compound 3, 6-diisopropyl-2,6-dimethyl nonane is

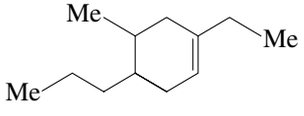
(1) 

(2) 

(3) 

(4) 

6. According to IUPAC convention, what is the name to the compound given below?



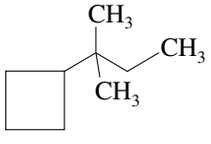
(1) 1-ethyl-5-methyl-4-propyl cyclohexene

(2) 2-ethyl-4-methyl-5-propyl cyclohexene

(3) 5-ethyl-1-methyl-2-propyl-4-cyclohexene

(4) 4-ethyl-2-methyl-1-propyl-4-cyclohexene

7. According to IUPAC convention, the correct name of the following compounds is



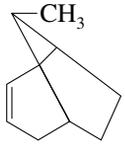
(1) 1-(1, 1-dimethylpropyl) cyclobutane

(2) 1-cyclobutyl-1, 1-dimethyl propane

(3) 2-cyclobutyl-2-methyl butane

(4) 1-(1-methylbutyl) cyclobutane

8. What is the systematic IUPAC name of the following compound?



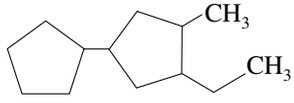
(1) 8-methyl bicyclo [3, 2, 1] oct-3-ene

(2) 8-methyl bicyclo [3, 2, 1] oct-2-ene

(3) 6-methyl bicyclo [3, 2, 1] oct-2- ene

(4) 6-methyl bicyclo [1, 2, 3] oct-2-ene

9. According to IUPAC convention, name of the following compound is



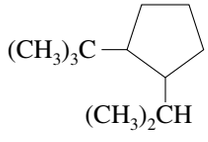
(1) 2-ethyl-4-methyl-1-cyclopentyl cyclopentane

(2) 2-ethyl-1-methyl-4-cyclopentyl cyclopentane

(3) 1-cyclopentyl-3-ethyl-4- methyl cyclopentane

(4) 4-cyclopentyl-1-ethyl-2- methyl cyclopentane

10. The correct IUPAC name of given substance is



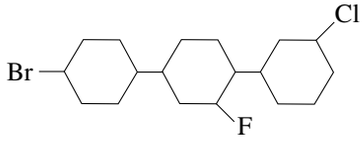
(1) 1-isopropyl-2-ter-butyl cyclopentane

(2) 1-ter-butyl-2-isopropyl cyclopentane

(3) 2-isopropyl-1-ter-butyl cyclopentane

(4) 2-ter-butyl-1-isopropyl cyclopentane

11. According to IUPAC convention, the systematic name of the compound given below is



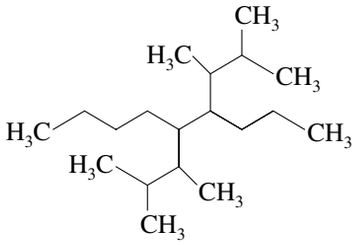
(1) 1-(3-chlorocyclohexyl)-4-(4-bromocyclohexyl)-2-fluorocyclohexane

(2) 5-(4-bromocyclohexyl)-2-(3-chlorocyclohexyl)-1-flouorocyclohexane

(3) 4-(4-bromocyclohexyl)-1-(3-chlorocyclohexyl)-2-fluorocyclohexane

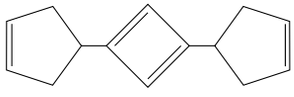
(4) 1-(4-bromocyclohexyl)-4-(3-chlorocyclohexyl)-3-fluorocyclohexane

12. What is the correct IUPAC name of the compound shown below?



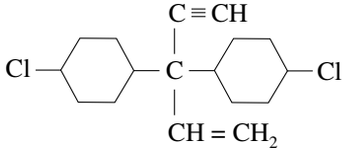
(1) 4-butyl-2, 3 6, 7-tetramethyl-5-propyl octane
(2) 4, 5-bis (1, 2-dimethyl propyl) nonane
(3) 5-(1, 2-dimethy lsopropyl)-2, 3-dimethyl-4-propyl nonane
(4) Both '2' and '3' are correct

13. What is the correct IUPAC name of the compound shown below?



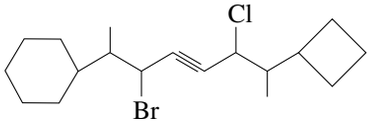
(1) Bis (cyclopentenyl) cyclobutadiene
(2) 1, 3-bis (3-cyclopentenyl) cyclobutadiene
(3) Dicyclopentene cyclobutadiene
(4) 4-[3-(3-cyclopentenyl)-1, 3-cyclobutadienyl] cyclopentene

14. What is the correct IUPAC name of the compound shown below?



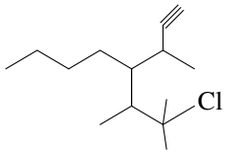
(1) 3, 3-bis-(chlorocyclohexyl) 1-penten-4-yne
(2) bis-(4-chlorocyclohexyl) 4-penten-1-yne
(3) 3, 3-bis-(4-chlorocyclohexyl)-1-penten-4-yne
(4) 3, 3-bis(4-chlorohexyl)-3-ethynyl prop-1-ene

15. What is the correct IUPAC name of the compound shown below?



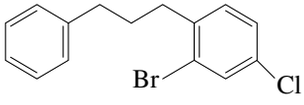
(1) 5-bromo-2-chloro-1-cyclobutyl-6-cyclohexyl-1, 6-dimethyl-3-hexyne
(2) 6-bromo-3-chloro-2-cyclobutyl-7-cyclohexyl-4-octyne
(3) 3-bromo-6-chloro-7-cyclohutyl-2-cyclohexyl-4-octyne
(4) 5-bromo-2-chloro-1-cyclobutyl-6-cyclohexyl-1-methyl-3-heptyne

16. What is the correct IUPAC name of the compound shown below?



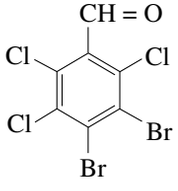
(1) 4-butyl-6-chloro-3, 5, 6-trimethyl-1-heptyne
(2) 4-butyl-6-chloro-3, 5, 6, 6-tetramethyl-1-heptyne
(3) 4-butyl-2-chloro-2, 3, 5-trimethyl-6-heptyne
(4) 4-(2-chloro-1, 2-dimethylpropyl)-3methyl-1-octyne

17. What is the correct IUPAC name of the following compound?



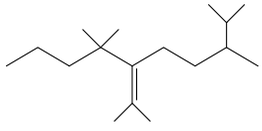
(1) 1-(2-bromo-4-chlorophenyl)-3-phenyl propane
(2) 3-bromo-2-(3-phenylpropyl) chlorobenzene
(3) 1-bromo-5-chloro-2-(3-phenylpropyl) benzene
(4) 2-bromo-4-chloro-1-(3-phenylpropyl) benzene

18. What is the correct IUPAC name of the compound given below?



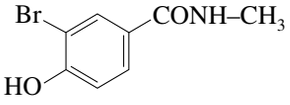
(1) 3, 4-dibromo-2, 5, 6-trichlorobenzaldehyde
(2) 1, 2-dibromo-3, 5, 6-trichlorobenzaldehyde
(3) 4, 5-dibromo-3, 3, 6-trichlorobenzaldehyde
(4) 5, 6-dibromo-1, 2, 4-trichlorobenzaldehyde

19. The IUPAC name of the compound shown below is



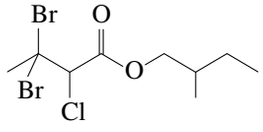
(1) 2, 4,4-timethyl-3-(3,4-dinethyl pentyl) hept-2-ene
(2) 2-isopropyl-6, 6-dimethyl 5-(methyl ethenyl) nonane
(3) 2-(methyl ethyl)-5-isopropylidene-6, 6-dimethyl nonane
(4) 2,6,7-trimethyl-3-(1′, 1′-dimethyl butyl) oct-2-ene

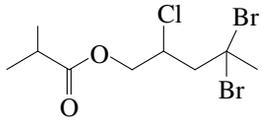
20. What is the correct IUPAC name of the compound shown below?

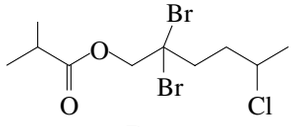


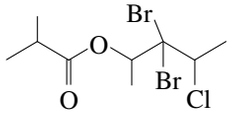
(1) 4-aminocarbonyl-3-bromo N-methyl phenol
(2) 3-bromo-4-hydroxy N-methyl benzene carboxamide
(3) 5-bromo-4-hydroxy N-methylbenzene carboxamide
(4) N-methyl 4-amido-3-bromophenol

21. Which of the following is correct structure of 3, 3-dibromo-2-chlorobutyl 2-methyl propanoate?

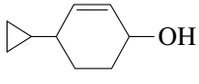
(1) 

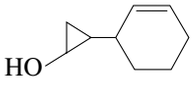
(2) 

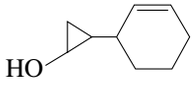
(3) 

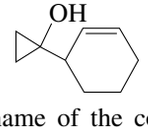
(4) 

22. Which is the correct structure of 2-(2-cyclohexenyl) cyclopropanol?

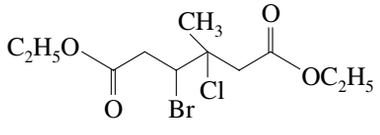
(1) 

(2) 

(3) 

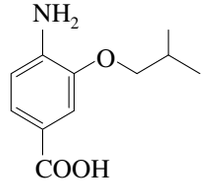
(4) 

23. What is the correct IUPAC name of the compound given below?



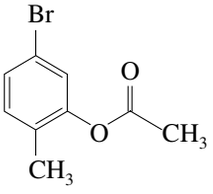
(1) 3-bromo-4-chloro-4-methyl ethyl hexanedioate
(2) Diethyl 4-bromo-3-chloro-3-methyl hexanedioate
(3) Ethyl 4-bromo-3-chloro-3-methyl hexanedioate
(4) Diethyl 3-bromo-4-chloro-4-methyl hexanedioate

24. What is IUPAC name of the compound given below?



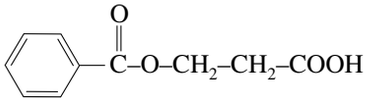
(1) 4-carboxy-2-(2′-methyl propoxy) aniline
(2) 4-amino-5-(2′-methyl propoxy) benzoic acid
(3) 4-amino-3- (2′-methyl propoxy) benzoic acid
(4) 4-amino-3-(2′-methyl propoxy) carboxy benzene

25. The correct IUPAC name of the compound given below is



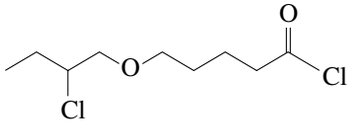
(1) 5-bromo-2-methyl phenyl ethanoate
(2) 3-bromo-6-methyl phenyl ethanoate
(3) 4-bromo-2-{oxy-(1-oxoethyl)} toluene
(4) Methyl 5-bromo-2-methyl benzoate

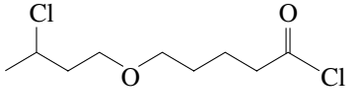
26. What is the correct IUPAC name of the compound shown below?

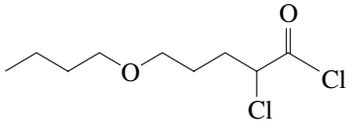


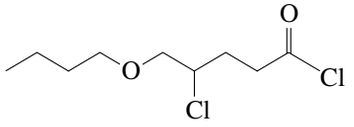
(1) 3-carboxy phenyl propanoic acid
(2) 3-(benzoyloxy) propanoic acid
(3) 3-hydroxy-3-oxoethyl benzoate
(4) 3-oxyphenyl carboxy propanoic acid

27. The correct structure of 5-(2-chlorobutoxy) pentanoyl chloride is

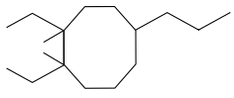
(1) 

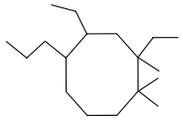
(2) 

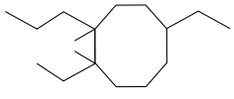
(3) 

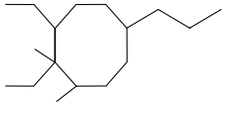
(4) 

28. The correct structural formula of 1,2-diethyl-1, 8-dimethyl-5-propyl cyclooctane is

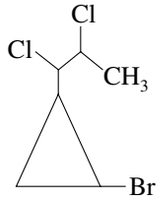
(1) 

(2) 

(3) 

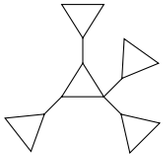
(4) 

29. The correct IUPAC name of the compound shown below is



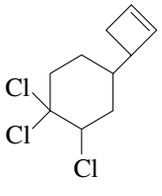
(1) 1-bromo-2-(1, 2-dichloropropyl) cyclopropane
(2) 2-bromo-1-(1, 2-dichloropropyl) cyclopropane
(3) 1-bromocyclopropyl-1, 2-dichloro propane
(4) 1-(2-bromocyclopropyl)-1, 2-dichloropropane

30. What is the IUPAC name of the compound shown below?



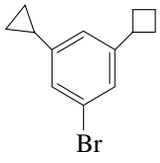
(1) Tetracyclopropyl cyclopropane
(2) Pentacyclopropane
(3) 1, 2, 2, 3-tetracyclopropyl cyclopropane
(4) 1, 1, 2, 3-tetracyclopropyl cyclopropane

31. What is the correct IUPAC name of the compound shown below?



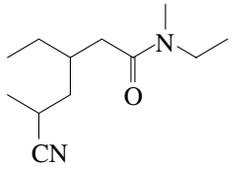
(1) 1, 1, 2-trichloro-4-cyclobutenyl cyclohexane
(2) 3-trichlorocyclohexyl cyclobutene
(3) 3-(3, 4, 4-trichlorocyclohexyl) cyclobutene
(4) 3, 4, 4-trichloro-1-cyclobutenyl cyclohexane

32. What is the correct IUPAC name of the compound shown below?



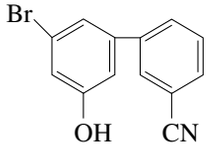
(1) 3-bromo-1-cyclobutyl-5-cyclopropyl benzene
(2) 3-bromo-1-cyclopropyl-5-cyclobutyl benzene
(3) 1-bromo-5-cyclobutyl-3-cyclopropyl benzene
(4) 1-bromo-3-cyclobutyl-5-cyclopropyl benzene

33. What is the correct IUPAC name of the following compound?



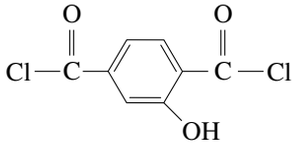
(1) 3-(2-cyanopropyl)-N-ethyl N-methyl pentanamide
(2) N-ethyl-3-(2-cyanopropyl) N-methyl pentanamide
(3) N, 3-diethyl-5-cyano N-methyl hexanamide
(4) 5-cyano-N, 3-diethyl N-methyl hexanamide

34. What is the correct IUPAC name of the compound shown below?



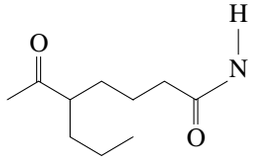
(1) 3-bromo-5-(3′-cyanophenyl) phenol
(2) 5-bromo-3-(3′-cyanophenyl) phenol
(3) 3-(3′-hydroxy-5′-bromophenyl) benzonitrile
(4) 3-(3′-bromo-5′-hydroxy phenyl) benzonitrile

35. What is the correct IUPAC name of the given compound?



(1) 2-hydroxy-1, 4-benzene dicarbonyl chloride
(2) 2, 4-dichloro carbonyl phenol
(3) 3-hydroxy-1, 4-benzene dicarbonyl chloride
(4) 1, 4-dicarbonyl chloride-3-hydroxy benzene

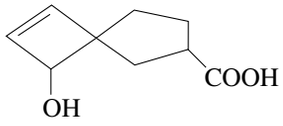
36. In the IUPAC name of the following compound, there is something wrong. Find the mistake.



N-ethyl-6-oxo-5 propyl heptanamide

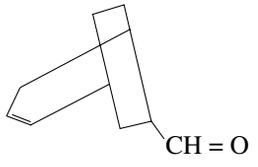
(1) Principal functional group is incorrectly chosen
(2) Incorrect prefix for locant is used
(3) Parent chain is incorrectly selected
(4) Locants name is not written is order of priority recommended by IUPAC

37. IUPAC name of the following compound is:



(1) 1-hydroxy spiro [3, 4] oct-2-ene-6-carboxylic acid
(2) 6-carboxy spiro [3, 4] oct-2-ene-1-ol
(3) 3-hydroxy spiro [3,4] oct-1-ene-6-carboxylic acid
(4) 2-carboxy spiro [3,4] oct-7-ene-6-ol

38. The IUPAC name of the following compound is:

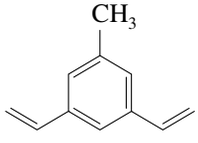


(1) Bicyclo [2,3,2] non-2-ene-6-carbaldehyde
(2) Bicyclo [3,2,2] non-5-ene-2-carbaldehyde
(3) Bicyclo [3,2,2] non-2-ene-6-carbaldehyde
(4) Bicyclo [3,2,0] non-2-ene-6-carbaldehyde

39. What is the correct IUPAC name of the compound shown below?

(1) 6-oxa spiro [2,3] octane
(2) 6-oxa spiro [4,3] octane
(3) 6-oxa spiro [3,3] heptane
(4) 6-oxa spiro [3,4] octane

40. What is the correct IUPAC name of the following compound?

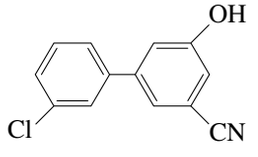


(1) 3, 5-diethenyl toluene
(2) 1, 3-diethenyl-5-methyl benzene
(3) 3-ethenyl-5-methyl styrene
(4) 1, 3, 5-triethenylmethyl benzene

EXERCISE 3

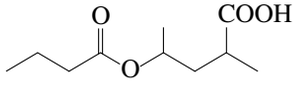
One and More Than One Option Correct Type Question

1. The correct statement regarding the given compound is/are



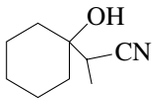
(1) Suffix of the name would be-ol
(2) Suffix of the name would be-nitrile
(3) Parent ring has two locants besides principal functional group
(4) Locant phenyl group is at fifth position of parent ring

2. What is/are true regarding the compound?



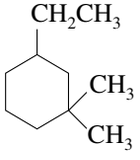
(1) It is a carboxy ester
(2) It is an alkanoyloxy acid
(3) Its IUPAC name is 4-carboxy-2-pentyl butanoate
(4) Its IUPAC name is 4-butanoyloxy-2-methyl pentanoic acid

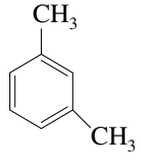
3. What is/are wrong according to IUPAC convention in the following naming?

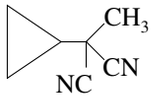


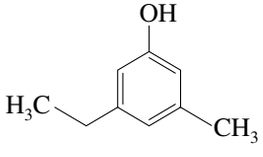
(1) Parent chain is incorrectly selected
(2) Parent chain has only three carbons
(3) Its IUPAC name is 1-(1-hydroxycyclohexyl)-1-methyl ethanenitrile
(4) Its IUPAC name is 2-(1-hydroxycyclohexyl) propanenitrile

4. Which of the following compound(s) and their IUPAC name is/are wrongly matched?

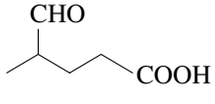
(1) 
l-ethy-3, 3-dimethyl cyclohexane

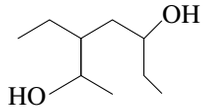
(2) 
Meta-dimethyl benzene

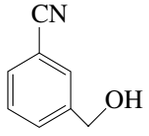
(3) 
2-cyclopropyl-2-methyl propane dinitrile

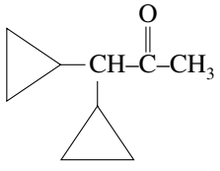
(4) 
3-ethyl-5-methyl phenol

5. Which of the following compounds and their names are correctly matched?

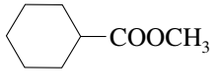
(1) 
4-formyl pentanoic acid

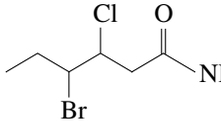
(2) 
1,3-diethyl-1,4-butanediol

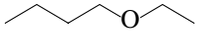
(3) 
3-hydroxymethyl benzonitrile

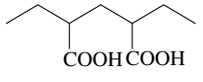
(4) 
1, 1-dicyclopropyl propanone

6. Which of the following structures and IUPAC name are incorrectly matched?

(1)  Methyl cyclohexanoate

(2)  4-bromo-3-chlorohexanamide

(3)  2-ethoxy pentane

(4)  3, 5-nonanedioic acid

7. If an alkane $C_{10}H_{22}$ has a quaternary carbon, two tertiary carbons and six methyl groups, which of the following could be one of its correct IUPAC name?
(1) 1, 2-dimethyl-1-tertiarybutyl butane
(2) 3-ethyl-2, 2, 4-trimethyl pentane
(3) 2, 2, 3, 4-tetramethyl hexane
(4) 2, 3, 4, 5-tetramethyl hexane

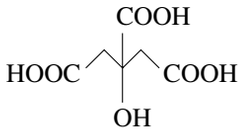
Statement Type Question

(1) If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I
(2) If both Statement-I and Statement-II are correct and Statement-II is not the correct explanation for Statement-I

(3) If Statement-I is correct and Statement-II is incorrect

(4) If Statement-I is incorrect and Statement-II is correct

8. Statement-I: The IUPAC name of citric acid is 2-hydroxy-propane-1, 2, 3-tricarboxylic acid.



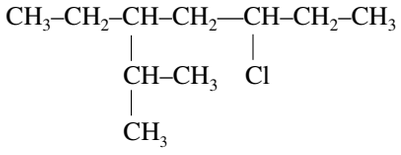
citric acid

Statement-II: When an unbranched C atom is directly linked to more than two like-functional groups, then it is named as a derivative of the parent alkane which does not include the C atoms of the functional group.

9. Statement-I: The IUPAC name of CH_3–CH=CH–C≡C–H is pent-3-en-1-yne and not pent-2-en-4-yne.

Statement-II: Lowest locant rule for multiple bond is preferred.

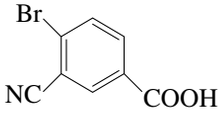
10. Statement-I: The IUPAC name for



Is 5-chloro-3-ethyl-2-methyl heptane and not 3-chloro-5-isopropyl heptane.

Statement-II: The parent carbon chain should contain larger number of alkyl substituents.

11. Statement-I: IUPAC name of the compound given below is 4-bromo-3-cyanobenzoic acid

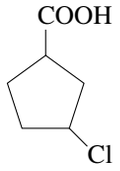


Statement-II: –COOH has higher priority than a cyanide group.

12. Statement-I: Dimethyl benzene can have three different IUPAC names

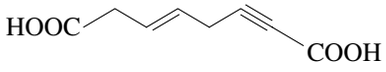
Statement-II: All three different names are for three positional isomers.

13. Statement-I: Following compound has its IUPAC name 3-chlorocyclopentanoic acid



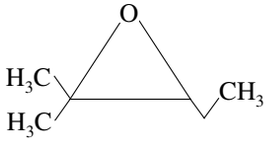
Statement-II: COOH is the principal functional group of compound which determines the suffix name.

14. Statement-I: IUPAC name of the following compound is oct-2-en-5-ynedioic acid



Statement-II: Double bond has preference over triple bond.

15. Statement-I: IUPAC name of the following compound is 2-ethyl-3, 3-dimethyl oxirane.



Statement-II: In oxirane, numbering starts from oxygen atom of the ring.

Comprehension Type Question

Passage #1 Q. 16–18

An aromatic compound has one cyanide and two chloride groups on benzene ring. In IUPAC system, cyanide has higher priority than chloride group, therefore determine suffix of parent name of the compound.

16. How many different IUPAC names can be assigned to the above mentioned compound?

(1) 2 (2) 3

(3) 4 (4) 6

17. What is IUPAC name of the compound above which is most polar?

(1) 2, 3-dichlorobenzonitrile

(2) 2, 4-dichlorobenzonitrile

(3) 2, 6-dichlorobenzonitrile

(4) 3, 4-dichlorobenzonitrile

18. Which is IUPAC name of the compound above which is least polar?

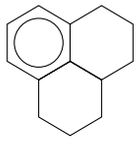
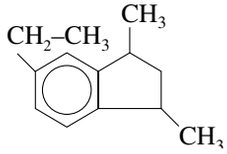
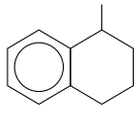
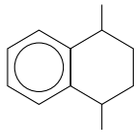
(1) 2, 3-dichlorobenzonitrile

(2) 2, 5-dichlorobenzonitrile

(3) 3, 4-dichlorobenzonitrile
(4) 3, 5-dichlorobenzonitrile

Column Matching Type Question

19. Match the column. (Matrix):

Column-I **Compounds**		*Column-II* **Number of Benzylic hydrogen**
(A)		(P) 2
(B)		(Q) 3
(C)		(R) 4
(D)		(S) 5

Code

	A	*B*	*C*	*D*
(1)	S	R	Q	P
(2)	R	S	P	Q
(3)	S	P	R	Q
(4)	Q	R	S	P

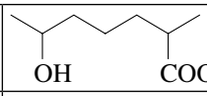
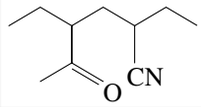
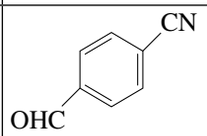
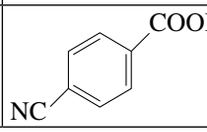
20. Match the IUPAC names from column-I with their features from column-II. There may be more than one match for the quantity from Column-I with the quantities from Column-II

Column-I		*Column-II*	
(A)	3, 3, 4, 4-tetramethyl-1-pentyne	(P)	has only three carbon collinear
(B)	2-butyne	(Q)	has four carbon colinear
(C)	1-butyne	(R)	substitution of H by Cl gives single product
(D)	2, 2, 5, 5-tetramethyl-3-hexyne	(S)	substitution of H by Cl gives three different products (excluding stereoisomers)

Code

	A	*B*	*C*	*D*
(1)	P	Q	R	S
(2)	P,S	Q,R	P,S	Q,R
(3)	P,Q	R,S	P,R	Q,S
(4)	P,R	PS	Q,R	R,S

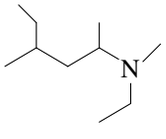
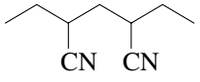
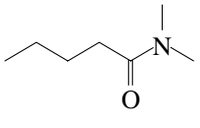
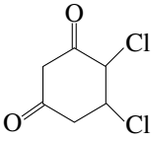
21.

Column-I		*Column-II*	
(A)		(P)	Name end with suffix 'anoic acid'
(B)		(Q)	Name end with suffix 'carboxylic acid'
(C)		(R)	Name end with suffix 'nitrile'
(D)		(S)	Parent chain/ring has six carbon atoms

Code

	A	*B*	*C*	*D*
(1)	P	R,S	R,S	Q,S
(2)	Q	R,S	R,S	Q,S
(3)	R	Q,S	P,R	R,S
(4)	S	P,Q	R,S	Q,S

22. Match the general formula from Column-I with the class they belong to in Column-II

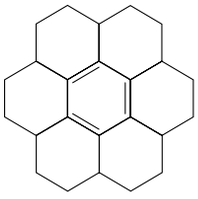
Column-I		*Column-II*
(A)		(P) has tertiary N-atom
(B)		(Q) has tertiary carbon atom
(C)		(R) has five carbons in the parent chain
(D)		(S) has six carbons in the parent chain

Code

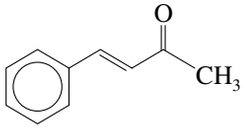
	A	*B*	*C*	*D*
(1)	P,R,S	P,R	Q	S
(2)	Q	P,R,S	P,S	Q,S
(3)	P,Q,S	Q,R	P,R	Q
(4)	Q,SP,	R	S	P

Single Digit Integer Type Question

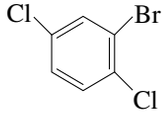
23. Total number of α-hydrogen in the given following compound is:



24. How many carbon atom present in the parent chain in the given following compound?



25. If the following compound is correctly named according to IUPAC convention what would be sum of the numbers representing positions of three halide locants?

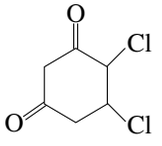


26. In the compound 7-ethyl 3-nonene-2, 5, 8-tricarboxylic acid, how many atoms are in sp^2-hybridisation state?

27. In 3-formy-2-methyl benzoic acid, what is the maximum number of hydrogen atoms which may lies in one single plane?

28. When name of hydrocarbon 3-(1-butenyl)-1, 5-hexadiene is rewritten correctly according to IUPAC convention, what would be the number of carbon atoms in the parent chain.

29. When the following compound is named correctly according to IUPAC convention, what would be the sum of position of two chlorine atoms?



30. How many secondary hydrogens are present in the alkyne named 3-ethyl-4-octyne?

EXERCISE 4

1. Which of the following compounds has incorrect IUPAC name: **[AIEEE-2002]**

(1) $CH_2–CH_2–CH_2–\underset{\underset{O}{\|}}{C}–O–CH_2–CH_3$

ethyl butanoate

(2) $CH_3–\underset{\underset{CH_3}{|}}{CH}–\underset{\underset{O}{\|}}{C}–\underset{\underset{CH_3}{|}}{CH}–CH_3$

2,4-dimethyl-3-pentanone

(3) $H_3C–\underset{\underset{OH}{|}}{CH}–\underset{\underset{CH_3}{|}}{CH}–CH_3$ 2-methyl-3-butanol

(4) $CH_3–CH_2–CH_2–CHO$ butanal

2. The IUAPC name of $CH_3COCH(CH_3)_2$ is **[AIEEE-2003]**

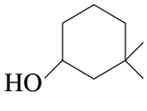
(1) 4-Methylisopropyl ketone

(2) 3-Methyl-2-butanone

(3) Isopropylmethyl ketone

(4) 2-Methyl-3-butanone

3. The IUPAC name of the compound is **[AIEEE-2004]**



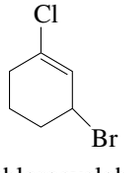
(1) 3,3-Dimethyl-1-hydroxy cyclohexane

(2) 1,1-Dimethyl-3-hydroxy cyclohexane

(3) 3,3-Dimethyl-1-cyclohexanol

(4) 1,1-Dimethyl-3-cyclohexanol

4. The IUPAC name of the compound shown below is **[AIEEE-2006]**

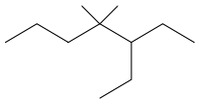


(1) 6-Bromo-2-chlorocyclohexene

(2) 3-Bromko-1-chlorocyclohexene

(3) 1-Bromo-3-chlorocyclohexene
(4) 2-Bromo-6-chlorocycohex-1-ene

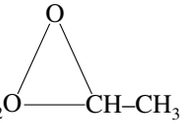
5. The IUPAC name of is- **[AIEEE-2007]**



(1) 1, 1-Diethyl-2-dimethylpentane
(2) 4, 4-Dimethyl-5, 5-diethylpentane
(3) 5, 5-Diethyl-4, 4-dimethylpentane
(4) 3-Ethyl-4, 4 dimethylheptane

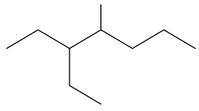
6. The correct decreasing order of priority for the functional groups of organic compounds in the IUPAC system of nomenclature is **[JEE Main-2008]**
(1) $-SO_3H$, –COOH, $-CONH_2$, –CHO
(2) –CHO, –COOH, $-SO_3H$, $-CONH_2$
(3) $-CONH_2$, –CHO, $-SO_3H$, –COOH
(4) –COOH, $-SO_3H$, $-CONH_2$, –CHO

7. The IUPAC name of neopentane is **[JEE Main-2009]**
(1) 2-methylbutane
(2) 2,2-dimethylpropane
(3) 2-methylpropane
(4) 2,2-dimethylbutane

8. The IUPAC name of the compound  is :

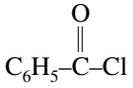
[JEE Main Online-2012]
(1) 1, 2-Epoxy propane (2) Propylene oxide
(3) 1, 2-Oxo propane (4) 1, 2-Propoxide

9. The correct IUPAC name of the following compound

 is **[JEE Main Online-2014]**

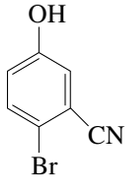
(1) 4-methyl-3-ethylhexane
(2) 3-ethyl-4-methylhexane
(3) 3,4-ethylemethylhexane
(4) 4-ethyl-3-methylhexane

10. The IUAPC name of the given compound is: **[IIT-2006]**



(1) Benzoylchloride
(2) Benzenecarbonylchloride
(3) Chlorophenyl ketone
(4) Phenylchloroketone

11. The IUPAC name of the following compound is- **[IIT-2009]**



(1) 4-Bromo-3-cyanophenol
(2) 2-Bromo-5-hydroxybenzonitrile
(3) 2-Cyano-4-hydroxybromobenzene
(4) 6-Bromo-3-hydroxybenzontrile

ANSWER KEY

EXERCISE # 1

1. (4)	2. (1)	3. (3)	4. (1)	5. (3)
6. (1)	7. (2)	8. (2)	9. (1)	10. (4)
11. (1)	12. (3)	13. (3)	14. (1)	15. (1)
16. (4)	17. (2)	18. (3)	19. (2)	20. (3)
21. (3)	22. (2)	23. (4)	24. (4)	25. (1)
26. (2)	27. (4)	28. (4)	29. (4)	30. (1)
31. (4)	32. (1)	33. (4)	34. (2)	35. (3)
36. (3)	37. (4)	38. (3)	39. (2)	40. (3)

EXERCISE # 2

1. (3)	2. (3)	3. (3)	4. (3)	5. (2)
6. (1)	7. (3)	8. (2)	9. (4)	10. (1)
11. (3)	12. (3)	13. (2)	14. (3)	15. (2)
16. (4)	17. (4)	18. (1)	19. (4)	20. (2)
21. (2)	22. (2)	23. (2)	24. (3)	25. (1)
26. (2)	27. (1)	28. (4)	29. (4)	30. (4)
31. (3)	32. (1)	33. (4)	34. (4)	35. (1)
36. (3)	37. (3)	38. (3)	39. (4)	40. (2)

EXERCISE # 3

1. (2,3)	2. (2,4)	3. (1,4)	4. (1,2)	5. (3,4)
6. (1,4)	7. (2,3)	8. (1)	9. (1)	10. (1)
11. (1)	12. (1)	13. (4)	14. (3)	15. (4)
16. (4)	17. (3)	18. (4)	19. (1)	20. (2)
21. (1)	22. (3)	23. (6)	24. (4)	25. (7)
26. (8)	27. (4)	28. (8)	29. (9)	30. (6)

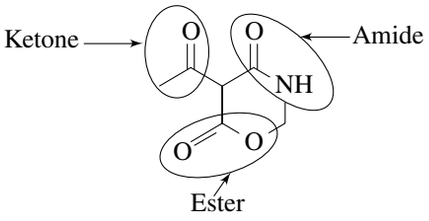
EXERCISE # 4

1. (3)	2. (2)	3. (3)	4. (2)	5. (4)
6. (4)	7. (2)	8. (1)	9. (2)	10. (2)
11. (2)				

HINT AND SOLUTION

EXERCISE # 1

1. [4]

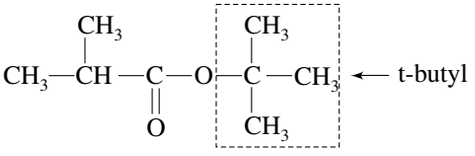


So ether group NOT present

2. [1]

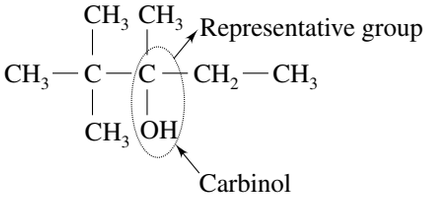
Double bond in between C–C known as olefinic bond.

3. [3]



t-Butyl isobutyrate

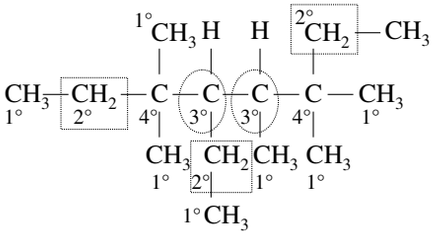
4. [1]



It consist 3-different alkyl radical which wright in alphabet order.

t-Butyl ethyl methyl carbinol

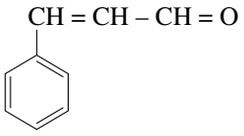
5. [3]



3° Carbon = 2

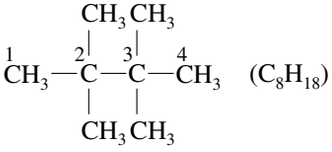
2° Hydrogen = 6

6. [1]



- All C are sp^2 hybridised
- It is planner
- IUPAC name – 3 phenyl-2 propenyl
- CHO group is not directly attach with benzen ring so it is not aromatic aldehyde.

7. [2]



(C_8H_{18})

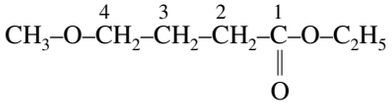
2, 2, 3, 3-tetra methyl butane

This structure have only 1°H

8. [2]

Principal functional group = 

Side chain = OCH_3 (methoxy)

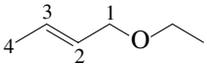


Ethyl-4-methoxy butanoate

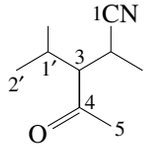
9. [1]

According to proirity of functional group

10. [4]



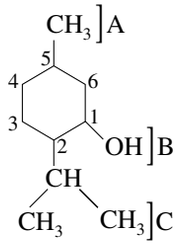
11. [1]



Principal functional group = CN

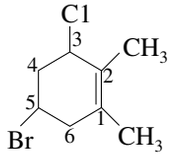
Side chain = $-\overset{\overset{O}{\|}}{C}-$, CH3, $CH(CH_3)_2$

12. [3]



—OH ⇒ Principal functional group has 1st locant number, then apply locant number rule A → 5, B → 1, C → 2

13. [3]



→ Numbering of parent chain start from double bonded C, by using alphabet rule

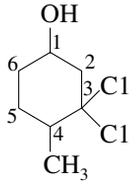
14. [1]

→ Maximum number of carbon containing ring selected as parent chain

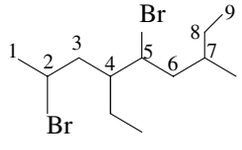
→ Cyclobutyl methyl is single complicated side chain

15. [1]

For numbering principal functional group (–OH) will be preferred



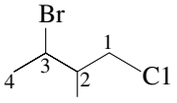
16. [4]



Select longest C chain

17. [2]

In option (2) parent chain is wrongly numbered, the correct numbering is



18. [3]

Molar mass = 84 is the multiple of 14

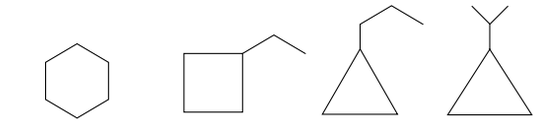
Hence molecular formula = $(CH_2)_n$

$\because \quad (12 + 2)_n = 84$

$n = 6$

$\because$ Molecular formula = C_6H_{12}

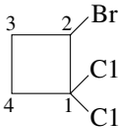
× has no double bond, it must be cycloalkane. Cyclo alkanes without methyl as locant are-



Cyclohereane | ethyl cyclobutane | propylcydo propane | isopropyl cyloprope

19. [2]

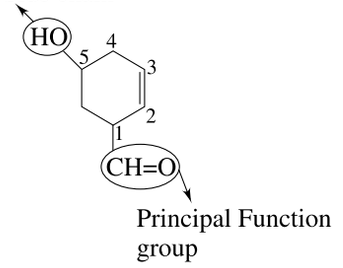
In option (2) parent chain wrongly numbered, correct numbering is



Correct name is 2-bromo-1, 1-dichloro cyclobutane according to least locant number rule

20. [3]

Side chain

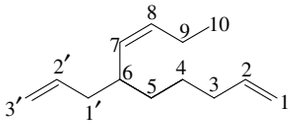


Principal Function group

Parent chain must be contain

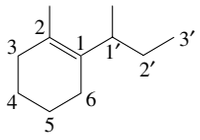
Principal functional group > multiple bond > side chain

21. [3]



Parent chain must contain maximum number of multiple bond and maximum number of C.

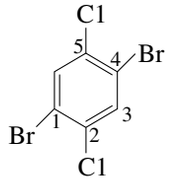
22. [2]



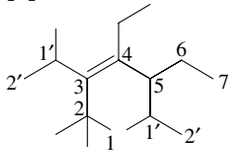
Apply alphabet rule with the preference of double bond

23. [4]

Numbering of parent chain according to alphabet rule

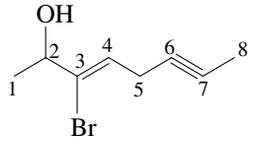


24. [4]

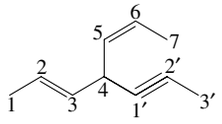


Apply least locant number rule with the preference of multiple bond.

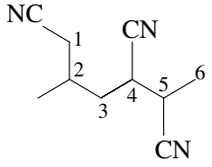
25. [1]



26. [2]

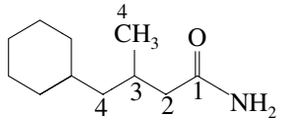


27. [4]



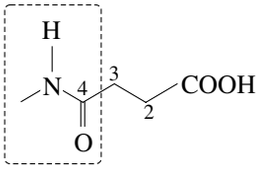
28. [4]

Open chain contain functional group so that it must be parent chain



Ring works as side chain

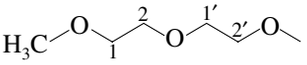
29. [4]



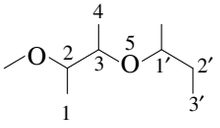
Side chain

3. (N. methly carbamoyl) propanoic acid

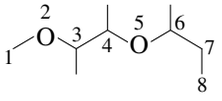
30. [1]



31. [4]



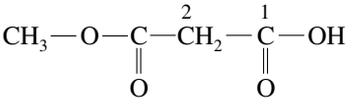
→ 2-methoxy-3-(1′ methyl propoxy) butane



As per OXA system

3, 4, 6-trimethyl-2,5-dioxa octane

32. [1]



2-carbomethoxy ethanoic acid

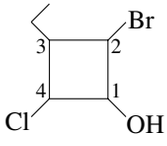
Principal functional group = COOH

Side Chain =  (esar group)

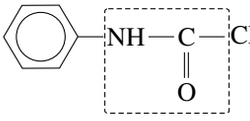
Ethanoyloxy

33. [4]

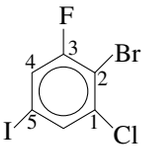
- Principal functional group = → OH
- Side chain → Bromo Chloro ethyl
- albhabet rule applies



34. [2]

 Principal functional group

35. [3]

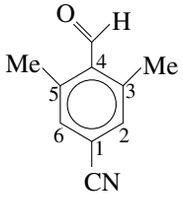


→ Apply locant number rule

→ followed by alphabet rule

2-bromo-1-chloro-3 fluoro 5-iodobenzene

36. [3]

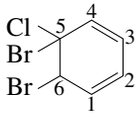


Priority – CN > –CH = O

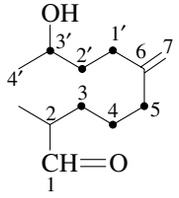
– CN ⇒ Principal functional group

– CH = O ⇒ Side chain

37. [4]



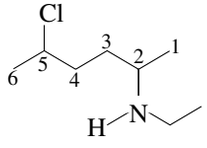
38. [3]



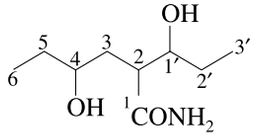
Parent chain must be preffer for numbering

functional group (–CH=O) > multiple bond (=) > side chain (–OH)

39. [2]

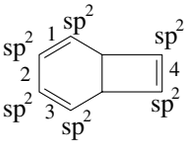


40. [3]



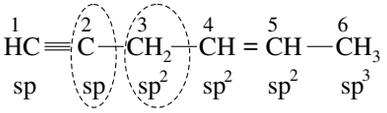
EXERCISE # 2

1. [3]



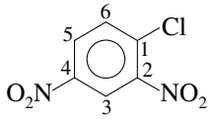
$sp^2 - sp^2$ sigma bonds = 4

2. [3]



3. [3]

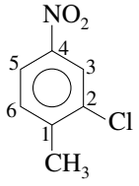
(1)



1-Chloro-2, 4-dinitro benzene (correct)

4-Chloro-1, 3-dinitro benzene (Wrong)

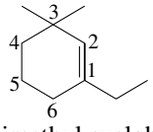
(2)



2-chloro-1methyl-4-nitro benzene (correct)

4-Methyl-5-chloronitro benzene (Wrong)

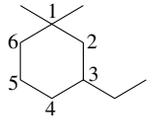
(3)



1-Ethyl-3,3-dimethyl cyclohexene (Correct)

Apply least locant number rule with the preference of multiple bond.

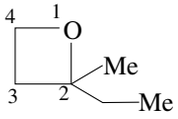
(4)



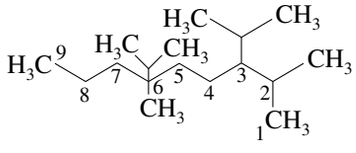
3-Ethyl-1,1-dimethyl cyclohexane (correct)

1-Ethyl-3,3-dimethyl cyclohexane (wrong)

4. [3]

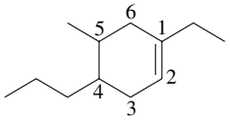


5. [2]



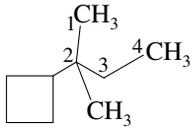
6. [1]

For numbering multiple bond preferred over side chain

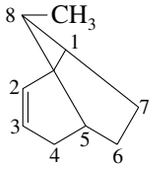


7. [3]

Parent chain must be contain greater number of side chain

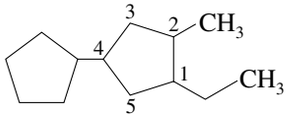


8. [2]

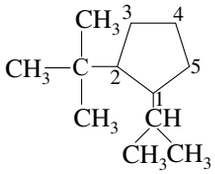


9. [4]

Apply least locant number rule as well abhabet rule

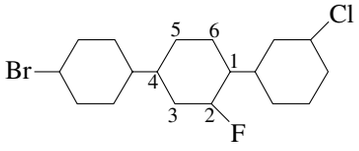


10. [1]



Selection of parent chain by alphabet rule

11. [3]

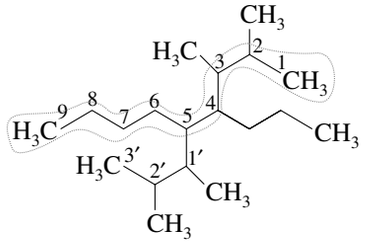


→ parent chain must be contain maximum number side chin

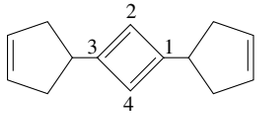
→ numbering of parent chain takes place by least locant number rule

12. [3]

Maximum number of continuous C-present in parent chain



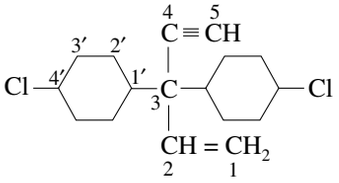
13. [2]



Parent chain must be contain maximum number of multiple bond.

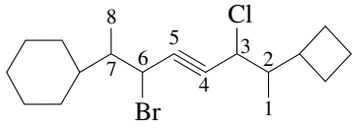
14. [3]

Parent chain must be contain maximum number of multiple bond



15. [2] Multiple bond (≡) containing chain selected as perent chain

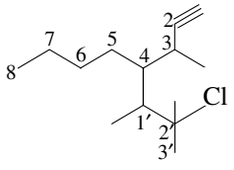
Alphabet rule applicable



16. [4]

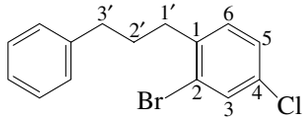
Parent chain must be contain following in given priority.

Principal function group > multiple bond > maximum number of carbon.



4-(2-chloro-1, 2-dimethylpropyl)-3methyl-1- octyne

17. [4]

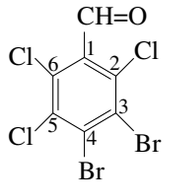


Numbering of parent chain according to least locant number rule.

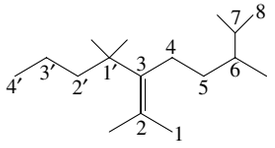
18. [1]

Principal functional group → –CH=O

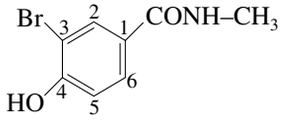
Numbering of parent chain (benzene ring) takes place according to Alphabet rule.



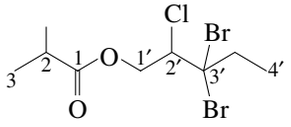
19. [4]



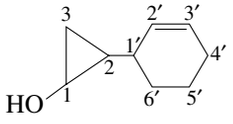
20. [2]



21. [2]

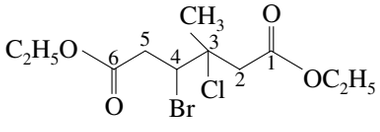


22. [2]

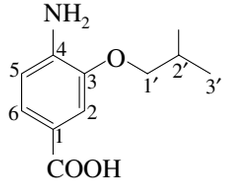


23. [2]

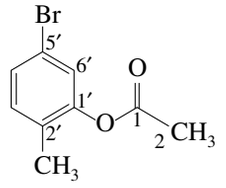
Numbering takes place according to least locant number rule



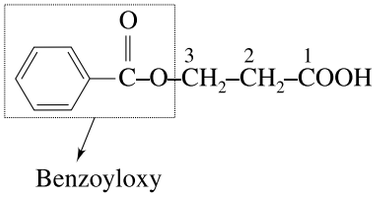
24. [3]



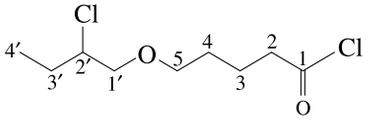
25. [1]



26. [2]

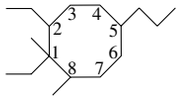


27. [1]



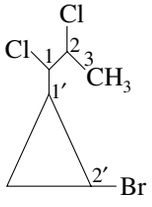
28. [4]

Use alphabet rule as well least locant number rule.



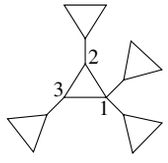
29. [4]

Maximum number side chain must be present in parent chain, when number of C in both (open/close) chain will be same

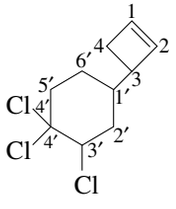


30. [4]

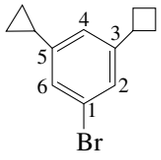
Apply locant number rule



31. [3] Multiple bond containing chain selected as parent chain



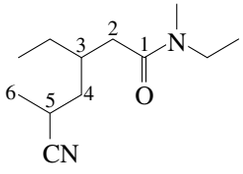
32. [1]



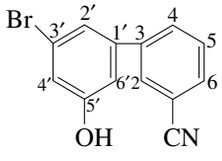
→ Aromatic ring has greater number of substituent, so that it must be parent chain

→ Numbering of parent chain takes place via alphabet rule

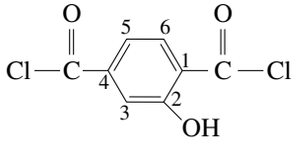
33. [4]



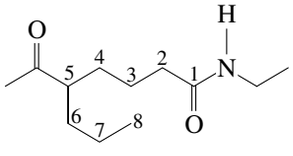
34. [4] Principal functional group (–C≡N). So that –C≡N containing chain selected as parent chain.



35. [1]



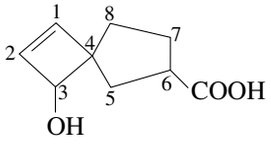
36. [3]



N-ethyl-6-oxo-5-propyl heptanamide (given)

Parent chain has 8 carbon so that given IUPAC name is wrong.

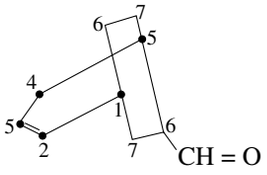
37. [3]



→ —COOH is Principal functional group

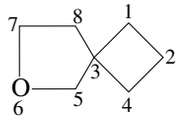
→ —OH (Side chain)

38. [3]



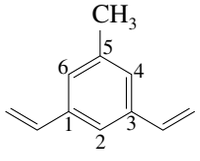
Bicyclo [3,2,2] non-2-cne-6-carbaldehyde

39. [4]



6-oxo-spiro [2,3] octane

40. [2]



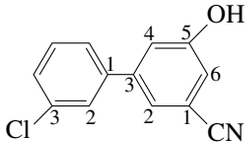
1, 3-diethenyl-5-methyl benzene

- Parent chain → benzene
- Side chain → ethenyl, methyl
- Numbering of parent chain according to Alphabet rule

EXERCISE # 3

1. [2, 3]

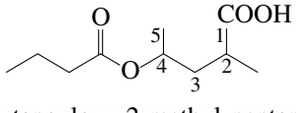
Cyanide has highest priority than hydroxyl group, hence suffix of the name would be nitrile. Other two locants on the parent phenyl ring are equidistant from –CN, numbering is done in alphabetical order as:



3-(3-chlorophenyl) 5-hydroxy benzonitrile

2. [2, 4]

Here, –COOH has higher priority than ester group, hence the compound is an alkanoyloxy acid, not a carboxy ester, Also,

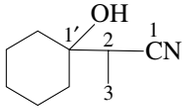


4-butanoyloxy-2-methyl pentanoic

As locant R–C– is named as alkanoyl.

3. [1, 4]

Cyanide has higher priority than hydroxy, compound would be numbered correctly as:



Parent chain has only three carbon.

Correct IUPAC name would be

2-(1-hydroxycyclohexyl)propane nitrile.

4. [1, 2]

(1) Numbering will start from carbon where two methyl groups are present and the name should be 3-ethyl-1, 1-dimethyl cyclohexane.

(2) Correct IUPAC name is 1, 3-dimethyl benzene (Meta is not used in IUPAC naming)

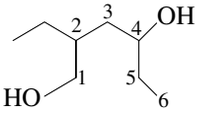
(3) It has correct name, carbons of two –CN groups are terminals of parent chain.

(4) It has correct name as –OH is the principal functional group with equidistant ethyl and methyl locants. Numbering is done in alphabetical order starting from carbon bearing –OH group.

5. [3, 4]

(1) Mentioned name is incorrect, carbon of –CHO is a part of parent chain as it gives the longest chain with more number of locants on it. The correct IUPAC name would be 4-methyl-5-oxopentanoic acid.

(2) The mentioned name is wrong as it has smaller parent chain. The correct name would be



2-ethyl-1, 4-hexanediol

(3) and (4) are correctly named.

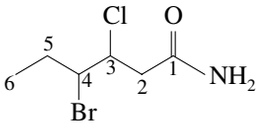
6. [1, 4]

(1) When carbon containing principal functional group is directly on a ring, normal suffix (hereoate) cannot be used. In present case, carboxylate suffix should have been used and correct IUPAC name would be "methyl cyclohexane carboxylate".

(4) When there are two carbon containing principal functional groups (now –COOH), their carbon atoms become terminals of the parent chain irrespective of chain length, The correct name of this compound would be 2-butyl-4-ethyl pentane-dioic acid.

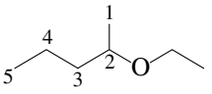
(3) and (4) have correct IUPAC names mentioned as:

(2)



4-bromo-3-choro hexanamide

(3)

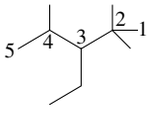


2-ethoxy pentane

7. [2, 3]

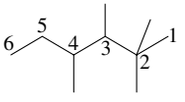
In option (1), the longest alky chain has not been considered as parent chain. Both (2) and (3) satisfy the given condition.

(2)



3-ethyl-2,2,4-trimethyl pentane

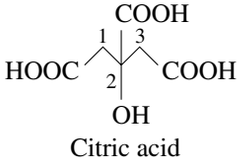
(3)



2,2,3-4-tetramethyl hexane

In (4), there is no quaternary carbon atom.

8. [1]



Citric acid

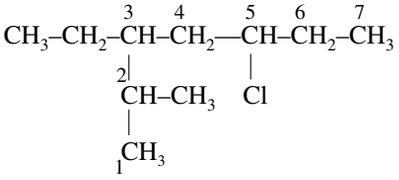
2-hydroxy-propane-1, 2, 3-tricarboxylic acid.

9. [1]

$\underset{5}{CH_3}\text{–}\underset{4}{CH}\text{=}\underset{3}{CH}\text{–}\underset{2}{C}\equiv\underset{1}{C}\text{–H}$ pent 3 en-1-yne

because Numbering takes place according to lowest locant rule.

10. [1]

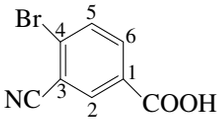


- When parent chain have same number of carbon from either side then maximum substituents contains chain must be preferred

• Numbering takes place according to lowest locant rule.

11. [1]

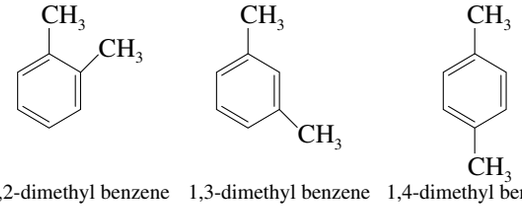
–COOH group has higher priority than –CN, hence numbering is started from the ring carbon where –COOH is present.



4-bromo-3-cyano benzio acid

12. [1]

There are only three positional isomers possible for dimethyl benzene



1,2-dimethyl benzene 1,3-dimethyl benzene 1,4-dimethyl benzene

Hence, the IUPAC name possible for dimethyl benzene.

13. [4]

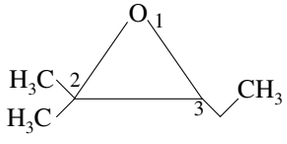
–COOH is directly on cyclopentane ring, its correct IUPAC name woud be 3-chlorocyclopentane carboxylic acid.

14. [3]

Double bond has no preference over triple bond. In the given dioic acid, both double and triple bonds are equidistant from terminals, numbering has been done in alphabetical order where 'ene' comes before y of 'yne'.

15. [4]

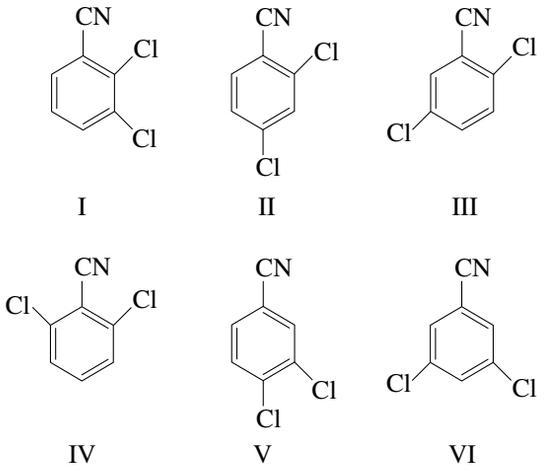
Numbering starts from oxygen in case of oxirane. However, the number series with smaller number at first occasion of difference will be the correct one as:



The correct IUPAC name of this compound is 3-ethyl-2, 2-dimethyl oxirane.

16. [4]

The six different isomers of the given compound are



17. [3]

The structure IV is most polar as the resultant of two C–Cl dipole vectors would be aligned with –CN dipole, would be added giving maximum dipole moment.

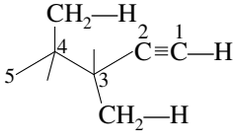
18. [4]

The structure VI is least polar because the resultant of two C–Cl dipole vectors would be at 180° angle to –CN dipole and in opposite direction.

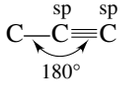
19. [1]

Carbon atom directly attached with benzene ring is benzylic C and H attached to such C- known as benzylic H.

20. [2]

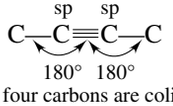
(A) 

Carbon 1, 2 and 3 are collinear as



Also, it has only three (underdline) non-equivalent hydrogen, gives three chloro alkynes in substitution reaction.

(A) → (P, S)

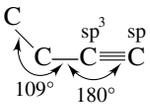
(B) 

All four carbons are colinear

Also, it has all six hydrogen equivalent, hence only one product after a hydrogen is substituted by chlorine.

(B) → (Q, R)

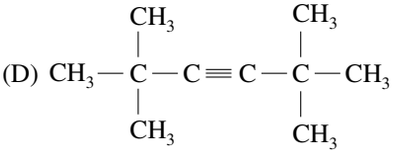
(C) $CH_3—CH_2—C\equiv C—H$



Only three carbons collinear

Also, it has three non-equivalent (underline) hydrogens, hence gives three different products after substitution of a H by Cl.

(C) → (P, S)

(D) 

Hence, the two sp-hybridised carbons and two α-carbon bonded to sp carbons are collinear.

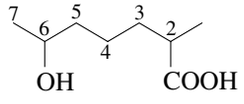
Also, all its hydrogen atoms are equivalent, gives only one chlorinated product on substitution of a H by Cl.

(D) → (Q, R)

21. [1]

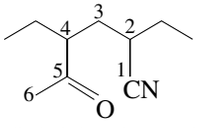
(A) → (P); (B) → (R, S); (C) → (R, S); (D) → (Q, S)]

(A) Naming ending with anoic acid and parent chain has seven carbon atoms.



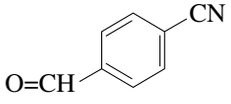
6-hydroxy-2-methyl heptanoic acid

(B) Name ending with nitrile and parent chain six carbon atoms.



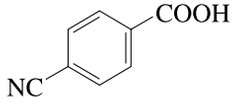
2,4-diethyl-5-oxohexanenitrile

(C) Name ending with nitrile and parent chain has six carbon atoms.



4-formylbenzontrile

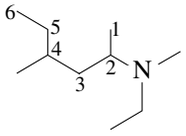
(D) Name ending with suffix nitrile and the parent phenyl ring has six carbon atoms.



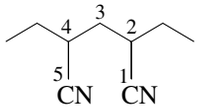
4-cyano benzene carboxylic acid

22. [3]

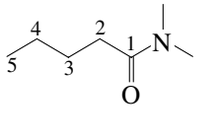
(A) → (P, Q, S); (B) → (Q, R); (C) → (P, R); (D) → (Q)

(A) 

It has 3° N-atom. Parent chain has six carbon atoms. It has C-4 and C-2 tertiary carbon.

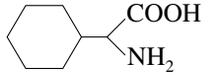
(B) 

It has no tertiary N-atom. C-2 and C-4 are tertiary carbon. Parent chain has 5 carbon.

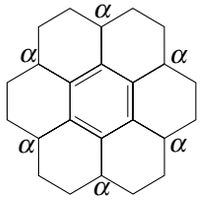
(C) 

Its nitrogen is tertiary. Parent chain has five carbon.

(D) It has two tertiary carbon. Parent chain has only two carbon.



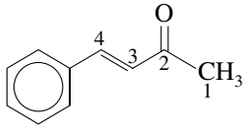
23. [6]



Each indicated α–C have 1α–H

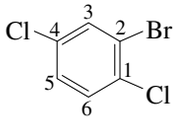
So total number of α–H = 6.

24. [4]



Functional group containing chain selected as parent chain.

25. [7] Apply least locoint number rule

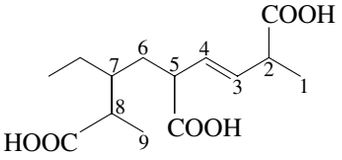


2-bromo-1,4-dichloro benzene

26. [8]

All three carbon of three –COOH are sp^2.

Three oxygen, one in each –COOH are sp^2.

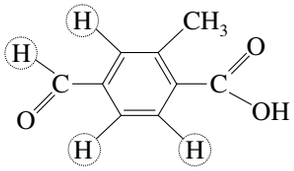


7-ethyl-3-noene-2,5,8-tricarboxyic acid

Both C-3 and C-4 carbons are sp^2.

27. [4]

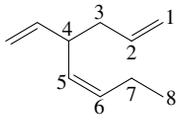
The structure of given compound is



Only hydrogen atoms attached to sp^2 hybridised carbon atoms can be coplanar. Labelled hydrogens are coplanar.

28. [8]

It has a further longer chain than the one indicated in the given name.

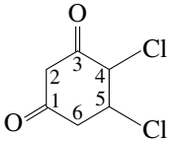


Given: 3-(-1-butenyl)-1, 5-hexadiene

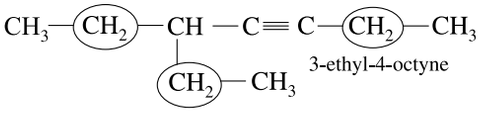
IUPAC: 4-ethenyl-1, 5-octadiene

29. [9]

When this compound is numbered correctly as sum of position of two chorine atoms is



30. [6]

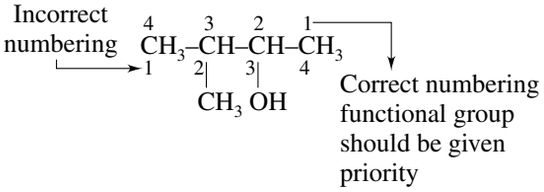


3-ethyl-4-octyne

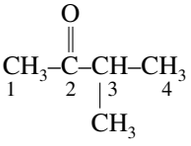
Al the hydrogens of $–CH_2–$ are secondary, hence 8 secondary H.

EXERCISE # 4

1. [3]



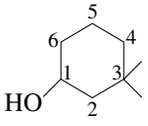
2. [2]



3-methyl butan-2-one or 3-methyl-2-butanone

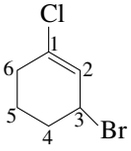
Keto (–C–) functional group is given priority.

3. [3]



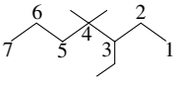
Carbon with –OH group is given C_1, thus it is 3,3-dimethyl-1-cyclohexanol.

4. [2]



Unsaturation (double bond) is given priority over halogen, So, the correct IUPAC name is 3-Bromo-1-chlorocyclohexene

5. [4]

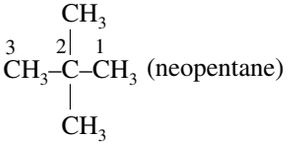


Numbering of parent chain takes place according to least locant number rule thus correct IUPAC name is 3-Ethyl-4, 4 dimethylheptane.

6. [4]

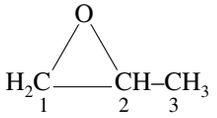
According to priority table of functional group.

7. [2]



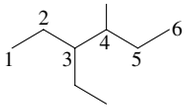
2,2-dimethylpropane.

8. [1]



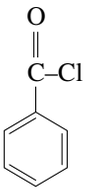
1, 2-Epoxy propane

9. [2]



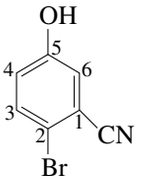
Alphabet rule applicable because least locant number rule failed thus correct IUPAC name is 3-ethyl-4-methylhexane

10. [2]



Parent chain is benzene ring so that correct IUPAC name is Benzenecarbonylchloride

11. [2]



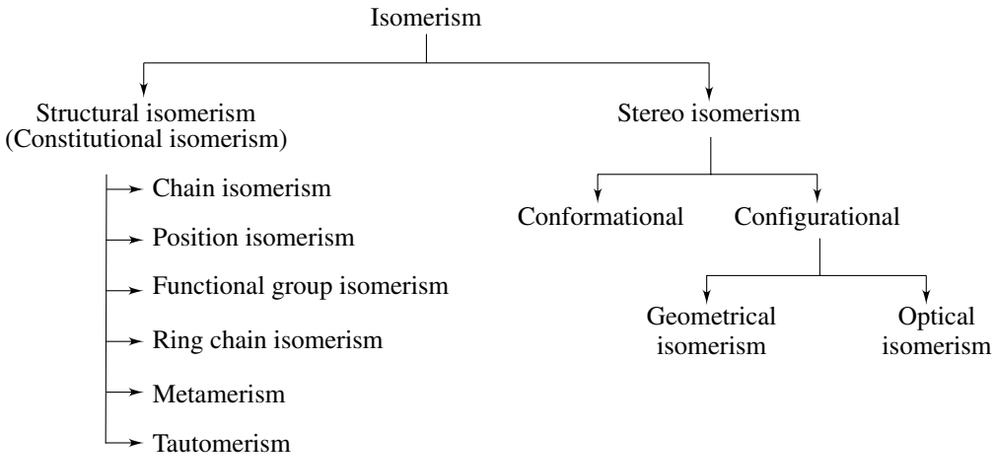
Principal group CN gets 1st locant number followed by least locant number rule thus correct IUPAC name is 2-Bromo-5-hydroxybenzonitrile.

CHAPTER 2

Isomerism

ISOMERISM

Compounds having same molecular formula but which differ in atleast some physical or chemical properties is known as isomers and the phenomena is said to be isomerism.



STRUCTURAL ISOMERISM

It is due to different molecular structural arrangement having same molecular formula so that properties will be different.

The structural isomerism may be classified into six categories. These are:

(i) **Chain Isomerism:** It is due to arrangement of carbon atom so that size of parent chain or size of side chain must be different.

(ii) **Position of isomerism:** It is due to different locant number of functional group or multiple bond or side chain along the same parent chain.

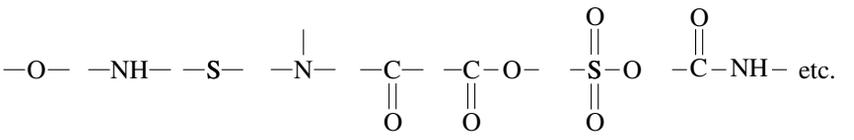
(iii) **Functional group isomerism:** It is due to presence of different functional group.

(iv) **Ring Chain Isomerism:** It is due to mode of linking of carbon atom so that same molecular formula correspond to both open and cyclic skeleton is known ring chain isomerism.

- For ring chain isomerism double bond equivalent (D.B.E) $\neq 0$.
- All ring chain isomers are always functional group isomers.

(v) **Metamerism:** It is due to different size of alkyl group along the same divalent functional group.

Condition: Polyvalent functional group containing substances will show metamerism.These are:



(vi) Tautomerism:

- Tautomerism is a special type of functional group isomerism which arises due to the oscillation of atom, mostly H-atom as proton between polyvalent atoms.
- Such isomers are directly and readily interconvertible under ordinary conditions, and the isomers are called tautomers.
- Tautomerism is chemical process and catalysed by acid or base.
- Tautomers exist in dynamic equilibrium.
- They have no separate existence under ordinary conditions.
- The other names of tautomerism are 'desmotroprism' or 'prototropy' etc.

Classification in Tautomerism

- **On the basis of migrated atom**

  Cation migrate → Cationotropy

  Proton migrate → Prototropy

  Anion migrate → Anionotropy
- **On the basis of system**

  Shiftting between 1, 2 atom – dyad system

  Shiftting between 1, 3 atom – triad system

  Shiftting between 1, 4 atom – tetrad system

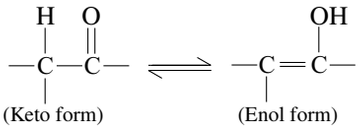
  Shiftting between 1, 5 atom – pentad system

Keto Enol Tautomerism

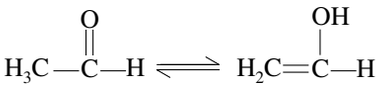
Condition: Carbonyl compound must have atleast one α-H or acidic-H

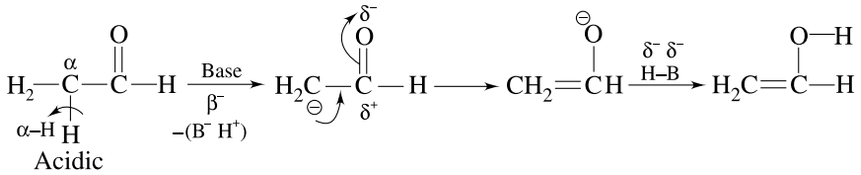
It is Triad system because shiffing of proton occured between 1, 3 position.

- When the tautomers exist in the two forms keto and enol then, such type of tautomerism is called keto-enol tautomerism.



Base catalysed tautomerism mechanism





- It is important to recognise that the enol is a real substance capable of independent existence it is not a resonance from of the carbonyl compound.
- **Following compound cannot show keto-enol tautomerism**

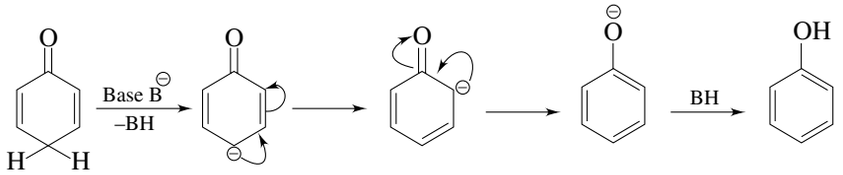
  (i) Carbonyl compounds do not have α-H can't show keto-enol tautomerism.

  (ii) Carboxylic acid and acid derivative except acid amide can't show keto-enol tautomerism.

(iii) For keto-enol tautomerism, the tautomeric form must be geometrically favourable.

- **Para tautomerism**

  When double-bond is present between α and β position (between C_3 and C_4) of cyclic ketone then 'H' of C_5 takes part in tautomerism, known as 1, 5 or para tautomerism.



- **% of enol in different compound**

  Enol content ∝ number of acidic H

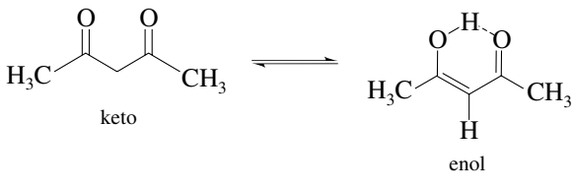
  ∝ stability of enolate ion

  ∝ stability of enol (due to intramolecular-H/aromatic character)

Comparison of Stability of Keto and Enol Forms

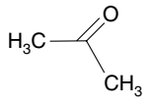
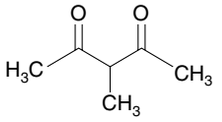
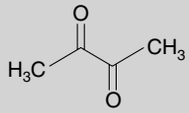
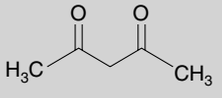
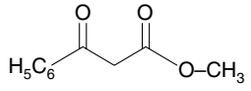
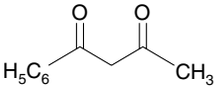
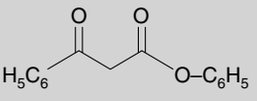
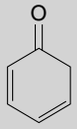
(i) In simple aldehydes and ketones, keto form is more stable than enol form because C=O bond is stronger than C=C bond.

(ii) In complex structures like 1,3-diketo compounds, enol form is more stable because it is stabilized by resonance as well as intramolecular hydrogen bonding.



Percentage Composition of Tautomeric Mixture

Percentage of enol content of some compounds is given below in the table.

Compounds	Enol percentage	Compound	Enol percentage
	0.00025		31.0
	0.0056		80.3
	4.8		89.00
	7.7		99.00

Calculation of Number of Structural Isomers

Profile-1: Isomers of Alkane

Molecular formula of alkane	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	C_9H_{20}	$C_{10}H_{22}$
Number of isomer	1	1	1	2	3	5	9	18	35	69

Trick: Number of isomer in alkane = (2n – 1), where n = number of isomer in previous alkane (except C_8H_{18})

Profile-2: Isomers of Alkyl Radical

Type of alkyl	$-CH_3$	$-C_2H_5$	$-C_3H_7$	$-C_4H_9$	$-C_5H_{11}$	$-C_6H_{13}$
Number of isomer	1	1	2	4	8	17

Profile-3: Isomers in different molecular formula

Step-1: Find D.B.E for given molecular formula.

Degree of unsaturated (DU)/Double bond equivalent (DBE) = $(C + 1) - \left(\frac{H + X - N}{2}\right)$

Step-II: Select nature of bonding between C-C

D.B.E	Possible bonding between C–C
0	(–) single bond
1	(=) double bond/| ring
2	1 (≡) triple bond | 2 (=) double bond | 1 (=) double bond + 1 ring | 2 ring
4	Benzene ring (3(=) double bond + 1 ring)

Step-III: Select the possible functional group

- If Molecular formula (M.F.) contains C, H only or C, H and (halogen), then draw and find out number of isomers (for alkane refer above table).
- If M.F. contains C, H, N, O, etc. then select possible functional group as follows:

M.F.	D.B.E	Possible functional group
$C_nH_{2n+2}O$	0	Alcohol/ether
$C_nH_{2n}O$	1	Aldehyde/ketone
$C_nH_{2n}O_2$	1	Carboxylic acid/ester/ hydroxy carbonyl
$C_nH_{2n+3}N$	0	1°/2°/3° amine
$C_nH_{2n-1}N$	2	Cyanide/isocyanide

Step-IV: Separate possible functional groups and radical parts then number of isomers of radical is equal to number structaur of some of corresponding functional group.

Stereo or Space Isomerism

Compound having same molecular formula and structural formula but differ due to spatial orientations of groups or atoms is known as stereo isomers and phenomenon is termed as stereo isomerism.

(1) Geometrical Isomerism

- Compound having same molecular formula but differ in their properties due to the difference in the orientations of attachment of same atoms or group in their molecule.
- It is caused due to the restricted rotation about double bond in open chain and about single bond in cyclo alkane.

Condition of Geometrical isomerism

1. Rotation must be restricted.
2. Each blocked atom must have pair of different groups/atoms.

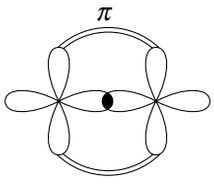
Geometrical isomerism is exhibited by following type of compounds.

(a) Compounds containing C = C, C = N, N = N, etc.

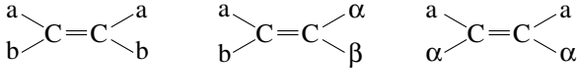
(b) Compounds containing cyclic structure.

1. Geometrical isomerism in alkene:

- Generally alkene show Geometrical isomerism because by the overlapping of two unhybridised carbon, formation of π–bond takes place which produce restricted rotation.



- All alkenes do not show Geometrical isomerism but not those in which both the double bonded carbon attach with different group or atoms.



Configuration of Geometrical isomer

1, *cis/trans* configuration:

- ***Cis* form:** Such isomer in which atleast one pair of similar groups/atoms attaches on the **same side** of double bonded carbon.
- ***Trans* form:** Such isomer in which atleast one pair of similar groups/atoms attaches on the **opposite side** of double bonded carbon.

ex.

(*cis*-2-Butene) (*trans*-2-Butene)

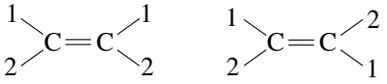
Comparison of properties of *cis* or *trans*-isomers: (With respect to 2-Butene)

S.No.	Properties	Answer	Reason
1.	Stability	*Trans* > *cis*	Trans have less mutual repulsion between the groups
2.	Dipole moment	*Cis* > *trans*	Trans have zero dipole moment
3.	Polarity	*Cis* > *trans*	Cis have more dipole moment so more polar
4.	Solubility in water	*Cis* > *trans*	Cis is more polar so more soluble in water
5.	Boiling Point (BP)	*Cis* > *trans*	Cis is more polar so more BP
6.	Melting Point (MP)	*trans* > *cis*	Trans is symmetrical molecule therefore better packing in crystal lattice, so it has more MP

E-Z Configuration:

E $\rightarrow$ Entgegen (opposite), Z $\rightarrow$ Zusammen (same)

- **E-form:** when two same priority groups attach on the **opposite side** of double bonded carbon, then it is called as E-form.
- **Z-form:** when two same priority groups attach on the **same side** of double bonded carbon, then it is called as Z-form



Z-form E-form

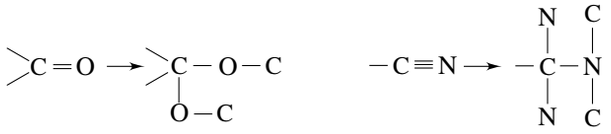
- **Priority rule:** Chan, Ingold and Prelong proposed a **sequence rule** (CIP Rule)

Rule-1 When atom or group of atoms which are directly attached to the stereogenic centre have higher atomic number will have higher priority.

Rule-2 When the atomic number is same, then higher atomic weight group or atom have higher priority

Rule-3 When both atomic number and atomic weight are same then priority will be decided by the next joining atom. If one of the atom from next joining atoms have higher atomic number then it corresponds to higher priority and so on.

Rule-4 If multiple bonded groups attach to the double bonded carbon, then they are considered in following manner.

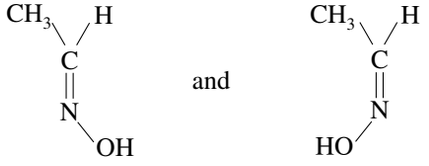


2. Geometrical isomerism in oxime: Oxime of aldehyde and oxime of unsymmetrical ketone also show geometrical isomerism except Oxime of formaldehyde.

- **In aldoximes**

  Syn isomer: When –OH group and H atom is on same side.

  Anti isomer: When –OH group and H atom is on opposite side.

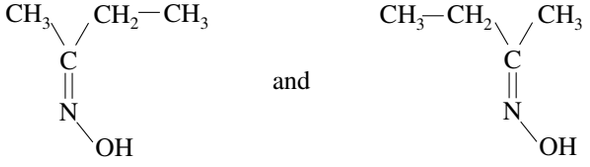


Syn-Acetaldoxime and Anti-Acetaldoxime

- **In unsymmetrical ketoxime**

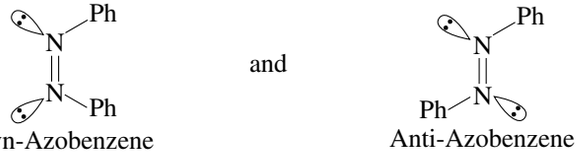
  Syn isomer: When –OH group and the alphabetically preferred alkyl are present on the same side of double bond, then it is called as syn form.

  Anti isomer: When –OH group and the alphabetically preferred alkyl are present on the opposite side of double bond, then it is called as Anti form.



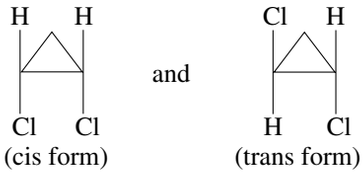
Syn-ethylmethyl ketoxime and Anti-ethylmethyl ketoxime

3. Geometrical isomerism in azo compounds: All azo compounds show geometrical isomerism
ex. Ph–N = N–Ph



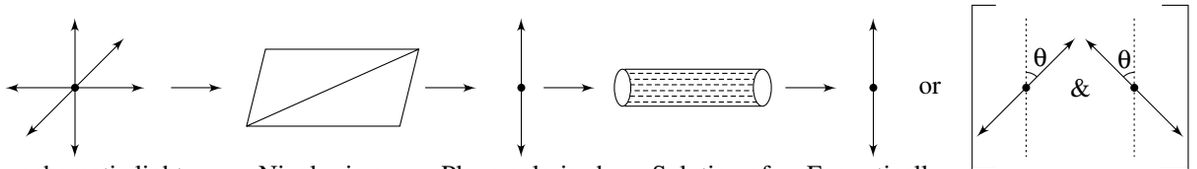
Syn-Azobenzene and Anti-Azobenzene

4. Geometrical isomerism in cycloalkane: In cyclic compound the rotation about C–C single bond is restricted because of the rigidity caused by the presence of other carbon of the ring which keep them tightly held, thus a disubstituted cyclic compound (having the two substitution at the separate carbon) will also show Geometrical isomerism.



(cis form) (trans form)

Optical Isomerism: It is due to behaviour of plane of polarised light. Certain organic compounds, have the ability to rotate plane of polarised light in either of the directions through certain angle when their solution is placed in the path of plane of polarised light known as optical active compounds. This property of substances is termed as **optical activity**.



Monochamotic light | Nicol prism | Plane polarised light | Solution of compound | For optically inactive | For optically acitive

Specific rotation: Optical rotation caused by 1 gm/ml solution in 1 dm length polarimeter tube at specific temp and source of the light.

$$\text{observed rotation} \propto \text{concentration} \times \text{length}$$

$$\theta = [\alpha]_D^T \times \text{concertration} \times \text{length}$$

$$[\alpha]_D^T = \frac{\theta}{\text{concertration} \times \text{length}}$$

$$[\alpha]_D^T = \frac{\theta}{c \times l}$$

- $$\text{Enantiomeric axis} = \frac{d - \ell}{d + \ell} \times 100 = \frac{\text{Optical Rotation}}{\text{Specific Rotation}} \times 100$$

θ = The observed rotation (Optical rotation)

α = Thereotical rotation (Specific rotation)

The magnitude of observed rotation (θ) depends upon following factors.

(1) Nature of substance.

(2) Nature of solvent.

(3) The concentration of the substance in tube. (C gm/mol)

(4) The length of the solution column. (l dm) [1 dm = 10 cm]

(5) The temperature of the experiment (t°C)

(6) The wavelength of the light used. (λÅ)

Optical Isomers

All these substances are known to exist in two stages.

(1) Optically active isomer:

(a) One rotating the plane of polarised light to the right is named **dextrorotatory** (Latin, Dexter-right) or direction (+) form.

(b) One rotating the plane of polarised light to the left this form is named **laevorotatory** (Latin, laevous = left) or direction (–) form.

(2) Optically inactive isomer:

(a) ***Meso compound:***

- Compound having two or more chiral carbons as well as POS, COS and AAOS is known as meso compounds.
- Meso compounds are optically inactive due to internal compensation.

- Meso are optically inactive, even though considered in optical isomer.
- Two different meso are diastereomers of each other.

(b) ***Racemic mixture:***

- An equimolar mixture of d and l isomer which does not rotate the plane polarised light hence it is optical inactive named (±)- mixture or **Racemic mixture**.
- Racemic mixture are optically inactive due to external compensation.
- Racemic mixture are optically inactive, and not considered in optical isomer.

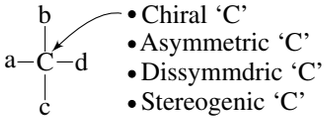
Theoretical Condition for optical activity:

- Compound must be chiral.
- Compound is non-superimposable on their mirror image.

Type-1: Optically active compound with chiral 'C'.

Chiral 'C': Carbon (sp^3) having all four different groups is called as chiral 'C'.

- Chirality is defined only at sp^3 hybridised atom not at sp or sp^2 atom.



$a \neq b \neq d \neq c$

- Compound having only one chiral C, their molecule must be chiral.
- Compound having more than one chiral C, their molecule may be or may not be chiral depending upon symmetry elements.

Symmetry elements:

(1) Plane of symmetry (POS) (σ)
(2) Centre of symmetry (COS) (i)
(3) Axis of symmetry (AOS) (C_n)
(4) Alternative symmetry(AAOS) (S_n)

POS: An imaginary plane which bisects the molecule into two equal half and equal half must be mirror image of each other is known as plane of symmetry.

COS: An imaginary point within a molecule through which draws a line in opposite directions and gets same atom at same distance is known as centre of symmetry. This rule is applicable for each atom.

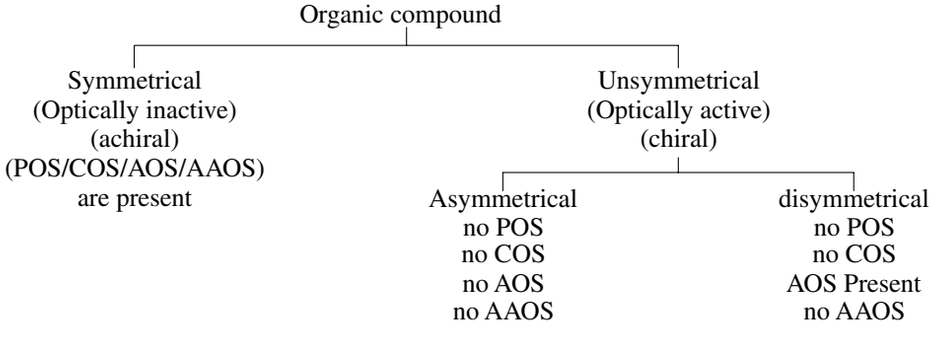
AOS: An imaginary axis through which rotates a molecule by minimum angle that molecule again reappears is known as axis of symmetry

$$n = \frac{360}{\theta}$$

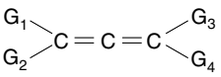
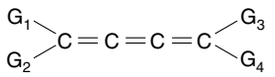
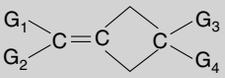
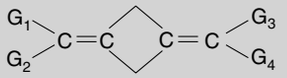
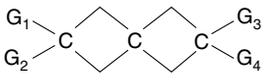
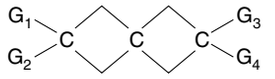
θ	360°	180°	120°	90°	72°	60°
C_n	C_1	C_2	C_3	C_4	C_5	C_6

• C_1 is not included in axis of symmetry.

AAOS: An imaginary symmetry element in which, first consider imaginary axis of symmetry after that consider imaginary POS $\perp$ with AOS and again it's molecule reappears then it is known as alternative axis of symmetry.



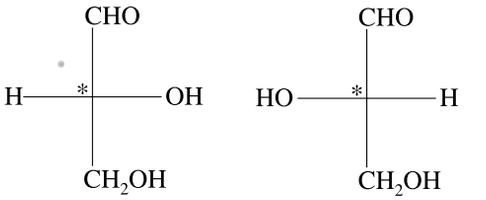
Type-2 Optically active compound without chiral 'C'

Continuous π-bond/ Ring/both	Even • non planer • optically active When $\boxed{G_1 \neq G_2}$, $\boxed{G_3 \neq G_4}$	Odd • Planner • Always inactives • Can show G.I. When $\boxed{G_1 \neq G_2}$, $\boxed{G_3 \neq G_4}$
(1) Allenes		
(2) Cyclo-alkylidenes		
(3) Spiranes		

Configuration of optical isomer

(1) D, L-SYSTEM (RELATIVE CONFIGURATION):

- It is applicable for only proper Fischer projection formula
- It is mostly used for assigning D/L configuration of carbohydrate (Poly hydroxy carbonyl compound) and protein (α-amino acid).
- It represents relative configuration with respect to glyceraldehydes.
- Following configuration of glyceraldehydes is considered as standard configuration.



D-glyceraldehyde (–OH is on R.H.S) L-glyceraldehyde (–OH is on L.H.S)

- In carbohydrate, group of only last chiral carbon compares with D/L glyceraldehydes

(2) R–S SYSTEM (ABSOLUTE CONFIGURATION):

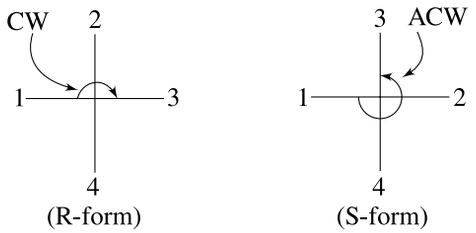
- R → Rectus (Right) S → Sinister (Left)
- R–S nomenclature is assigned as follow:

Rules of R-S configuration in Fischer formula

Step-I: By the set of **sequence rule**, we give the priority order of atom or group connected though the chiral carbon.

Step-II: If atom/group of minimum priority is present on the vertical line, then put arrow 1 → 2 → 3.

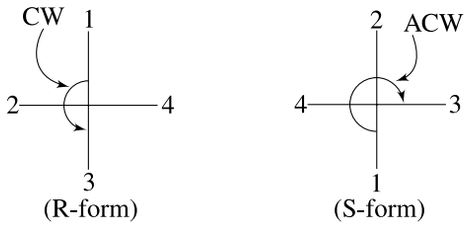
If it is clockwise ⇒ R but Anti clockwise ⇒ S



(R-form) (S-form)

Step-III: If minimum priority group present on the horizontal line, then put arrow 1 → 2 → 3

If it is clockwise ⇒ S but anticlockwise ⇒ R



Rule of R-S configuration in wedge dash formula

Step-I: By the set of sequence rule, we give the priority order of atom or group connected though the chiral carbon.

Step-II: If atom/group of minimum priority is present on upward the plane (broken line), then put arrow $1 \rightarrow 2 \rightarrow 3$.

If it is clockwise $\Rightarrow$ R but Anti clockwise $\Rightarrow$ S

Step-III: Step-II must be satisfied first by **golden rule** as given below.

By interchanging odd pair of groups across the chiral carbon, its R–S configuration will be opposite.

By interchanging even pair of groups across the chiral carbon, its R–S configuration will remain same

Enantiomers

- *d* and ℓ form of any compound is called enantiomer.
- Non-superimposable mirror image are called enantiomers.
- Opposite configuration of any compound are called enantiomers.

Properties of enantiomers

(1) Enantiomers have chiral molecule (optically active).

(2) Enantiomers have identical physical properties like BP, MP, refractive index, density, etc.

(3) They rotate PPL in opposite direction but to the equal extent of optical rotation.

(4) They have identical chemical properties, however their rate of reaction will differ if they combine with other optically active reagents.

$$\left.\begin{array}{l} R + X \xrightarrow{k_1} P \\ S + X \xrightarrow{k_2} P \end{array}\right\} \text{ X is optically inactive, then } K_1 = K_2$$

$$\left.\begin{array}{l} R + Y \xrightarrow{k_3} P \\ S + Y \xrightarrow{k_4} P \end{array}\right\} \text{ Y optically active, then } K_3 \neq K_4$$

Diastereomers: Such configurational isomers which are neither mirror images nor superimposable on each other are called as diastereomers.

Properties of diastereomers

(1) They are generally optically active, however geometrical isomers are exceptions.

(2) They have different physical properties like MP, BP, density, solubilities and value of specific rotation.

(3) They are separated by fractional distillation, fractional crystallisation and chromatography, etc.

(4) They exhibit similar but not identical chemical behaviour.

Pseudo chiral carbon: Those achiral carbon converted into chiral carbon whenever stereochemistryof one of the valency will change.

Prochiral carbon: Those achiral carbon converted into chiral carbon if one of the valency changes by different group.

Calculation of stereo isomer

Type-1: Compound showing only geometrical isomers

Case-1 If $R_1 \neq R_2$ (Unsymmetrical Compound)

(R_1–CH=CH–CH=CH–R_2)

Number of Geometrical isomers = 2^n

n → number of stereogenic (double bond) centre

Case-2 If $R_1 = R_2$ (Symmetrical Compound)

(R_1–CH = CH–CH=CH–R_2)

Number of Geometrical isomers = $2^{n-1} + 2^{p-1}$

If n is even number then, $p = \frac{n}{2}$;

If n is odd number then, $p = \frac{n+1}{2}$

Type-2: Compound showing only **Optical isomers**

Compound	Optically active isomer (a) or Number of d and ℓ isomer	Number of meso isomer (m)	Total number of optical isomer (a + m)
(1) Unsymmetrical	2^n	0	2^n
(2) Symmetrical n = even number	2^{n-1}	$2^{n/2-1}$	$2^{n-1} + 2^{n/2-1}$
(3) Symmetrical n = odd number	$2^{n-1} - 2^{\frac{n-1}{2}}$	$2^{\frac{n-1}{2}}$	2^{n-1}

n = number of chiral carbon

Type-3: Compound showing both **Optical isomers and Geometrical isomers**

(1) Compound Unsymmetrical

Number of stereo isomer = 2^n

n = Number of chiral carbon and Number of π-bonds which showing geometrical isomersism

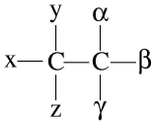
(2) Compound symmetrical – draw and check

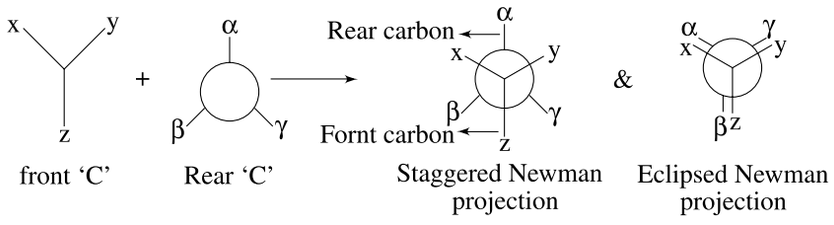
Conformational isomerism: Such non-identical arrangements of atoms or group in a molecule obtained by the free rotation about a single bond that can easily be reconverted at room temperature are known as conformational isomers or conformers.

Condition: Molecule must have at least only 3 continuous σ bonds.

Projection of Tetrahedral Carbon Atom:

1. Newman projection: The two σ bonded carbon atoms represented by circle by one behind the other so that only the front carbons are depicted from the centre of the circle while C–H bonds of back carbon are drawn from the circumference of circle as

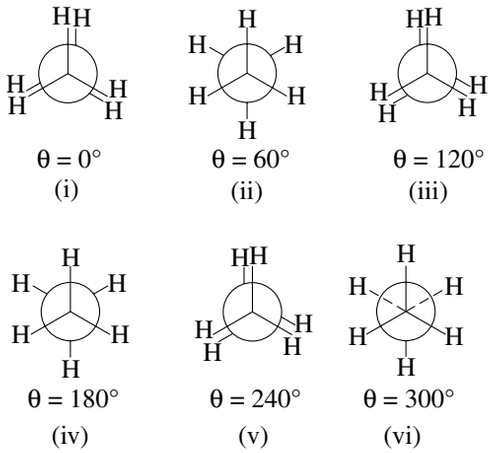




2. Sawhorse Projection: The two σ bonded e expressed by slanted and elongated line

Eclipsed sawhorse projection & Staggered sawhorse projection

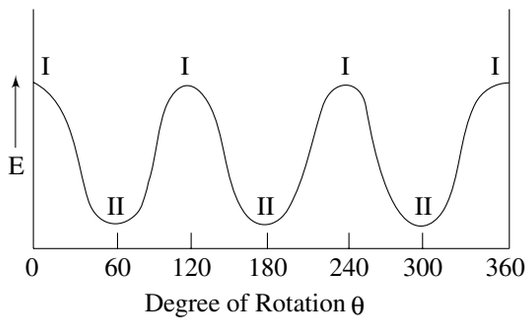
Conformation of ethane:



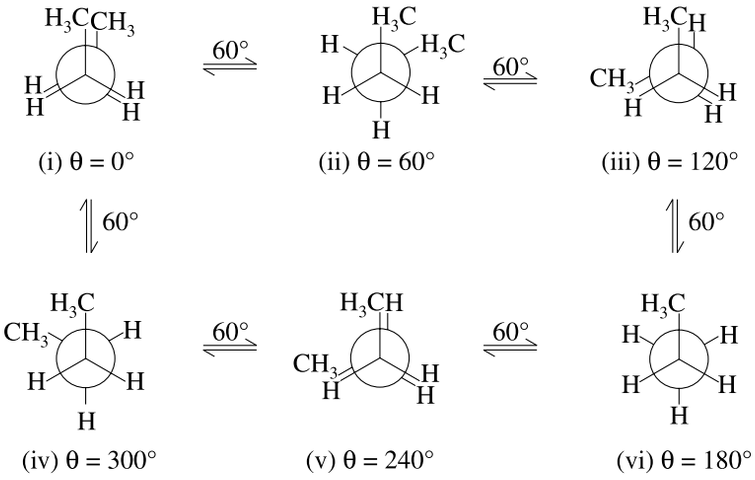
- Ethane molecule contains infinite number of conformers
- The extreme conformation of ethane molecules is staggered and eclipsed
- All other conformer erist in between 0° + 60° known as skew form.
- The energy of staggered conformation is lower than eclipsed conformation by 2.8 kcal/mole (11.7 kJ/mole).
- Staggered conformation is more stable than the eclipsed conformation
- The mixture contains 99% staggered conformation and 1% eclipsed conformation.
- Eclipsed and staggered conformations are not isolated from the mixture.

Order of Stability Staggered > Skew > Eclipsed

Energy Level Comparison of Conformations of Ethane



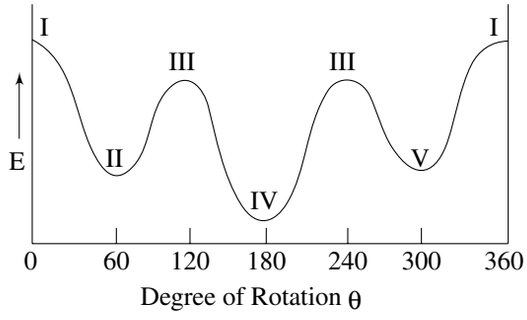
Conformations of Butane (CH_5–CH_2–CH_2–CH_3):



(i) = Fully eclipsed form (CH_3 group eclipsed by CH_3 group)
(ii) = (vi) = partial staggered form
(iv) = *anti* or *trans* (Staggered)
(iii) = (v) = partial eclipsed form (CH_3 group eclipsed by H)
Stability order: iv > ii > iii > i

Order of Stability Anti > Gauche > Partially Eclipsed > Fully Eclipsed

Energy Level Comparison of Conformations of n-butane

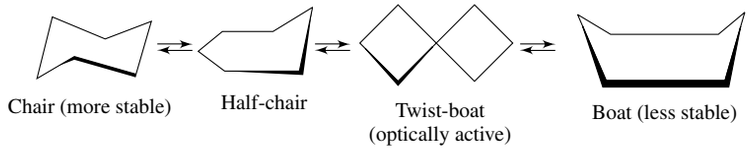


Cycloalkanes

In cyclopropane and cyclobutane (both planar), C–C–C angle are 60° and 90° respectively. Cyclopentane and cyclohexane (considered planar though non-planar) with C–C–C angles 180° and 120° respectively.

Baeyer or angle strain	Cyclopropane	Cyclobutane	Cyclopentane	Cyclohexane
$\frac{1}{2}$ [109°28′ – angle]	24°44′	9°44′	0°44′	–5°16′

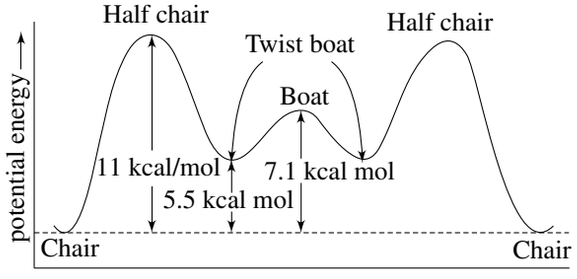
Conformations of Cyclohexane: A cyclohexane ring can assume many shapes and any single cyclohexane molecule is in a continuous state of flexing or flipping into different shapes which are illustrated as follows:



Interconversion of chair forms is known as conformational inversion and occurs by rotation about carbon-carbon bonds.

The most stable conformation of cyclohexane is the chair form.

Relative energies of the conformation of cyclohexane molecule



Actual conformers of cyclohexane with relative energy are as follows :

Conformer	Chair	Twist boat	Boat	Half chair
Relative energy	0.000 kJ mol^{-1}	22.2 kJ mol^{-1}	28.9 kJ mol^{-1}	44 kJ mol^{-1} (approx.)

The relative stability of conformations of cyclohexane decreases in the order:

Chair 〉 Twist boat 〉 Boat 〉 Half chair

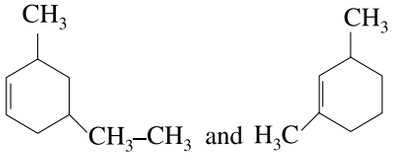
The potential energy barrier for transformation of chair form to other forms is about 37.8-46.0 kJ mol^{-1}

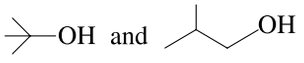
SOLVED EXAMPLE

1. Which are not position isomers?

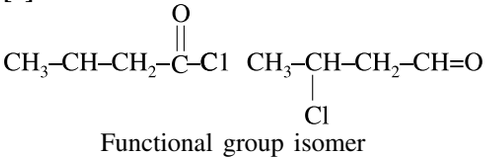
(1) $CH_3–\underset{\underset{CH_3}{|}}{CH}–\underset{\underset{CH_3}{|}}{CH}–CH_3$ and $CH_3–\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}–CH_2–CH_3$

(2) $CH_3–\underset{\underset{H}{|}}{C}–CH_2–\underset{\underset{Cl}{|}}{C}=O$ and $CH_3–\underset{\underset{Cl}{|}}{CH}–CH_2–\underset{\underset{H}{|}}{C}=O$

(3) 

(4) 

Sol. **[2]**



Functional group isomer

2. Which of the following statements regarding ethanoic acid and methyl methanoate are correct?

I. They are functional group isomers with molecular formula $C_2H_4O_2$.

II. They belong to same homologous series.

III. They have different chemical properties.

(1) I and II (2) I and III

(3) II and III (4) I, II and III

Sol. **[2]**

$CH_3–COOH$ $H–\overset{\overset{O}{\|}}{C}–OCH_3$

Ethanoic acid Methyl methanoate

→ m.f. = $C_2H_4O_2$

→ functional group differ, So belong different homologous series and also have different chemical Properties.

3. Organic compound with molecular formula $C_4H_8O_2$ cannot have the functional group

(1) carboxylic acid (2) ester

(3) dialdehyde (4) cyclic diol

Sol. **[3]**

$$D.B.E = (C + 1) - \frac{H + X - N}{12}$$

$$= (4 + 1) - \left(\frac{8}{2}\right) = 1$$

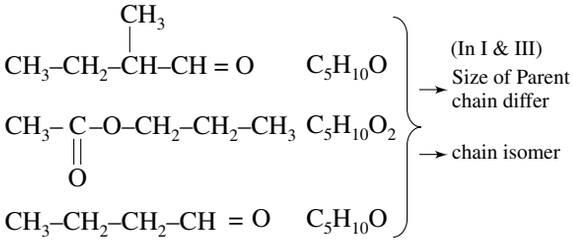
In dialdehyde, D.B.E = 2 (not possible)

4. Which of the following Compounds are structural isomers of $C_5H_{10}O$?

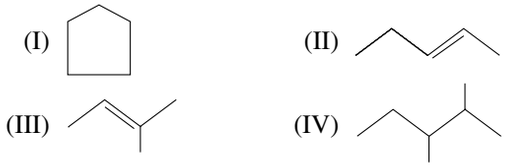
I. 2-methyl butanal
II. Propyl ethanoate
III. Pentanal

(1) I and II (2) I and III
(3) II and III (4) I, II and III

Sol. **[2]**

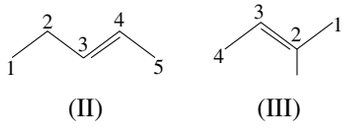


5. Select pair of chain isomers from the following



(1) I and II (2) II and IV
(3) I and IV (4) II and III

Sol. **[4]**



(II) (III)

P.C differ so they becomes Chain isomer

6. An alkyne has molar mass 96. How many different isomer (excluding stereochemical designation) are possible considering all of them to be internal alkynes?

(1) 3 (2) 4
(3) 6 (4) 8

Sol. **[3]**

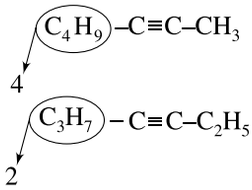
$C_nH_{2n-2} = 96$

$12n + 2n–2 = 96$

$14n = 98$

$n = 7$

m.f. = C_7H_{12}



number of possible alkyne = 4 + 2 = 6

7. How many structural isomers are possible for compounds containing C, H and O atoms only with their molar masses 100 as well as the isomers are simultaneously ketones?

(1) 3 (2) 4
(3) 5 (4) 6

Sol. **[4]**

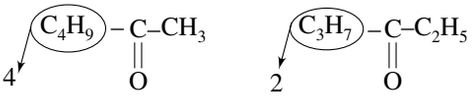
General formula of ketone $C_nH_{2n}O$

$12n + 2n + 16 = 100$

$14n = 84$

$n = 6$

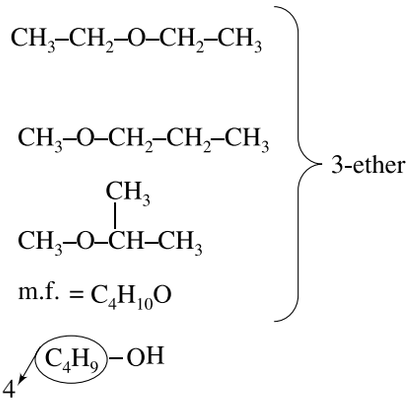
$C_6H_{12}O$



8. An organic compound has three ether isomers and it is the smallest ether which satisfy this condition. Which of the following is true regarding this compound?

(1) Only one alcohol isomer exist
(2) Four alcohol isomers exist and they are all constitutional isomers
(3) Five alcohol isomers exist and they are positional isomers of each other
(4) Molecular formula of the compound is $C_5H_{12}O$

Sol. **[2]**



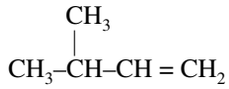
9. How many alkene isomers are possible for compound with molecular formula C_5H_{10}?

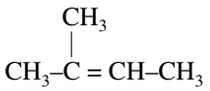
(1) 3 (2) 4
(3) 5 (4) 6

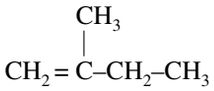
Sol. **[4]**

$CH_3–CH_2–CH_2–CH = CH_2$

$CH_3–CH_2–CH = CH–CH_3$ (cis/trans)







alkene isomer = 6

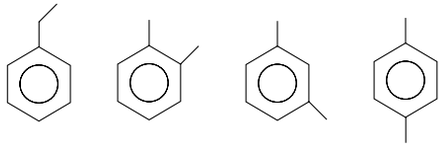
10. How many structural isomer are possible with the molecular formula C_8H_{10}

(1) 3 (2) 4

(3) 5 (4) 6

Sol. **[2]**

$$D.U = (8 + 1) - \frac{10}{2} = 4$$

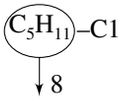


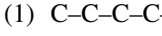
11. How many different secondary halide names can be assigned to the compounds with molecular formula $C_5H_{11}Cl$ (excluding stereoisomers)?

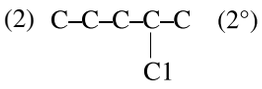
(1) 3 (2) 4

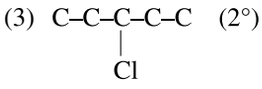
(3) 5 (4) 7

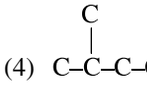
Sol. **[1]**

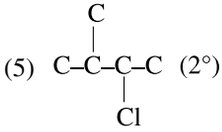


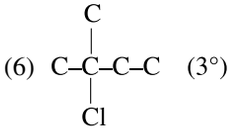
(1) 

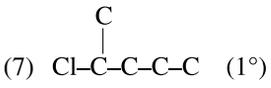
(2) 

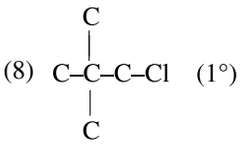
(3) 

(4) 

(5) 

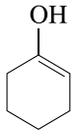
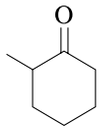
(6) 

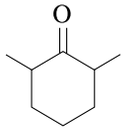
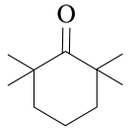
(7) 

(8) 

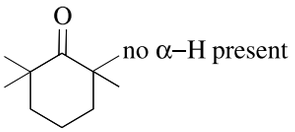
2° halide isomer = 3

12. Which of the following compound will not undergo tautomerism?

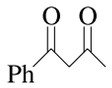
(1)  (2) 

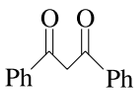
(3)  (4) 

Sol. **[4]**

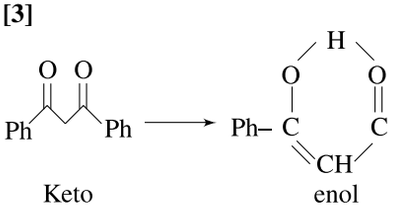


13. Which of the following compound has highest enol content?

(1)  (2) 

(3)  (4) 

Sol. **[3]**



→ Stabilised by intramolecular H-bond

→ Phenyl group, further stabilised via Resonance

14. Which of the following compounds will not show geometrical isomerism?

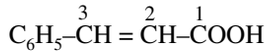
(1) 3-Phenyl-2-propenoic acid

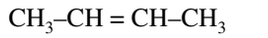
(2) 2-Butene

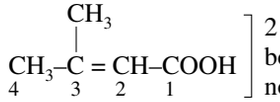
(3) 3-Methyl-2-butenoic acid

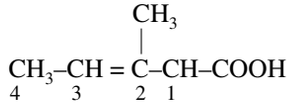
(4) 3-Methyl-2-pentenoic acid

Sol. **[3]**









15. Which of the following will have zero dipole moment?

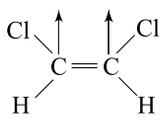
(1) *cis*-1, 2-Dichloroethene

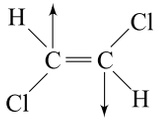
(2) *trans*-1, 2-Dichloroethene

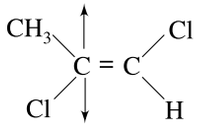
(3) *trans*-1, 2-Dichloropropene

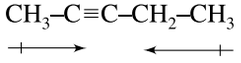
(4) 2-Pentyne

Sol. **[2]**

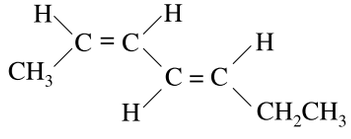








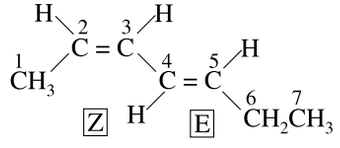
16. What is the IUPAC name of the following compound?



(1) hepta-(2E, 4Z) diene (2) hepta (2E, 4E) diene

(3) hepta-(2Z, 4E) diene (4) hepta-(2Z, 4Z)diene

Sol. **[3]**



(2Z, 4E)

17. Which of the following compounds exhibits stereioisomerism?

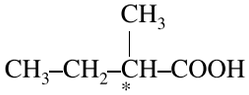
(1) 2-Mehylbutene

(2) 3-Methylbutyne

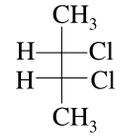
(3) 3-Methylbutanoic acid

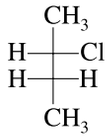
(4) 2-Methylbutanoic acid

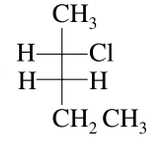
Sol. **[4]**

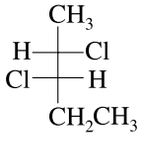


18. Which of the following is a meso compound:

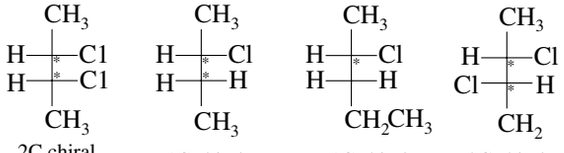
(1) 

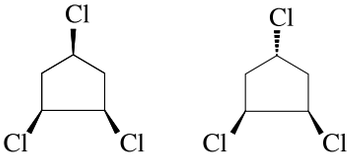
(2) 

(3) 

(4) 

Sol. **[1]**



19. 

Relation between (a) and (b) is:

(1) Enantiomer (2) Diastereomer

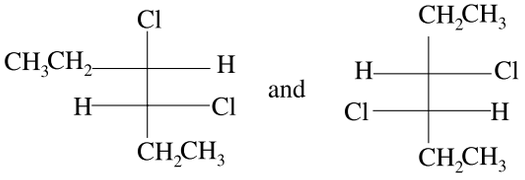
(3) Identical (4) Structural isomer

Sol. **[2]**

Stereoisomer not mirror image

Diastereomer

20. The pair of molecules shown are



(1) enantiomers

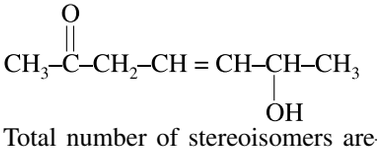
(2) diastereomers

(3) constitutional isomers

(4) two conformations of the same molecule

Sol. **[2]**

For comparison of Fischer projection, like groups should be present on vertical and horizontal lines.

21. 

Total number of stereoisomers are–

(1) 4 (2) 6

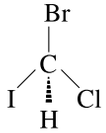
(3) 8 (4) 12

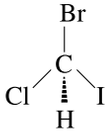
Sol. **[1]**

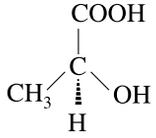
n = 2

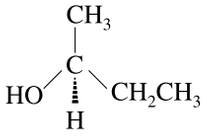
number of streoisomer = $2^2 = 4$

22. Which of the following representations have an R configuration?

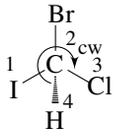
(1) 

(2) 

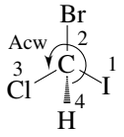
(3) 

(4) 

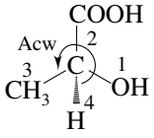
Sol. **[1]**



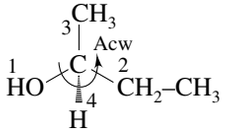
(R)



(S)



(S)



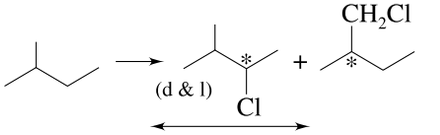
(S)

23. How many chiral compounds are possible on mono-chlorination of 2-methyl butane?

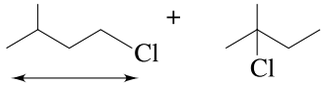
(1) 8 (2) 2

(3) 4 (4) 6

Sol. **[3]**



In each one chiral Carbon present, chiral molecule



No chiral Carbon present, achiral molecule

24. An optically pure compound x gave an $[\alpha]_D^{25} = +20.0°$. A mixture of X and its enantiomer Y gave $[\alpha]_D^{25} = +10°$. The ratio of X to Y in the mixture is:

(1) 2 : 1 (2) 1 : 3

(3) 3 : 1 (4) 1 : 2

Sol. **[3]**

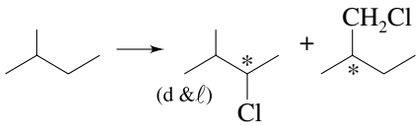
Enantiomeric axis of d = $\frac{10}{20} = \frac{1}{2} \times 100 = 50\%$

Racemic mix = 50%

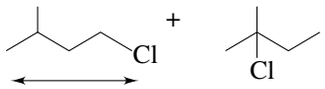
d = 25%, ℓ = 25

Total d = 50 + 25 = 75%, ℓ = 25%

$\frac{d}{\ell} = \frac{75}{25} = 3:1$

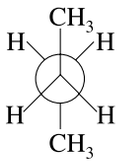


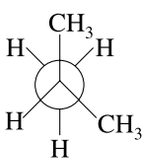
In each one chiral Carbon present, chiral molecule

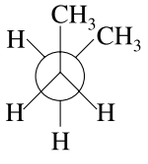


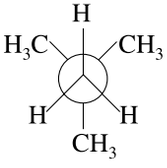
No chiral Carbon present, achiral molecule

25. The most stable conformer of 2-methyl propane is

(1) 

(2) 

(3) 

(4) 

Sol. **[2]**

Only option (2) belongs 2-methyl propane and also it is more stable

EXERCISE 1

1. Which of the following statements are correct?

I. A pair of positional isomers differs in the position of the same functional group.

II. A pair of structural isomers have the same relative molar mass

III. A pair of functional group isomers belongs to different homologous series.

(1) I and II (2) I and III

(3) II and III (4) I, II and III

2. Assuming a hydrocarbon C_5H_{10} without any double bond, how many different structures exist that contain only one alkyl group?

(1) 1 (2) 2

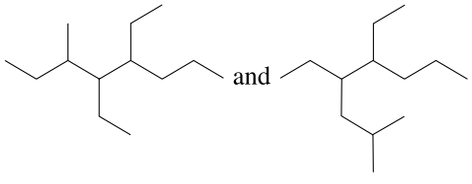
(3) 3 (4) 5

3. Which name is not possible with molecular formula C_6H_{10}?

(1) 2-hexyne (2) 3-hexyne

(3) 4-methyl-2-pentyne (4) 3-cyclopropylpropyne

4. Given compound shows which type of isomerism?



(1) Chain isomerism

(2) Positional isomerism

(3) Functional group isomerism

(4) Metamerism

5. How many structural isomers of molecular formula C_3H_6BrCl?

(1) 4 (2) 5

(3) 6 (4) 7

6. The total number of stable acyclic compounds having the molecular formula C_4H_8O is:

(1) 4 (2) 7

(3) 11 (4) 14

7. Which of the following statements concerning 3, 4-dibromo-1-pentene and 3, 5-dibromo-2-pentene are correct?

I. They have same molecular formula $C_5H_8Br_2$

II. They are positional isomers

III. They have similar chemical properties.

(1) I and II (2) I and III

(3) II and III (4) I, II and III

8. Number of structural isomers of compound having molecular formula C_4H_7Cl is:

(1) 4 (2) 8

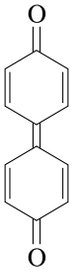
(3) 12 (4) 16

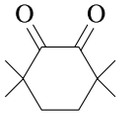
9. How many amide isomers are possible for C_4H_9ON?

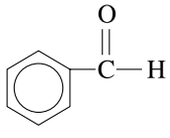
(1) 4 (2) 5

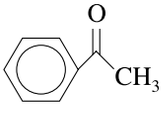
(3) 6 (4) 8

10. Which of the following compounds will undergo tautomerism?

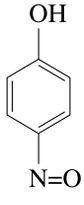
(1) 

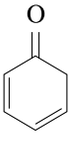
(2) 

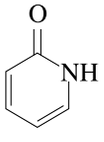
(3) 

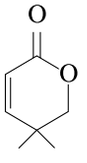
(4) 

11. Which of the following compounds cannot show tautomerism?

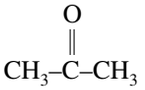
(1) 

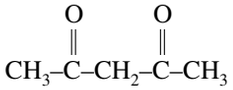
(2) 

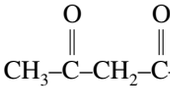
(3) 

(4) 

12. Order of stability of enol content:

(a) 

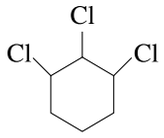
(b) 

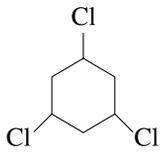
(c) 

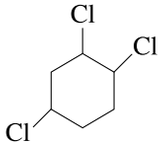
(1) a > b > c (2) b > a > c

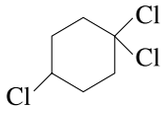
(3) b > c > a (4) a > b > c

13. Which of the following compounds does not have any geometrical isomer?

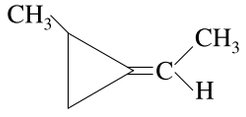
(1) 

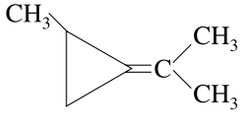
(2) 

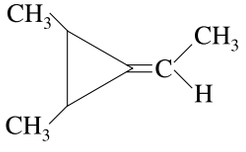
(3) 

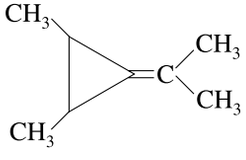
(4) 

14. Which of the following will show optical isomerism as well as geometrical isomerism?

(1) 

(2) 

(3) 

(4) 

15. The correct order of the substituent in each of the following set in order of priority according to CIP rule

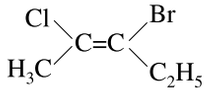
(1) –Cl > –OH > –SH > H

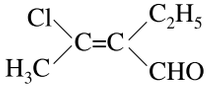
(2) $-CH_2-Br > -CH_2-Cl > -CH_2-OH > -CH_3$

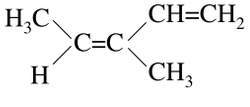
(3) –CH = O > –OH > $-CH_3$ > –H

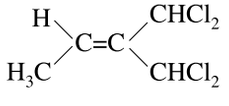
(4) $-OCH_3 > -N(CH_3)_2 > -CH_3 > -CD_3$

16. The E-isomer among the following is

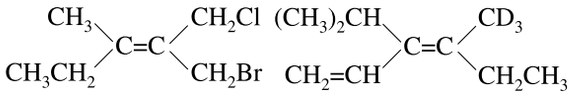
(1) 

(2) 

(3) 

(4) 

17. Consider the following compounds,



(i) (ii)

The correct E/Z configurational notations for the compounds I to II are respectively-

(1) Z, Z (2) E, Z

(3) E, Z (4) E, E

18. A cyclic dichloride has a total five constitutional plus geometrical isomers. Which of the following satisfy this condition without altering the carbon skeleton?

(1) Dichloromethyl cyclopropane

(2) Dichlorocyclobutane

(3) Dichlorocyclopentane

(4) Dichlorocyclohexane

19. How many cyclic isomers exists (structural and geometrical only) for $C_3H_3Cl_3$?

(1) 2 (2) 3

(3) 4 (4) 5

20. Which of the following compounds is a meso compound?

(1) 

(2) 

(3) 

(4) 

21. Which of following is not capable of existing enantiomers

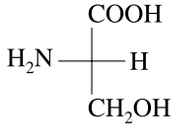
(1) 1, 3-dichloro butane

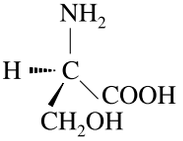
(2) 1, 2-dibromo propane

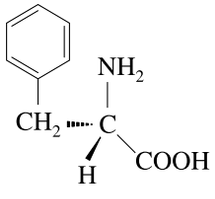
(3) 1, 4-dichloro pentane

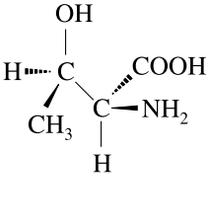
(4) 3-ethyl pentane

22. Which of the following is not correct representation of L-amino acids

(1) 

(2) 

(3) 

(4) 

23. Which isomer below has a stable intramoecular H-bond?

(1) *trans*-3-fluoro propenoic acid

(2) *Cis*-3-fluoro propenoic acid

(3) 2-fluoro propenoic acid

(4) 4-fluoro-3-methyl-3-pentenoic acid

24. If solution of a compound (30 g/100 mL of solution) has measured rotation of +15° in a 2 dm log sample tube, the specific rotation of this compound is

(1) +50° (2) +25°

(3) +15° (4) +7.5°

25. What is true regarding a meso form of a compound?

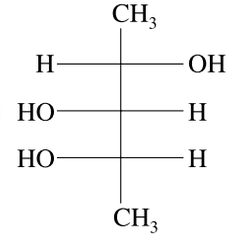
(1) A meso form is achiral due ot the presence of an axis of symmetry

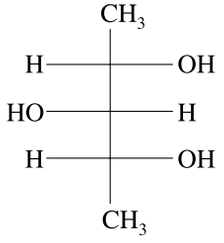
(2) A meso form does not contain any chiral carbon

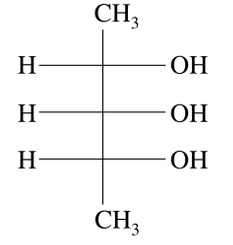
(3) A meso form cannot be isolated from its optically active stereoisomer by fractional crystallisation

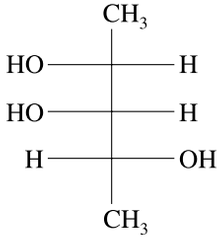
(4) A meso form is achiral due to internal compensation of optical rotation

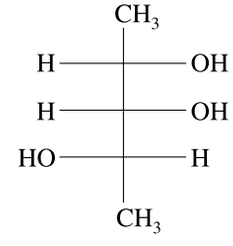
26. Which structures represent(s) diastereomers of l?

(I)


(II)


(III)


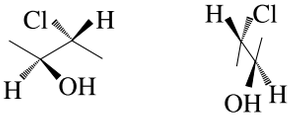
(IV)


(V)


(1) Only II (2) II and III

(3) II and IV (4) III and IV

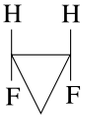
27. Relation between given pair is:

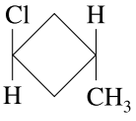


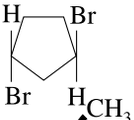
(1) Enantiomer (2) Diastereomers

(3) Identical (4) Structural isomer

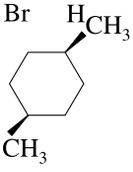
28. Which compound does not possess a plane of symmetry?

(I)


(II)


(III)


(IV)


(V)


(1) I, II and V (2) I, III and IV

(3) II, III and IV (4) III and IV

29. Dextrorotatory α-pinene has a specific rotation n $[\alpha]_D^{20}$ = + 51.3°. A sample of α-pinene containing both the enantiomers was found to have a specific rotation value $[\alpha]_D^{20}$ = + 30.8°. The percentages of the (+) and (–) enantiomers present in the sample are, respectively:

(1) 70% and 30% (2) 80% and 20%

(3) 20% and 80% (4) 60% and 40%

30. What is wrong about enantiomers of 2-chloropropanoic acid?

(1) Have same solubility in water

(2) Have same pK_a value

(3) Have same refractive Index

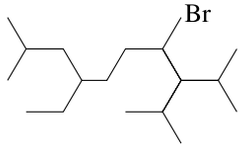
(4) Have same rate of reactions with (+)-2-butanol

31. How many stereoisomers exist for the compound 4-(1-propenyl) cyclohexene?

(1) 2 (2) 3

(3) 4 (4) 5

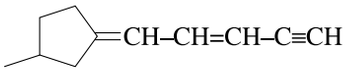
32. Calculate the number of stereoisomerism for



(1) 2 (2) 4

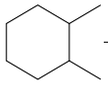
(3) 8 (4) 6

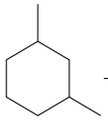
33. The number of stereoisomers possible for the compound is-



(1) 2 (2) 4
(3) 6 (4) 8

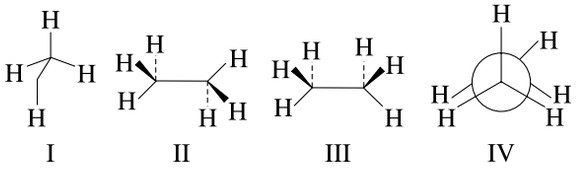
34.


→ a (stereoisomers)


→ b (stereoisomers)

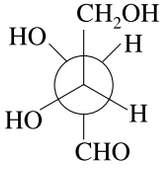
a and b are stereoismers sum of (a + b = ?)
(1) 4 (2) 6
(3) 8 (4) 12

35. Which of the following represents the staggered conformation of ethane?

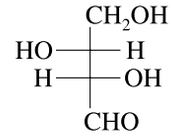


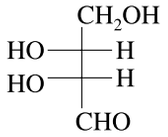
(1) I and II (2) I, II and III
(3) I and III (4) II, III and IV

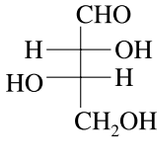
36. Consider the following Newman projection.

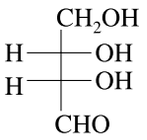


Which of the following is the correct representation of the same compound in Fischer projection formula (ignore conformational aspect)?

(1) 

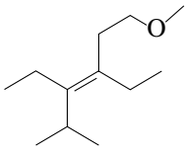
(2) 

(3) 

(4) 

37. Which is true about conformers of 1, 1, 2, 2-tetrachloroethane?
(1) The most stable conformer has dihedral angle of 60° between all adjacent chlorine atoms
(2) In the least stable conformer, two Cl-atoms are eclipsing one another while other two Cl-atoms are eclipsed to hydrogen atoms
(3) In the most stable conformer, dihedral angle between hydrogen atoms is 60°
(4) The most stable conformer is non-polar

38. Consider the following structure



Its IUPAC name is
(1) (Z)-3, 4-diethyl-1-methoxy-5-methyl-3-hexene
(2) (E)-3, 4-diethyl-1-methoxy-5-methyl-3-hexene
(3) (E)-3, 4-diethyl-6-methoxy-2-methyl-3-hexene
(4) (Z)-3, 4-diethyl-6-methoxy-2-methyl-3-hexene

39. Which of the following statements is incorrect about cis and trans isomers ?
(1) *cis*-2-butene can be converted into *trans*-2-butene by irradiation
(2) In general *trans* isomers have zero dipole moment
(3) On heating, fumaric acid (a *trans* acid) gives an anhydride
(4) On heating, maleic acid (a *cis* acid) gives an anhydride

40. The in correct statement concerning various conformers of 2-fluoroethanol is/are
(1) Anti-conformer is the most stable conformer
(2) There is intramolecular H-bonding in its most stable conformer
(3) The most stable conformer has greater steric strain than 2nd most stable conformer
(4) Dissolving in water lower the percentage of most stable conformer

EXERCISE 2

1. How many different isomer can be given to bromodichlorobenzene?

(1) 3 (2) 4

(3) 6 (4) 7

2. How many cycloalkene isomers exist for C_5H_8 which contain at least one methyl locant directly present on the ring?

(1) 2 (2) 4

(3) 5 (4) 6

3. How many structural isomers exist for C_4H_8O which are simultaneously ether? Also there is no atom sp^2-hybridised.

(1) 3 (2) 4

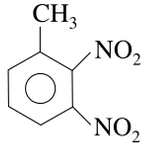
(3) 6 (4) 7

4. A hydrocarbon has molecular formula $X(C_6H_6)$. Also, X has triple bonds as the only type of unsaturation, i.e., it has neither double bonds nor any ring structure. How many different IUPAC name can be assigned to X?

(1) 3 (2) 4

(3) 5 (4) 7

5.

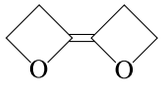


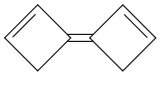
Number of positional isomer are:

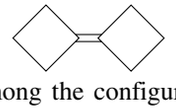
(1) 4 (2) 5

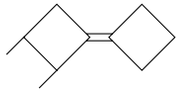
(3) 6 (4) 7

6. Which of following compound will not show geometrical isomerism?

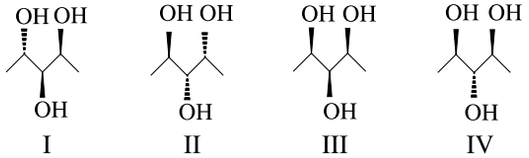
(1) 

(2) 

(3) 

(4) 

7. Among the configurations

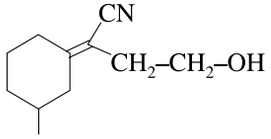


The meso pair is-

(1) I and II (2) I and IV

(3) III and IV (4) II and III

8. False statement about the following compound is–



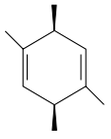
(1) It is having two stereocentres

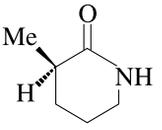
(2) Its configuration at double bond is E

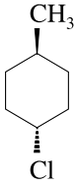
(3) It shows optical isomerism

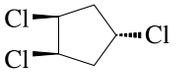
(4) It shows geometrical isomerism

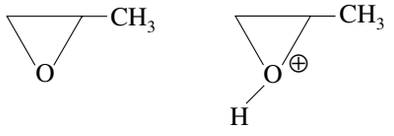
9. Which of the following compound is chiral?

(1) 

(2) 

(3) 

(4) 

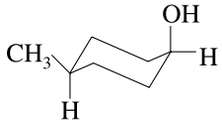
10. 

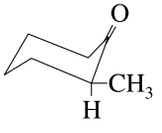
Number of chiral center present in above compounds are:

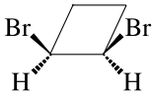
(1) 1, 1 (2) 1, 2

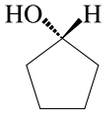
(3) 2, 1 (4) 2, 3

11. Which of the following molecule is chiral?

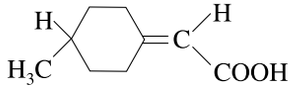
(1) 

(2) 

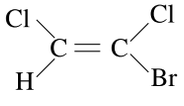
(3) 

(4) 

12. Consider the following structures,



(X)



(Y)

Which one of the following statements is correct about the structures (X) and (Y)?

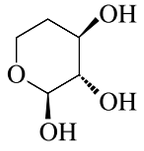
(1) Both (X) and (Y) exhibit enantiomerism

(2) Both (X) and (Y) exhibit distereomerism

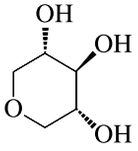
(3) (X) exhibits enantiomerism while (Y) exhibits distereomerism

(4) (X) exhibits distereomerism while (Y) exhibits enantiomerism

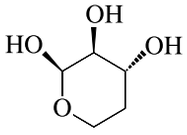
13. Which two of the following compounds are identical?



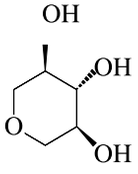
(I)



(II)



(III)

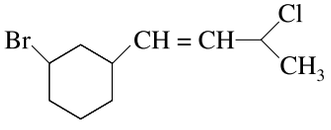


(IV)

(1) I & II (2) II & IV

(3) III & IV (4) I & III

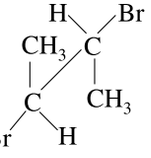
14. How many stereo isomers are possible for the following molecule?

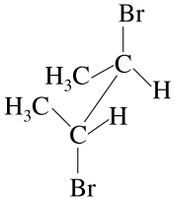


(1) 4 (2) 8

(3) 16 (4) 32

15. The structures shown here are related as being:



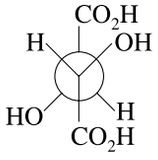


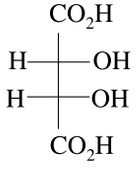
(1) Conformers (2) Enantiomorphs

(3) Geometrical isomers (4) Diastereoisomers

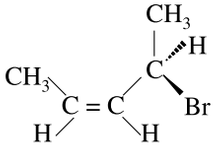
16. Which of following pair is Diastereomers?

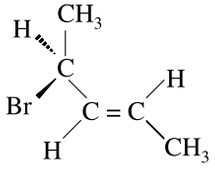
(1)



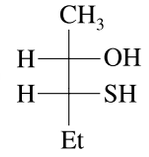


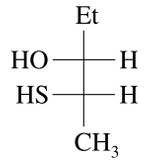
(2)



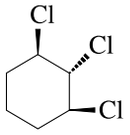


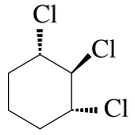
(3)



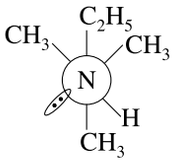


(4)

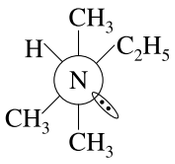




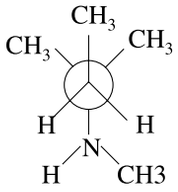
17.



(I)



(II)



(III)

Which of the following statements is correct?

(1) I and II are conformational isomers while II and III are functional isomers

(2) I and II are functional isomers while II and III are conformational isomers

(3) I and II are functional isomers while I and III are conformational isomers

(4) I and II are functional isomers while I and III are metamer isomers

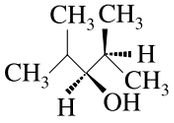
18. The total number of dimethylphenols having the molecular formula $C_8H_{10}O$ is:

(1) 3 (2) 4

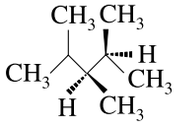
(3) 6 (4) 8

19. Which of the following structures represents a chiral compound?

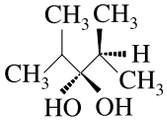
(1)



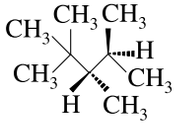
(2)



(3)



(4)

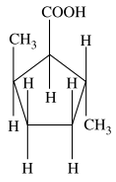


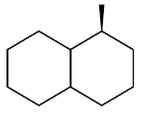
20. (+)-mandelic acid has a specific rotation of 158°. What would be the observed specific rotation of a mixture of 25% (–)-mandelic acid and 75% (+)-mandelic acid?

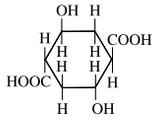
(1) +118.5° (2) –118.5°

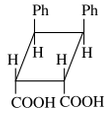
(3) –79° (4) +79°

21. Which species exhibits a plane of symmetry?

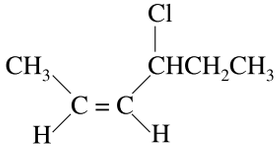
(1) 

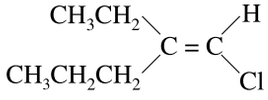
(2) 

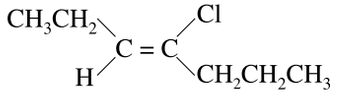
(3) 

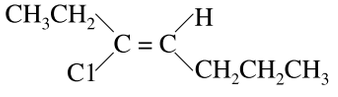
(4) 

22. Which of the following represents Z-3-chloro-3-heptene?

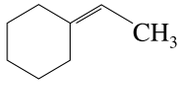
(1) 

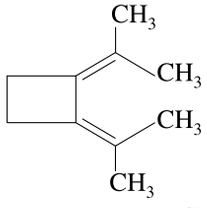
(2) 

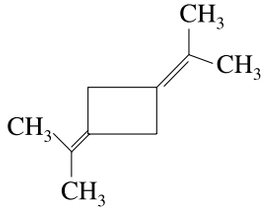
(3) 

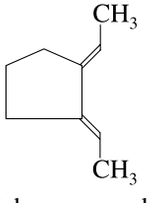
(4) 

23. Which compound below can show geometrical isomerism?

(1) 

(2) 

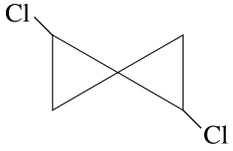
(3) 

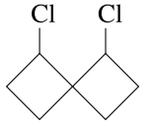
(4) 

24. Which compound below is capable of showing geometrical isomerism?

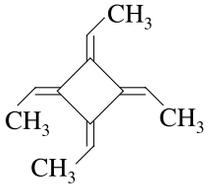
(1) $CH_3–CH=C=CH–CH_3$

(2) $CH_3–CH=C=C=CH–CH_3$

(3) 

(4) 

25. How many geometrical isomers exist for the molecule shown below?



(1) 2 (2) 3

(3) 5 (4) 6

26. If chlorocyclohexane is subjected to further chlorination, how many different isomers (geometrical plus structural only) of dichlorocyclohexane would be produced?

(1) 3 (2) 5

(3) 6 (4) 7

27. The correct statement regarding elements of symmetry and chirality of compound is

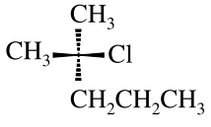
(1) Presence of an axis of symmetry destroy chirality

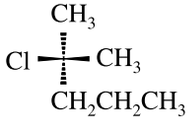
(2) Centre of symmetry has no role to play in chirality of a compound

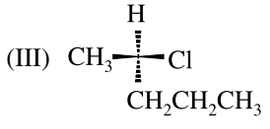
(3) A compound with either plane or centre of symmetry is always achiral

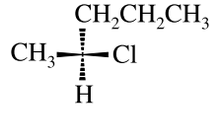
(4) A compound with an axis of symmetry simultaneously contain centre of symmetry

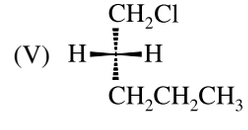
28. Consider the following set of molecules

(I) 

(II) 

(III) 

(IV) 

(V) 

The pairs of enantiomers are

(1) I, II, III and IV (2) I and II

(3) III and IV (4) IV and V

29. How many stereoisomers are possible for the compound 2, 5-heptadiene-4-ol?

(1) 2 (2) 3

(3) 4 (4) 5

30. A stereoisomer of cyclobutane-1,2-diol has lower solubility in water than its other stereoisomer, which is this isomer and why?

(1) Trans, lower dipole moment

(2) *Cis*, higher dipole moment

(3) *Cis*, intramolecular H-bonding

(4) *Trans*, intramolecular H-bonding

31. Which of the following correctly ranks the cycloalkanes in order of increasing ring strain per methylene group?

(1) Cyclopropane < Cyclobutane < Cyclopentane < Cyclohexane

(2) Cyclohexane < Cyclopentane < Cyclobutane < Cyclopropane

(3) Cyclohexane < Cyclobutane < Cyclopentane < Cyclopropane

(4) Cyclopropane < Cyclopentane < Cyclobutane < Cyclohexane

32. The correct statement concerning conformers of 1, 2-dichloroethane is

(1) It's gauche conformer has higher potential energy than an eclipsed conformer in which H–Cl aoms are eclipsing

(2) Syn-periplanar conformer is most stable

(3) Increasing temperature decreases dipole moment of 1, 2-dichloroethane

(4) The two gauche conformers are enantiomers

33. Which of the following is achiral

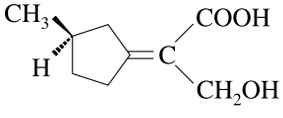
(1) 2-bromo bicyclo [1, 1, 0] butane

(2) 2-fluoro bicyclo [2, 2, 2] octane

(3) 2-chloro bicyclo [2, 1, 1] hexane

(4) 5-chloro bicyclo [2, 1, 1] hexane

34. In the compound

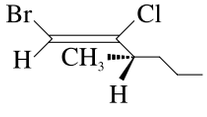


The configurations at the chiral centre and the double bond are respectively,

(1) R and E (2) R and Z

(3) S and Z (4) S and E

35.



The configurations at the chiral centre and the double bond are respectively,

(1) R and E (2) R and Z

(3) S and Z (4) S and E

36. If a hydrogen of 1, 3-pentadiene is substituted by chlorine, how many different isomer (excluding stereochemical designation) can be assigned to the chlorinated dienes?

(1) 2 (2) 3

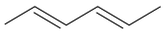
(3) 4 (4) 5

37. How many different structural isomers exist for C_5H_8 that have only sp^3-hybridised carbon atoms?

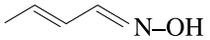
(1) 3 (2) 4

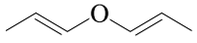
(3) 5 (4) 7

38. Which compound below has four stereoisomers?

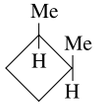
(1) 

(2) H – N = N – N = N – H

(3) 

(4) 

39.



Incorrect statement about this compound is:

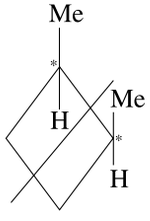
(1) It shows geometrical isomerism

(2) It possess centre of symmetry

(3) It possess plane of symmetry

(4) It shows optical isomerism

Sol. **[2]**



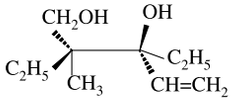
POS present

COS absent

C* present

G.I. present

40. The absolute configuration of the below figure is:



(1) 2R, 3S (2) 3R, 4S

(3) 2S, 3R (4) 3S, 4R

EXERCISE 3

One and More Than One Option Correct Type Question

1. The correct statement(s) regarding the isomers of compound N-ethyl-N-methyl-1-propanamine is/are

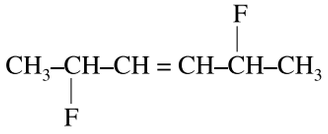
(1) A pair of enantiomers remain in dynamic equilibrium

(2) Addition of HCl results in the formation of enantiomeric hydrochloride salts

(3) Addition of a pure enantiomer of 2-methyl butanoic acid to the solution of amine results in formation of a pair of diastereomeric salts

(4) Its enantiomers can be separated by gas chromatography

2. Consider the following molecule



The correct statement/s concerning above molecule is/are

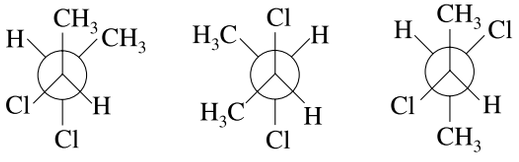
(1) It has a total of six stereoisomers

(2) It's meso form upon ozonolysis followed by Zn-hydrolysis gives racemic mixture

(3) It's optically active isomers, each upon ozonolysis followed by Zn-hydrolysis given a single enantiomer

(4) It has only two optically active isomers

3. The correct statement(s) concerning the following Newmann's projections is/are



(I) (II) (III)

(1) I and II correspond to conformers of enantiomers of 2, 3-dichlorobutane

(2) I and III are two conformers of the same enantiomer of 2, 3-dichlorobutane

(3) III is the most stable conformer of meso-2, 3-dichlorobutane

(4) I and II are conformers of a pair of diastereomers of 2, 3-dichlorobutane

4. Which of the following statements is/are correct ?

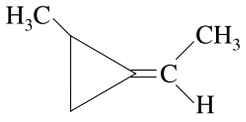
(1) A meso compound has chiral centres but exhibits no optical activity

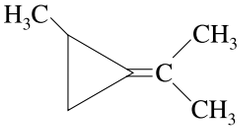
(2) A meso compound has no chiral centres and thus are optically inactive

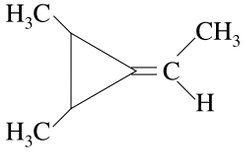
(3) Meso compounds are superimposable on their mirror images even though they contain chiral centres

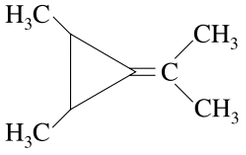
(4) Meso compounds do not show optical activity due to external compensation of optical rotation

5. Which of the following will show optical isomerism as well as geometrical isomerism?

(1) 

(2) 

(3) 

(4) 

6. The correct statement (s) concerning aldehydes of general formula $C_5H_{10}O$ is/are

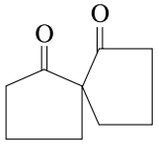
(1) It has total five aldehyde isomers

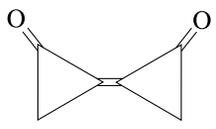
(2) Two of the aldehydes are chiral

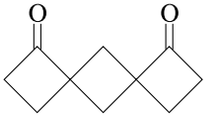
(3) Two of the aldehyde isomers have no enol

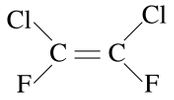
(4) All enols of aldehyde isomers are diastereomeric

7. Which compound below can have a non-polar stereoisomers?

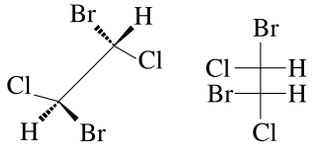
(1) 

(2) 

(3) 

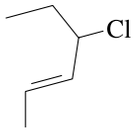
(4) 

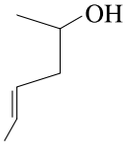
8. The correct statement(s) concerning the following structures is/are

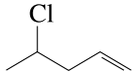


(1) P and Q are enantiomers
(2) P and Q are diastereomers
(3) Both are optically active
(4) P is optically inactive while Q is optically active

9. Which of the following compounds can show geometrical & optical isomerism.

(1) 

(2) 

(3) 

(4) 

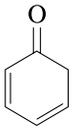
Statement Type Question

(1) If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I
(2) If both Statement-I and Statement-II are correct and Statement-II is not the correct explanation for Statement-I
(3) If Statement-I is correct and Statement-II is incorrect
(4) If Statement-I is incorrect and Statement-II is correct

10. Statement-I: Molecules that are non-superimposable on their mirror images are chiral

Statement-II: All chiral molecules have chiral centres.

(1) If both statement-I and statement-II are true but statement-II is not a correct explanation of the statement-I
(2) If both statement-I & statement-II are true & the statement-II is a correct explanation of the statement-I
(3) If statement-I is true and statement-II is false
(4) If statement-I is false and statement-II is true

11. Statement-I: Percentage enol content for 

is almost 100%.

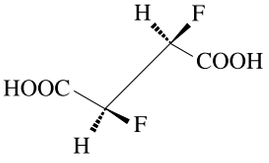
Statement-II: Due to aromaticity, stability of enol increases, hence percentage enol content also increases.

(1) Statement-1 is true, statement-II is true and statement-II is correct explanation for statement-I
(2) Statement-1 is true, statement-II is true and statement-II is NOT the correct explanation for statement-I
(3) Statement-I is true, statement-II is false
(4) Statement-I is false, statement-II is true

12. Statement-I: Fluoroethanal has two stereomeric enols in which *cis* enol predominates at equilibrium.

Statement-II: Intramolecular H-bonding increases the stability of a stereomer.

13. Statement-I: The compound shown below is optically inactive.



Statement-II: Compound shown above possesses axis of rotation.

14. Statement-I: Enantiomers differ in their chemical action with other enantiomer.

Statement-II: A pair of enantiomers have different orientation of collision with another enantiomer forming different transition state.

Comprehension Type Question

Passage (Q. 15–17)

Organic compound with molecular formula C_3H_6O has one degree of unsaturation. One degree of unsaturation can be present in the form of a pi-bond or a ring structure. Pi-bond can be formed between carbon atoms or between carbon and oxygen atom.

15. How many isomers exist for this compound that have a ring structure?

(1) 1 (2) 2
(3) 3 (4) 4

16. If only carbonyl isomers (aldehyde and ketone) are considered, how many corresponding enol isomers would be possible?

(1) 1 (2) 2
(3) 3 (4) 4

17. How many isomers of this compound exist that have no stereoisomer?

(1) 2 (2) 4
(3) 6 (4) 7

Passage (Q. 18–20)

The two major contributors of conformers of 1,2-dichloroethane are anti and gauche. At 32°C in gas phase, the measured dipole moment of 1,2-dichloroethane is 1.12 D.

The dipole moment of a mixture of X and Y is given by the relationship

$$\mu^2 = N_x\mu_x^2 + N_\gamma u_\gamma^2$$

Here, N = mole fraction of each kind of molecule. From bond moment measurement, it has been estimated that gauche conformer of 1, 2-dichloroethane should have a dipole moment of about 3.2 D.

18. What per cent of conformers of 1,2-dichloroethane is anti, at 32°C?

(1) 12% (2) 36%

(3) 60% (4) 89%

19. What is true about percentage of gauche conformer?

(1) There is only one gauche conformer is about 12%

(2) There is only one gauche conformer in about 64%

(3) There is racemic mixture, although inseparable, of gauche conformers, about 12%

(4) There is racemic mixture, although inseparable, of gauche conformers, about 64%

20. What happens if temperature if increased to 52°C?

(1) Percentage of gauche conformers decreases and that of anti-conformers

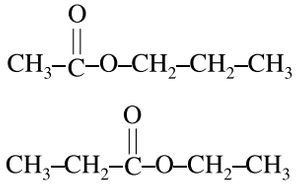
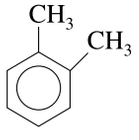
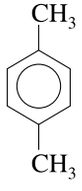
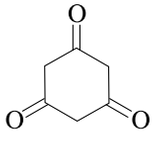
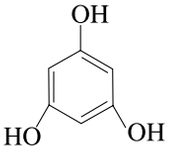
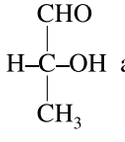
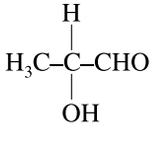
(2) Percentage of both gauche and anti conformers increases

(3) No change in percentage of anti and gauche conformers occur

(4) Percentage of both anti and gauche conformers decreases

Column Matching Type Question

21. Match List I with List II and select the correct answer from the codes given below the lists:

List-I	***List-II***
(A)  and	(P) Enantiomer
(B)  	(Q) Position isomers
(C)  and 	(R) Metamers
(D)  and 	(S) Tautomers

Codes:

	A	**B**	**C**	**D**
(1)	R	Q	S	P
(2)	R	Q	P	S
(3)	P	Q	R	S
(4)	Q	R	S	P

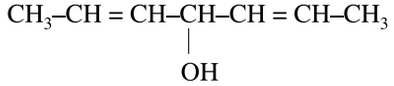
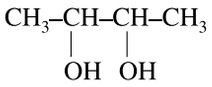
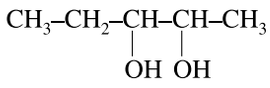
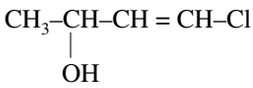
22. Match the quantity from Column I with the types of isomerism from Column II.

Column I	*Column II*
(i) Pentene	(p) Has two positional isomers.
(ii) 1-methoxypropene	(q) Has two geometrical isomers.
(iii) Dichlorocyclopropane	(r) Has six geometrical isomers.
(iv) 2, 4, 6-octatriene	(s) Has more than four cyclic isomers.

Codes

	(i)	(ii)	(iii)	(iv)
(1)	p, q, s	p, s	p, r, s	p, s
(2)	p	q	r	s
(3)	p, s	p, q, r	s, p, q	p
(4)	q, r	p, s	r, s	q

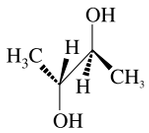
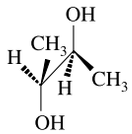
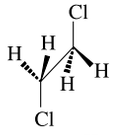
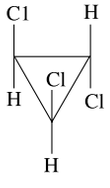
23. Consider the molecules in Column I and match them with their stereochemical properties from Column II.

Column I	*Column II*
(i) 	(P) Have only three stereoisomers
(ii) 	(Q) Have four stereoisomers
(iii) 	(R) Have only two optically active isomers.
(iv) 	(S) Have more than two pairs of diastereomers.

Codes

	(i)	(ii)	(iii)	(iv)
(1)	q, r, s	p, r	q, s	q, s
(2)	p	q	r	s
(3)	p, q	q, s	r	q
(4)	p, q, r	r, s	q, r	p, q

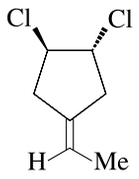
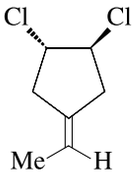
24. Match the structures on the left Column I with the properties on the right Column II.

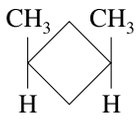
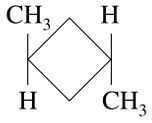
Column I	*Column II*
(i) 	(p) Has plane of symmetry
(ii) 	(q) Has axis of symmetry
(iii) 	(r) Has centre of symmetry
(iv) 	(s) Rotate plane polarised light

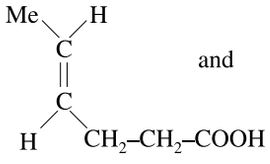
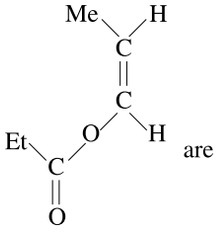
Codes

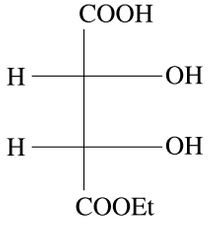
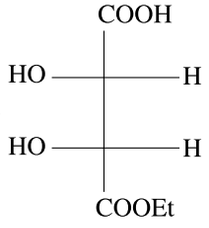
	(i)	(ii)	(iii)	(iv)
(1)	r,s	p,q	q,r	p,s
(2)	p,q,r,s	r,s	p	q
(3)	p,r	q,s	p,q,r	p,q
(4)	p	q	r	s

25. ***Column I*** ***Column II***

(A)  and  are (P) Structural isomers

(B)  and  are (Q) Enantiomers

(C)  and  are (R) Compounds which are geometrical isomer and diastereoisomers

(D)  and  are (S) Compound are geometrical isomers and enantiomers

(1) (A)→(R); (B)→(Q); (C)→(P); (D)→(S)

(2) (A)→(Q); (B)→(R); (C)→(P); (D)→(Q)

(3) (A)→(R); (B)→(Q); (C)→(S); (D)→(P)

(4) (A)→(R); (B)→(S); (C)→(Q); (D)→(S)

26. ***Column-I*** ***Column-II***
(Compound) ***(Number of isomer)***

(A)  (P) 2

(B)  (Q) 3

(C)  (R) 4

(D)  (S) 6

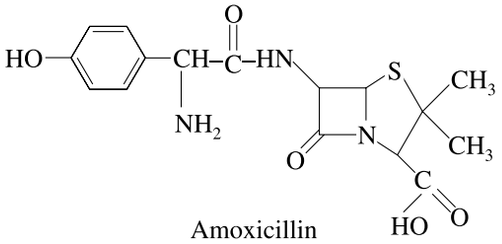
(1) (A)→(Q); (B)→(R); (C)→(P); (D)→(P)
(2) (A)→(R); (B)→(P); (C)→(Q); (D)→(P)
(3) (A)→(R); (B)→(Q); (C)→(P); (D)→(P)
(4) (A)→(R); (B)→(Q); (C)→(Q); (D)→(P)

Single Digit Integer Type Question

27. How many isomers, each containing a phenyl ring, are possible for C_9H_{12}?

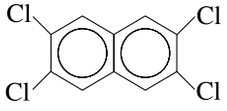
28. How many different isomers of alkene with molecular formula C_7H_{14}, on catalytic hydrogenation, can give 3-methyl hexane?

29. Total number of chiral centers in amoxicillin, which belongs to the family of semisynthetic penicillins.

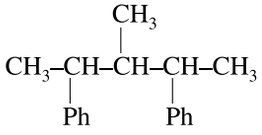


Amoxicillin

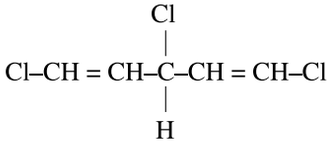
30. Total number of plane of symmetry present in given compound is



31. How many pairs of diastereomers can be made for the compound shown below?



32. Find out the total number of stereoisomers of the given following compound.



33. How many different structural isomers exist for C_3H_6O in which no atom is sp^2 or sp-hybridised?

34. Consider the following reaction

$$(X)\ C_6H_{12} \xrightarrow[Ni]{H_2} C_6H_{14} \xrightarrow[h\nu]{Cl_2} C_6H_{13}Cl(Y)$$

(4 positional isomers)

How many different isomers of X satisfy the above condition?

EXERCISE 4

1. Stereo-Isomerism includes **[AIEEE-2002]**
(1) Geometrical isomerism only
(2) Optical isomerism only
(3) Both geometrical & optical isomerism
(4) Position & Functional isomerism

2. Which of the following does not show geometrical isomerism– **[AIEEE-2002]**
(1) $CH_3–CH=CH–CH_3$
(2) $CH_3–CH_2–CH=CH_2$
(3) $CH_3–\underset{\displaystyle Cl}{\underset{|}{C}}=CH–CH_3$
(4) $ClHC=CH–CH_2–CH_3$

3. Racemic mixture is formed by mixing two– **[AIEEE-2002]**
(1) Isomeric compounds
(2) Chiral compounds
(3) Meso compounds
(4) Enanitiomers with chiral carbon

4. Geometrical isomerism is not shown by **[AIEEE-2002]**
(1) 1, 1-dichloro-1-pentene
(2) 1, 2-dichloro-1-pentene
(3) 1, 3-dichloro-2-pentene
(4) 1, 4-dichloro-2-pentene

5. Racemic mixture is– **[AIEEE-2002]**
(1) A mixture of chiral carbons
(2) A mixture of isomers
(3) A mixture of aldehydes and ketones
(4) A mixture of alcohols and ethers

6. Following types of compounds (as I and II)
(i) $CH_3CH=CHCH_3$
(ii) $CH_3–\underset{\displaystyle CH_2CH_3}{\underset{|}{CH}}–OH$ **[AIEEE-2002]**

Are studied in terms of isomerism in

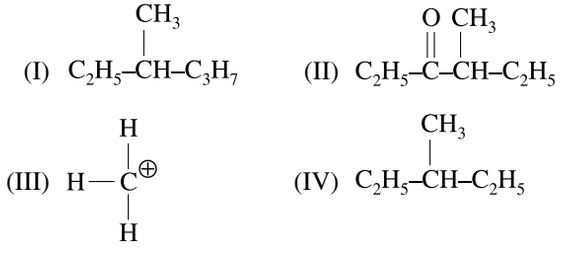
(1) chain isomerism

(2) position isomerism

(3) conformers

(4) stereoisomerism

7. Among the following four structures i to iv **[AIEEE-2003]**



It is true that–

(1) Only (III) is a chiral compound

(2) Only (II) and (IV) are chiral compounds

(3) All four are chiral compounds

(4) Only (I) and (II) are chiral compounds

8. Which of the following compounds is not chiral? **[AIEEE-2004]**

(1) 1-chloropentane

(2) 2-chloropentane

(3) 1-chloro-2-methyl pentane

(4) 3-chloro-2-methyl pentane

9. Which of the following will have a meso isomer also **[AIEEE-2004]**

(1) 2-Chlorobutane

(2) 2, 3-Dichlorobutane

(3) 2, 3-Dichloropentane

(4) 2-Hudroxypropanoic acid

10. For which of the following parameters, the structural isomers C_2H_5OH and CH_3OCH_3 would be expected to have the same values? (Assume ideal behaviour) **[AIEEE-2004]**

(1) Heat of vaporisation

(2) Vapour pressure at the same temperature

(3) Boiling points

(4) Gaseous densities at the same temperature and pressure

11. Which type of isomerism is shown by 2,3-dichlorobutane **[AIEEE-2005]**

(1) Optical (2) Diastereo isomerism

(3) Structural (4) Geometric

12. Increasing order of stability among the three main conformations (i.e., Eclipse, Anti, Gauche) of 2-fluoroethanol is **[AIEEE-2006]**

(1) Gauche, Eclipse, Anti

(2) Eclipse, Anti, Gauche

(3) Anti, Gauche, Eclipse

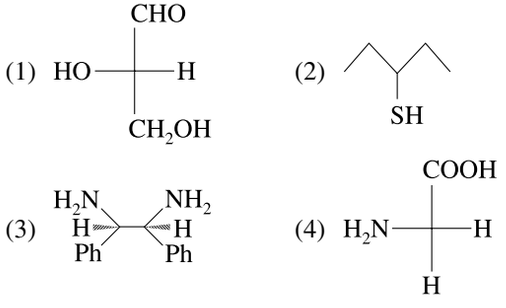
(4) Eclipse, Gauche, Anti

13. Which one of the following conformation of cyclohexane is chiral? **[AIEEE-2007]**

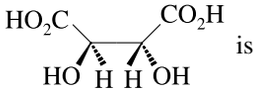
(1) Twist boat (2) Rigid

(3) Chair (4) Boat

14. Which of the following molecules is expected to rotate the plane of plane-polarised light? **[AIEEE-2007]**



15. The absolute configuration of the compound is **[AIEEE-2008]**



(1) R, R (2) R, S

(3) S, R (4) S, S

16. The alkene that exhibits geometrical isomerism is **[AIEEE-2009]**

(1) Propene (2) 2-methyl propene

(3) 2-butene (4) 2-methyl-2-butane

17. The number of stereoisomers possible for a compound of the molecular formula CH_3–CH=CH–CH(OH)–Me is **[AIEEE-2009]**

(1) 3 (2) 2

(3) 4 (4) 6

18. Out of the following the alkene that exhibits optical isomerism is– **[AIEEE-2010]**

(1) 2-methyl-2-pentene (2) 3-methyl-2-pentene

(3) 4-methyl-1-pentene (4) 3-methyl-1-pentene

19. Identify the compound that exhibits tautomerism **[AIEEE-2011]**

(1) 2-Butene (2) Lactic acid

(3) 2-Pentanone (4) Phenol

20. How many chiral compounds are possible on monochlorination of 2-methyl butane? **[AIEEE-2012]**

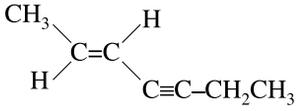
(1) 2 (2) 4

(3) 6 (4) 8

21. Maleic acid and fumaric acids are: **[AIEEE-2012]**

(1) Tautomers
(2) Chain isomers
(3) Geometrical isomers
(4) Functional isomers

22. The IUPAC name of the following compounds is **[JEE Main Online-2012]**

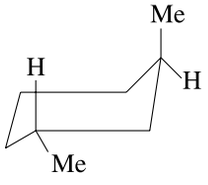


(1) (Z) – 5 – heptene – 3 – yne
(2) (Z) – 2 – heptene – 4 – yne
(3) (E) – 5 – heptene – 3 – yne
(4) (E) – 2 – heptene – 4 – yne

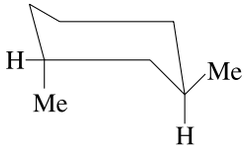
23. Monocarboxylic acids are functional isomers **[JEE Main Online-2013]**

(1) Ethers (2) Amines
(3) Esters (4) Alcohols

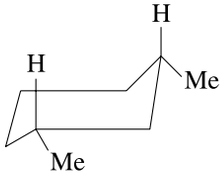
24. Arrange in the correct order of stability (decreasing order) for the following molecules– **[JEE Main Online-2013]**



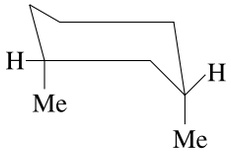
(I)



(II)



(III)



(IV)

(1) I > II > III > IV (2) IV > III > II ≈ I
(3) III > I ≈ II > IV (4) I > II ≈ III > IV

25. Which one of the following acids does not exhibit optical isomerism– **[JEE Main Online-2014]**

(1) Lactic acid (2) Tartaric acid
(3) Maleic acid (4) α-amino acid

26. Which of the following compounds will exhibit geometrical isomerism? **[JEE-Main-2015]**

(1) 1-Phenyl-2-butene
(2) 3-Phenyl-1-butene
(3) 2-Phenyl-1-butene
(4) 1, 1-Diphenyl-1-propane

27. The number of structural isomers for C_6H_{14} is– **[JEE Main Online-2015]**

(1) 6 (2) 4
(3) 3 (4) 5

28. The optically inactive compound from the following is– **[JEE Main Online-2015]**

(1) 2-chloropropanal
(2) 2-chlorobutane
(3) 2-chloro-2-methylbutane
(4) 2-chloropentane

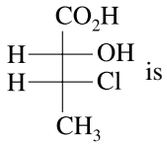
29. Which of the following pairs of compounds are positional isomers– **[JEE Main Online-2015]**

(1) $CH_3–CH_2–CH_2–\underset{\underset{O}{\|}}{C}–CH_3$ and $CH_3–CH_2–\underset{\underset{O}{\|}}{C}–CH_2–CH_3$

(2) $CH_3–CH_2–CH_2–\underset{\underset{O}{\|}}{C}–CH_3$ and $CH_3–\underset{\underset{CH_3}{|}}{CH}–C(=O)–CH_2–CHO$

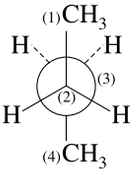
(3) $CH_3–CH_2–CH_2–CH_2–CHO$ and $CH_3–CH_2–CH_2–\underset{\underset{O}{\|}}{C}–CH_3$

(4) $CH_3–CH_2–\underset{\underset{O}{\|}}{C}–CH_2–CH_3$ and $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!\!CH–CH_2–CHO$

30. The absolute configuration of  is **[JEE-main-2016]**

(1) (2S, 3R) (2) (2S, 3S)
(3) (2R, 3R) (4) (2R, 3S)

31. If C_2 in above compound is rotated by 120° angle in anticlockwise direction along $C_2–C_3$, which of the following form will be produced **[IIT-2004]**



(1) Partial eclipsed
(2) Perfectly eclipsed
(3) Perfectly staggered
(4) Gauche conformation

32. $\mu_{obs} = \Sigma\mu_i X_i$ where μ_I is the dipole moment of stable conformer and X_i is the mole fraction of that conformer. **[IIT-2005, Subjective type]**

(a) Write stable conformer for $Z–CH_2–CH_s–Z$ in Newman's projection.

If $\mu_{solution}$ = 1.0 D and mole fraction of anti form

= 0.82, find μ_{gauche}

(b) Write most stable meso conformer of $(CHDY)_2$

If (i) Y = CH_3 about C2-C3 rotation and

(ii) Y = OH about C1-C2 rotation

33. $CH_2–\underset{\displaystyle CH_3}{\underset{|}{CH}}–CH_2–CH_3 \xrightarrow{Cl_2/hv}$ N (no. of isomers)

$\xrightarrow{\text{Fractuional distillation}}$ (F), (N) and (F) are: **[IIT-2006]**

(1) 6, 4 (2) 4, 4

(3) 6, 6 (4) 3, 3

34. The number of structural isomers for C_6H_{14} is **[IIT-2007]**

(1) 3 (2) 4

(3) 5 (4) 6

35. **Statement-I:** Molecule that are non superimposable on their mirror images are chiral.

Statement-II: All chiral molecules have chiral centres. **[IIT-2007]**

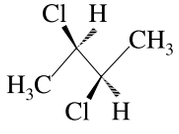
(1) If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I.

(2) If both Statement-I and Statement-II are correct and Statement-II is not the correct explanation for Statement-I.

(3) If Statement-I is correct and Statement-II is incorrect.

(4) If Statement-I is incorrect and Statement-II is correct.

36. The correct statement about the compound given below is **[IIT-2008]**



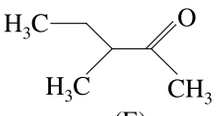
(1) The compound is optically active

(2) The compound possesses center of symmetry

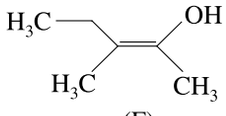
(3) The compound possesses plane of symmetry

(4) The compound possesses axis of symmetry

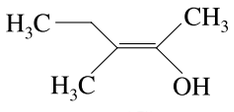
37. Which is correct statement concerning the structures E, F and G is **[IIT-2008]**



(E)



(F)



(G)

(1) E, F and G are resonance structures

(2) E, F and E, G are tautomers

(3) F and G are geometrical isomers

(4) F and G are diastereomers

38. Give the total number of cyclic structural as well as stereo isomers possible for a compound with the molecular formula C_5H_{10}. **[IIT-2009, Integer type]**

39. The correct statement about the compound $H_3C(HO)HC–CH=CH–CH(OH)CH_3(X)$ is **[IIT-2010]**

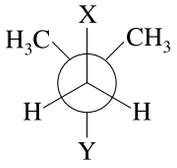
(1) The total number of stereo isomers possible for X is 6

(2) The total number of distereomers possible for X is 3

(3) If the stereochemistry about the double bond in X is trans, the number of enantiomers possible for X is 4

(4) If the stereochemistry about the double bond in X is *cis*, the number of enantiomers possible for X is 2

40. In the Newman projection for 2, 2-dimethylbutane **[IIT-2010]**



X and Y can respectively be

(1) H and H (2) H and C_2H_5

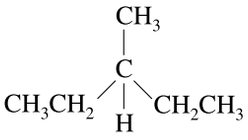
(3) C_2H_5 and H (4) CH_3 and CH_3

41. The total number of cyclic isomers possible for a hydrocarbon with the molecular formula C_4H_6 is **[IIT-2010]**

(1) 5 (2) 4

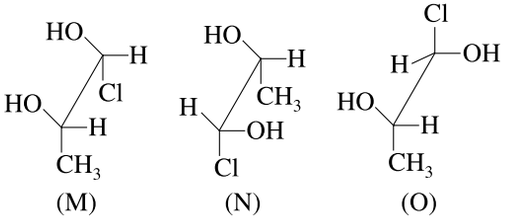
(3) 2 (4) 3

42. The maximum number of isomers (including stereoisomers) that are possible on monochlorination of the following compound, is– **[IIT-2011]**

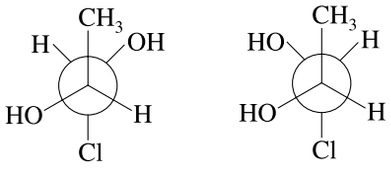


(1) 5 (2) 6
(3) 5 (4) 8

43. Which of the given statement(s) about N, O, P and Q with respect to M is (are) correct? **[IIT-2012]**



(M) (N) (O)



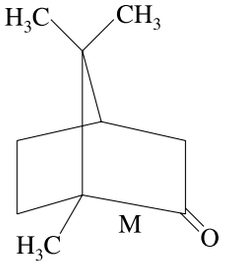
(P) (Q)

(1) M and N are non-mirror image Stereoisomers
(2) M and Q are identical
(3) M and P are enantomers
(4) M and Q are identical

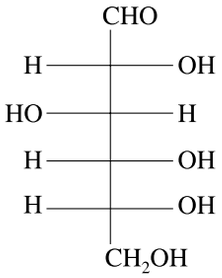
44. The correct combination of names for isomeric alcohols with molecular formula $C_4H_{10}O$ is/are **[JEE-Adv-2014]**

(1) tert-butanol and 2-methylpropan-2-ol
(2) tert-butanol and 1, 1-dimethylethan-1-ol
(3) n-butanol and butan-1-ol
(4) isobutyl alcohol and 2-methylpropan-1-ol

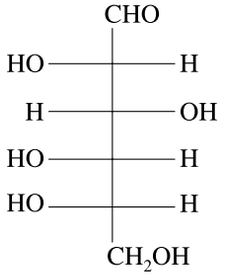
45. The total number of stereoisomers that can exist for M is **[JEE-Adv-2015, Integer type]**

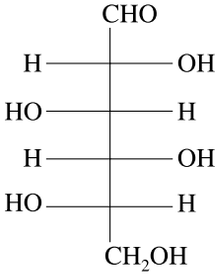


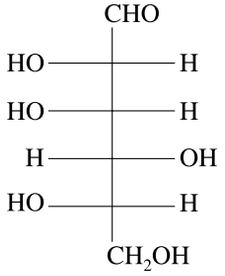
46. The Structure of D-(+)-glucose is **[JEE-Adv-2015, Integer type]**

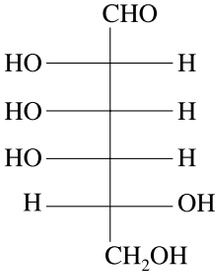


The structure of L-(–)-glucose is

(1) 

(2) 

(3) 

(4) 

ANSWER KEY

EXERCISE # 1

1. (1)	2. (2)	3. (4)	4. (2)	5. (2)
6. (4)	7. (4)	8. (3)	9. (4)	10. (4)
11. (4)	12. (3)	13. (4)	14. (1)	15. (2)
16. (2)	17. (1)	18. (2)	19. (2)	20. (3)
21. (4)	22. (2)	23. (2)	24. (2)	25. (4)
26. (2)	27. (1)	28. (4)	29. (2)	30. (4)
31. (3)	32. (2)	33. (3)	34. (2)	35. (1)
36. (1)	37. (4)	38. (2)	39. (3)	40. (1)

EXERCISE # 2

1. (3)	2. (4)	3. (3)	4. (3)	5. (3)
6. (3)	7. (3)	8. (1)	9. (2)	10. (2)
11. (2)	12. (3)	13. (2)	14. (3)	15. (4)
16. (2)	17. (4)	18. (3)	19. (4)	20. (4)
21. (4)	22. (4)	23. (4)	24. (2)	25. (2)
26. (4)	27. (3)	28. (3)	29. (3)	30. (3)
31. (2)	32. (4)	33. (1)	34. (2)	35. (3)
36. (4)	37. (3)	38. (3)	39. (2)	40. (3)

EXERCISE # 3

1. (1,2,3)	2. (1,2,3)	3. (1,3,4)	4. (1,3)	
5. (1,3,4)	6. (1,2,4)	7. (2,3,4)	8. (2,4)	
9. (1,2)	10. (3)	11. (1)	12. (1)	13. (4)
14. (1)	15. (4)	16. (3)	17. (4)	18. (4)
19. (3)	20. (3)	21. (1)	22. (3)	23. (1)
24. (3)	25. (2)	26. (3)	27. (8)	28. (9)
29. (4)	30. (3)	31. (5)	32. (4)	33. (2)
34. (3)				

EXERCISE # 4

1. (3)	2. (2)	3. (4)	4. (1)	5. (1)
6. (4)	7. (4)	8. (1)	9. (2)	10. (4)
11. (1)	12. (2)	13. (1)	14. (1)	15. (1)
16. (3)	17. (3)	18. (4)	19. (3,4)	20. (2)
21. (3)	22. (4)	23. (3)	24. (3)	25. (3)
26. (1)	27. (4)	28. (3)	29. (1)	30. (1)
31. (4)	32. (1)	33. (1)	34. (3)	35. (3)
36. (1,4)	37. (2,3,4)	38. (7)	39. (1,4)	40. (2,4)
41. (1)	42. (4)	43. (1,2,3)	44. (1,3,4)	45. (2)
46. (1)				

HINT AND SOLUTION

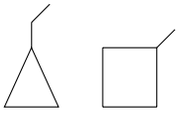
EXERCISE # 1

1. [1]

As per definition

2. [2]

- Given molecular formula C_5H_{10} corresponds to C_nH_{2n} so that isomers should be alkene and cyclo alkane.
- C_5H_{10} do not have double bond so it must be cyclo alkane.
- Alkyl containing cyclo alkane are



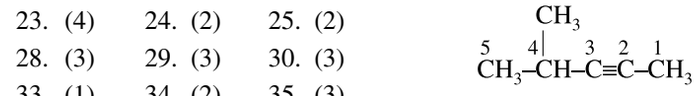
3. [4]

$CH_3–CH_2–CH_2–C\equiv C–CH_3$

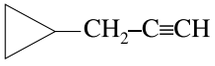
2-hexyne (C_6H_{10})

$CH_3–CH_2–C\equiv C–CH_2–CH_3$

3-hexyne (C_6H_{10})

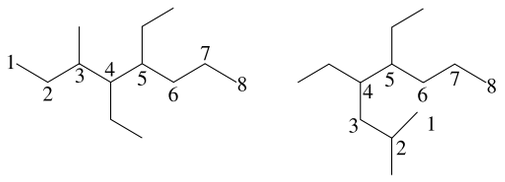


2-methyl 2-pentyne (C_6H_{10})



3-cyclo propyl propyne (C_6H_8) hence it is not possible.

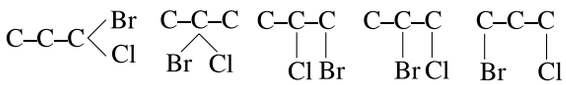
4. [2]



Locant position (3, 4, 5) & (2, 4, 5) differ along same parent chain

5. [2]

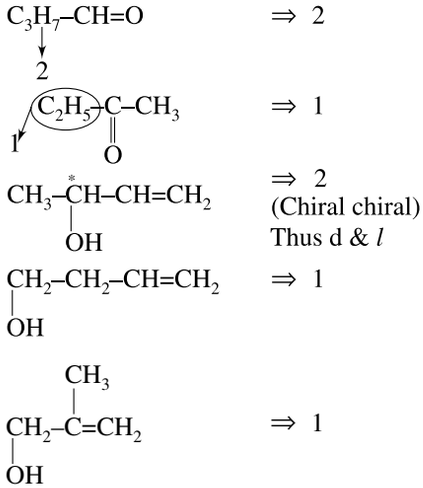
$$\text{D.B.E} = (C + 1) \frac{H + X - N}{2} = 3 + 1 - \frac{6 + 2}{2} = 0$$



6. [4]

Molecular formula C_4H_8O correspond to $C_nH_{2n}O$ so that isomers are

Aldehyde / ketone / unsaturated alcohol / unsaturated ether



$CH_2=CH-O-CH_2-CH_3 \Rightarrow 1$
$CH_2=CH-CH_2-O-CH_3 \Rightarrow 1$
$CH_3-CH=CH-O-CH_3 \Rightarrow 2$

(GI)
$CH_2=C(CH_3)-O-CH_3 \Rightarrow 1$

$CH_2(OH)-CH(CH_3)-CH=CH-CH_3 \Rightarrow 2$ (GI)

Total isomer = 14
No unsaturation.

7. [4]

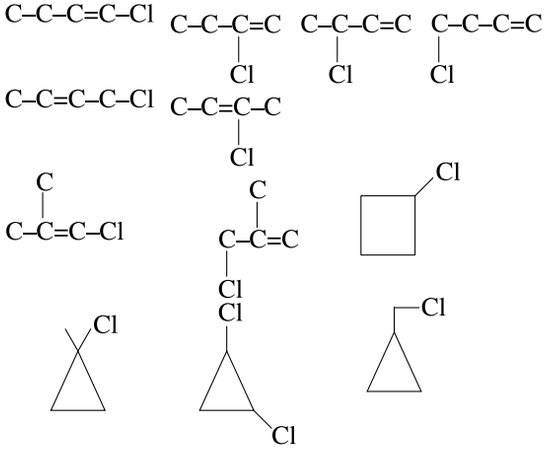
$CH_3-\overset{5}{C}H(Br)-\overset{4}{C}H(Br)-\overset{3}{C}H-\overset{2}{C}H=\overset{1}{C}H_2$ → M.F = $C_5H_8Br_2$
→ Position isomer
$CH_2(Br)-CH_2-C(Br)=CH-CH_3$ → functional group same so chemical properties are same

8. [3]

M.P. = C_9H_7Cl

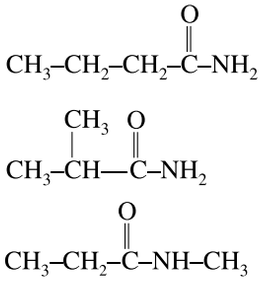
D.B.E. = $(C + 1) - \left(\frac{H + X - N}{2}\right)$

$= (4 + 1) - \frac{7 + 1 - 0}{2} = 1$

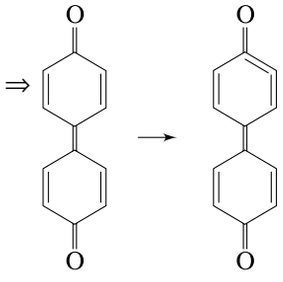


number of isomer = 12

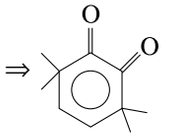
9. [4]

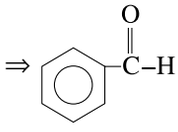


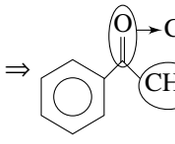
10. [4]



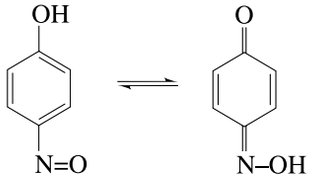
Geometrically unfavourable

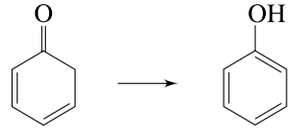

No α – H

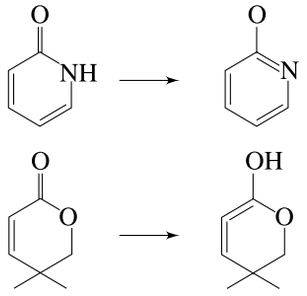

No α – H


Carbonyl group
α – H
Show tautomerism

11. [4]

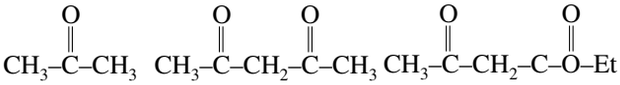






Geometrically unfavourable

12. [3]



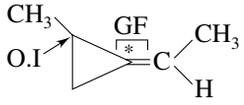
(a) (Monocarbonyl) (b) (β–dicarbonyl) (c) (β–ketoester)

∵ (b > c > a) (refer key concept)

13. [4]

Same substituents at same Carbon

14. [1]

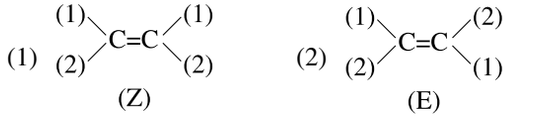


Each blocked atom consist of pair of different groups, so that it shows G.I.

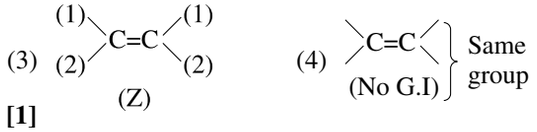
15. [2]

Use sequence rule or CIP rule

16. [2]

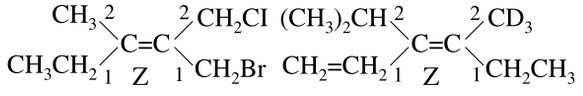


(Z) (E)



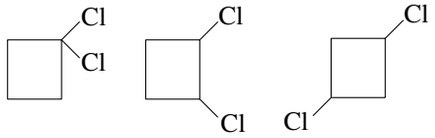
(Z) Same group

17. [1]



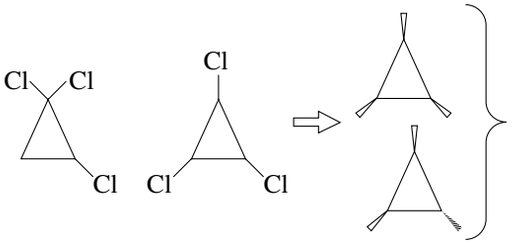
I II

18. [2]



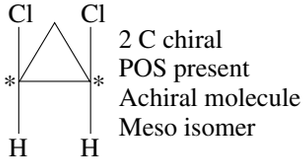
Cis and *trans* *Cis* and *trans*

19. [2]



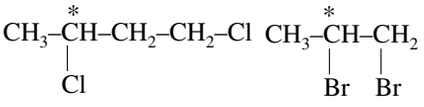
Total isomer = 3

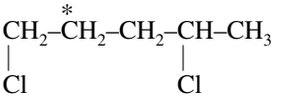
20. [3]

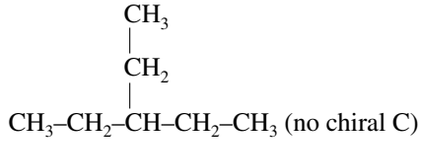


2 C chiral
POS present
Achiral molecule
Meso isomer

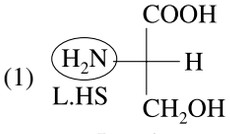
21. [4]



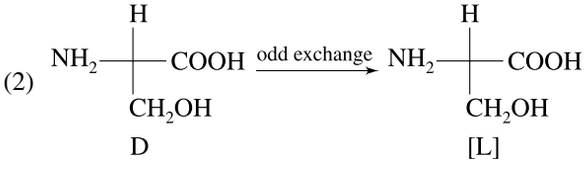




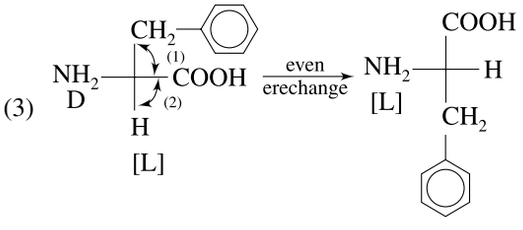
22. [2]



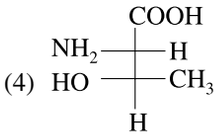
L series



D [L]

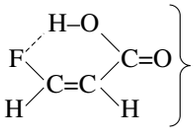


D [L] [L]

(4) 

L Series

23. [2]


Stable, six membered ring due to intra molecular H-bonding

24. [2]

$$C = \frac{30\ g}{100\ mL} = 0.3\ g/mL$$

$$\{\alpha\}_T^{\lambda} = \frac{\alpha}{\ell.C} = \frac{15}{0.3 \times 2} = +\ 25^\circ$$

25. [4]

A meso form, although containing chiral carbons is optically inactive due to the presence of plane of symmetry. Optical activity of one half of the molecule is exactly cancelled by other half, i.e., internally compensated.

26. [2]

II and III are meso form of hence diastereomers

27. [1]

Hint: Calculating R-S Configration of both chiral carbon & compare with R-S configration of other combound.

→ Opposite configulation bf some locant carbon shows enantiomerism.

28. [4]

III and IV are enantiomeric so that they do not have plane of symmetry.

29. [2]

Enantionmeric axis (d) = $\frac{30.8}{51.3} \times 100 = 60\%$

Racemic mix = 40%

d = 20% $\quad \ell$ = 20%

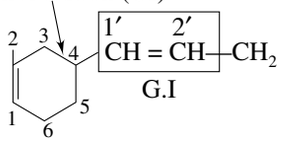
Total d = 60 + 20 = 80% $\quad \ell$ = 20

30. [4]

Pair of enantiomers react differently with a pure enantiomer of other compound.

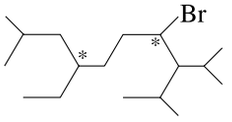
31. [3]

Chiral carbon (OI)


G.I

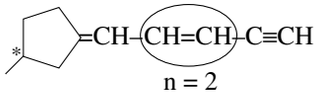
4-(1–propenyl) cyclohexene n = 2 (stereogenic centre)
number of stereo isomer = $2^2 = 4$

32. [2]



Chiral carbon = 2, number of S.I. = $2^2 = 4$

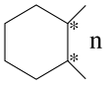
33. [2]



n = 2

number of S.I. = 2^2
= 4

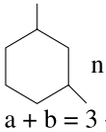
34. [2]


n = 2 (symmetrical)

$a = 2^{n-1} + 2^{\frac{n}{2}-1}$

$= 2^{2-1} + 2^{\frac{2}{2}-1}$

$= 2 + 1 = 3$

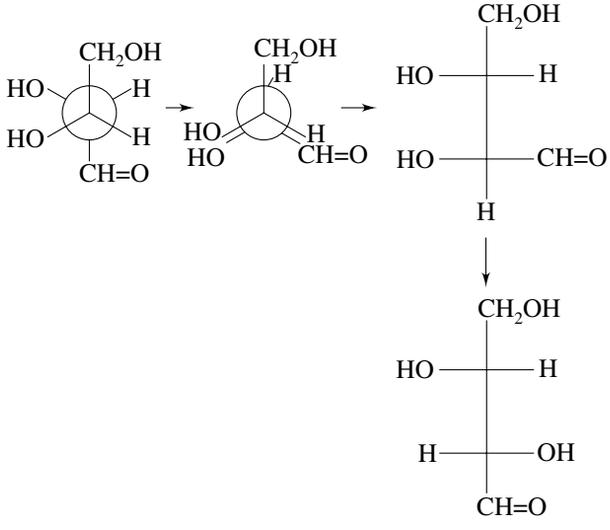

n = 2 (Symmetrical)

a + b = 3 + 3 = 6

35. [1]

By viewing structure properly

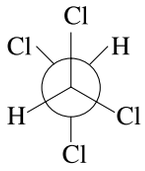
36. [1]



Only eclipsed form will convert into fisher projection.

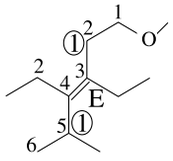
37. [4]

The most stable conformer is



Non-polar

38. [2]

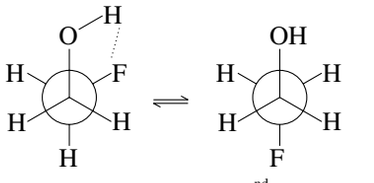


Numbering of parent chain takes place according to locant number rule.

39. [3]

refer Key Concept

40. [2]



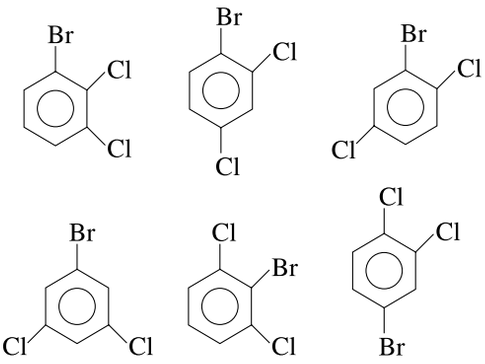
Most stable I

2nd most stable II

Conformer II has less steric strain than I.

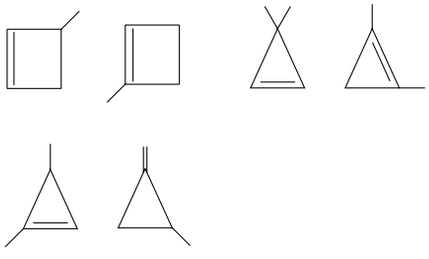
EXERCISE # 2

1. [3]

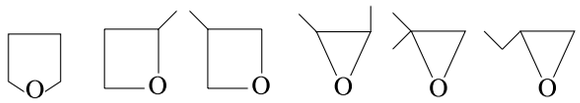


Number of isomer = 6

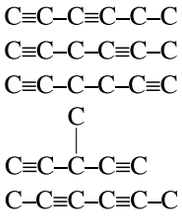
2. [4]



3. [3]

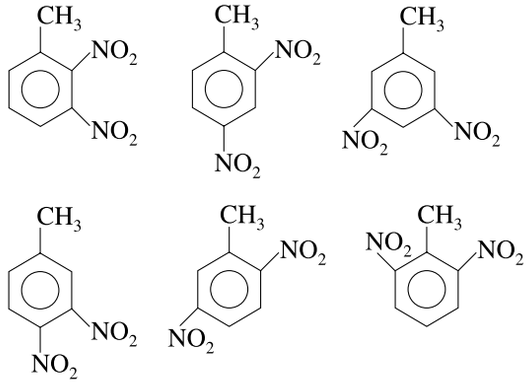


4. [3]



Number of alkyne isomer = 5

5. [3]



6. [3]

Condition for G.I.

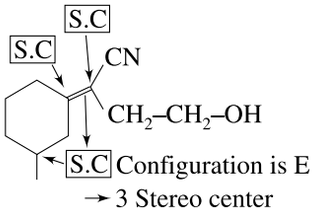
Each double bonded atom consist of pair of different group.

7. [3]

(I), (II) POS absent (optically active compound)

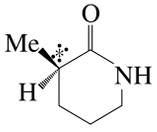
(III), (IV) POS present (Meso compound)

8. [1]



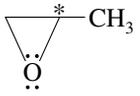
Number of isomer = 6

9. [2]

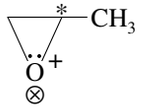


1 C chiral so molecule chiral

10. [2]

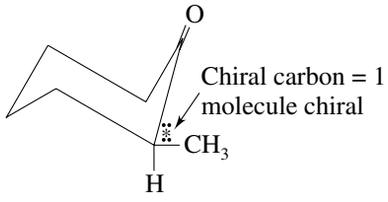


Chiral centre = 1



Chiral centre = 2

11. [2]



12. [3]

X → Show optical isomerism because (ring + double bond = even number)

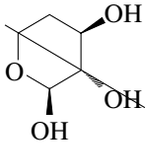
→ Exhibits enantiomerism.

Y → Show geometrical isomerism

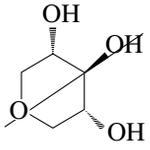
→ Exhibits distereomerism.

13. [2]

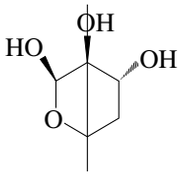
(II) and (IV) are identical



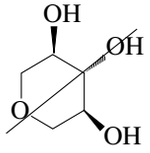
(I)
POS absent
Optically active



(II)
POS present
Meso

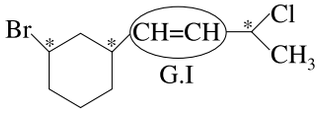


(III)
POS absent
Optically active



(IV)
POS present
Meso

14. [3]

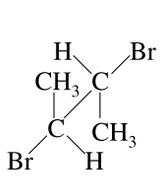


n = 4

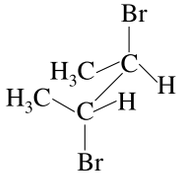
Number of Stereo isomer = $2^4 = 16$

15. [4]

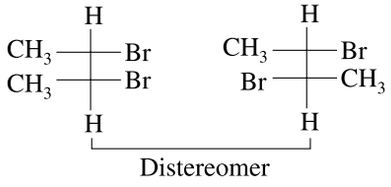
Eclipsed form of show Sawhorse be change into Fischer form.



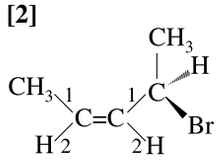
I



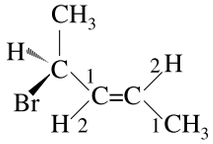
II



16. [2]



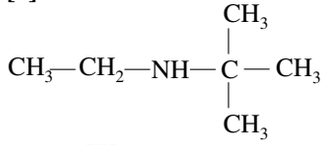
[Z]



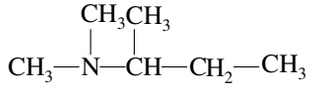
[E]

→ Diastereomers

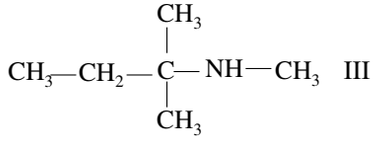
17. [4]



I



II

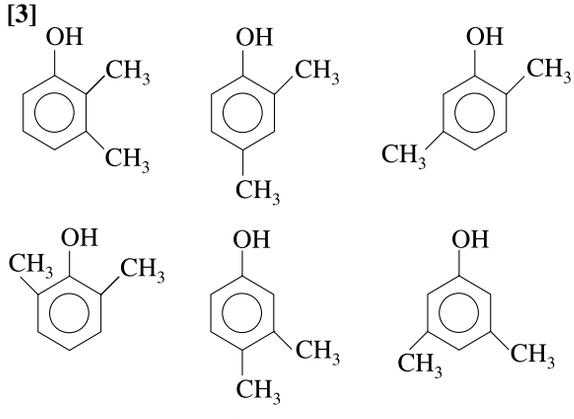


III

I & II – Functional Group will be differ.

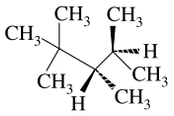
I & III – Alkyl groups will differ along same functional group. Hence they are metamers.

18. [3]



Number of isomer=6

19. [4]



- 1 carbon is chiral so that molecule is always chiral.
- In rest 1, 2, 3 potion no chiral carbon is present.

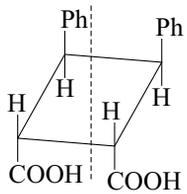
20. [4]

$$\text{Enantiomeric axis} = \frac{d - \ell}{d + \ell} = \frac{\text{Observed rotation}}{\text{Specific rotation}}$$

$$\Rightarrow \quad \frac{75 - 25}{75 + 25} = \frac{\text{Observed rotation}}{+158}$$

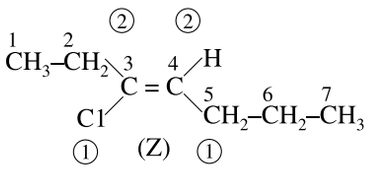
$$\text{Observed rotation} = \frac{158}{2} = +79°$$

21. [4]



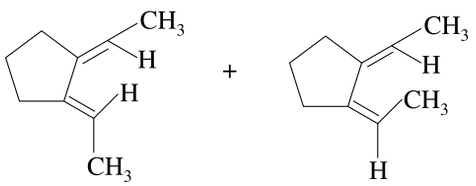
Equal half have mirror image of one another so that POS is present.

22. [4]



In rest other option, either E-form or double bond at 2nd carbon of parent chain

23. [4]



24. [2]

When there is three consecutive double bonds, terminals lie in the same plane giving geometrical isomerism

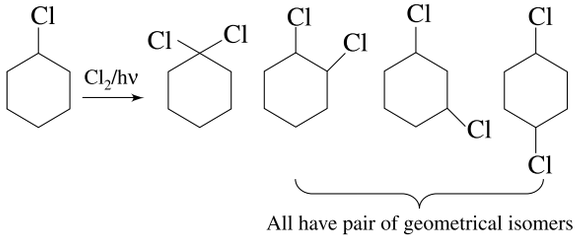
25. [2]

→ *Cis-cis*

→ *trans-trans*

→ *cis-trans*

26. [4]



All have pair of geometrical isomers

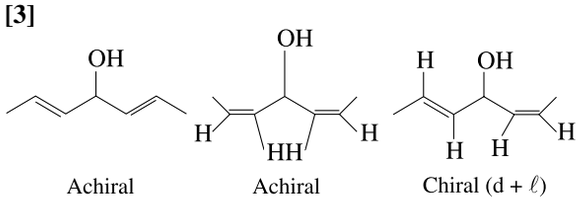
27. [3]

Presence of either plane of symmetry or centre of symmetry makes a molecule superimposable its mirror image, Presence or absence of axis of symmetry has no role to play in optical activity.

28. [3]

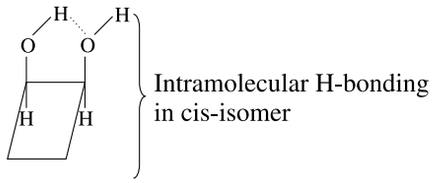
III and IV both are chiral and mirror images of one another.

29. [3]



Achiral Achiral Chiral (d + ℓ)

30. [3]

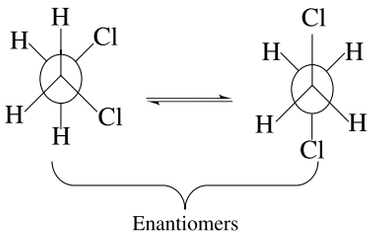


Intramolecular H-bonding in cis-isomer

31. [2]

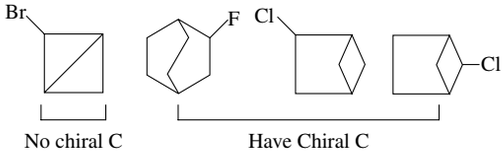
Cyclohexane has least angle strain. Cyclopropane has highest angle strain and angle strain decreases with increase in ring size reaches minimum in cyclohexane

32. [4]



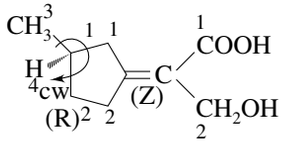
Enantiomers

33. [1]

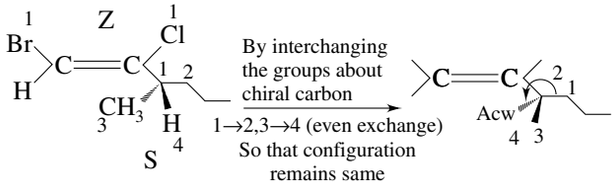


No chiral C Have Chiral C

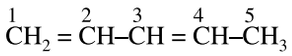
34. [2]



35. [3]



36. [4]

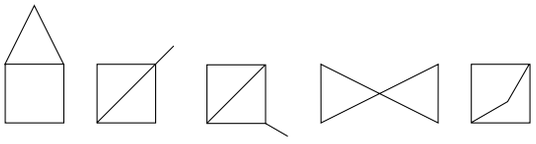


Type of C = 5

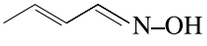
Type of H = 5

Number of monochloro product = type of H = 5

37. [3]



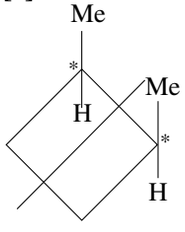
38. [3]



It is unsymmetrical compound having 2-stereogenic double bond

Number of S.I = $2^2 = 4$

39. [2]



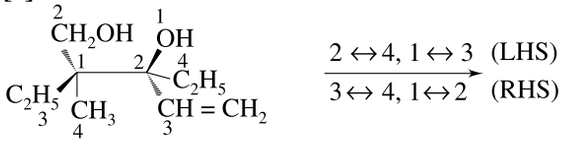
POS present

COS absent

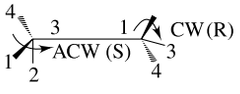
C* present

G.I. present

40. [3]



$\xrightarrow[3 \leftrightarrow 4,\ 1 \leftrightarrow 2]{2 \leftrightarrow 4,\ 1 \leftrightarrow 3}$ (LHS) (RHS)



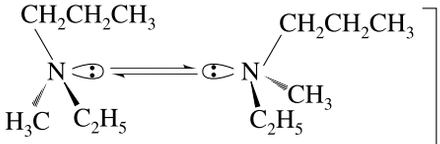
- Least proirity group always takes at inward the plane.
- By even exchange between the groups about chiral carbon then configuration remains same.
- Locant number of chiral carbon decided by IUPAC rule

EXERCISE # 3

One and More Than One Option Correct Type Question

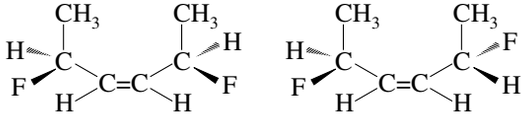
1. [1, 2, 3]

It show fluxional inversion at nitrogen and the two enantiomers remain in dynamic equilibrium

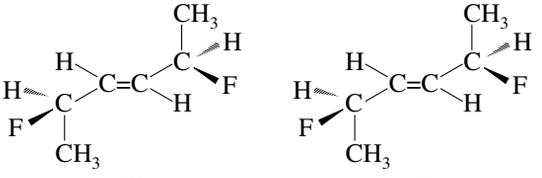


(I) (II)

2. [1, 2, 3]



(I) Meso (II) Chiral (d + l)



(III) Meso (III) Chiral (d + l)

Total six isomers, two optically incactive and four optically active. Both I and III upon ozonolysis followed by Zn-hydrolysis produces racemic mixture. II and IV on similar treatment yields a single optically active product in each case.

3. [1, 3, 4]

I and II conformers of enantiomers.

III is most stable due to largest groups at maximum distance.

I is enantiomeric while III is meso, hence I and II are diastereomers.

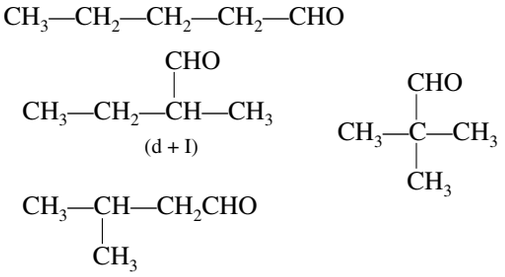
4. [1, 3]

Meso form is optically inactive as it is superimposable on its mirror image. In meso form, optical activity of one half is compensated by other half of the molecule, i.e., internally compensated.

5. [1, 3, 4]

Option 2 has a chiral carbon, show optical isomerism but cannot show geometrical isomerism.

6. [1, 2, 4]

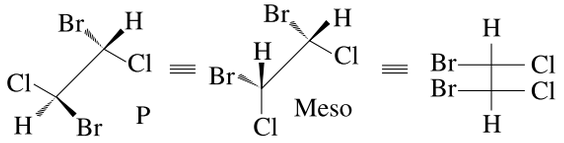


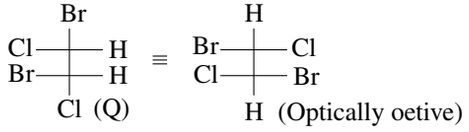
Total five aldehyde isomers. Out of five above shown aldehydes, two are chiral. All of the above aldehydes are capable of showing keto-enol tautomerism have diastereomeric enols.

7. [2, 3, 4]

All these have functional groups are in same plane can be non-polar. In (1), the two rings are in different plane, always polar.

8. [2,4]





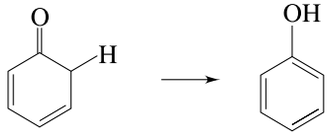
9. [1,2]

10. [3]

Statement-I is true but II is false. Because allene type substance do not have chiral centre even that they have chiral molecule.

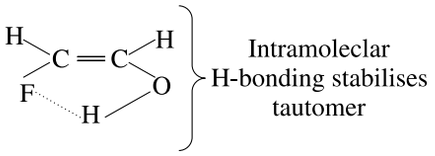
11. [1]

enol content ∝ stability of enol



≈100% enol content
aromatic substance

12. [1]



13. [4]

Compound is optically active inspite of possessing axis of symmetry.

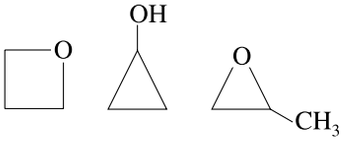
14. [1]

Enantiomers have opposite orientation of groups at chiral carbon.

Comprehension Type Question

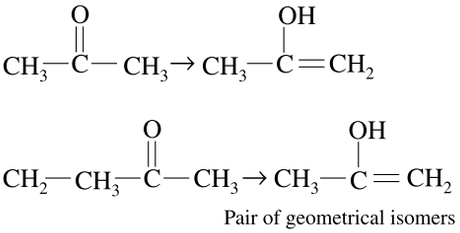
Passage (15 to 17):

15. [4]



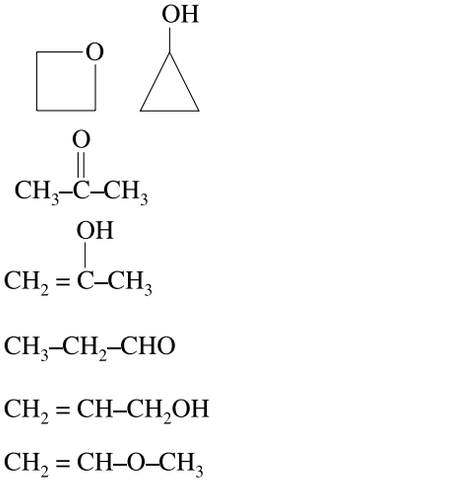
Chiral (d + l)

16. [3]



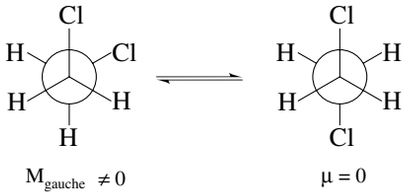
Pair of geometrical isomers

17. [4]



Passage (Q. 18 to 20):

18. [4]



$1.12\ D = (3.2)^2x + 0(1 - x)$

$x = 0.11$

Mole fraction of anti = $1 - x = 0.89$

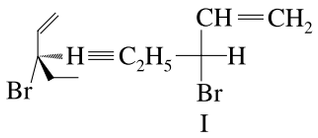
% anti-conformer = 89%

19. [3]

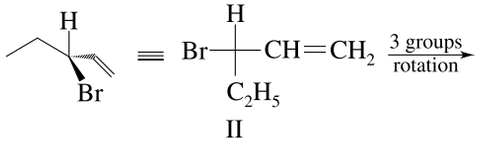
The two gauche conformers are enatiomers, combined they are 11%

20. [3]

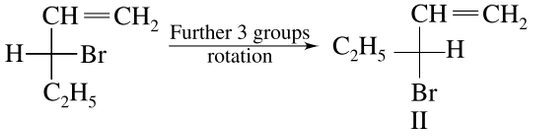
Increasing temperature will decrease percentage of both anti and gauche conformers as it will increase percentages of less stable eclipsed conformers.



I



II

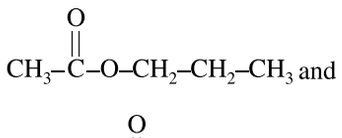


II

I and II are here same isomers.

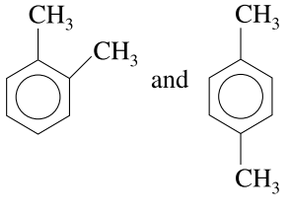
Column Matching Type Question

21. [1]

(A) 

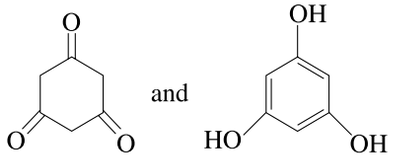
(R) metamers

Size of alkyl differ along same bivalent functional group

(B) 

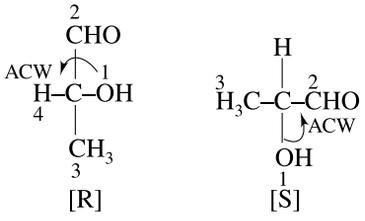
(Q) Position isomers

Locant number will be differ along same parent chain

(C) 

(S) Tautomers

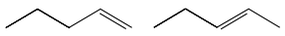
Functional group will be differ due to migration of proton

(D) 

(P) Enantiomer

22. [3]

(i) Pentene has several cyclic isomers.

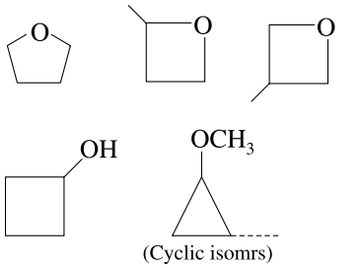


Cis + trans

Hence, (i) → (p, q, s)

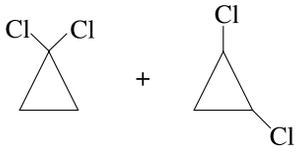
(ii) CH_3–CH=CH–OCH_3, shows *cis-trans* isomerism

1-methoxy propene

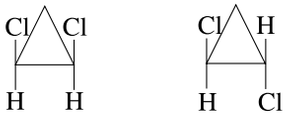


Hence, (ii) → (q, s)

(iii) Dichlorocyclopropane

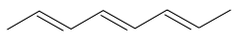


(Positional isomers)



(Geometrical isomers)

Hence, (iii) → (p, q)

(iv) 

(2, 4, 6-ocatriene)

It has several positional isomers and six geometrical isomers, i.e.,

cis-cis-cis

trans-trans-trans

cis-trans-cis

trans-cis-trans

cis-cis-trans

trans-trans-cis

It has several ring isomers.

∴ (iv) → (r, s)

23. [1]

(i) → (q, r, s); (ii) → (p, r);

(iii) → (q, s); (iv) → (q, s)

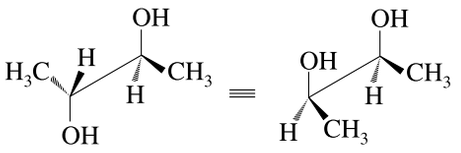
(i) *cis-cis* and *trans-trans* are achiral while *cis-trans* is chiral giving total four stereoisomers.

(ii) Diastereomers can be both optically active, inactive can be separated meso form consist of plane of symmetry.

(iii) Meso form is optically inactive, usually consists of plane of symmetry.

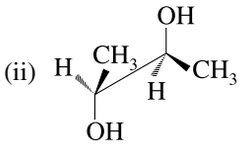
(iv) Racemic mixture consists of equal amount of enantiomers, hence optically inactive. However, it can be resolved into enantiomers.

24. [3]

(i) 

Has centre of symmetry Has plane of symmetry

(i) → (p, r)

(ii) 

It has C-2 axis of symmetry passing through centre of C_2–C_3 bond. However, this compound is optically active.

(ii) → (q, s)

(iii) Compound is achiral, has all three types of symmetry.

(iii) → (p, q, r)

(iv) It ahs both plane and axis of symmetry.

(iv) → (p, q)

25.

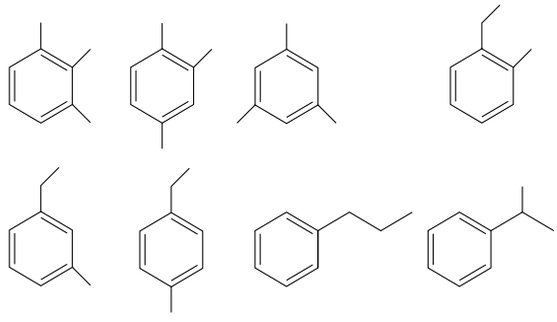
Sol. (A)→(Q); (B)→(R); (C)→(P); (D)→(Q)

26.

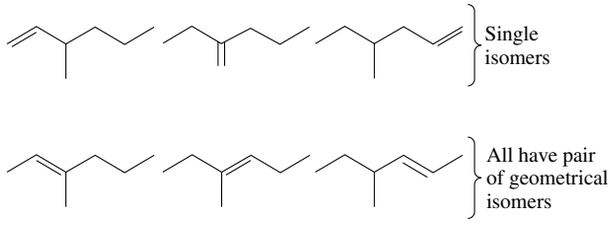
Sol. (A)→(R); (B)→(Q); (C)→(P); (D)→(P)

Single Digit Integer Type Question

27. [8]

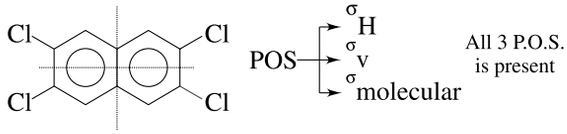


28. [9]

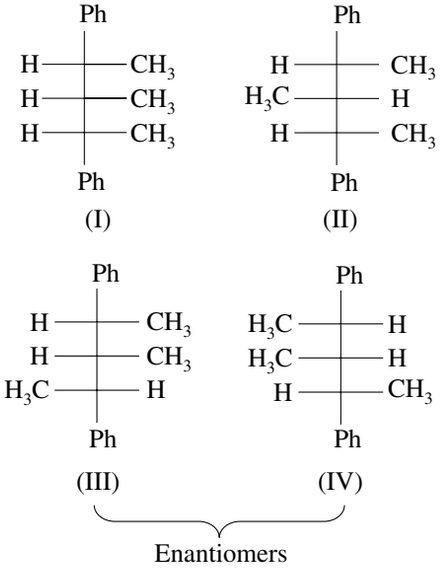


29. [4]

30. [3]



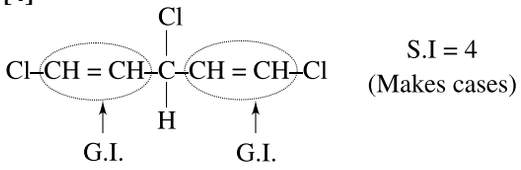
31. [5]



Pair of diastereomers are

I + III, I + IV, II + III, II + IV and I + II.

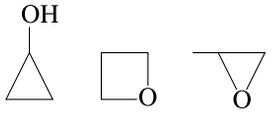
32. [4]



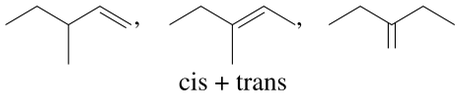
S.I = 4
(Makes cases)

33. [2]

Given condition (no sp & sp^2 atom) satisfied only when ring isomer exist



34. [3]



cis + trans

EXERCISE # 4

1. [3]

Geometrical & Optical isomerism are different type of Stereo-Isomerism.

2. [2]

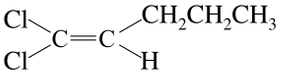
two groups or atoms attached to doubly bonded carbon atoms should be different for G.I.

$CH_3–CH_2–CH=CH_2$

3. [4]

Racemic mixture is an equimolar mixture of enantiomers.

4. [1]

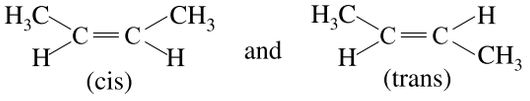


two groups or atoms attached to doubly bonded carbon atoms should be different for G.I.

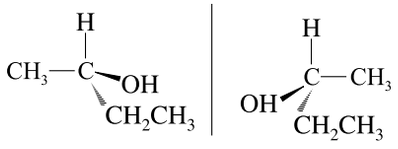
5. [1]

Racemic mixture is mixture of chiral carbons

6. [4]



Geometrical isomers (cis-trans)



Molecule is optically active enantiomers

Geometrical isomers and enantiomers both are stereoisomers.

7. [4]

Chiral compounds are those which have one chiral centre, i.e., all four atoms or groups attached to same carbon are different. Here, I and II are chiral but III and IV are achiral compounds.

8. [1]

Chiral carbon has all the four different groups attached to it.

(1) $CH_3CH_2CH_2CH_2CH_2Cl$ (no chiral carbon atom)

(2) $CH_3\overset{*}{C}HCH_2CH_2CH_3$ (one chiral carbon atom)
Cl

(3) $CH_3CH_2CH_2\overset{*}{C}HCH_2Cl$ (one chiral carbon atom)
Cl

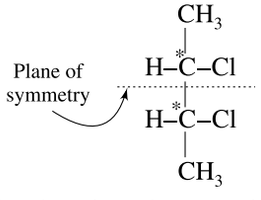
(4) $CH_3–\overset{*}{C}H–\overset{*}{C}HC–H_2CH_3$ (two chiral carbon atoms)
Cl Cl

9. [2]

(1) $CH_3–\overset{*}{C}H–CH_2CH_3$
Cl

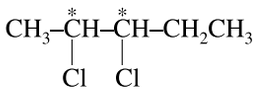
One asymmetric carbon atom, forms *d*-and *l*-optical isomers.

(2)

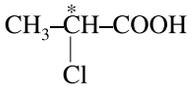


Meso due to intemal compensation

Two asymmetric carbon atoms, forms *d*-, *l*-and meso forms.

(3) 

Two asymmetric carbon atoms but does not have symmetry. Hence, meso form is not formed.

(4) 

One asymmetric carbon atom, meso form is not fomed

10. [4]

In CH_3CH_2OH, there is intermolecular H-bonding while it is absent in isomeric ether CH_3OCH_3.

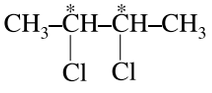
Larger heat is required to vaporise CH_3CH_2OH, as compared to CH_3OCH_3, thus (1) is incorrect.

CH_3CH_2OH is less volatile than CH_3OCH_3, thus vapour pressures are different, thus (2) is incorrect.

Boiling point of CH_3CH_2OH > CH_3OCH_3, thus (3) is incorrect.

Density = $\frac{\text{mass}}{\text{volume}}$, due to ideal behaviour at a given temperature and pressure, volume and molar mass are same. Hence, they have same vapour density.

11. [1]

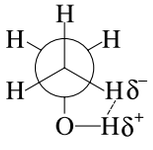


There are two chiral C-atom (*)

Thus, it shows optical isomerism.

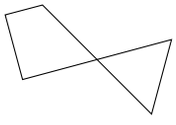
12. [2]

HO–CH_2–CH_2–F



Gauche-conformation is comparatively more stable due to hydrogen linkage in between F and H (at O-atom), hence increasing order of stability is eclipsed, anti (staggered), gauche.

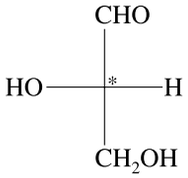
13. [1]



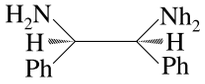
Chair form is unsymmetrical and has absence of any element of symmetry.

14. [1]

The molecule, which is optically active, has chiral centre, is expected to rotate the plane of polarised light.

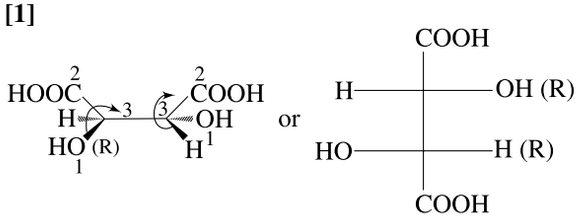


One chiral centre hence, optically active



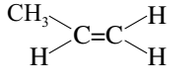
Two chiral centres, but plane of symmetry within molecule hence, optically inactive.

15. [1]

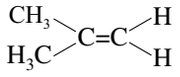


16. [3]

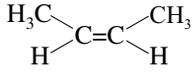
Geometrical isomerism is shown by those alkenes only in which atoms or groups attached to each carbon atom are different. Thus,



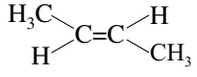
Propene
(three-atoms H linked to doubly bonded C-atoms are same, thus no geometrical isomerism)



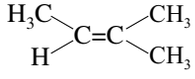
2-methyl propene
(no geometrical isomerism)



cis-2-butene
(methyl group and H-atom linked to doubly bonded C-atom lie on same side, hence, cis isomer)



Trans-2-butene
H-atom lie on opposite side to one another, hence, trans isomer



2-methyl-2-butene
(no geometrical isomerism)

17. [3]

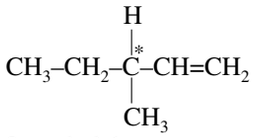
There are four stereoisomers

cis (R), *cis* (S), *trans* (R), *trans* (S)

18. [4]

Optical isomerism is shown by the carbon compounds which possess atleast one chiral carbon.

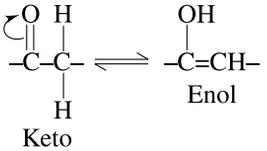
Thus, 3-methyl-1-pentene possess a chiral carbon, hence it shows optical isomerism



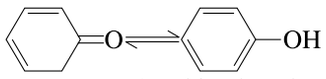
3-methyl-1-pentence
(It has one chiral centre)

19. [3,4]

Tautomerism is due to spontaneous interconversion of two isomeric forms with different functional groups into one another. The term tautomer means constitutional isomers that undergo such rapid interconversion that cannot be independently isolated



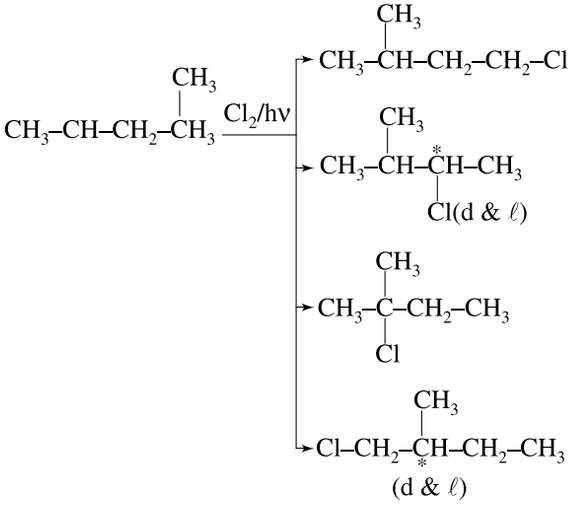
Keto Enol



Keto Enol in phenol

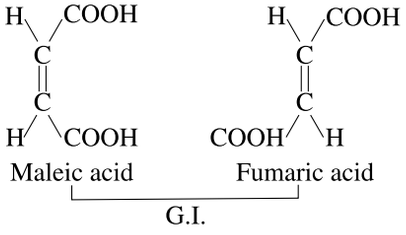
Thus, (3) 2-pentanone and (4) Phenol exhibit tautomerism.

20. [2]



- Each chiral carbon ($\overset{*}{C}$) cantaining substance have two chiral molecule
- Total chiral molecule

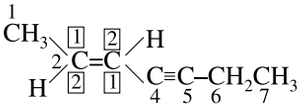
21. [3]



Maleic acid Fumaric acid

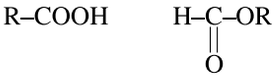
G.I.

22. [4]



(E) – 2 – heptene – 4 – yne

23. [3]



Carboxylic acid and ester have same M.F

- Hence mono carboxylic acid in functional group isomer of ester.

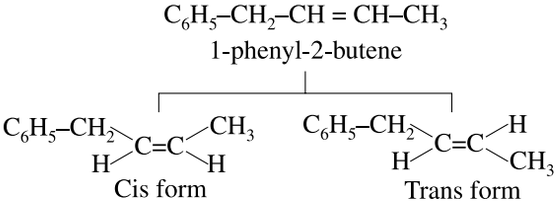
24. [3]

25. [3]

All other have at least one chiral C so they will show optical isomerism only maleic acid have no chiral carbon, thus it do not show optical isomerism

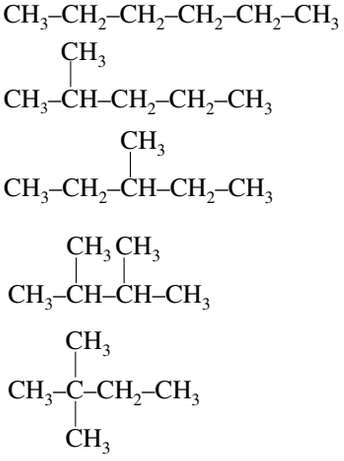
26. [1]

For G.I. each double bonded carbons have pair of different group/atom



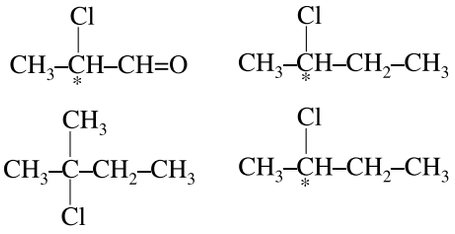
Cis form Trans form

27. [4]



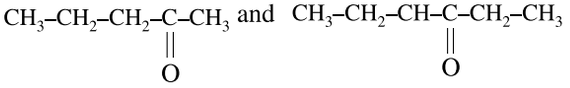
Total structural. isomer = 5

28. [3]



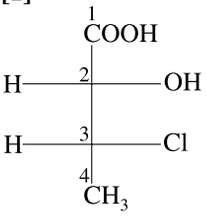
No chiral carbon
op. inactive

29. [1]



Same MF, but locant number of functional group will differ along same parcent carbon chain so it is pair of position isomer

30. [1]



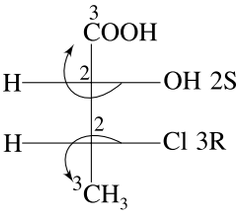
For C-2, order of priority of substituents is

OH > CH(Cl)(CH_3) > COOH (According to CIP rules)

For C-3, order of priority of substituents is

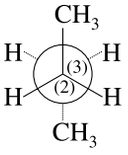
Cl > CH(OH)(COOH) > CH_3 (According to CIP rules)

Hence

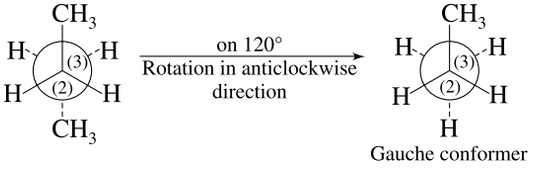


31. [4]

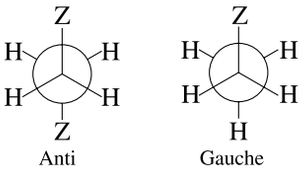
Here, when C_2 is rotated anticlockwise 120° about C_2–C_3 bond the resulting conformer is gauche conformer.



Hence



32. [1]



Mole-fractin of anti form = 0.82

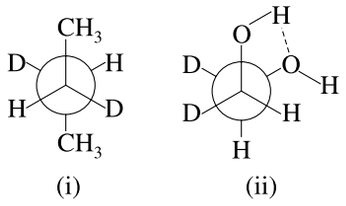
Mole-fraction of gauche form = 0.18

$\mu_{obs} = 1\ D \Rightarrow 1 = \mu_{anti} \times 0.82 + \mu_{gauche} \times 0.18$

$\because \quad \mu_{anti} = 0 \Rightarrow 1 = \mu_{gauche} \times 0.8$

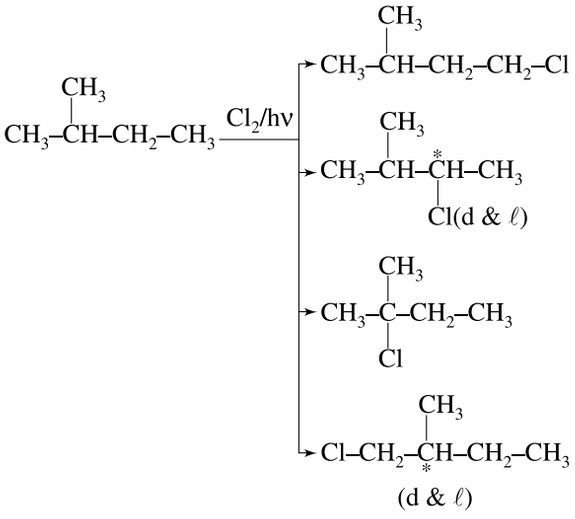
$$\mu_{gauche} = \frac{1}{0.18} = 5.55\ D$$

(b)



Structure (ii) is more stable than its anti-conformer because of intramolecular H-bonding

33. [1]

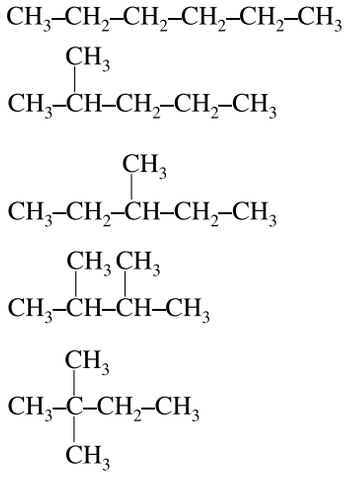


N $\xrightarrow[\text{distillation}]{\text{Fractional}}$ F = 4

Separation of d and ℓ isomers do not takes place by fractional distillation

- Total number of structural isomers (N) = 6

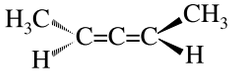
34. [3]



Total structural isomer = 5

35. [3]

Molecules that are non-superimposable on its mirror image are optically active and known as chiral molecule. However, for chirality of molecule, presence of chiral centre is not essential

e.g., 

Molecule is chiral but does not possesses any chiral carbon

36. [1,4]

The compound is optically active as well as it possesses a two-fold axis of symmetry

37. [2,3,4]

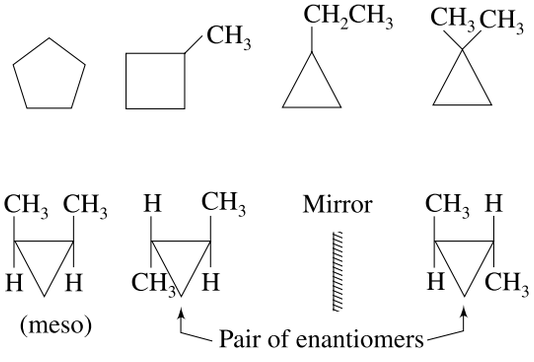
E, F and G are not resonance structures because movement of hydrogen between E and F are involved.

E, F and E, G are tautomers in which E is keto form and both F and G are enol form of the same E.

F and G are geometrical isomers.

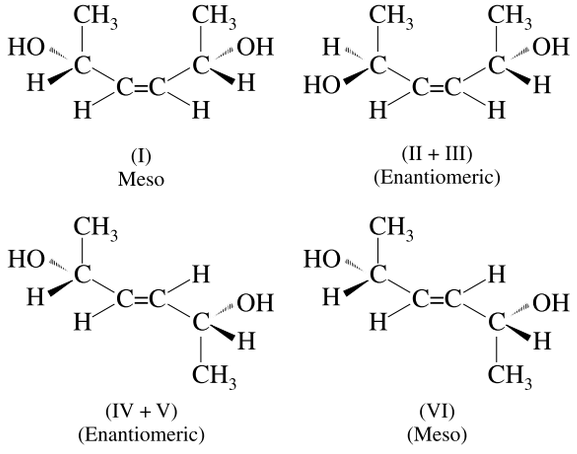
F and G are diastereomers as they are stereoisomers but not related by mirror image relationship.

38. [7]

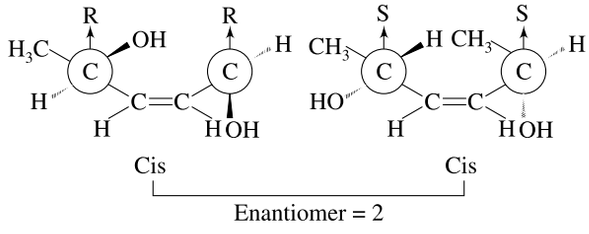


Total seven isomers.

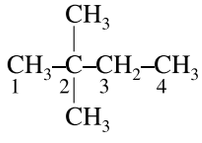
39. [1,4]



Total six isomers, in both *cis* and *trans* forms, there are two enantiomers each.



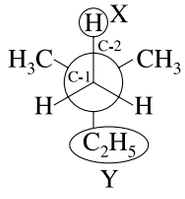
40. [2,4]



Conformation projection along C_1–C_2

C_1 contains all three Hs

So, X = H



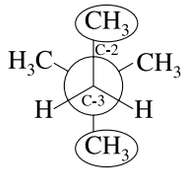
C_2 contains two methyl and one ethyl group

So, Y = C_2H_5

Conformational projection along C_2–C_3

C_2 contains three methyl groups (C_2 from the back carbon in the given structure)

So, Y = CH_3



C_3 contains two Hs and one methyl group

[C_3 form front carbon in the given structure]

So, X = CH_3

C_3 contains two Hs and one methyl group

(C_3 form front carbon in the given structure)

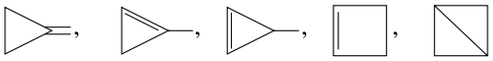
So, X = CH_3

Isomerism (Stereochemistry)

Conceptual (Structural visualisation) III

41. [1]

C_4H_6 can have five cyclic isomers

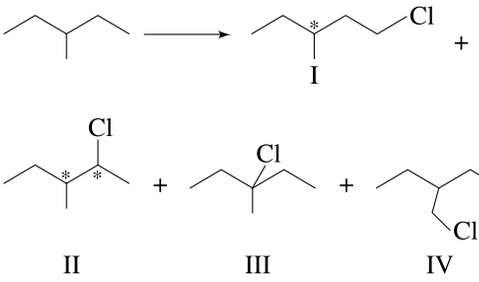


Isomerism (organic)

Structural manipulation

III

42. [4]



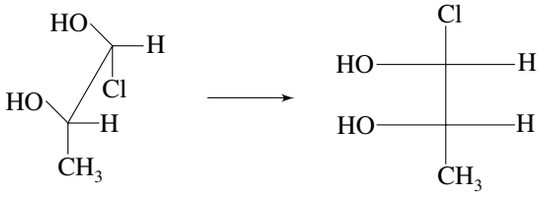
I has one chiral carbon = two isomers

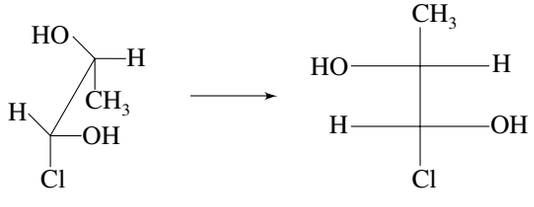
II has two chiral carbons and no symmetry = four isomers.

III and IV have not chiral carbon, no stereoisomers.

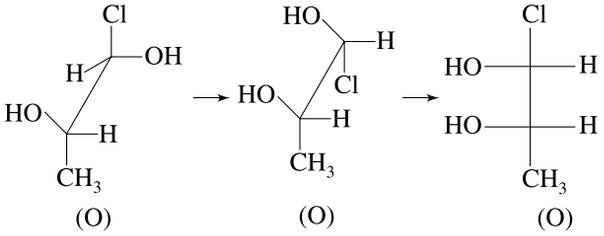
43. [1,2,3]

Converting all of them into Fischer projection.





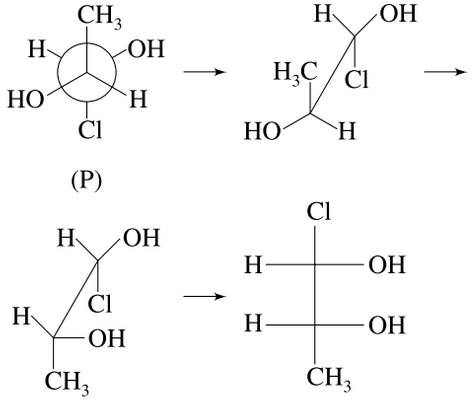
Since, M and N have –OH on same side and opposite side respectively, they cannot be mirror image, they are diastereomers.



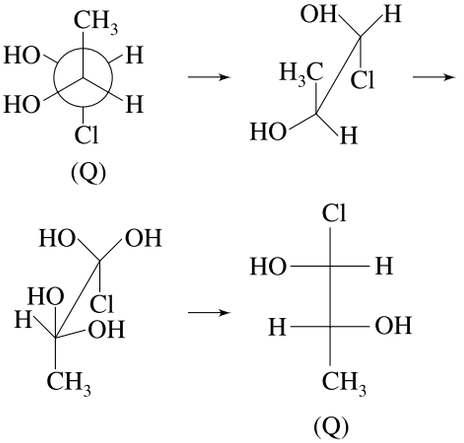
M and O are identical.

Note: Fischer projection represents eclipsed form of Sawhorse projection.

For comparison purpose, similar types of eclipsed conformers must be drawn, i.e., both vertically up or both vertically down.



M and P are non-superimposable mirror images, hence, enantiomers.



M and Q are non-identical they are diastereomers.

44. [1,3,4]

Plan this problem is based on structure and nomenclature of organic compound.

Draw structure of each compound and write IUPAC name of the given compound.

Match the molecular formula of given compound with molecular formula of compound given in choices.

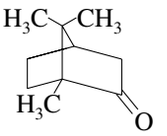
The combination of names for possible isomeric alcohols with molecular formula $C_4H_{10}O$ is/are

Formula	Names
$CH_3CH_2CH_2CH_2OH$	n-butyl alcohol/n-butanol/butan-1-ol
$CH_3–CH_2–CH(CH_3)–OH$	Isobutyl alcohol/2-methyl propan-1-ol
$CH_3–CH(CH_3)–CH_2–OH$	Secondary butyl alcohol/butan-2-ol
$CH_3–C(CH_3)_2–OH$	Tertiary butyl alcohol/2-methyl propan-2-ol

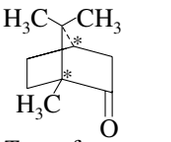
Hence, choices (1), (3) and (4) are correct

45. [2]

Although the compound has two chiral carbons (indicated by stars), it does not has four optically active isomers as expected. It is due to its existence in *cis*-form only



cis-form



Trans-form
(only hypothetical)

The above shown transformation does not exist due to restricted rotation about the bridge head carbons, hence only *cis*-form and its mirror image exist.

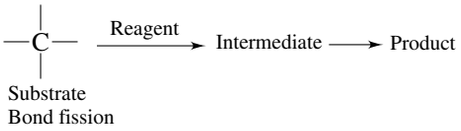
46. [1]

L-(–)-glucose is enantiomer of D-(+)-glucose with hydroxyl group on left of vertical at C-5 (L-configuration).

CHAPTER 3

General Organic Chemistry

MECHANISMS OF REACTIONS



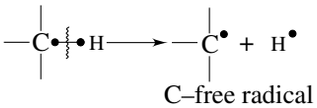
BREAKING OF COVALENT BOND (BOND FISSION)

The fission of a covalent bond can take place in two ways depending upon the nature of the given compound, the nature of attacking reagent and the reaction conditions.

(1) Homolytic fission or homolysis.

(2) Heterolytic fission or heterolysis.

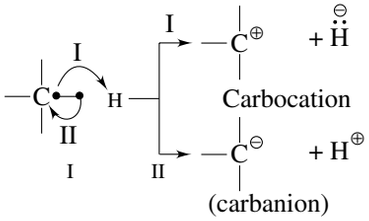
(1) Hemolytic bond fission (Homolysis): Such fission in which bond pair is equally distributed in between respective atoms, which leads the formation of free radical is known as homolysis.



Favorable conditions

1. When the EN difference between two atoms is zero or near zero.
2. Reaction is carried out at high temp. ($T \geq 500°$)
3. In presence of sunlight.
4. When reagent is radical.
5. In presence of peroxide or tetraethyl lead (TEL)
6. In presence of Non-polar solvent.
7. In gaseous phase of reacting mixture.

(2) Heterolytic bond fission (Heterolysis): Such fission in which bond pair completely transfers towards one of the atoms, which leads the formation of ions is known as heterolysis.



Favorable conditions

(1) When EN difference between two atoms is very high.

(2) Reaction is carried out at low temp.

(3) In presence of ionic reagent.
(4) In presence of polar solvents.
(5) In liquid phase of reacting mixture.

Note: Energy needed for heterolysis is always greater than energy needed for homolysis.

Attacking Reagent

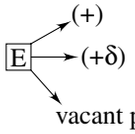
Most of the attacking reagent can be classified as follows:

(1) Electrophiles
(2) Neucleophiles
(3) Ambiphiles
(4) Free Radicals

(1) Electrophiles:

- They are e^- loving species.
- They are e^- deficient reagent.
- They are e^- pair acceptor from any donor.
- They are also behave as Lewis acid.

Identification:



Some of the electrophiles are listed below:

Type-I: +vely charged electrophile (E^+)

All cation except cation of IA, IIA, H_3O^+, $NH_4^{\oplus}$

$\overset{\oplus}{H}$, $\overset{\oplus}{C}H_3$, $\overset{\oplus}{C}l$, $\overset{\oplus}{N}O_2$, $N\overset{\oplus}{O}$, $S\overset{\oplus}{O}_3H$, etc.

Type-II: Neutral electrophile

(i) Vacant p orbital $BeCl_2$, BF_3, $AlCl_3$, $\ddot{C}H_2$, $\ddot{C}Cl_2$, etc.
(ii) Vacant d orbital $SnCl_2$,$SnCl_4$, $ZnCl_2$, $FeBr_3$, $SbCl_5$, etc

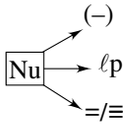
Type-III: After bond break

(i) Like YZ_n type molecule EN(y) < E.N.(z), $n \geq 2$
CO_2, CCl_4, NF_3, SO_3, etc
(ii) Halogen molecule Br–Br, Cl–Cl, I–I

(2) Neucleophiles:

- They are nucleus loving species.
- They are e^- rich reagent.
- They are e^- pair donor to any acceptor.
- They also behave as Lewis base.

Identification:



Some of the Neucleophiles are listed below:

Type-I: (–)vely charged nucleophile (nu)

All anions $\overset{\ominus}{H}$, $\overset{\ominus}{C}H_3$, $\overset{\ominus}{O}H$, $\overset{\ominus}{F}$, $\overset{\ominus}{N}H_2$, $\overset{\ominus}{N}_3$, $CH{\equiv}\overset{\ominus}{C}$, $R–COO^-$, etc.

Type-II: Neutral nucleophile

(i) Compound with the atom having at least one ℓp.

$H_2\ddot{O}$, $\ddot{N}H_3$, $\ddot{P}H_3$, CH_3–OH, CH_3–NH_2

(ii) Compound with the atom having π-bond

Alkene/Alkyne type R – CH = CH_2, R–C ≡ CH, Benzene, etc.

Type-III: All organometallic compounds

R Mgx, R_2 Zn, R_2LiCu, ete.

Type-IV: *Ambident nucleophile:* two or more nucleophilic site in a molecule.

$C \equiv \overset{\ominus}{N}$, $N\overset{\ominus}{O}_2$, $S\overset{\ominus}{O}_3$, NH_2OH, etc.

(3) Ambiphiles: Such reagent which behave both as electrophile as well nucleophile is known as ambiphile.

Organic substance in which carbon-atom directly attaches with highly EN atom with multiple bond behaves as ambiphile.

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3,\ CH_3-C\equiv N,\ CH_3-\underset{\underset{O}{\|}}{C}-Cl,\ CH_3-\underset{\underset{O}{\|}}{C}-NH_2,\ \text{etc.}$$

(4) Free Radicals:

- They are neutral species.
- They are e^- deficient reagent.
- They consist of unpaired e^- or odd e^-
- They are highly reactive.
- Requirement of one electron form completing their octet.

$\dot{H}$, $\dot{C}H_3$, $\dot{C}\ell$, R–$COO^{\bullet}$, $O\dot{H}$, etc.

REACTION INTERMEDIATES

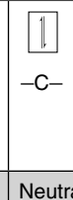
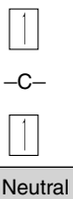
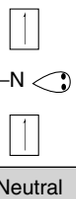
In the study of organic chemistry following intermediates are important.

(i) Carbocation
(ii) Carbanion
(iii) Carbon free radical
(iv) Carbene
(v) Nitrene

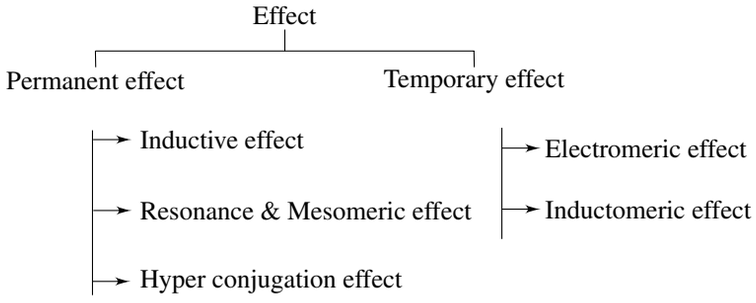
Carbocation, Carbanion and Carbon free radical are of following type

Property	Carbocation	Carbanion	Carbon free radical
Representation			
Bond fission	Heterolysis	Heterolysis	Homolysis
Electrical nature	Positive	Negative	Neutral
Number of electrons in valence shell	6	8	7
Hybridisation	sp^2	sp^3	sp^2
Shape	Planar	Pyramidal	Planar
Number of unpaired e(n)	0	0	1
Magnetic moment ($\mu = \sqrt{n(n+2)}$ B.M.)	0	0	1.73 BM
Magnetic nature	Diamagnetic	Diamagnetic	Paramagnetic
Reagent	Electrophile	Nucleophile	Electrophile

- Carbene and Nitrene each are of following two types:

Property	Singlet carbene	Triplet carbene	Singlet nitrene	Triplet nitrene
Representation				
Electrically nature	Neutral	Neutral	Neutral	Neutral
Number of electrons in valence sheet	6	6	6	6
Hybridisation	sp^2	sp	sp^2	sp
Shape	V-shape	Linear	Linear	Linear
Stability	Less	More	Less	More

FACTORS INFLUENCING THE COVALENT BOND



INDUCTIVE EFFECT (I-EFFECT)

$\delta_0 \quad \delta\delta\delta_+ \; \delta\delta_+ \quad \delta_+$
$C_4—C_3—C_2—C_1—Z \; \{EN© < EN(z)\}$
(Source)

- Due to partial displacement of bond pair towards more EN atom, polarisation of carbon chain takes place, known as I effect.
- Cause → due to difference in E.N.

Characteristics

1. It is a permanent effect.
2. It is a weak effect because only partial charge develops.
3. It is operated by σ bond (works in between σ bond).
5. Shifted bond pair never loses parent orbital.
6. I–effect is distance dependent.

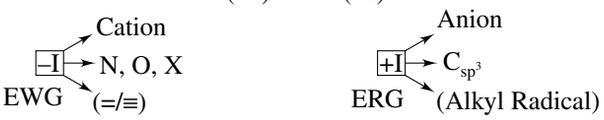
+I EFFECT/–I EFFECT

1. **+I effect:** Such atom/group which repels σ electrons as compared to H-atom are +I group and observed effect is +I effect.
   - +I effect showing group ⇒ Electron repelling group (E.R.G.)
2. **–I effect:** Such atom/group which attracts σ electrons as compared to H-atom are –I group and observed effect is –I effect.
   - –I effect showing group ⇒ Electron withdrawing group. (E.W.G.)

Identification:

Trick:

$$E.N.(Csp^3) < E.N(z)$$
$$(+I) \qquad (-I)$$



–I series.

$$-\overset{\oplus}{N}F_3 > \overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > -\overset{\oplus}{S}R_2 > -NO_2 > -C\equiv N > -COOH > -COOR > -CH=O > -F >$$
$$-OR > -OH > Cl > Br > I > -NH_2 > -C\equiv CH > Phenyl > -CH=CH_2 > H.$$

+I series: $= \overset{\ominus}{N}H_2 > O^{\ominus} > -COO > R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}(3°) > R-\underset{(2°)}{\overset{\overset{R}{|}}{CH}} > R-\underset{(1°)}{CH_2} > -CH_3 > T > D > H$

Application of I effect:

1. **Stability of reaction intermediate:**

   Stability of $-\overset{|}{C}^{\oplus} \propto +I \propto \frac{1}{-I}$

   Stability of $-\overset{|}{C}^{\ominus} \propto -I \propto \frac{1}{+I}$

   Stability of $-\overset{|}{C}^{\bullet} \propto +I \propto \frac{1}{-I}$

   trick → Like to Like stability

   $-\overset{|}{C}^{\oplus}$ (|) $\quad +I \quad$ Stability↑

   $-\overset{|}{C}^{\oplus}$ (|) $\quad -I \quad$ Stability↑

Note: I factor works only when bonding nature of charged atom is same (EN same)

2. **Acidic Strength:**

   According to Bronsted theory

   Acidic strength ∝ stability of anion

   Acidic strength $\propto -I \propto \frac{1}{+I}$

   Acid strength ↑ Ka ↑ Pk_a ↓ PH ↓

3. **Basic Strength:**

   Basic strength $\propto +I \propto \frac{1}{-I}$

   Base strength ↑ k_b ↑ Pk_b ↓ PH ↑

   Some facts:

   - I effect works only when source group is same.
   - Between strength and distance, distance must be preferred over strength.
   - Between strength and number of –I group, number must be preferred over strength.

Basic strength of 1°/2°/3° amine

Due to steric hindrance of three alkyl group, donation of lone pair becomes difficult so that it is less basics (basic strength decreases) **As per NCERT**

In aqueous solution

(i) R = – CH_3

$2° > 1° > 3° > NH_3$

(ii) R = $–C_2H_5$

$2° > 3° > 1° > NH_3$

In vapour state

$3° > 2° > 1° > NH_3$

Note: If medium is not given then basic strength is compared only in aqueous solution.

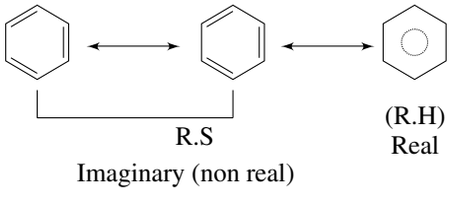
RESONANCE AND MESOMERIC EFFECT

Such hypothetical phenomena in which one of the substance can be represented by more than one imaginary structure known as resonance.

Permanent electron delocalisation of π-bond in nuclear framework or carbon chain is known as resonance.

→ These imaginary non-real structures are known as resonating strength (R.S) or canonical structure.

→ One of the real structure formed by contribution of all canonical form known as resonating hybrid (R.H).



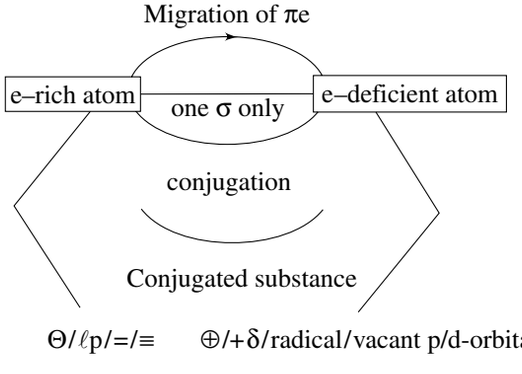
Cause: It is due to de-localisation of π $-e^-$ in conjugate substance.

Condition for resonance:

(1) Molecule or its part must be planar i.e., participating atom lies in same plane.

(2) Molecule must be in conjugation.

- When e^- rich and e^- deficient atoms are separated by only one σ-bond, then such atoms are said be in conjugation.
- Such substance which consists of at least 2-conjugated atoms is known as conjugated substance.
- In conjugate substance, migration of πe from e–rich to e–deficient atom takes place, is known as de-localisation



- Double/triple bond may be e^- rich or e^- deficient depending upon nature of other part.

(1) **Rules for directing arrow in resonance:**

(1) π-electron migrates towards cation during resonance.

(2) Anion electron migrates towards π-bond during resonance.

(3) Homolytic cleavage of π-bond takes place if radical show resonance.

(4) Lone pair electron migrates towards π-bond.

(1) $C=C\overset{\curvearrowright}{\underset{\sigma}{}}A^{\oplus} \longleftrightarrow \overset{\oplus}{C}-C=A$

(2) $\overset{\curvearrowleft}{C}=C\overset{\curvearrowleft}{\underset{\sigma}{}}A^{\ominus} \longleftrightarrow \overset{\ominus}{C}-C=A$

(3) $\overset{\curvearrowleft}{C}\overset{\curvearrowright}{=}C\overset{\curvearrowleft}{\underset{\sigma}{}}A^{\bullet} \longleftrightarrow {}^{\bullet}C-C=A$

(4) $C=C\overset{\curvearrowright}{\underset{\sigma}{}}C=\overset{\curvearrowright}{C} \longleftrightarrow \overset{\oplus}{C}-C=C-\overset{\ominus}{C}$

(5) $\overset{\curvearrowleft}{C}=C-\overset{\curvearrowleft}{\ddot{A}} \longleftrightarrow \overset{\ominus}{C}-C=\overset{\oplus}{A}$

(6) $C=C\overset{\curvearrowright}{\underset{\sigma}{}}C=\overset{\curvearrowright}{O} \longleftrightarrow \overset{\oplus}{C}-C=C-\overset{\ominus}{O}$

(7) $\overset{\oplus}{C}\overset{\curvearrowleft}{\underset{\sigma}{}}\ddot{O} \longleftrightarrow C=\overset{\oplus}{O}$

(8) $A^{\oplus}-\overset{\curvearrowleft}{B}^{\ominus} \longleftrightarrow A=B$

Properties of resonating structures:

(1) Resonating structures (R.S.) are imaginary structures, so they can't be isolated.

(2) Resonating hybrid (R.H.) is the real structure so that it can be isolated.

(3) R.H can be formed by equal or unequal contribution of individual R.S.

(4) The whole property of conjugate substance can be explained by only R.H.

(5) R.S can explain the properties according to their contributed proportion.

(6) Conjugate substance is always represented by most contributed R.S.

(7) There is no equilibrium that exists between R.S.

(8) R.S can be separated by the symbol (↔)

(9) The stability of R.H is always greater than any individual R.S

(10) In R.H, πe^{-} is distributed equally throughout the conjugated part.

Delocalised πe

e^{-} of π-bond or negative charge or ℓp takes part in conjugation known as delocalized πe

(i) When more than one π bond or lone pair of same atom is present in conjugation then only one of them takes part in delocalisation

(ii) When positive, negative, ℓp, radical is present in conjugation in addition with π bond then only π-π conjugate predominantly takes place

Hint: At conjugate atom: $1\ell p \Rightarrow 2\pi e$, $1(-) \Rightarrow 2\pi e$, $1(\bullet) \Rightarrow 1\pi e$, $1(=) \Rightarrow 2\pi e$

Stability of resonating structure:

Generally stability of R.S ∝ Contribution

(1) More the covalent bond more stable is R.S.

(2) Neutral molecule is more stable than ionic molecule if octet is complete.

(3) Complete octet of each atom is highly stable R.S.

(4) Negative charge is more preferred on high electro negative atom and positive charge is preferred on less electronegative atom.

(5) Charge separation means heterolytic cleavage which is highly unstable and known as heterovalent R.S.

(6) Similar charge at neighbour position is highly unstable and opposite charge is stable at neighbour position.

Note: Those R.S. having same stability, same potential energy, same contribution towards resonating hybrid are known as equivalent resonating structure.

Mesomeric effect: Permanent delocalisation of π-e of a functional group to the single bond is known as mesomeric effect.

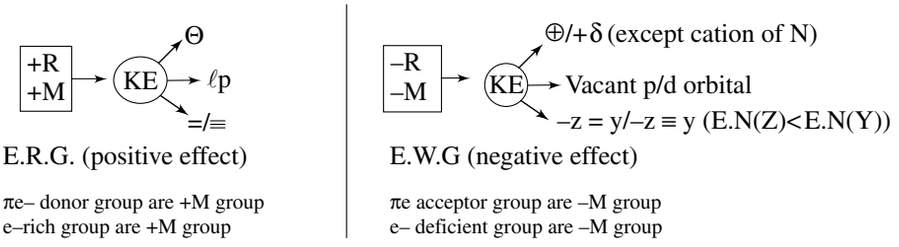
Cause: De-localisation of πe^- in conjugate substance.

Characteristic:

1. It is permanent effect.
2. It is a strong effect because real charge develops.
3. It is operated by π-bond (πe).
4. M-effect is a distance independent.
5. M-effect works in only conjugate substance.

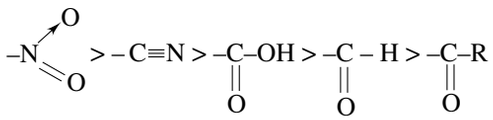
+M/–M effect

(1) Identification

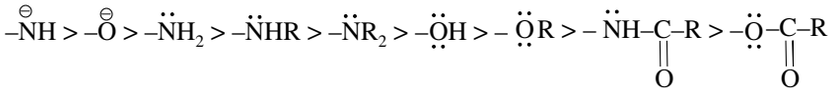


KE (Key element) ⇒ Atom is directly attached with conjugate part.

- Order of –M-effect of some standard species is:



- Order of +M-effect of some standard species is:

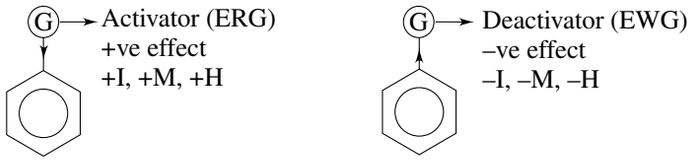


Comparison of M and I effect:

Mesomeric effect	**Inductive effect**
(1) This operates on π-bond	(1) This operate on σ-bond
(2) Distance independent	(2) Distance dependent
(3) It is more dominant because of complete charge	(3) It is less dominant because of partial charge
(4) In benzene M-effect is applicable at only ortho/ para positions	(4) In benzene I-effect is applicable at all 3-ortho-meta, para position
(5) Resonance is a stabilising effect	(5) In neutral molecule inductive effect is destabilising effect
(6) M-effect work only in conjugate substance	(6) I-effect works in both conjugate and non-conjugate substance

Note: In Halogen (–Cl, –Br, –I) , –N = O, etc. –I-effect dominants over +M-effect.

Activator/deactivator: Such groups which increase the e^- density of benzene ring are known as activators and those which decrease the e^- density of benzene ring are known as deactivators.



Overall M and I effect i.e., ERG/EWG

	Group at Benzene ring	Effect	Overall effect	Activator and De-activator	Directive Nature for Ar–SE
1.	$-\overset{\ominus}{N}H, -\overset{\ominus}{O}$	+M, +I	positive effect/ERG	Activator	O/P director
2.	$-\ddot{O}H, -\ddot{N}H_2$ $-NH-\overset{\overset{O}{\|\|}}{C}-R, -O-\overset{\overset{O}{\|\|}}{C}-R$	+M, –I +M > –I	positive effect/ERG	Activator	O/P director
3.	$-CH=CH_2$ $-C_6H_5$	+M, –I (+M > –I)	positive effect/ERG	Activator	O/P director
4.	Alkyl $-CH_3$,$-C_2H_5$	+H, +I	positive effect/ERG	Activator	O/P director
5	–X, (F, Cl, Br, I) –N=O	+M, –I –I > + M	negative effect/EWG	De-activator	O/P director
6.	$-NO_2$, – CH = O –CN, – COOH	–M,–I	negative effect/EWG	De-activator	Meta director
7.	$-CCl_3$, $-CF_3$	–H,–I	negative effect/EWG	De-activator	Meta director
8.	$-\overset{\oplus}{N}R_3$, $-\overset{\oplus}{N}H_3$	Only –I	negative effect/EWG	De-activator	Meta director

Strength of activator (ERG):

$$\underset{\text{Strong activator}}{\underbrace{-\overset{\ominus}{N}H > \overset{\ominus}{O} > -NR_2 > -NH_2 > -OH}} > \underset{\text{Moderate activator}}{\underbrace{-OR > -NH-\overset{\overset{O}{\|}}{C}-R > -O-\overset{\overset{O}{\|}}{C}-R}} > \underset{\text{Weak activator}}{\underbrace{\text{alkyl} > \text{phenyl} > H}}$$

Strength of deactivator (EWG):

$$\underset{\text{Strong De-activator}}{\underbrace{-\overset{\ominus}{N}H_3 > \overset{\ominus}{-}NO_2 > CF_3 > -CCl_3}} > \underset{\text{Moderate De-activator}}{\underbrace{-CN > -SO_3H - CH=O > -COOH}} > \underset{\text{Weak De-activator}}{\underbrace{-F > -Cl > -Br > -I > H}}$$

Application of Resonance:

(1) Hybridisation: When negative charge or ℓp atom is present in conjugation, such atoms are always in sp^2 hybridised state.

(2) Bond length/bond energy/bond strength:

$$\text{Bond length of single bond} \propto \frac{1}{\text{Resonance}}$$

$$\text{Bond length of double bond} \propto \text{Resonance}$$

$$\text{Bond length} \propto \frac{1}{\text{bond energy}} \propto \frac{1}{\text{bond strength}}$$

(3) Resonance energy: Energy is released whenever localised electron interconverts into delocalised electron.

(4) Aromaticity:

(I) Aromatic substances: Such substances which fulfill the following conditions are known as aromatic substance.

(a) Molecule must be cyclic

(b) Ring must be planar

(c) Continuous conjugation throughout ring

(d) Obey Huckel rule

$\boxed{4n + 2 = \pi e}$

{n = 0, 1, 2, 3 ...} s

- Aromatic substances are diamagnetic in nature.

(II) Anti-aromatic substances:

(a) Molecule must be cyclic

(b) Ring must be planar

(c) Continuous conjugation throughout ring

(d) $\boxed{4n = \pi e^-}$

{n = 1, 2, 3…}

- Anti-aromatic substances are paramagnetic in nature.

(III) Non-aromatic substances: Such cyclic substances which are neither aromatic nor anti-aromatic, are non-aromatic substances.

Stability order of cyclic substances:

Aromatic > Non-Aromatic > Anti-aromatic

Annulene: Such monocyclic substances in which alternate single and double bond are present in a ring, are known as Annulene.

Annulene (4)

Annulene (6)

Annulene (8)

Annulene [8], [10], [12] are non-planar due to repulsion between adjacent H-atom.

(5) Stability of reaction intermediate:

Profile-1: In different type of conjugation

(1) Conjugate substance is more stable than non-conjugate substance, except antiaromatic substance.

(2) In conjugate substance

Stability ∝ Resonance ∝ Number of R.S ∝ Number of conjugated position

(3) When negative, positive, ℓ.p, are aromatically stablised then such conjugate substances are most stable even that less Number of R.S

(4) Equally contributed R.S. containing conjugate substance is more stable even that less Number of R.S

- Aromatic stable substance > conjugate substance (equal contributor) > conjugate substance (unequal contributor) > non-conjugate substance

Profile-2: In same type of conjugation

$$\text{Stability of } -\overset{|}{\underset{|}{C}}{}^{\oplus} / -\overset{|}{\underset{|}{C}}{}^{\bullet} \propto \text{ERG (+ve)} \propto \frac{1}{\text{EWG (–ve)}}$$

$$\text{Stability of } -\overset{|}{\underset{|}{C^{\ominus}}} \propto \text{EWG (–ve effect)} \propto \frac{1}{\text{ERG (+ve effect)}}$$

(6) Acidic strength

Profile-1: In different type of conjugation

Acidic strength ∝ stability of anion

Acidic strength ∝ Delocalisation (Resonace)

Profile-2: In same type of conjugation

$$\text{Acidic strength} \propto \text{EWG(negative)} \propto \frac{1}{\text{ERG(positive)}}$$

(7) Basic strength

Profile-1: In different type of conjugation

Basic strength ∝ e^--donating tendency

$$\text{Base strength} \propto \frac{1}{\text{Delcalisation of } \ell p \text{ (Resonance)}}$$

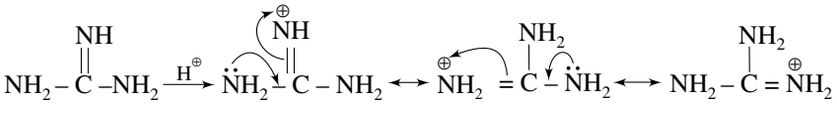
Profile-2: In same type of conjugation

$$\text{Base strength} \propto \text{ERG} \propto \frac{1}{\text{EWG}}$$

Profile-3: Base strength of guanidine

Guanidine is most basic nitrogenous organic substance

Explanation:



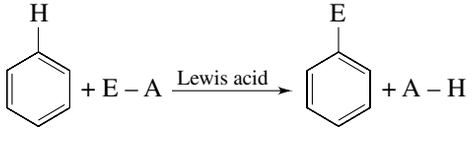
3 equal contributor canonical form
Most stable cation

Basic strength ∝ stability of conjugate cation

(8) Aromatic Electrophilic Substitution Reactions

The reactions in which one or more hydrogen atoms of the benzene ring are replaced by an electrophile are called electrophilic aromatic substitution reactions.

These reactions are of the general type shown below:



EFFECT OF SUBSTITUENTS ON REACTIVITY AND ORIENTATION

When substituted benzene undergo electrophilic attack, groups already on the ring affect both the rate of the reaction and the site of attack therefore substituent groups affect both reactivity and orientation in electrophilic aromatic substitutions.

We can divide substituent groups into two classes according to their influence on the reactivity of the ring. Those that cause the ring to be more reactive than benzene itself we call activating groups. Those that cause the ring to be less reactive than benzene we call deactivating groups.

Theory of Orientation

A group attached to benzene has a directing influence on the electrophilic substitution reaction. Two types of groups have been classified based on their orientation effects.

Activating Group

A group that releases electrons to benzene ring is an activating group. It directs the incoming electrophile to *ortho* or *para* position. Examples include

Strongly activating: $-NH_2$, $-NHR$, $-NR_2$, $-OH$, $-OCH_3$

Moderately activating: $-NHCOCH_3$, $-OCOCH_3$

Weakly activating: $-CH_3$, $-CH{=}CH_2$, $-C_6H_5$

Deactivating Group

A group that withdraws electrons from benzene is a deactivating group. It directs the incoming electrophile to *meta* position. Examples include

Strongly deactivating: $-\overset{+}{N}(CH_3)_3$,$-NO_2$, $-CN$, $-SO_3H$

Moderately deactivating $-CHO$, $-COR$, $-COOR$, $-COOH$, $-COCl$

*Weakly deactivating: F, –Cl, –Br, –I (*o/p* director)

Mode of Orientation

Case-I: Activating Groups: Ortho para Directors

Case-II: Deactivating Groups: Meta Directors

Case-III: Halo Substituents: Deactivating Ortho-Para Directors

EFFECT OF SUBSTITUTENTS ON REACTIVITY

In presence of different substituents on benzene ring, rate of reaction increased or decreased is known as substitution effect.

$$\text{Reactivity of ArsE} \propto \text{Activating power} \propto \frac{1}{\text{Deactivating power}}$$

Aromatic Electrophilic Substitution Reactions of Polysubstituted Benzene

What happens when two or more substituent groups are attached to the benzene ring? Where is the electrophile likely to attack? Some qualitative rules have been formulated to answer this question.

(i) The most activating group will control orientation.

(ii) No substitution occurs between two meta substituents because of crowding.

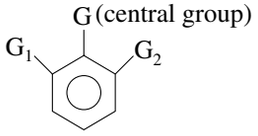
(iii) When both groups are meta directors, it is difficult to introduce third group.

Reactions of aromatic substance are following Reaction:

Reaction	Reagent	$E^{\oplus}$
Chlorination	$Cl_2/FeCl_3$ Cl_2/Fe	$Cl^{\oplus}$
Nitration	HNO_3/H_2SO_4	$\overset{\oplus}{N}O_2$
Sulphonation	Conc. H_2SO_4	SO_3 Neutral
Friedel–Craft reaction	$R{-}Cl/AlCl_3$ $R{-}\underset{\underset{O}{\|\|}}{C}{-}Cl/AlCl_3$	$R^{\oplus}$ $R{-}C^{\oplus}{=}O$

(9) Ortho effect:

(1) SIR effect (Steric inhibition of resonance)



Due to maximum repulsion by G_1 and G_2 groups, central group G comes out of the plane of benzene ring so that group G can't participate in resonance with ring is known as SIR or ortho effect

Condition for SIR effect:

(1) Central group 'G' must be bulky.

Bulky group → –COOH, $-SO_3H$, $-\overset{\overset{O}{\|}}{C}-Cl$, $-\overset{\overset{O}{\|}}{C}-NH$, CMe_3, $-NR_2$, $-NO_2$, –Br, – I, etc.

Smaller group → –OH, $-OCH_3$, $-NH_2$, $-CH_3$, –F, –Cl, etc.

(2) G_1 and G_2 may or may not be bulky but must be occupied at both the ortho positions of G

Note: For –COOH, $-SO_3H$, presence of only one group at ortho-position is sufficient for SIR effect.

- Ortho substituted benzoic acid is more acidic because its conjugate base will be more stable due to steric crowding.

Steric Inhibition in protonation (S.I.P.)

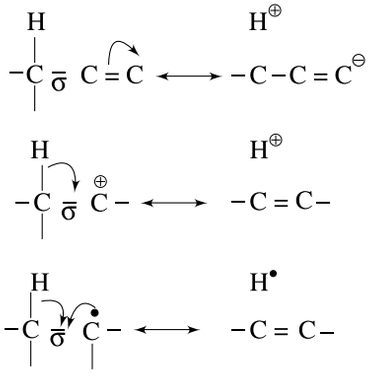
- Only for basic strength.
- Ortho substituted aniline are weaker bases because their conjugate acids are unstable due to van der Waal repulsion.
- Exception: No SIP effect is observed in case of OCH_3 group only.

Hyperconjugation effect (H-effect):

Backer Nathan effect (No bond Resonance)

When at least one C–H bond is separated by only one σ bond with π bond/ positive charge/ radical then delocalisation σ bond of C–H takes place is known as H-effect or σ–π conjugation.

Types of hyperconjugation:



- Order of effectiveness M > H > I

Some facts:

- Allylic hydrogen and benzylic hydrogen are more reactive due to hyper conjugation.
- In alkene or alkyne bond length are not ideal single bond having double bond character and vice-versa.
- Saytzeff rule will be explained by hyperconjugation because more the substituted alkene more stable because of more α-hydrogen.
- Hyperconjugation can be applied on alkene, alkyne, cation and radical.

+H effect: Alkyl group increases e-density of benzene ring by the delocalisation of σ bond

Power of +H group

(i) In different alkyl group

+H power ∝ Number of α-H

$CH_3- > CH_3-CH_2- > (CH_3)_2-CH- > (CH_3)_3-C-$

(ii) In isotopic hydrogen

$-CH_3 > -CD_3 > -CT_3$

Reverse Hyperconjugation (–H effect)

–H group ⇒ $-CZ_3$

Ex. $-CF_3$, $-CF_3$, $-CCl_3$, $-C(NO_3)_3$

Application of hyper conjugation:-

(1) Stability

(i) Stability of alkenes ∝ Number of α-H

(ii) Stability of alkyl carbocations ∝ Number of α-H

(iii) Stability of alkyl free radical ∝ Number of α-H

(2) Heat of hydrogenation

$CH_2=CH_2 + H_2 \rightarrow CH_3-CH_3$

(1) ΔH (HOH) ∝ Number of π-bond

(2) If number of π-bonds is same

$$\Delta H \text{ (HOH)} \propto \frac{1}{\text{stability of alkene}}$$

(3) Heat of combustion

$CH_2=CH_2 + O_2 \rightarrow 2CO_2 + 2H_2O$

(1) ΔH (HOC) ∝ Number of C & H

(2) If number of carbons is same

$$\Delta H \text{ (HOC)} \propto \frac{1}{\text{stability of alkene}}$$

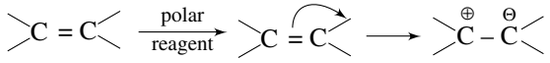
ELECTROMERIC EFFECT

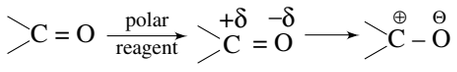
Condition: Compound must have π bond

–C=C–, –C≡C–, –C=O, –C≡N, etc.

- The effect involving the complete transfer of shared pair of electrons of pi bond in the presence of polar reagent is known as electromeric effect (E effect).

  It is a temporary effect and is brought into play instantaneously at the demand of the attacking reagent. However, as soon as the attacking reagent is removed, original electronic condition is restored.





Nucleophilicity (Strength of Nucleophile): The relative reactivity of nucleophile is known as nucleophilicity.

Nucleophilicity can be compared as given below:

(1) A negatively charged nucleophile is always a more reactive nucleophile than its conjugate acid. Thus HO^- is a better nucleophile than H_2O and RO^- is better than ROH.

(2) In a group of nucleophiles in which the nucleophilic atom is the same or belong to same period,

$$\boxed{\text{Nucleophilicities} \propto \text{Basicities}}$$

(3) In a group of nucleophiles in which the nucleophilic atom is the same and the category of anion is also same then,

$$\boxed{\text{Nucleohilicities} \propto \frac{1}{\text{steric hindrance}}}$$

(4) In a group of nucleophiles in which the nucleophilic atom is the different, then nucleophilicities are depends upon nature of solvent:

(i) In Polar Protic Solvents $\boxed{\text{Nucleophilicities} \propto \text{Size}}$

(ii) In Polar Aprotic Solvents $\boxed{\text{Nucleohilicities} \propto \frac{1}{\text{Size}}}$

Relative Nucleophilicity in Protic solvents:

$$SH^- > CN^- > I^- > OH^- > N_3^- > Br^- > CH_3CO_3^- > Cl^- > F^- > H_2O$$

Leaving Groups(or nucleofuge): In alkyl halides the leaving group is the halogen substituent – it leaves as a halide ion. To be a good leaving group the substituent must be able to leave as a relatively stable, weakly basic molecule or ion.

$$Nu:^- + R - L \rightarrow R - Nu + :L^-$$

SOLVED EXAMPLE

1. Which of the following compounds easily undergoes homolytic bond fission?

(1) CH_3–Cl (2) CH_3–CH=O

(3) H–O–O–H (4) NH_2–CH_3

Sol. **[3]**

H–O–O–H

Due Least E.N. difference.

2. Which of the following represents the mode of hybridisation sp^2–sp^2–sp–sp from left to right?

(1) CH_2=CH–C≡N (2) HC≡C–C≡CH

(3) CH_2=C=C=CH_2 (4) CH_2=CH–CH=CH_2

Sol. **[1]**

CH_2=CH–C≡N

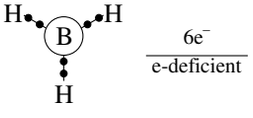
sp^2 sp^2 sp sp

3. Which of the following is an electron deficient molecule?

(1) CH_3CH_3 (2) BH_3

(3) SiH_4 (4) PH_3

Sol. **[2]**



4. One of the following pairs represents a set of nucleophile:

(1) CN^- and NH_3 (2) $AlCl_3$ and Cl^-

(3) H^+ and H_2O (4) Br^+ and $\ddot{C}\,Cl_2$

Sol. **[1]**

e-rich species are nucleophile (refer key concept.)

5. The decreasing order of –I effect of the following is:

I. $H_3N^{\oplus}$ **II.** NO_2

III. CN **IV.** COOH

(1) I > II > III > IV (2) II > I > III > IV

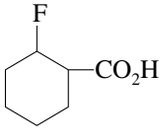
(3) I > II > III > IV (4) II > I > IV > III

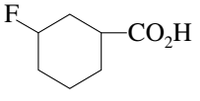
Sol. **[1]**

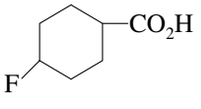
$\underset{\text{cation}}{-NH_3^+} > -NO_2 > -CN > -COOH$ (refer key concept.)

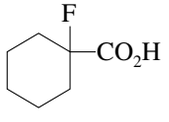
$\downarrow$ –I effect

6. Which of the following has highest K_a value?

(1) 

(2) 

(3) 

(4) 

Sol. **[4]**

Acidic strength ∝ –I Power ∝ K_a

Also –I power decresed as distance increses

7. Which of following has lowest pK_a value?

(1) $Cl–CH_2–CO_2H$ (2) $Cl–\underset{\displaystyle Cl}{\underset{|}{CH}}–CO_2H$

(3) $Cl_3C–CO_2H$ (4) $CH_3–CO_2H$

Sol. **[3]**

Acidic strength $\propto -I \propto K_a \propto \frac{1}{pK_a}$

As number of –I group increases, –I power further increases hence pK_a value decreases.

8. Arrange the following compound in order of decreasing acidity

$CH_3–CH_2–OH\,(\alpha); CH_3–CH_3–\overset{\oplus}{O}H_2(\beta); CH_3–O–CH_3\,(\gamma)$

(1) $\alpha > \beta > \gamma$ (2) $\beta > \alpha > \gamma$

(3) $\gamma > \beta > \alpha$ (4) $\alpha > \gamma > \beta$

Sol. **[2]**

$$\underset{\text{acid Strength} \downarrow}{\underline{\text{Cation} > \text{Alcohol} > \text{ether}}}$$

9. Amongst the amines $C_6H_5NH_2$ (I), CH_3NH_2 (II), $(CH_3)_2NH$ (III) and $(CH_3)_3N$ (IV) the order of basicity (in aqueous medium) is–

(1) I < IV < II < III (2) IV < III < II < I

(3) I < II < III < IV (4) II < III < IV < I

Sol. **[1]**

$\underset{\substack{\ell p \text{ delocalised} \\ \text{least basic}}}{C_6H_5–NH_2(I)}$ $\underbrace{\underset{(1°)}{CH_2–NH_2(II)}\ \underset{(2°)}{(CH_3)_2–NH(III)}}_{\ell p\text{-localised more basic}}$ $\underset{(3°)}{(CH_3)_3N(IV)}$

Also as per N.C.E.R.T result if R = $–CH_3$

Basic strength 2° > 1° > 3°

Hence order of basic strength in aqueous solution

(I) < (IV) < (II) < (III)

10. The order of decreasing stability of the anions

$\underset{I}{(CH_3)_3C^-}$ $\underset{II}{(CH_3)_2CH^-}$ $\underset{III}{CH_3CH_2^-}$ $\underset{IV}{C_6H_5CH_2^-}$ is–

(1) I > II > III > IV (2) IV > III > II > I

(3) IV > I > II > III (4) I > II > IV > III

Sol. **[2]**

$$\underset{\substack{\text{Resonance} \\ \text{Stability}}}{(IV)} > \underbrace{(III) > (II) > (I)}_{\substack{+I \text{ Power} \uparrow \\ \text{Stability of Carbanion} \downarrow}}$$

11. In the formate ion $\left(H—\overset{\displaystyle O}{\overset{\|}{C}}—O^-\right)$, the two carbon-oxygen bonds are found to be equal. This is because

(1) the formate ion $HCOO^-$ is obtained by the removal of a proton from HCOOH

(2) the carbon atom in $HCOO^-$ is sp^2 hybridised

(3) the formate ion is a tautomeric mixture of

$H—\overset{\displaystyle O}{\overset{\|}{C}}—O^-$ and $O=\overset{\ominus}{C}—OH$

(4) the formate ion is a resonance hybrid of the two equivalent resonance structures

$H—\overset{\displaystyle O}{\overset{\|}{C}}—O^-$ and $H—\overset{\displaystyle O^{\ominus}}{\overset{|}{C}}=O$

Sol. **[4]**

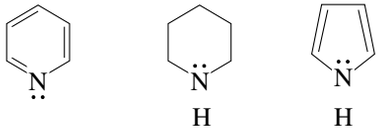
$H–\overset{\displaystyle O}{\overset{\|}{C}}–O^- \longleftrightarrow H–\overset{\displaystyle O^-}{\overset{|}{C}}=O$

(Resonance)

Equal contributor

Resonating hybrid $\Rightarrow$ $H—\overset{\displaystyle O^{\delta-}}{\overset{\|}{C}}—O^{\delta-}$

12. The hybridisation states of the nitrogen atoms at in pyridine, piperidine and pyrrole are respectively:

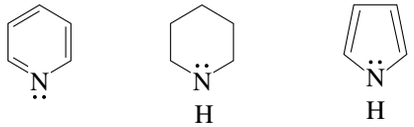


Pyridine Piperidine Pyrrole

(1) sp^2, sp^3 and sp^2 (2) sp^2, sp^3 and sp^3

(3) sp^3, sp^3 and sp^3 (4) sp^2, sp^2 and sp^2

Sol. **[1]**

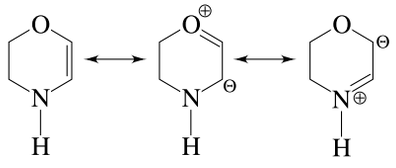


Pyridine Piperidine Pyrrole

sp^2 sp^3 sp^2

(ℓp delocalised)

13.



(I) (II) (III)

The least stable canonical structure among these is:

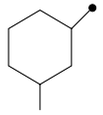
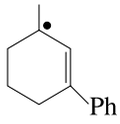
(1) I (2) II

(3) III (4) all are equally stable

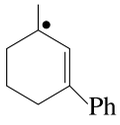
Sol. **[2]**

→ In (II) Str., more EN atom carries positive charge, less stable

14. Which one of the following is most stable?

(1) 
(2) 
(3) 
(4) 

Sol. **[3]**



Resonance & 3α – H(+H Effect)

most stable

15. Pyridine is less basic than triethyl amine because:

(1) Pyridine has aromatic character

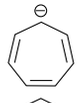
(2) Nitrogen in pyridine is sp^2 hybridised

(3) Pyridine is a cyclic system

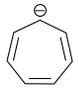
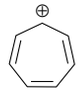
(4) Lone pair of nitrogen is delocalised in pyridine

Sol. **[4]** ℓp of N in pyridine is de-localised so that it is less basic than triethyl amine.

16. Which is an aromatic compound?

(1) 
(2) 
(3) 
(4) 

Sol. **[2]**


4n=8
Anti Aromatic ;

4n + 2 = 6
Aromatic ;


Non planar
non aromatic ;

non planar
non aromatic

17. Which of the following is the strongest nucleophile?

(1) $EtO^{\ominus}$
(2) $\overset{\ominus}{O}H$
(3) $\overset{\ominus}{C}N$
(4) $I^{\ominus}$

Sol. **[1]**

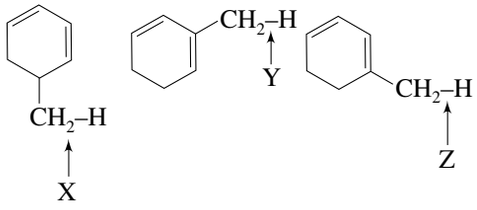
Nucleophilicity is parallel to basicity

Acidity : HI > HCN > H_2O > EtOH

Basicity and nucleophilicity:

$I^{\ominus} < \overset{\ominus}{C}N < \overset{\ominus}{O}H < EtO^{\ominus}$

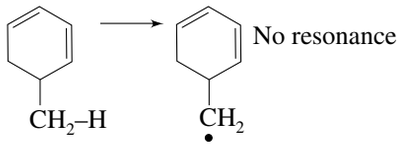
18. Which of the following is the correct order for bond energy for C–H bonds in these compounds?

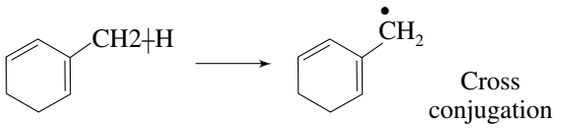


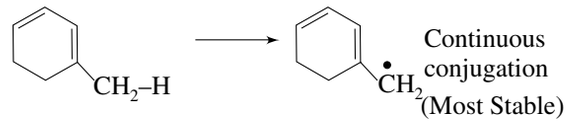
(1) Y > Z > X
(2) X > Z > Y
(3) X > Y > Z
(4) Z > X > Y

Sol. **[3]**

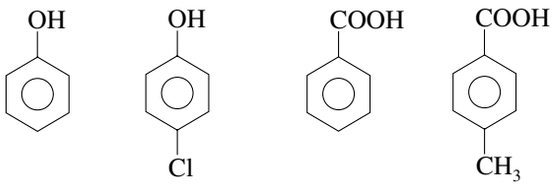
$$\text{Bond energy} \propto \frac{1}{\text{stablity of free radical}}$$





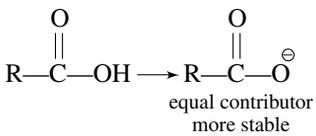


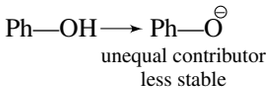
19. The correct order of decreasing acidity of the compounds is:



(1) III > IV > II > I
(2) IV > III > I > II
(3) III > II > I > IV
(4) II > III > IV > I

Sol. **[1]**





Acidic strength ∝ stability of anion

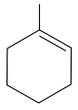
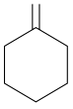
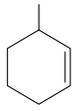
Thus R—COOH > Ph–OH (Acid strength)

when functional group (source group) is same

$$\text{Acid strength} \propto \text{EWG} \propto \frac{1}{\text{ERG}}$$

Hence III > IV > II > I

20. Compare heat of hydrogenation of the following:

(i)  (ii)  (iii) 

(1) i > ii > iii (2) iii > ii > i

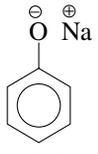
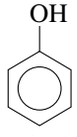
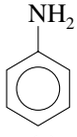
(3) ii > i > iii (4) ii > iii > i

Sol. **[2]**

ΔH Heat of hydrogenation

$$\propto \frac{1}{\text{sterbility of alkene}} \propto \frac{1}{\text{number } \alpha - H}$$

21. Compare rate of EAS

 (a)  (b)  (c)  (d)

(1) a > b > c > d (2) a > c > b > d

(3) c > a > b > d (4) c > b > a > d

Sol. **[2]**

Rate of Ar – $S_E \propto$ ERG

ERG power ($-O^{\ominus}$ > – NH_2 > –OH)

22. Which among the following statements are incorrect?

(1) $\ddot{C}F_2$ is more stable than $\ddot{C}Cl_2$

(2) $\ddot{C}Cl_2$ is more stable than $\ddot{C}Br_2$

(3) singlet $\ddot{C}H_2$ is more stable than triplet $\ddot{C}H_2$

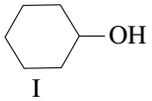
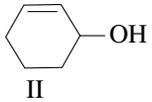
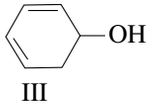
(4) Singlet $\ddot{C}H_2$ has planar geometry

Sol. **[3]**

:CF_2 > **:**CCl_2 > **:**CBr_2 > **:**Cl_2 ⟶ Stability

Triplet $\ddot{C}H_2$ is more stable than singlet $\ddot{C}H_2$. Hence it is incorrect.

23. Identify the correct order of the ease of dehydration of the following compounds.

 I  II  III

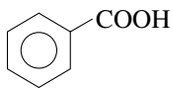
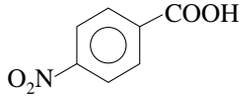
(1) I > II > III (2) III > II > I

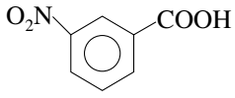
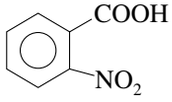
(3) I > III > II (4) III > I > II

Sol. **[2]**

Rate of dehydration ∝ stability of carbocation

24. Which of the following compounds has the highest pK_a value?

(1)  (2) 

(3)  (4) 

Sol. **[1]**

When functional. group (–COOH) same

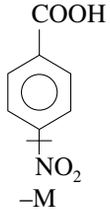
Acidic strength ∝ EWG ∝ $\frac{1}{pKa}$

Acid strength ∝ $K_a \propto \frac{1}{pKa}$

no effect

lessAcidiC

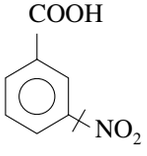
pKA ↑



–M

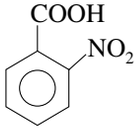
–I|dist. ↑

$(EWG)_2$



Meta position only

–I $(EWG)_3$

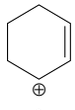
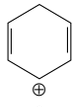


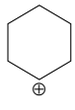
–Mda

–I ↑ dist. ↓

$(EWG)_1$

25. Least stable carbocation amongst following is:

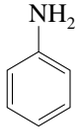
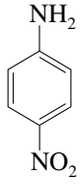
(1)  (2) 

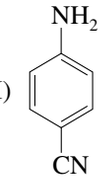
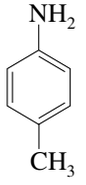
(3)  (4) 

Sol. **[3]**

→ Due to Bredt's rule +ve charge cannot be placed at the bridgehead carbon.

26. Consider the following compounds:

(I)  (II) 

(III)  (IV) 

Arrange these compounds in decreasing order of their basicity:

(1) I > II > III > IV (2) II > III > I > IV

(3) IV > I > III > II (4) IV > I > II > III

Sol. **[3]**

Base strength $\propto$ + M, +I $\propto \frac{1}{-M, -I}$

27. Which of the following has highest leaving group ability?

(1) $\overset{\ominus}{N}H_2$ (2) $H_3C-\underset{\underset{O}{\|}}{C}-O^{\ominus}$

(3) $\overset{\ominus}{O}CH_3$ (4) $I^{\ominus}$

Sol. **[4]**

Leaving ability $\propto$ acid strength of conjugate acid

$\propto \frac{1}{\text{base strength of anion}}$

$\rightarrow$ HI is most acidic hence I^- is good leaving group

28. What is the decreasing order of stability of the ions?

(I) $H_3C-HC^{+}-CH_3$ (II) $H_3C-HC^{+}-O-CH_3$

(III) $H_3C-HC^{+}-C(=O)-CH_3$

(1) I > II > III (2) II > III > I

(3) III > I > II (4) II > I > III

Sol. **[4]**

$CH_3-\overset{+}{C}H-CH_3$

Incomplete octet and less EN carbon atom carries +ve charge, Hence more stable than III but less stable than II

$CH_3-\overset{+}{C}H-\ddot{O}CH_3 \leftrightarrow CH_3-CH=\overset{+}{O}-CH_3$

Complete octet (Most stable)

$CH_3-\overset{\oplus}{C}H-\underset{\underset{O}{\|}}{C}-CH_3 \leftrightarrow CH_3-CH=\underset{\underset{O^{+}}{|}}{C}-CH_3$

Incomplete octet and more EN oxygen atom carries +ve charge hence less stable

Therefore correct stability after is:

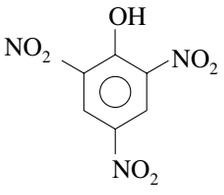
(II) > (I) > (III)

29. Arrange 2, 4, 6-trinitrophenol (I); 2, 4-dinitrophenol (II); *o*-nitrophenol (III) and *p*-nitrophenol (IV) in order of acidity:

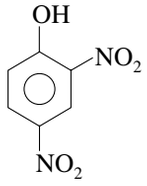
(1) I > II > III = IV (2) IV > III > II > I

(3) I > II > IV > III (4) III > II > I > IV

Sol. **[3]**

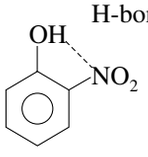


(I)

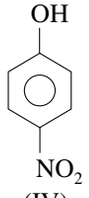


(II)

Intra-molecular H-bond



(III)



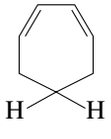
(IV)

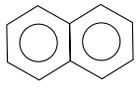
$\Rightarrow$ Removal of Proton becomes difficult, so it is less acidic than para nitrophenol

Acidic strength $\propto -M, -I \propto \frac{1}{+M, +I}$

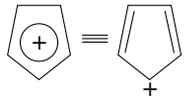
(I) > (II) > (IV) > (III)

30. Which one of the following substances is aromatic?

(1)  (2) 

(3)  (4) 

Sol. **[4]**

(1) 

4n = 4

n = 1

anti aromatic

(2) non-planar

(3) non-planar due to repulsion between adjacent H-atom

(4) 4n + 2 = 10

n = 2

EXERCISE 1

1. In the compound $CH_2=CH-CH_2-CH_2-C\equiv CH$, the ($C_2$–$C_3$) bond is of the type:

(1) $sp - sp^2$ (2) $sp^3 - sp^3$

(3) $sp - sp^3$ (4) $sp^2 - sp^3$

2. Which of the following series contains electrophile only?

(1) H_2O, SO_3, $\overset{\oplus}{N}O_2$ (2) NH_3, H_2O, BI_3

(3) ROH, NH_3, $\overset{\oplus}{N}O_2$ (4) $AlCl_3$, SO_3, $\overset{\oplus}{Cl}$

3. Give the correct order of increasing acidity of the following compounds.

$ClCH_2COOH$ (I) CH_3CH_2COOH (II)

$ClCH_2CH_2COOH$ (III) $(CH_3)_2CHCOOH$ (IV)

CH_3COOH (V)

(1) V < II < IV < I < III

(2) IV < II < V < III < I

(3) III < I < IV < II < V

(4) V < IV < II < I < III

4. Which of the following acids has lowest pK_a value?

(1) $CH_3-\underset{NO_2}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OH$ (2) $\underset{NO_2}{\underset{|}{CH_2}}-CH_2-\overset{O}{\overset{\|}{C}}-OH$

(3) $\underset{Cl}{\underset{|}{CH_2}}-\overset{O}{\overset{\|}{C}}-OH$ (4) $CH_3-\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-OH$

5. A nucleophile is called an ambident nucleophile if:

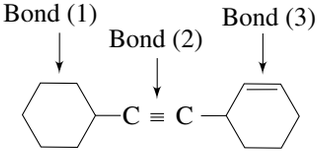
(1) It is capable of acting as nucleophile as well as an electrophile

(2) Its attacking atom has two lone pairs

(3) It has two possible electron donating sites

(4) It can act lewis acid

6. Rank the indicated bonds in each compounds in order of increasing bond strength:



(1) 1 < 2 < 3 (2) 3 < 1 < 2

(3) 1 < 3 < 2 (4) 2 < 3 < 1

7. Arrange the following groups in order of decreasing *m*-directing strength. $-\overset{+}{N}R_3$, –CN, $-NO_2$, –COOH

(1) $-\overset{+}{N}R_3 > -NO_2 > -CN > -COOH$

(2) $-COOH > -CN > -NO_2 > -\overset{+}{N}R_3$

(3) $-CN > -NO_2 > -COOH > -\overset{+}{N}R_3$

(4) $-NO_2 > -CN > -\overset{+}{N}R_3 > -COOH$

8. (I) $CH_3-O-CH=CH-CH=CH_2$

(II) $CH_3-O-\overset{\oplus}{C}H-CH=CH-\overset{\oplus}{C}H_2$

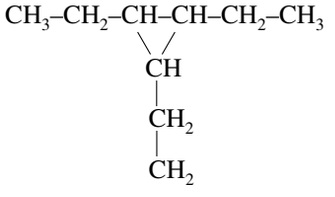
(III) $CH_3-\overset{\oplus}{O}=CH-CH=CH_2-\overset{\oplus}{C}H_2$

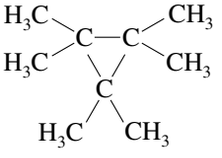
Among these three canonical structures (through more are possible) what would be their relative contribution in the hybrid:

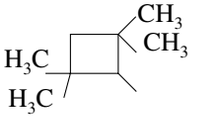
(1) I > II > III (2) III > II > I

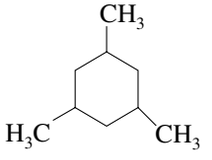
(3) I > III > II (4) III > I > II

9. An organic compound has molecular formula C_9H_{18}. Its all carbon atoms are sp^3 hybridised and its all hydrogen atoms are identical. Its structural formula can be:

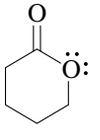
(1) 

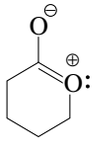
(2) 

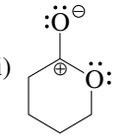
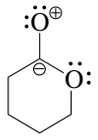
(3) 

(4) 

10. Stability order of the following resonating structure will be–

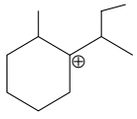
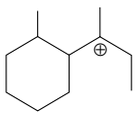
(i) 

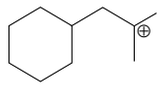
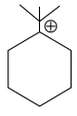
(ii) 

(iii)  (iv) 

(1) i > ii > iii > iv (2) ii > i > iii > iv
(3) iii > ii > i > iv (4) i > iii > ii > iv

11. Which carbocation is the most stable?

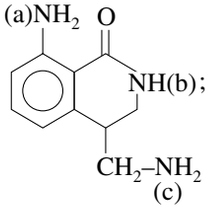
(1)  (2) 

(3)  (4) 

12. Compare acidic strength–

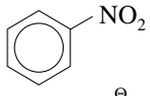
(i) $CHCl_3$ (ii) CHF_3
(iii) $CH_3–CH_3$

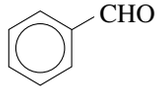
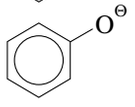
(1) i > ii > iii (2) ii > i > iii
(3) iii > i > ii (4) ii > iii > i

13. 
(a)NH_2 O NH(b); Basic strength order is– $CH_2–NH_2$ (c)

(1) a > b > c (2) b > a > c
(3) c > a > b (4) c > b > a

14. Electrophile $\overset{\oplus}{N}O_2$ attacks the following:

(I)  (II) 

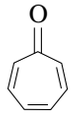
(III)  (III) 

In which cases $\overset{\oplus}{N}O_2$ will attack at meta position

(1) II and IV (2) II and III
(3) II and IV (4) I only

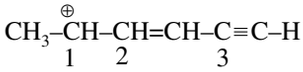
15. Which of the structures below would be aromatic?

(i)  (ii) 

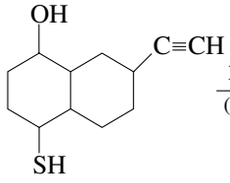
(iii)  (iv) 

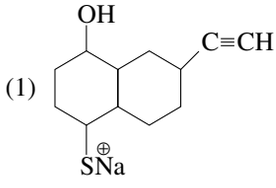
(1) i and iv (2) i, iii and iv
(3) iii and iv (4) ii

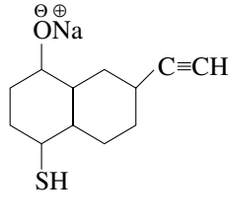
16. What is the hybridisation of C_1, C_2, C_3 carbon in the following compound?

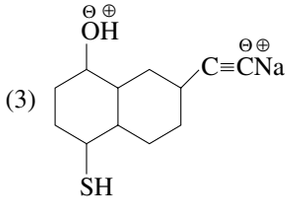

$CH_3–\overset{\oplus}{C}H–CH=CH–C\equiv C–H$
1 2 3

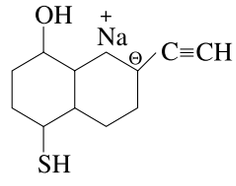
(1) sp^3, sp^3, sp^3 (2) sp^3, sp^2, sp^2
(3) sp^3, sp^2, sp (4) sp^2, sp^2, sp

17. 
OH, C≡CH, SH; $\xrightarrow[\text{(1 mole)}]{NaNH_2}$ (A); Product (A) is:

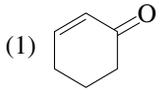
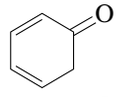
(1) 
OH, C≡CH, $\overset{\oplus}{S}Na$

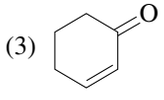
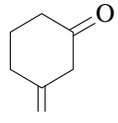
(2) 
$\overset{\ominus}{O}\overset{\oplus}{Na}$, C≡CH, SH

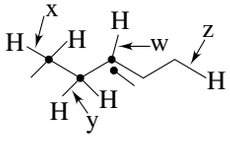
(3) 
$\overset{\ominus}{O}\overset{\oplus}{H}$, $C\equiv\overset{\ominus}{C}\overset{\oplus}{N}a$, SH

(4) 
OH, $\overset{+}{N}a$, $\overset{\ominus}{}$, C≡CH, SH

18. Which of the following has longest C – O bond?

(1)  (2) 

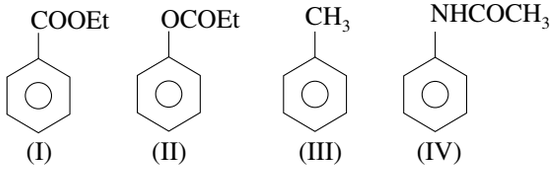
(3)  (4) 

19. 
x, H, H, H, w, z, H, H, H, y

Arrange the (C–H) bonds x, y and z in decreasing order of their bond dissociation energies in homolysis

(1) y > x > z > w (2) z > x > w > y
(3) w > x > z > y (4) y > z > w > x

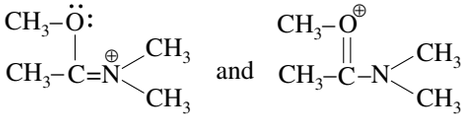
20. Find the correct order of electron density at benzene ring:

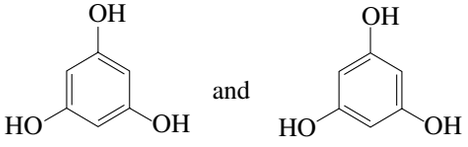

COOEt, OCOEt, CH_3, $NHCOCH_3$

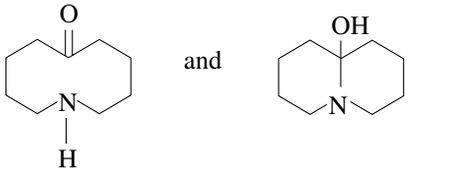
(I) (II) (III) (IV)

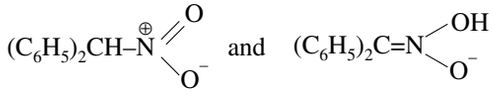
(1) IV > III > II > I (2) I > II > III > IV
(3) IV > II > I > III (4) IV > II > III > I

21. Which of the following pairs of structure are resonance structure?

(i)  and

(ii) 

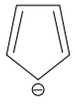
(iii) 

(iv) 

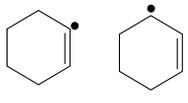
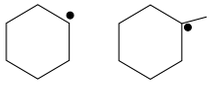
(1) (i) and (iv) (2) (ii) and (iii)
(3) (i) and (ii) (4) All of these

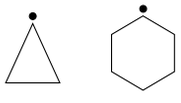
22. Which of the following anions is resonance destabilised?

(1)  (2) 

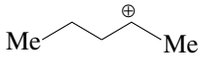
(3)  (4) 

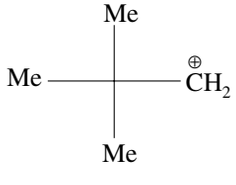
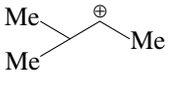
23. In which of the following pairs, 1st is more stable than 2nd?

(1)  (2) 

(3)  (4) $Ph_3C^{\bullet}$, $(CH_3)_3C^{\bullet}$

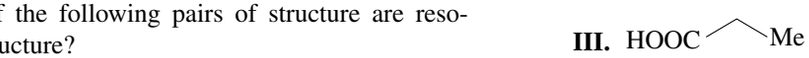
24. Which of the following carbocations is most stable?

(1)  (2) 

(3)  (4) 

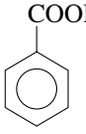
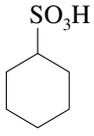
25. The decreasing order of the acidic character is:

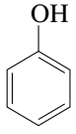
I. COOC–≡–H **II.** 

III. 

(1) I > II > III (2) III > II > I
(3) II > I > III (4) III > I > II

26. Which of the following is least acidic?

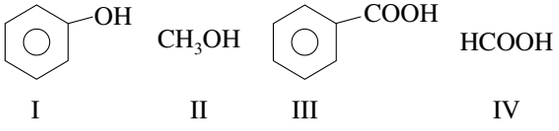
(1)  (2) 

(3)  (4) 

27. Amongst NO_2, CH_3, OCH_3, Br, CMe_3, the decreasing order of groups or atoms having negative inductive effect is:

(1) $NO_2 > Br > OCH_3 > CMe_3 > CH_3$
(2) $NO_2 > OCH_3 > Br > CMe_3 > CH_3$
(3) $NO_2 > Br > OCH_3 > CH_3 > CMe_3$
(4) $Br > NO_2 > OCH_3 > CH_3 > CMe_3$

28. The correct order of the decreasing pK_a values of the compounds is:



I II III IV

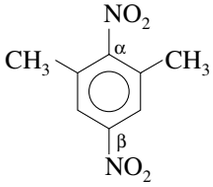
(1) I > II > III > IV (2) II > I > III > IV
(3) III > IV > I > II (4) IV > III > I > II

29. The order of ease of heterolysis of following t-butyl compound is:

(I) $(CH_3)_3C–OH$ (II) $(CH_3)_3C–OAc$
(III) $(CH_3)_3C–Cl$

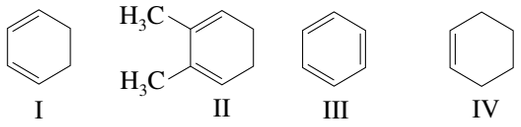
(1) I < II < III (2) III < II < I
(3) I < III < II (4) II < I < III

30. Compare C–N bond length α, β as indicated:



(1) α > β (2) α = β
(3) α < β (4) can't be predicted

31. The decreasing order of bond length of C=C in the following compounds is:

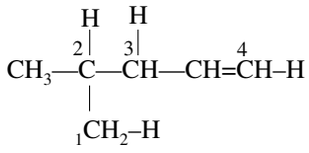


I II III IV

(1) II > I > IV > III (2) III > II > I > IV

(3) II > III > I > IV (4) IV > I > II > III

32. C_1–H, C_2–H, C_3–H and C_4–H the homolytic bond dissociation energy is in the order:



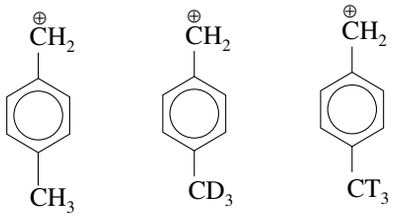
(1) C_2–H > C_3–H > C_4–H > C_1–H

(2) C_1–H > C_4–H > C_2–H > C_3–H

(3) C_2–H > C_3–H > C_1–H > C_4–H

(4) C_4–H > C_1–H > C_3–H > C_2–H

33. Arrange the following cation in increasing order of stability

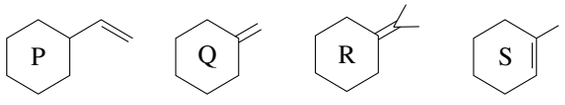


(A) (B) (C)

(1) A < B < C (2) A < C < B

(3) C < A < B (4) C < B < A

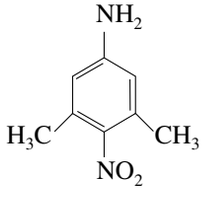
34. Arrange the following alkenes in increasing order of their enthalpy of hydrogenation (–ΔH):



(1) R < S < Q < P (2) R < S < P < Q

(3) P < Q < R < S (4) P < Q < S < R

35. Which of the following effects of —NO_2 group operates on —NH_2 group in this molecule?



(1) Only –I effect

(2) Only – M effect

(3) Both –I and –M effect

(4) Only + M effect

36. The decreasing order of –I effect of the orbitals is:

I. sp **II.** sp^2

III. sp^3

(1) I > II > III (2) III > II > I

(3) I > III > II (4) II > III > I

37. Electrophile in the case of chlorination of benzene in the presence of $FeCl_3$ is:

(1) Cl^+ (2) Cl^-

(3) Cl (4) $FeCl_3$

38. Identify the strongest nucleophile.

(1) CH_3CH_2SH (2) $CH_3COO^{\ominus}$

(3) CH_3NH_2 (4) $NC-\overset{\ominus}{C}H_2$

39. Among the following the correct order of basicity is:

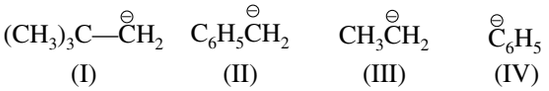
(1) $\overset{\ominus}{NH_2} > \overset{\ominus}{OH} > \overset{\ominus}{RO} > RCOO^{\ominus}$

(2) $\overset{\ominus}{NH_2} > \overset{\ominus}{RO} > \overset{\ominus}{OH} > RCOO^{\ominus}$

(3) $RCOO^{\ominus} > \overset{\ominus}{NH_2} > \overset{\ominus}{RO} > OH^{\ominus}$

(4) $RCOO^{\ominus} > \overset{\ominus}{RO} > \overset{\ominus}{NH_2} > OH^{\ominus}$

40. Identify the correct order of stability among the following carbanions



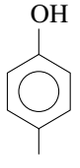
(I) (II) (III) (IV)

(1) I > III > IV > II (2) I > IV > III > II

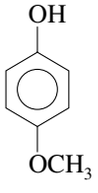
(3) II > III > IV > I (4) II > IV > III > I

41. Value of pK_a will be minimum for:

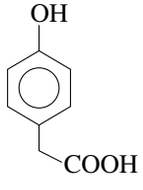
(1)



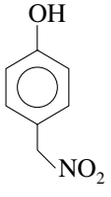
(2)



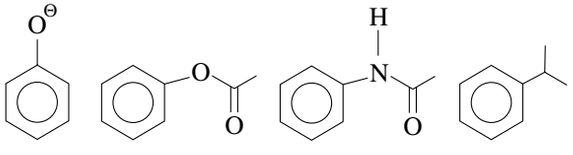
(3)



(4)



42. The order of reactivity of the compounds

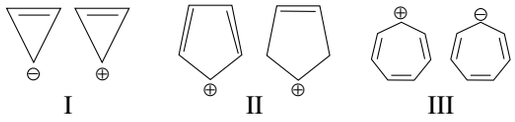


(I) (II) (III) (IV)

Towards substitution with a given electrophile is:

(1) IV > III > II > I (2) I > II > III > IV
(3) III > II > I > IV (4) I > III >II > IV

43. In which pair second ion is less stable than first?

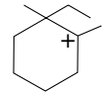
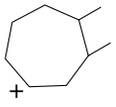


I II III

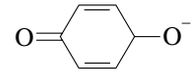
(1) (I) and (II) (2) (II) and (III)
(3) only (II) (4) only (III)

44. Which of the following carbocation will undergo favourable rearrangement?

(1)  (2) 

(3)  (4) 

45. In which of the following, all C–O bonds are not of equal length?

(1)  (2) $CH_3–COO^-$

(3) CO_3^{2-} (4) NO_2^-

46. Arrange *o*-toluic acid (I), *m*-toluic acid (II), *p*-toluic acid (III) and benzoic acid (IV) in order of decreasing acid strength.

(1) I > II > III > IV (2) I > II > IV> III
(3) III > IV> I > II (4) I > IV > II > III

47. In the given ionic reaction, designate the nucleophile and the leaving group

$CH_3–CH_2–Br + NaI \longrightarrow CH_3–CH_2–I + NaBr$

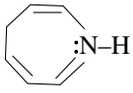
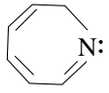
(1) $Nu^{\ominus} = Br^{\ominus}$, $L^{\ominus} = I^{\ominus}$
(2) $Nu^{\ominus} = I^{\ominus}$, $L^{\ominus} = Br^{\ominus}$
(3) $Nu^{\ominus} = I^{\ominus}$, $L^{\ominus} = \overset{\ominus}{C}H_2CH_3$
(4) $Nu^{\ominus} = \overset{\ominus}{C}H_2CH_3$, $L^{\ominus} = Br^{\ominus}$

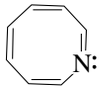
48. The decreasing order of nucleophilicities of the following is

I. $Br^{\ominus}$ **II.** $MeO^{\ominus}$
III. $Me_2N^{\ominus}$ **IV.** $Me_3C^{\ominus}$

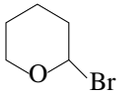
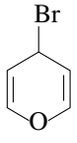
(1) I > II > III > IV (2) IV > III > II > I
(3) IV > III > I > II (4) II > I > III > IV

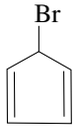
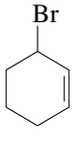
49. Which of the following is best classified as heterocyclic aromatic compound?

(1)  (2) 

(3)  (4) 

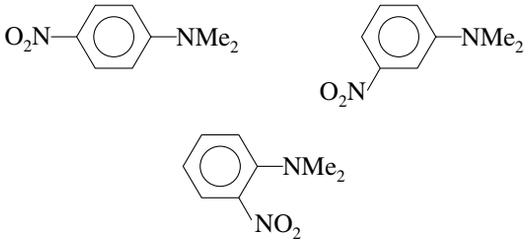
50. Among the following which is more reactive toward $AgNO_3$?

(1)  (2) 

(3)  (4) 

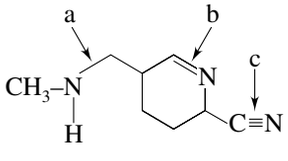
EXERCISE 2

1. The correct order of resonance energy in the following is:



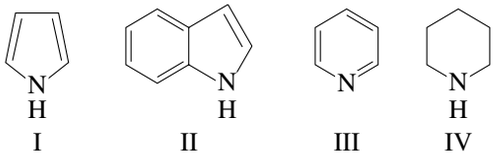
(1) II > I > III (2) I > II > III
(3) III > II > I (4) II > III > I

2. Rank the indicated bond in the given compound in order of decreasing bond strength:



(1) a > b > c (2) c > b > a
(3) b > c > a (4) c > a > b

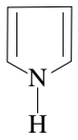
3. The correct order of basicity of the compounds is-



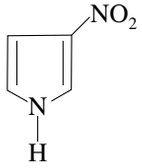
I II III IV

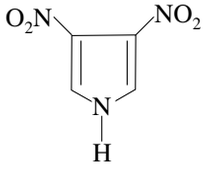
(1) IV > III > II > I (2) III > IV > I > II
(3) IV> III > I > II (4) III > IV > II > I

4. The weakest base amongst the following is:

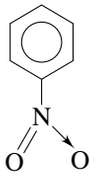
(1) 

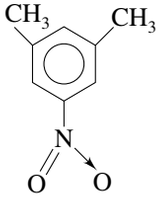
(2) 

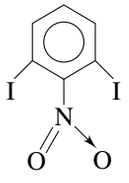
(3) 

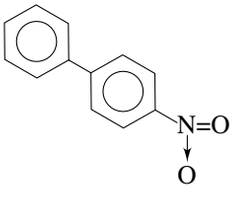
(4) 

5. In which of the following molecules, $-NO_2$ group is not coplanar with phenyl ring?

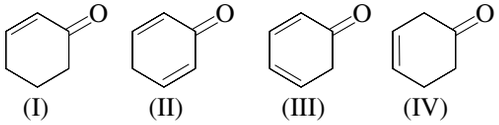
(1) 

(2) 

(3) 

(4) 

6. Among these compounds, which one has maximum resonance energy?

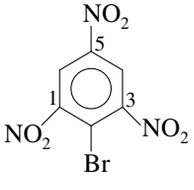


(I) (II) (III) (IV)

(1) I (2) II

(3) III (4) IV

7. Which of the following statements would be true about this compound?



(1) All three C–N bonds are of same length

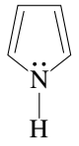
(2) C_1–N and C_3–N bonds are of same length but shorter than C_5–N bond

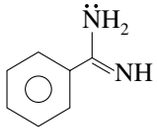
(3) C_1–N and C_3–N bonds are of same length but longer than C_5–N bond

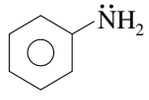
(4) C_1–N and C_3–N bonds are of different length but both are longer than C_5–N bond

8. The decreasing order of basic characters of the following is:

I. 

II. 

III. 

IV. 

(1) III > I > IV > II (2) II > I > IV > II

(3) IV > III > II > I (4) I > II > III > IV

9. The decreasing order of nucleophilicities of the following is:

I. H_2O **II.** EtOH

III. $MeCOO^{\ominus}$ **IV.** $\overset{\ominus}{O}H$

V. $EtO^{\ominus}$

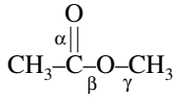
(1) I > II > III > V > IV

(2) I > II > III > IV > V

(3) IV > V > III > II > I

(4) V > IV > III > II > I

10. α, β and γ are three (C–O) bonds in methyl acetate;

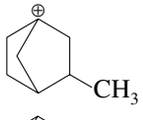


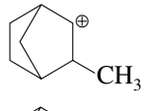
the bond lengths are in the order:

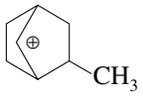
(1) α > β > γ (2) α < β < γ

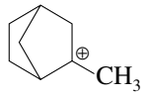
(3) α = β = γ (4) α < β = γ

11. Which of the following carbonium ion is the most stable?

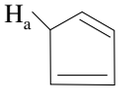
(1) 

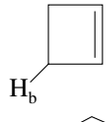
(2) 

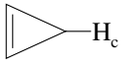
(3) 

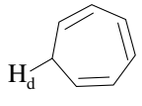
(4) 

12. Which of the following will have the lowest pK_a value?

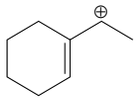
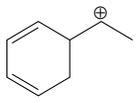
(1) 

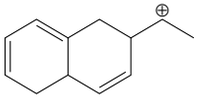
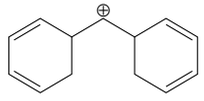
(2) 

(3) 

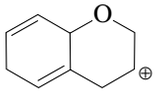
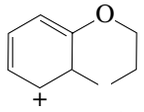
(4) 

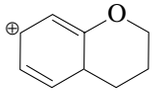
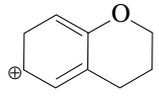
13. The most stable carbocation is:

(1)  (2) 

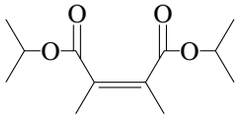
(3)  (4) 

14. Which of the following is most stable cation?

(1)  (2) 

(3)  (4) 

15. A synthetic cockroach repellent has following structure,



The compound contains:

(1) sp^3 and sp^2-hybridised carbon atom

(2) Only sp^2-hybridised carbon atom

(3) sp, sp^2 and sp^3-hybridised carbon atom

(4) Only sp^3-hybridised carbon atom

16. The correct order of increasing nucleophilicity in protic solvent is:

(1) $SH^{\ominus} > CN^{\ominus} > I^{\ominus} > OH^{\ominus} > N_3^{\ominus}$

(2) $N_3^{\ominus} > OH^{\ominus} > I^{\ominus} > CN^{\ominus} > SH^{\ominus}$

(3) $CN^{\ominus} > SH^{\ominus} > I^{\ominus} > OH^{\ominus} > N_3^{\ominus}$

(4) $OH^{\ominus} > CN^{\ominus} > SH^{\ominus} > I^{\ominus} > N_3^{\ominus}$

17. Which of the following is anti aromatic?

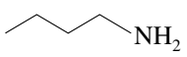
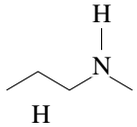
(1) Cyclopentadienyl anion

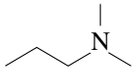
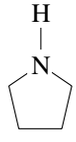
(2) Cyclopentadienyl cation

(3) Cycloheptatrienyl cation

(4) Anthracene

18. What is the increasing order of basic strength of the following compounds in aqueous solution?

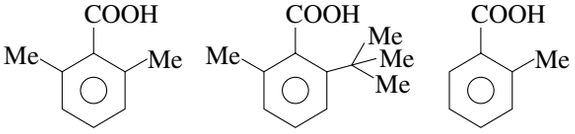
(I)  (II) 

(III)  (IV) 

(1) I < II < III < IV (2) I < II < IV < III

(3) III < I < II < IV (4) III < I < IV < II

19. Arrange in increasing order of pK_b value of given substance:

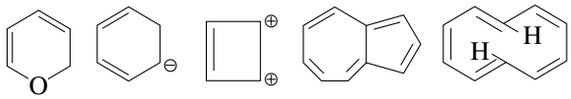


(I) (II) (III)

(1) I < II < III (2) III < I < II

(3) II < I < III (4) II < III < I

20. Which of the following compounds are aromatic?

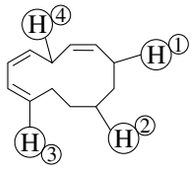


(I) (II) (III) (IV) (V)

(1) III and IV (2) I and II

(3) II, III and IV (4) III, IV and V

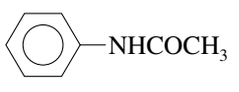
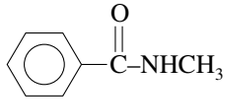
21. Arrange them in increasing bond dissociation energy of C–H bond:

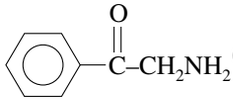
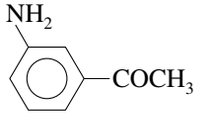


(1) 1 > 2 > 3 > 4 (2) 4 > 3 > 2 > 1

(3) 4 > 1 > 3 > 2 (4) 3 > 2 > 1 > 4

22. The correct order of basic strength of the following is:

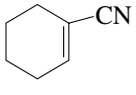
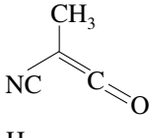
(I)  (II) 

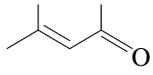
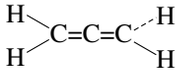
(III)  (IV) 

(1) I > II > III > IV (2) IV > II > III > I

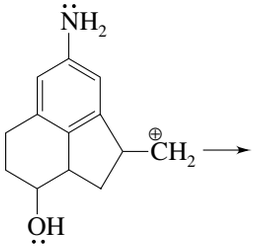
(3) III > IV > II > I (4) III > II > IV > I

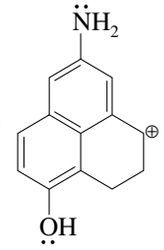
23. Which of the following molecules does not contain sp^3 hybridised carbon atoms?

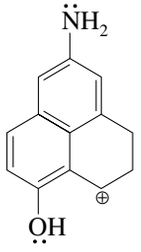
(1)  (2) 

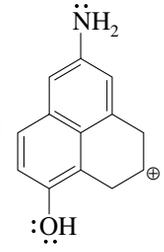
(3)  (4) 

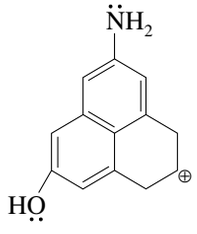
24. Following carbocation rearranges to from:



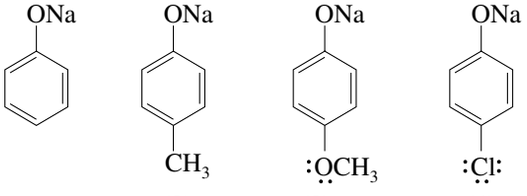
(1) 

(2) 

(3) 

(4) 

25. The correct nucleophilicity order is:

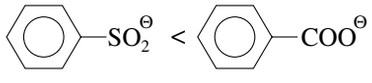


(1) (2) (3) (4)

(1) 1 > 2 > 3 > 4 (2) 3 > 2 > 1 > 4

(3) 3 > 2 > 4 > 1 (4) 2 > 1 > 3 > 4

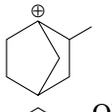
26. The correct leaving group ability has been mentioned in the option

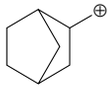
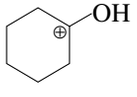
(1) 

(2) $CF_3SO_3^{\ominus} > CCl_3SO_3^{\ominus}$

(3) $I^{\ominus} < {}^{\ominus}CN$ (4) ${}^{\ominus}NH_2 > {}^{\ominus}OH$

27. Find out correct stability order in the following carbocations:

(I)  (II) 

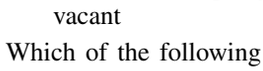
(III)  (IV) 

(1) IV > I > III > II (2) IV > III > I > II

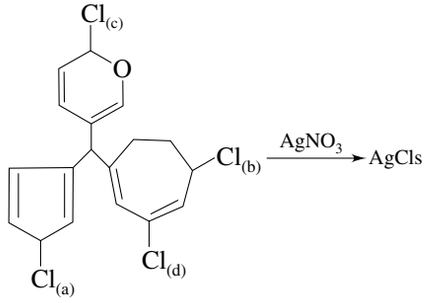
(3) I > IV > III > II (4) I > III > IV > II

28. The most unstable carbanion among the following is:

(1) $H_5C_6 - \ddot{C}H_2^{\ominus}$ (2) $\ddot{C}Cl_3^{\ominus}$

(3)  (4) $:\overline{C}_6H_5$

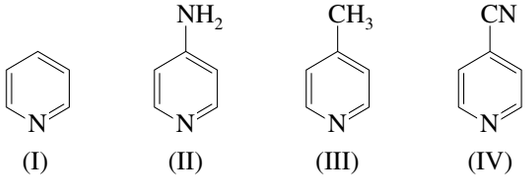
29. Which Cl will eliminate with fastest rate in the form of $Cl^{\ominus}$ to form AgCl?



(1) $Cl_{(c)}$ (2) $Cl_{(b)}$

(3) $Cl_{(a)}$ (4) $Cl_{(d)}$

30. The correct order of increasing basic nature for the following compounds is:

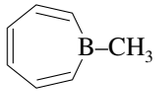


(I) (II) (III) (IV)

(1) IV < I < III < II (2) I < II < III < IV

(3) IV < III < II < I (4) II < IV < I < III

31. The compound shown is planar and all the carbon-carbon bond lengths are the same. What can you deduce about the bonding of boron from these observations?



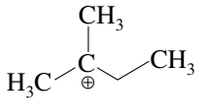
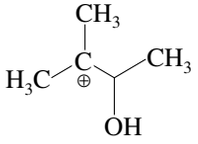
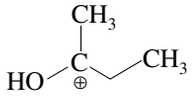
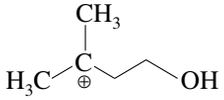
(1) The boron is sp^2-hybridised and the p-orbital contains an unshared pair of electrons

(2) The boron is sp^2-hybridised and a hybrid orbital contains an unshared pair of electrons

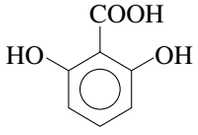
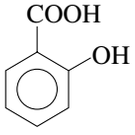
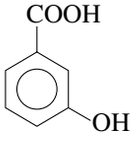
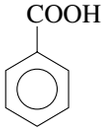
(3) The boron is sp^2-hybridised and a hybrid orbital is vacant

(4) The boron is sp^2-hybridised and the p-orbital is vacant

32. Which of the following cations is the most stable?

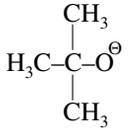
(1) 
(2) 
(3) 
(4) 

33. The decreasing order of acidic character of the following is:

(I) 
(II) 
(III) 
(IV) 

(1) I > II > III > IV (2) III > IV > II > I
(3) IV > III > II > I (4) I > II > IV > III

34. Consider the following nucleophiles (A) and (B)

(A)  (B) $HO^{\ominus}$

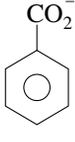
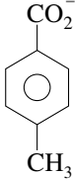
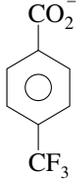
Select correct statements about (A) and (B)

(1) A is weaker nucleophile and weaker base compared to B which is stronger nuclephile and stronger base
(2) A is stronger nucleophile and stronger base compared to B which is weaker nuclephile and weaker base
(3) A is weaker nucleophile and stronger base compared to B which is strong nuclephile and weaker base
(4) None of these

35. Which of the following is the incorrect order of bond lengths?

(1) C – C > C = C > C ≡ C > C ≡ N
(2) C = N > C = O > C = C > C = S
(3) C = C > C = N > C = O > C ≡ N
(4) C – C > C = C > C ≡ C > C – H

36. Arrange in increasing order of leaving group ability:


(I)

(II)

(III)

(1) II < I < III (2) I < III < II
(3) III < II < I (4) I = II = III

37. Arrange these compounds in the increasing order of their aromatic character

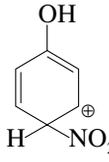
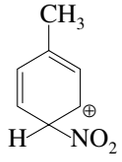

(A)

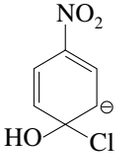
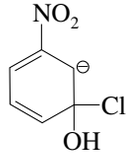
(B)

(C)

(1) C, B, A (2) A, B, C
(3) A, C, B (4) A = B = C

38. Consider the following statement:

(I)  is more stable than 

(II)  is more stable than 

(1) I and II both are correct
(2) I and reverse of II are correct
(3) II and reverse of I are correct
(4) I and II both are incorrect

39. Arrange the CH_3COO^-, $C_6H_5O^-$ and $C_6H_5SO_3^-$ anions as leaving group in the decreasing order if the pK_a values of their conjugate acids are 4.5, 10 and 2.6 respectively

(1) $C_6H_5SO_3^- > CH_3COO^- > C_6H_5O^-$
(2) $C_6H_5O^- > CH_3COO^- > C_6H_5SO_3^-$
(3) $CH_3COO^- > C_6H_5SO_3^- > C_6H_5O^-$
(4) $CH_3COO^- > C_6H_5SO_3^- > C_6H_5O^-$

40. The order of decreasing nucleophilicities of the following species is:

(1) $CH_3\overset{\ominus}{S} > CH_3\overset{\ominus}{O} > CH_3C\overset{\ominus}{O}O > CH_3OH$
(2) $CH_3C\overset{\ominus}{O}O > CH_3\overset{\ominus}{S} > CH_3\overset{\ominus}{O} > CH_3OH$
(3) $CH_3OH > CH_3\overset{\ominus}{S} > CH_3C\overset{\ominus}{O}O > CH_3\overset{\ominus}{O}$
(4) $CH_3\overset{\ominus}{O} > CH_3OH > CH_3C\overset{\ominus}{O}O > CH_3\overset{\ominus}{S}$

EXERCISE 3

One and More Than One Option Correct Type Question

1. Among the following which statement is correct?

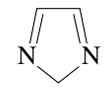
(1) 4 nitrophenol is more acidic than 3,5-dimethyl-4-nitrophenol

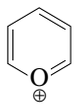
(2) Among R_2NH,  and $R-C\equiv\ddot{N}$ weakest base is $R-C\equiv\ddot{N}$

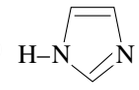
(3) Bridge head carbocation is rarely formed

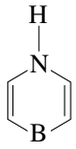
(4) p-fluorophenol is stronger acid than p-chlorophenol

2. Which of the following are aromatic?

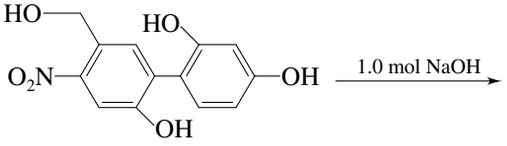
(1) 

(2) 

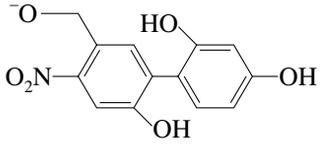
(3) 

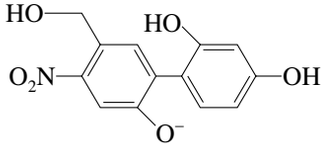
(4) 

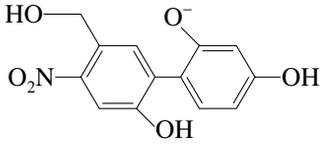
3. Predict the major product in the following reaction.

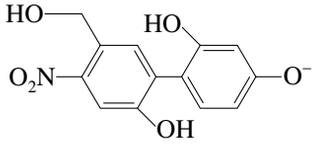


1.0 mol

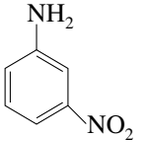
(1) 

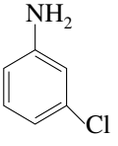
(2) 

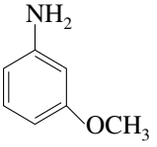
(3) 

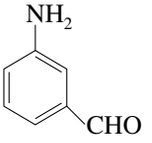
(4) 

4. Which of the following is/are more basic than its own para-isomer?

(1) 

(2) 

(3) 

(4) 

5. In which of the following the first anion is more stable than the second?

(1) $O_2N-\overset{\ominus}{C}H_2$ and $F-\overset{\ominus}{C}H_2$

(2) $\overset{\ominus}{C}F_3$ and $\overset{\ominus}{C}Cl_3$

(3) $F_3C-\overset{\ominus}{C}H_2$ and $Cl_3C-\overset{\ominus}{C}H_2$

(4) $CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H_2$ and $H_2N-\overset{\ominus}{C}H_2$

6. In the vinyl cation, the positively charged carbon is sp hybridised. Which statement about the hybridisation type of the negatively charged carbon in the vinyl carbanion is incorrect?

(1) The carbon is sp hybridised to help to stabilise the orbital with the lone pair

(2) The carbon is sp hybridised to maximise s-character in the orbital with the lone pair

(3) The carbon is sp hybridised to minimise repulsion between the bonding and non-bonding electrons

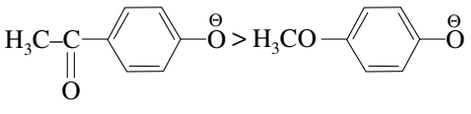
(4) The carbon is sp^2 hybridised to minimise angle strain around pi-bond

7. Which of the following is correct order of nucleophilicity in CH_3OH ?

(1) $\ddot{N}H_3 < \ddot{N}H_2 - \ddot{N}H_2$

(2) $CH_3CH_2\overset{\ominus}{O} > \overset{\ominus}{O}H > CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}$

(3) $F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$

(4) 

8. What is/are true regarding a reactive intermediate formed in a reaction?

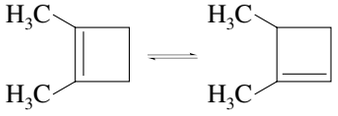
(1) It is the species present at the maxima of the activation energy diagram

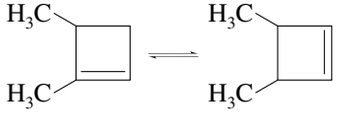
(2) It is formed for infinitesimal time only, cannot be isolated practically

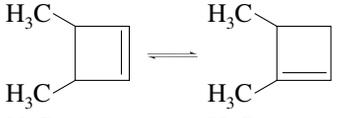
(3) The most stable reactive intermediate leads to the formation of major product

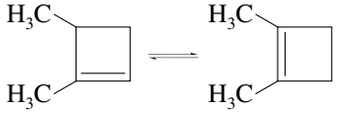
(4) It is responsible for more than one product in a reaction

9. Which of the following process is/are exothermic?

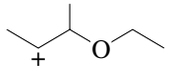
(1) 

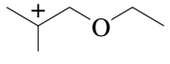
(2) 

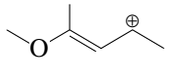
(3) 

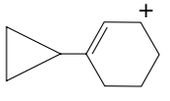
(4) 

10. Which of the following carbocation (s) undergo favourable rearrangement into more stable one?

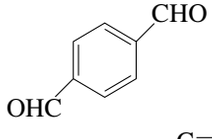
(1) 

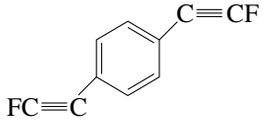
(2) 

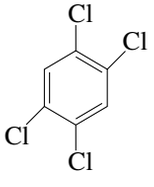
(3) 

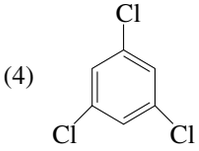
(4) 

11. Which of the following (s) is/are non-polar?

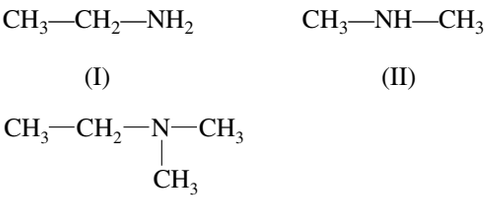
(1) 

(2) 

(3) 

(4) 

12. Consider the following amines.



(I) (II)

(III)

Which of the following statements is/are correct regarding their basicity?

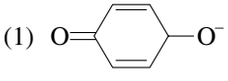
(1) In aqueous solution, the increasing basicity is I < II < III

(2) In gas phase, the basic strength follows the order I < II < III

(3) The pKa values of these amines in gas phase is in the order III < II < I

(4) In aqueous solution, II evolve maximum heat on the basis of per mol when neutralised by adding excess of HCl

13. In which of the following, all C—O bonds are of equal length?

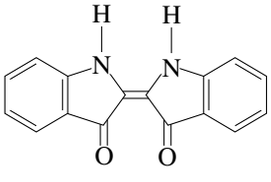
(1) 

(2) $CH_3—COO^-$

(3) HCO_3^-

(4) NO_2^-

14. Consider the molecule indigotin



The correct statement (s) regarding the compound (indigotin) is/are

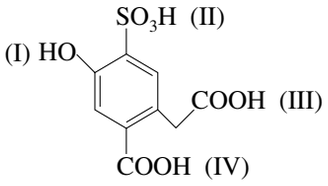
(1) In exhibit geometrical isomerism and its trans isomer is more stable

(2) It exhibit enantiomerism

(3) Its 'CiS' isomer has greater solubility in water than the trans one

(4) It is a planar molecule with very large resonance stabilisation energy

15. Which of the following statement applies correctly regarding acidity of the following acid?



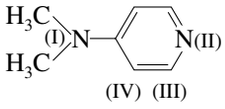
(1) One mole of acid would require 4.0 mol of NaOH for complete neutralisation

(2) Proton labelled II will be deprotonated first during neutralisation

(3) On treatment with $NaHCO_3$, its one mole would require two moles of base

(4) The acid is stronger than both benzene sulphonic acid and benzoic acid

16. Which of the following deduction regarding following base is/are true?



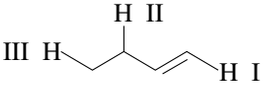
(1) Nitrogen I is protonated first during stepwise neutralisation

(2) Nitrogen II is protonated first during stepwise neutralisation

(3) Conjugate acid has a resonance structure with complete valence shells of all atoms

(4) $-OCH_3$ group at IV will increase basic strength while the same from positions III will decrease basic strength

17. The correct statement(s) concerning the labelled hydrogens in the following molecule is/are



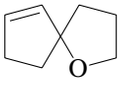
(1) II undergo easiest homolytic bond fission in a chemical reaction

(2) Amongst the labelled hydrogens, C—H II has greatest bond length

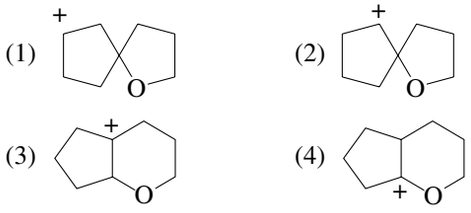
(3) Amongst the labelled hydrogens C—H I has the shortest bond length

(4) Hydrogens labelled I and II take part in hyperconjugation

18. Alkenes on electrophilic attack by H^+ forms carbocation. Which is/are the probable carbocation possible in this reaction?



$\xrightarrow{H+}$ Most stable carbocation



Assertion and Reason Type Question

(1) If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I

(2) If both Statement-I and Statement-II are correct and Statement-II is not the correct explanation for Statement-I

(3) If Statement-I is correct and Statement-II is incorrect

(4) If Statement-I is incorrect and Statement-II is correct

19. Statement-1: In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.

Statement-2: The amino group being completely protonated in strongly acidic solution, the lone pair of electrons of the nitrogen is no longer available for resonance.

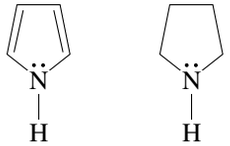
20. Statement-1: $Me-\overset{\oplus}{C}H_2$ is more stable than $MeO-CH_2^{\oplus}$

Statement-2: Me is a + I group where as MeO is a – I group

21. Statement-1: $\ddot{C}F_2$ is good electrophile than $:CCl_2$

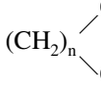
Statement-2: Electronegativity of F is greater than electronegativity of Cl.

22. Statement-1: Pyrrolidine (II) is more basic than pyrrole (I)



Statement-2: Protonated pyrrole has resonance stabilisation of positive charge in aromatic ring.

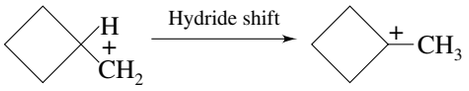
23. Statement-1: The difference between Ka_1, and Ka_2 for dicarboxylic acids of type



decreases as n increases

Statement-2: On increasing n the – I effect of – COOH group decreases (Ka_1, decreases) also + I effect of $-COO^-$ group decreases (Ka_2 increases)

24. **Statement-I:** Following is a favourable rearrangement of carbocation:

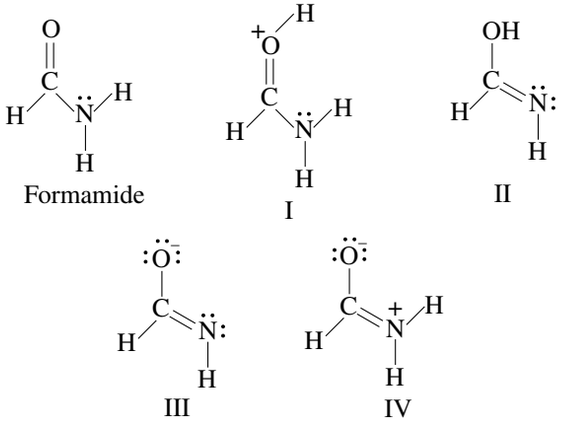


Statement-II: A tertiary alkyl carbocation is more stable than primary alkyl carbocation.

Comprehension Type Question

Comprehension (Q. 25–27)

Amide is a conjugated system, exhibit resonance, Following are formamide and structures that bear some relationship to the Lewis structure of formamide.



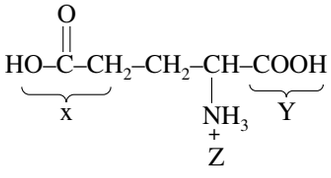
25. Which is a resonance contributor to formamide?
(1) Only I (2) Only II
(3) Only III (4) Only IV

26. Which represents a conjugate acid of formamide?
(1) Only I (2) Only II
(3) Only III (4) Only IV

27. Which is capable of showing stereoisomerism?
(1) Only I (2) Only II
(3) Only III (4) Only IV

Comprehension (Q. 28–30)

Consider the following amino acid (protonated) to answer the next three questions.



28. the order of acidic strength of X, Y and Z is
(1) X > Y > Z (2) Z > X > Y
(3) Y > Z > X (4) Y > X > Z

29. If the amino acid shown above is treated with 1.0 mole of NaOH, the species formed is

(1) $\bar{O}CO–CH_2CH_2–\underset{\overset{+}{NH_3}}{\underset{|}{CH}}–COOH$

(2) $HOOC–CH_2CH_2–\underset{\overset{+}{NH_3}}{\underset{|}{CH}}–COO^-$

(3) $HOCO–CH_2CH_2–\underset{NH_2}{\underset{|}{CH}}–COOH$

(4) $HOOC–CH_2CH_2–\underset{NH_3}{\underset{|}{CH}}–O^-$

30. If the above amino acid is treated with excess of NaOH, what would be formed?

(1) $\bar{O}OC–CH_2CH_2–\underset{NH_2}{\underset{|}{CH}}–COO^-$

(2) $HOOC–CH_2CH_2–\underset{NH_2}{\underset{|}{CH}}–COO^-$

(3) $\bar{O}OC–CH_2CH_2–\underset{\overset{+}{NH_2}}{\underset{|}{CH}}–COO^-$

(4) $\bar{O}OC–CH_2CH_2–\underset{NH_2}{\underset{|}{CH}}–COOH$

Column Matching Type Question

31. Match the following: (More than one option in column-II may match with single option in column-I). Match the hybridisation state of below listed carbon atoms.

$CH_2=C=CH–CH_2–C\equiv C–CH_2–NH_2$

Column-I ***Carbon atoms***	***Column-I*** ***Hybridization state***
(A) C_1	(P) sp
(B) C_2	(Q) sp^2
(C) C_5	(R) sp^3
(D) C_6	(S) dsp^2

(1) A → P; B → Q; C → R; D → S
(2) A → S; B → P; C → Q; D → R
(3) A → R; B → Q; C → P; D → S
(4) A → R; B → P; C → Q; D → P

32.

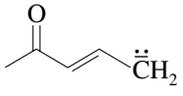
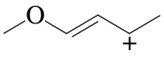
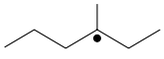
Column-I	***Column-II***
(A) $A - B \rightarrow A^+ + :B^-$	(p) Free radical
(B) $CH_3\overset{\oplus}{C}H–CH_3$	(q) Heterolytic cleavage
(C) $A - A \rightarrow \dot{A} + \dot{A}$	(r) Carbocation

(D) $CH_2N_2 \rightarrow \ddot{C}H_2 + N_2$ (s) Nucleophile

(E) $CH_3\ddot{\underset{..}{O}}H$ (t) Carbene

(1) A → q; B → r; C → p; D → s; E → t
(2) A → q; B → p; C → r; D → t; E → s
(3) A → r; B → q; C → p; D → t; E → s
(4) A → q; B → r; C → p; D → t; E → s

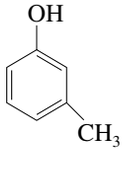
33. Column-I has listed some common reactive intermediates and column-II has listed some of the properties possessed by these intermediates. Match the quantity from column-I with the quantities from Column-II

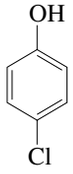
Column-I	***Column-II***
(A) 	(p) Has more stable resonance structure
(B) 	(q) Paramagnetic
(C) 	(r) Hyperconjugation stabilises the intermediates
(D) $:CH_2$	(s) Acts as a strong Lewis acid

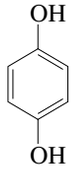
(1) A → q; B → p; C → q, s; D → p, r
(2) A → p; B → q; C → r; D → s
(3) A → s; B → r; C → p; D → q
(4) A → p; B → p, r, s; C → q, r; D → q, s

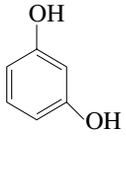
Single Digit Integer Type Question

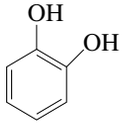
34. How many of the following are stronger acid than phenol?

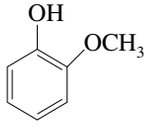

I

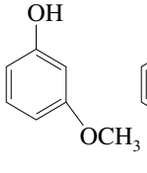

II

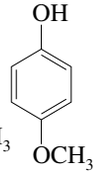

III

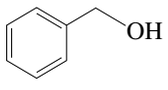

IV

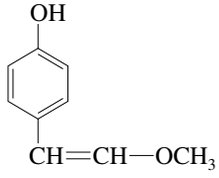

V


VI

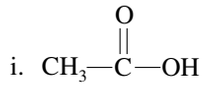

VII

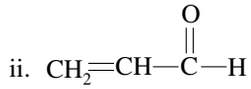

VIII

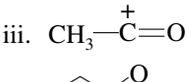

IX

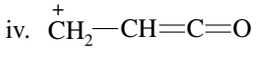

X

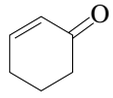
35. In how many of the following, at least one of the C—O bond is weaker than the C—O bond in acetaldehyde?

i. 

ii. 

iii. 

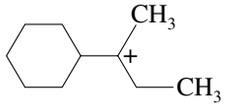
iv. 

v. 

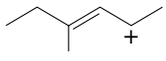
vi. CO_3^{2-}

vii. NCO^-

36. The total number of contributing structures showing hyperconjugation for the following carbocation is

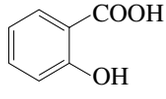


37. If the following carbocation is formed in a chemical reaction that finally bonds with bromide nucleophile, how many different bromination products are expected?



38. In carbene ($:CH_2$), what is the maximum number of valence electrons that may have same spin direction?

39. From the list below how many of them are stronger acid than benzoic acid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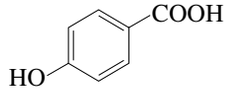
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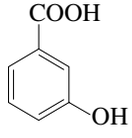
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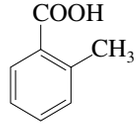
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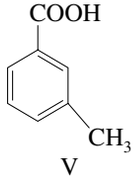
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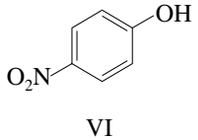
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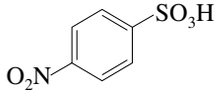
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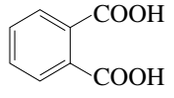
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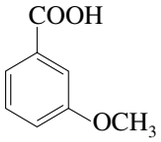
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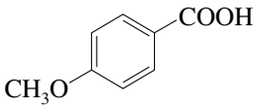
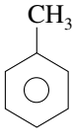
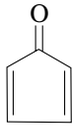
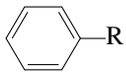

X

40. X = N Number of compound unstable at room temperature.

(a) 
(b) 
(c) 
(d) 
(e) 
(f) 

EXERCISE 4

1. In the following benzyl/allyl system **[AIEEE-2002]**

$R–CH=CH_2$ or 

(R is alkyl group)

Increasing order of inductive effect is-

(1) $(CH_3)_3C– > (CH_3)_2CH– > CH_3CH_2–$

(2) $CH_3CH_2– > (CH_3)_2CH– > (CH_3)_3C–$

(3) $(CH_3)_2CH– > CH_3CH_2– > (CH_3)_3C–$

(4) $(CH_3)_3C– > CH_3CH_2– > (CH_3)_2CH–$

2. The correct order of increasing basic strength of the bases NH_3, CH_3NH_2 and $(CH_3)_2NH$ is **[AIEEE-2003]**

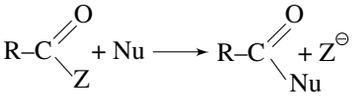
(1) $NH_3 < CH_3NH_2 < (CH_3)_2NH$

(2) $CH_3NH_2 < (CH_3)_2NH < NH_3$

(3) $CH_3NH_2 < NH_3 < (CH_3)_2NH$

(4) $(CH_3)_2NH < NH_3 < CH_3NH_2$

3. Rate of the reaction **[AIEEE-2004]**



Is fastest when Z is-

(1) Cl (2) NH_2

(3) OC_2H_5 (4) $OCOCH_3$

4. Consider the acidic nature of the carboxylic acids- **[AIEEE-2004]**

(a) PhCOOH (b) $o–NO_2C_6H_4COOH$

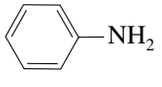
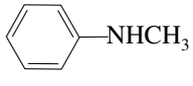
(c) $p–NO_2C_6H_4COOH$ (d) $m–NO_2C_6H_4COOH$

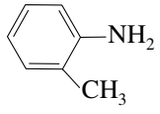
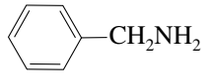
Which of the following order is correct ?

(1) a > b > c > d (2) b > d > c > a

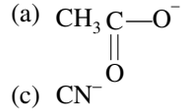
(3) b > d > a > c (4) b > c > d > a

5. Which of the following is the strongest base- **[AIEEE-2004]**

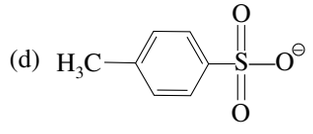
(1)  (2) 

(3)  (4) 

6. The decreasing order of nucleophilicity among the nucleophiles **[AIEEE-2005]**

(a)  (b) CH_3O^-

(c) CN^-

(d) 

(1) (d) > (c) > (b) > (a) (2) (a) > (b) > (c) > (d)

(3) (c) > (b) > (a) > (d) (4) (b) > (c) > (a) > (d)

7. Amongst the following the most basic compound is **[AIEEE-2005]**

(1) Aniline (2) benzylamine

(3) p-nitroaniline (4) acetanilide

8. The increasing order of stability of the following free radicals is– **[AIEEE-2006]**

(1) $(C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$

(2) $(C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C} < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$

(3) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H$

(4) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$

9. $CH_3Br + Nu^- \rightarrow CH_3 – Nu + Br^-$

The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) A to D is **[AIEEE-2006]**

[Nu– = (A) PhO^-, (B) AcO^-, (C) HO^-, (D) CH_3O^-]

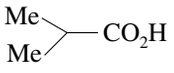
(1) D > C > B > A (2) A > B > C > D

(3) B > D > C > A (4) D > C > A > B

10. Among the following acids, which has the lowest pK_a value? **[AIEEE-2006]**

(1) $(CH_3)_2CH–COOH$ (2) CH_3CH_2COOH
(3) CH_3COOH (4) HCOOH

11. The correct order of increasing acid strength of the compounds- **[AIEEE-2006]**

(A) CH_3CO_2H (B) $MeOCH_2CO_2H$
(C) CF_3CO_2H (D) 

(1) B<D<A<C (2) D<A<C<B
(3) D<A<B<C (4) A<D<C<B

12. Which one of the following is the strongest base in aqueous solution? **[AIEEE-2007]**

(1) Trimethylamine (2) Aniline
(3) Dimethylamine (4) Methylamine

13. Presence of a nitro group in a benzene ring **[AIEEE-2007]**

(1) activates the ring towards electrophilic substitution
(2) renders the ring basic
(3) deactivates the ring towards nucleophilic substitution
(4) deactivates the ring towards electrophilic substitution

14. Arrange the carbanions, $(CH_3)\overset{\ominus}{C}$, $\overset{\ominus}{C}Cl_3$, $(CH_3)_2\overset{\ominus}{C}H$, $C_6H_5\overset{\ominus}{C}H_2$, in order of their decreasing stability- **[AIEEE-2009]**

(1) $(CH_3)_2\overset{\ominus}{C}H > \overset{\ominus}{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_3\overset{\ominus}{C}$
(2) $\overset{\ominus}{C}Cl_3 > C_6H_5\overset{\ominus}{C}H_2 > (CH_3)_2\overset{\ominus}{C}H > (CH_3)_3\overset{\ominus}{C}$
(3) $(CH_3)_3\overset{\ominus}{C} > (CH_3)_2\overset{\ominus}{C}H > C_6H_5\overset{\ominus}{C}H_2 > \overset{\ominus}{C}Cl_3$
(4) $C_6H_5\overset{\ominus}{C}H_2 > \overset{\ominus}{C}Cl_3 > (CH_3)_3\overset{\ominus}{C} > (CH_3)_2\overset{\ominus}{C}H$

15. The correct order of increasing basicity of the given conjugate bases (R=CH_3) is **[AIEEE-2010]**

(1) $RCOO^- > HC \equiv \bar{C} > \bar{R} < \bar{N}H_2$
(2) $\bar{R} < CH \equiv \bar{C} < RCOO^- < \bar{N}H_2$
(3) $RCOO^- < \bar{N}H_2 < CH \equiv \bar{C} < \bar{R}$
(4) $RCOO^- < CH \equiv \bar{C} < \bar{N}H_2 < \bar{R}$

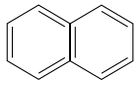
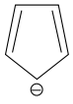
16. Consider thiol anion ($RS^{\ominus}$) and alkoxy anion ($RO^{\ominus}$). Which of the following statements is correct? **[AIEEE-2011]**

(1) $RS^{\ominus}$ is less basic but more nucleophilic than $RO^{\ominus}$
(2) $RS^{\ominus}$ is more basic and more nucleophilic than $RO^{\ominus}$
(3) $RS^{\ominus}$ is more basic but less nucleophilic than $RO^{\ominus}$
(4) $RS^{\ominus}$ is less basic and less nucleophilic than $RO^{\ominus}$

17. The correct order of acid strength of the following compounds is: **[AIEEE-2011]**

(A) Phenol (B) p-Cresol
(C) m-Nitrophenol (D) p-Nitrophenol
(1) D > C > A > B (2) B > D > A > C
(3) A > B > D > C (4) C > B > A > D

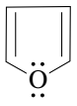
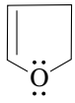
18. The non aromatic compound among the following is– **[AIEEE-2011]**

(1)  (2) 
(3)  (4) 

19. Ortho-Nitrophenol is less soluble in water than p- and m-Nitrophenols because– **[AIEEE-2012]**

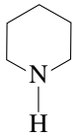
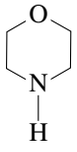
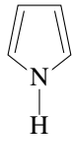
(1) o-Nitrophenol shows intramolecular H-bonding
(2) o-Nitrophenol shows intermolecular H-bonding
(3) Melting point of o-Nitrophenol is lower than those of m-and p-isomers.
(4) o-Nitrophenol is more volatile in steam than those of m-and p-isomers

20. Which of the following compounds are antiaromatic **[AIEEE Online-2012]**

(I)  (II) 
(III)  (IV) 
(V)  (VI) 

(1) (III) and (VI) (2) (V) and (VI)
(3) (I) and (V) (4) (I) and (IV)

21. In the following compounds: **[AIEEE Online-2012]**

(1)  (II) 
(III)  (IV) 

The order of basicity is as follows:

(1) IV > III > II > I (2) II > III > I > IV

(3) I > III > II > IV (4) III > I > II > IV

22. Dipole moment is shown by:

[AIEEE Online-2012]

(1) trans-2, 3-dichloro-2-butene

(2) 1, 2-dichlorobenzene

(3) 1, 4-dichlorobenzene

(4) trans-1, 2-dinitroethene

23. Which of the following cannot be represented by resonance structures?

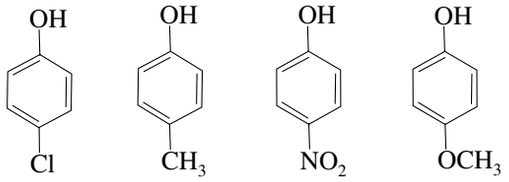
[AIEEE Online-2012]

(1) Dimethyl ether (2) Carboxylate anion

(3) Toluene (4) Nitrate anion

24. Arrange the following compounds in order of decreasing acidity:

[JEE Main online-2012]



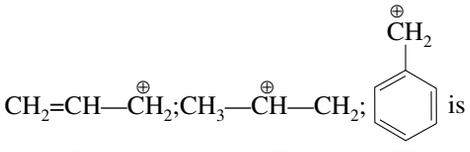
(I) (II) (III) (IV)

(1) III > I > II > IV (2) IV > III > I > II

(3) II > IV > I > III (4) I > II > III > IV

25. The order of stability of the following carbocations

[JEE Main Online-2013]



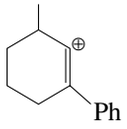
(I) (II) (III)

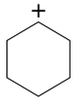
(1) I > II > III (2) III > I > II

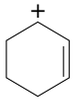
(3) III > II > I (4) II > III > I

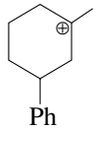
26. Which one of the following is the most stable?

[JEE Main Online-2013]

(1) 

(2) 

(3) 

(4) 

27. The order of basicity of amines in gaseous state is

[JEE Main Online-2013]

(1) 1° > 2° > 3° > NH_3 (2) 3° > 2° > NH_3 > 1°

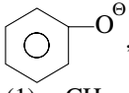
(3) 3° > 2° > 1° > NH_3 (4) NH_3 > 1° > 2° > 3°

28. In nucleophilic substitution reaction, order of halogens as incoming (attacking) nucleophile is should be-

[JEE Main Online-2013]

(1) $Br^- > I^- > Cl^-$ (2) $I^- > Br^- > Cl^-$

(3) $Cl^- > Br^- > I^-$ (4) $Cl^- > I^- < Br^-$

29. Which one of the following substituents at position is most effective in stabilising the phenoxide 

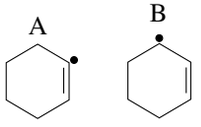
, ion? **[JEE Main Online-2014]**

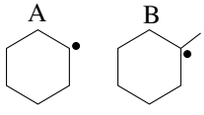
(1) $–CH_3$ (2) $–OCH_3$

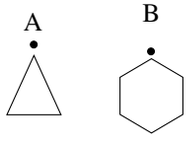
(3) $–COCH_3$ (4) $–CH_2OH$

30. In which of the following pairs A is more stable than B?

[JEE main Online-2014]

(1) 

(2) 

(3) 

(4) A B
$Ph_3C^\bullet$, $(CH_3)_3C^\bullet$

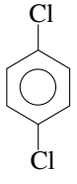
31. Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value?

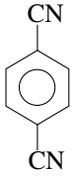
[JEE Main Online-2014]

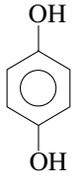
(1) CH_3NH_2 (2) $(CH_3)_3N$

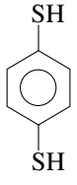
(3) $C_6H_5NH_2$ (4) $(CH_3)_2NH$

32. or which of the following molecule significant $\mu \neq 0$? **[JEE Main Online-2014]**

(a) 

(b) 

(c) 

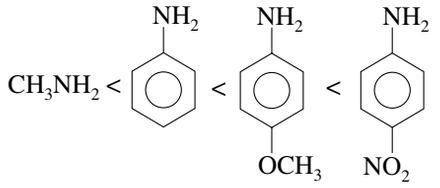
(d) 

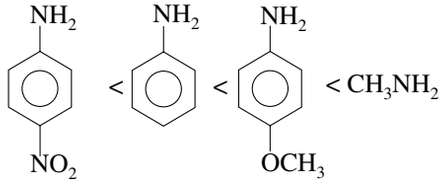
(1) a and b (2) only c

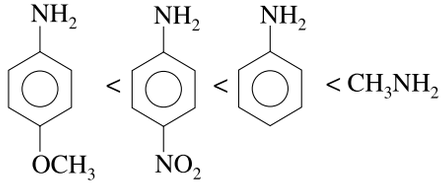
(3) c and d (4) only a

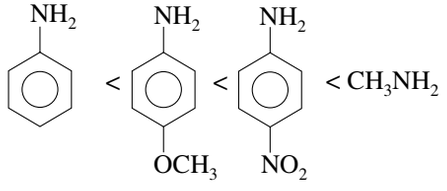
33. Arrange the following amines in the order of increasing basicity

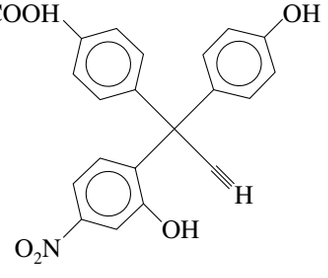
JEE Main Online-2015]

(1) 

(2) 

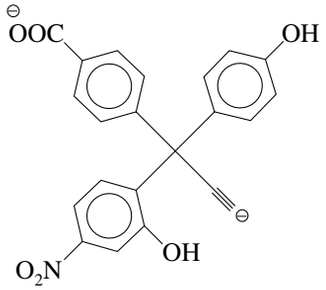
(3) 

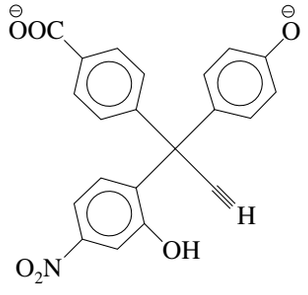
(4) 

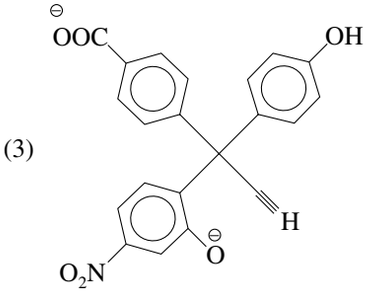
34. 

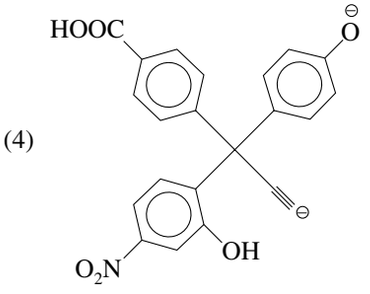
[IIT-2003]

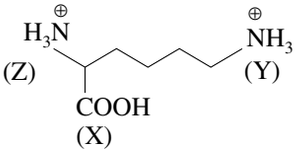
When X is made to react with 2 eq. of $NaNH_2$ the product formed will be -

(1) 

(2) 

(3) 

(4) 

35. (Z) 

(X) (Y)

Correct order of acidic strength is:

[IIT-2004]

(1) x > y > z (2) z > y > x

(3) y > z > x (4) x > z > y

36. For-1-methoxy-1, 3-butadiene, which of the following resonating structure is least stable?

[IIT-2005]

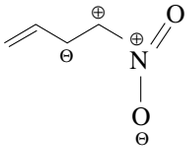
(1) $\overset{\ominus}{C}H_2–\overset{\oplus}{C}H–CH–CH=CH–O–CH_3$

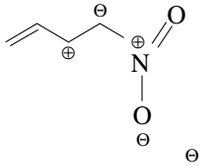
(2) $\overset{\ominus}{C}H_2–CH=CH–CH–\overset{\oplus}{O}–CH_3$

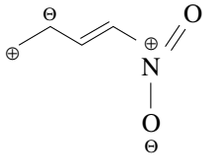
(3) $CH_2=CH–\overset{\oplus}{C}H=\overset{\ominus}{C}H–O–CH_3$

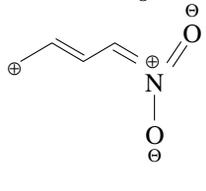
(4) $CH_2=CH–\overset{\ominus}{C}H–CH=\overset{\oplus}{O}–CH_3$

37. Among the following, the least stable resonance structure is: **[IIT-2007]**

(1) 

(2) 

(3) 

(4) 

38. **Statement-1**: *p*-Hydroxybenzoic acid has a lower boiling point that *o*-hydroxybenzoic

Statement-2: *o*-Hydroxybenzoic acid has intramolecular hydrogen bonding. **[IIT-2007]**

(1) If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I

(2) If both Statement-I and Statement-II are correct and Statement-II is not the correct explanation for Statement-I

(3) If Statement-I is correct and Statement-II is incorrect

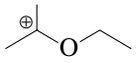
(4) If Statement-I is incorrect and Statement-II is correct

39. Hyperconjugation involves overlap of the following orbitals **[IIT-2008**

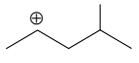
(1) $\sigma - \sigma$ (2) $\sigma - p$

(3) $p - p$ (4) $\pi - \pi$

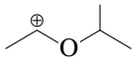
40. The correct stability order for the following species is- **[IIT-2008]**



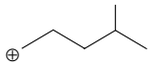
(I)



(II)



(III)

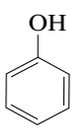


(IV)

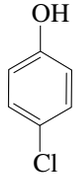
(1) II > IV > I > III (2) I > II > III > IV

(3) II > I > IV > III (4) I > III > II > IV

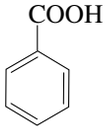
41. The correct acidity order of the following is **[IIT-2009]**



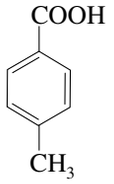
(I)



(II)



(III)

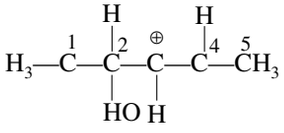


(IV)

(1) III > IV > II > I (2) IV > III > I > II

(3) III > II > I > IV (4) II > III > IV > I

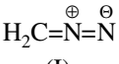
42. In the following carbocation, H/CH_3 that is most likely to migrate to the positively charged carbon is- **[IIT-2009]**



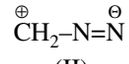
(1) CH_3 at C – 4 (2) H at C– 4

(3) CH_3 at C – 2 (4) H at C – 2

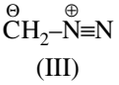
43. The correct stability order of the following resonance structures is-



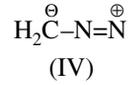
(I)



(II)



(III)



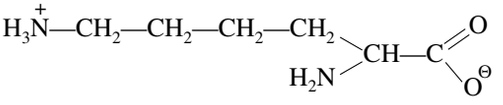
(IV)

[IIT-2009]

(1) I > II > IV > III (2) I > III > II > IV

(3) II > I > III > IV (4) III > I > IV > II

44. Out of the following the alkene that exhibits optical isomerism is

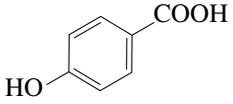


[IIT-2010]

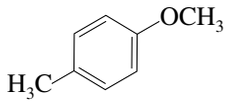
(1) 1 (2) 2

(3) 3 (4) 4

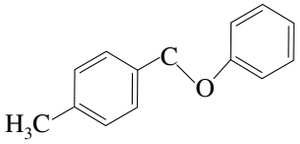
45. The compounds P, Q and S **[IIT-2010]**



(P)



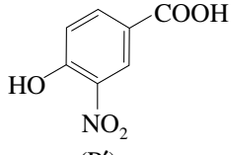
(Q)



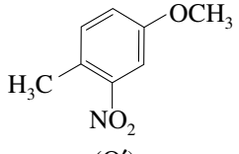
(S)

were separately subjected to nitration using HNO_3/ H_2SO_4 mixture. The major product formed in each case respectively, is

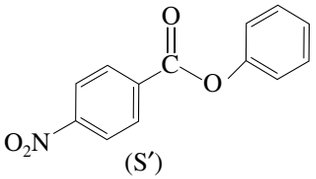
(1)



(P′)

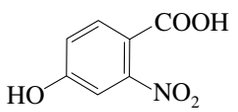


(Q′)

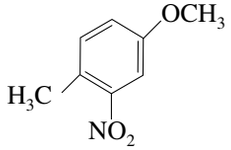


(S′)

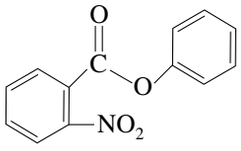
(2)



(P′)

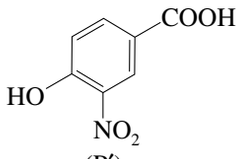


(Q′)

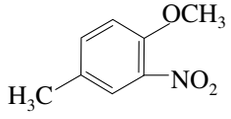


(S′)

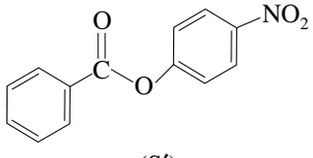
(3)



(P′)

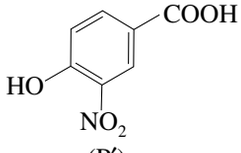


(Q′)

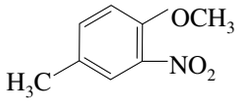


(S′)

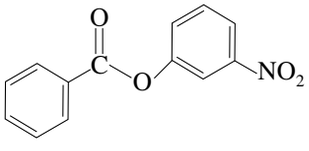
(4)



(P′)



(Q′)



(S′)

46. Among the following compounds, the most acidic is- **[IIT-2011]**

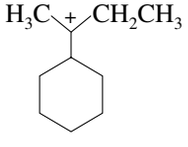
(1) p-nitrophenol

(2) p-hydroxybenzoic acid

(3) o-hydroxybenzoic acid

(4) p-toluic acid

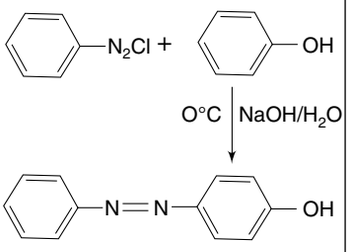
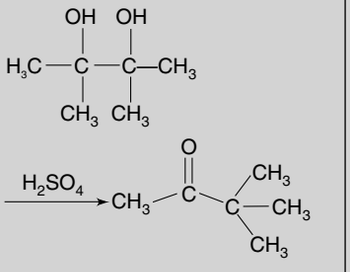
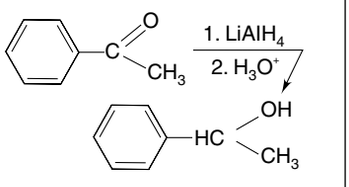
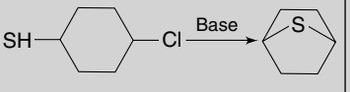
47. The total number of contributing structures showing hyperconjugation (involving C–H bonds) for the following carbocation is **[IIT-2011]**



(1) 6 (2) 4

(3) 3 (4) 2

48. Match the column reaction in Column I with appropriate options in Column II. **[ITT Adv. 2011]**

	Column I		Column II
i.		p.	Racemic mixture
ii.		q.	Addition reaction
iii.		r.	Substitution reaction
iv.		s. t.	Coupling reaction Carbocation intermediate

Codes

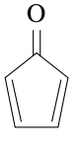
	i	ii	iii	iv
(1)	r, s	t	p, q	q
(2)	p	r, s	q, s	t
(3)	r, s	p	t	r, s
(4)	q	t	p, t	q, r

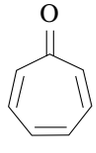
49. Which of the following molecules, in pure form, is (are) **unstable** at room temperature?

[IIT-2012]

(1) 

(2) 

(3) 

(4) 

50. In allene (C_3H_4), the type(s) of hybridisation of the carbon atoms, is (are) **[ITT Adv. 2012]**

(1) sp ad sp^3 (2) sp and sp^2

(3) only sp^3 (4) sp^2 and sp^3

51. The hyperconjugative stabilities of tert-butyl cation and 2-butene, respectively, are due to **[IIT-2013]**

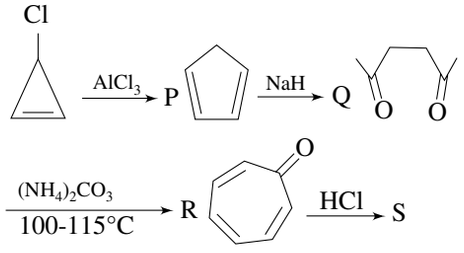
(1) $\sigma \rightarrow$ p(empty) and $\sigma \rightarrow \pi^*$ electron delocalisations

(2) $\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi$ electron delocalisations

(3) $\sigma \rightarrow$ p (filled) and $\sigma \rightarrow \pi$ electron delocalisations

(4) p(filled) $\rightarrow \sigma \rightarrow \pi^*$ electron delocalisations

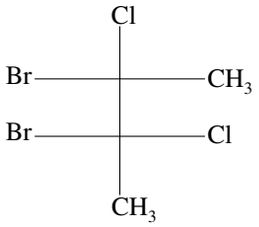
52. Among P, Q, R and S, the aromatic compound(s) is/are **[IIT Adv. 2013 (MCQ)]**



(1) P (2) Q

(3) R (4) S

53. The total number(s) of stable conformers with non-zero dipole moment for the following compound is (are) **[JEE(Adv)-2014]**



54. Hydrogen bonding plays a central role in the following phenomena: **[JEE Adv-2014 (MCQ)]**

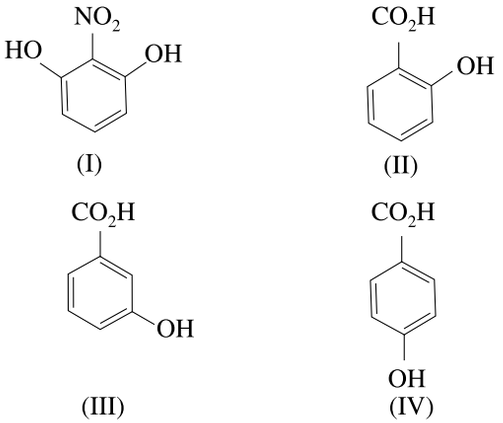
(1) Ice floats in water

(2) higher lewis basicity of primary amines than tertiary amines in aqueous solutions

(3) Formic acid is more acidic than acetic acid

(4) Dimerisation of acetic acid in benzene

55. The correct order of acidity for the following compounds is **[JEE(Adv)-2016]**



(1) I > II > III > IV (2) III > I > II > IV

(3) III > IV > II > I (4) I > III > IV > II

ANSWER KEY

EXERCISE # 1

1. (4)	2. (4)	3. (2)	4. (4)	5. (3)
6. (3)	7. (1)	8. (3)	9. (2)	10. (1)
11. (3)	12. (1)	13. (3)	14. *	15. (3)
16. (4)	17. (1)	18. (2)	19. (3)	20. (4)
21. (3)	22. (3)	23. (4)	24. (1)	25. (1)
26. (3)	27. (3)	28. (2)	29. (1)	30. (1)
31. (2)	32. (4)	33. (4)	34. (1)	35. (1)
36. (1)	37. (1)	38. (1)	39. (2)	40. (4)
41. (4)	42. (4)	43. (4)	44. (2)	45. (1)
46. (4)	47. (2)	48. (2)	49. (4)	50. (2)

EXERCISE # 2

1. (2)	2. (2)	3. (3)	4. (4)	5. (3)
6. (3)	7. (3)	8. (1)	9. (4)	10. (2)
11. (4)	12. (1)	13. (1)	14. (2)	15. (1)
16. (1)	17. (2)	18. (4)	19. (2)	20. (1)
21. (4)	22. (4)	23. (4)	24. (1)	25. (2)
26. (2)	27. (1)	28. (4)	29. (1)	30. (1)
31. (4)	32. (3)	33. (1)	34. (3)	35. (2)
36. (1)	37. (3)	38. (1)	39. (1)	40. (1)

EXERCISE # 3

1. (1,2,3)	2. (2,3,4)	3. (3)	4. (1,4)	
5. (1,3)	6. (1,2,3)	7. (1,2)	8. (2,3,4)	
9. (3,4)	10. (1,2)	11. (1,2,3,4)		
12. (2,3,4)	13. (2,3)	14. (1,3,4)	15. (1,2,4)	
16. (2,3)	17. (1,2,3)	18. (4)	19. (4)	20. (3)
21. (4)	22. (3)	23. (1)	24. (4)	25. (4)
26. (1)	27. (2)	28. (4)	29. (2)	30. (3)
31. (4)	32. (4)	33. (4)	34. (3)	35. (5)
36. (6)	37. (8)	38. (4)	39. (6)	40. (3)

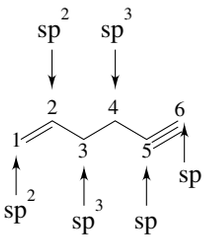
EXERCISE # 4

1. (1)	2. (1)	3. (1)	4. (4)	5. (4)
6. (4)	7. (2)	8. (4)	9. (4)	10. (4)
11. (3)	12. (3)	13. (4)	14. (2)	15. (4)
16. (1)	17. (1)	18. (4)	19. (1)	20. (2)
21. (3)	22. (2)	23. (1)	24. (1)	25. (2)
26. (3)	27. (3)	28. (2)	29. (3)	30. (4)
31. (4)	32. (4)	33. (2)	34. (3)	35. (4)
36. (3)	37. (1)	38. (4)	39. (2)	40. (4)
41. (1)	42. (4)	43. (2)	44. (2)	45. (3)
46. (3)	47. (1)	48. (1)	49. (2,3)	50. (2)
51. (1)	52. (1,2,3,4)	53. (3)	54. (1,2,4)	55. (1)

HINT AND SOLUTION

EXERCISE # 1

1. [4]



Hence, C_2 and C_3 are sp^2-and sp^3-hybridised

2. [4]

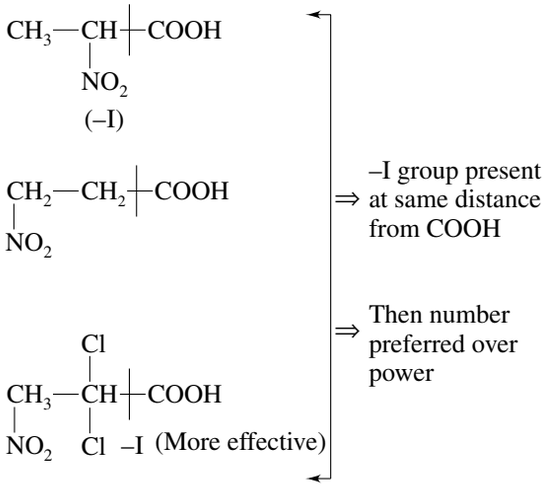
e-deficient species are electrophile

3. [2]

Acid strength $\propto$ – I $\propto \frac{1}{+I}$

Also –I power increases as the distance from source group decreases

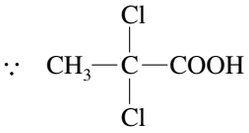
4. [4]



For – I (Preferable order)

→ Distance > Number > Power

Acidic strength $\propto$ – I Power $\propto \frac{1}{+I \text{ power}} \propto \frac{1}{PK_a}$

$\because$ 

⇒ Most + effective – I most Acidic least PKa

Between number and strength, number dominates in the groups having –I effect.

5. [3]

Nuclophile having two nucleophilic site (e^-–denating site) is ambident nucleophle.

6. [3]

Bond-1	Bond-2	Bond-3
sp^3-sp^3	sp-sp	sp^2-sp^2

% s $\propto$ E.N $\propto$ bond strength

(1) < (3) < (2)

7. [1]

$$-NR_3 > -NO_2 > -CN > -COOH$$

↓ De-activating power

↓ m-directing strength

8. [3]

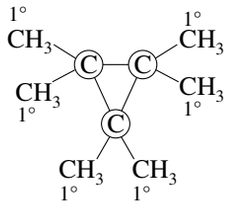
(I) Structure → non polar (most stable)

(II) Structure → Incomplete octet

(III) Structure → Complete octet

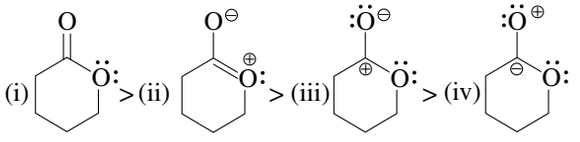
$\therefore$ (I) > (III) > (II)

9. [2]



→ All 1°C attach with 4°C so 1°H are identical

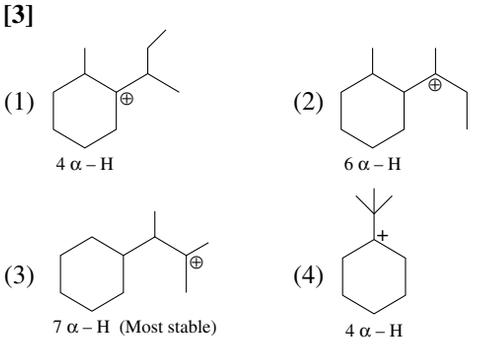
10. [1]



non polar | complete octet | More E.N –ve | More E.N +ve

Incomplete octet

11. [3]



4 α – H | 6 α – H | 7 α – H (Most stable) | 4 α – H

12. [1]

$CHCl_3 \longrightarrow \overset{\ominus}{C}Cl_3$ Most stable, due to pπ-dπ bonc

Most acidic

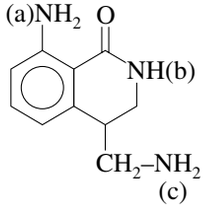
$CHF_3 \longrightarrow \overset{\ominus}{C}F_3$ EWG stabilised anion

$CH_3–CH_3 \longrightarrow CH_3\overset{\ominus}{C}H_2$

ERG, destabilised anion

Stability of anion ∝ Acid strength of conjugate

13. [3]



c > a > b

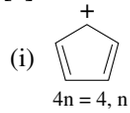
l.p localised | less de-localised | more de-localised

(due to cross conjugation)

14. [2]

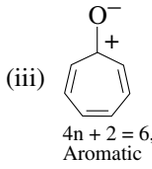
De-activating group are meta director.

15. [3]



4n = 4, n = 1
Anti aromatic

4n = 4, n = 1
Anti aromatic



4n + 2 = 6, n = 1
Aromatic

4n + 6 = 2, n = 0
Aromatic

16. [4]

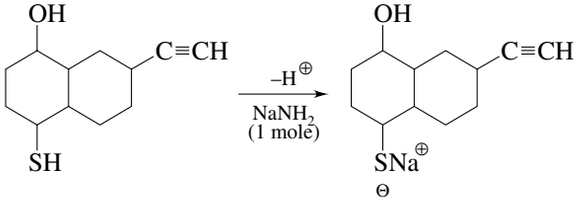
$CH_3–\overset{\oplus}{C}H–CH=CH–C\equiv C–H$

(1) (1) (3)

sp^2 sp^2 sp

17. [1]

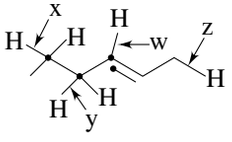
Removal of most acidic H takes place, according to size factor, Acidic strength ∝ size



18. [2]

Resonance ∝ bond length of double bond

19. [3]



$\overset{-x}{\dot{C}H_2}–CH_2–CH=CH–CH_3$ (H effect only)

$\overset{-y}{CH_3}–\dot{C}H–CH=CH–CH_3$ (R + H) effect

$\overset{-w}{CH_3–CH_2}–\dot{C}=CH–CH_3$ More EN caries radical (like +ve) unstable

$\overset{-z}{CH_3–CH_2–CH=CH–}\dot{C}H_2$ Only R effect

Bond dissociation energy (B.D.E)

$$\propto \frac{1}{\text{stability of carbon free radical}}$$

20. [4]

e-density of benzene ring ∝ E.R.G Power

Thus $–NHCOCH_3$ > –OCOEt > $–CH_3$ > COOEt

21. [3]

In reasonating structures atoms always at same position only migration of e^- takes place.

22. [3]

π . π conjugation dominant (– ve) is not in conjugation

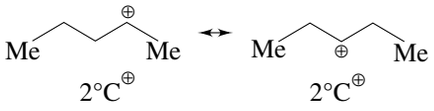
23. [4]

$Ph–\overset{\bullet}{C}(Ph)–Ph$ > $CH_3–\overset{\bullet}{C}(CH_3)–CH_3$

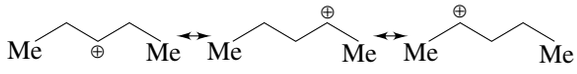
Resonance stable

24. [1]

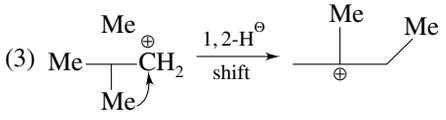
Here (1) is stable because it would not change to other stable carbocation. It can only change $2°C^{\oplus}$ to $2°C^{\oplus}$.

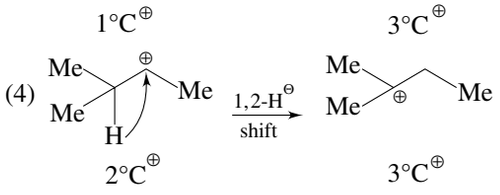


On the other hand, (2) can change to two $2°C^{\oplus}$ structures.



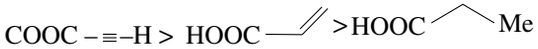
Furthermore, (3) is stabilised by 1, 2-Me shift and (2) is stabilised by 1, 2-$H^{\oplus}$ shift.





So (1) is most stable.

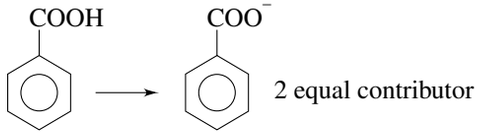
25. [1]



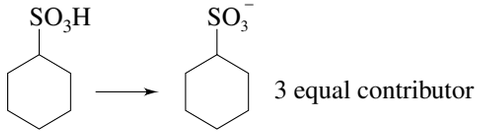
Acidic order: $sp > sp^2 > sp^3 (C \equiv C > C = C > C - C)$

26. [3]

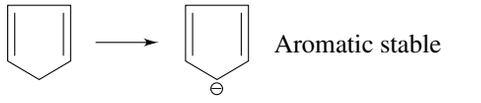
Acidic strength ∝ stability of conjugate anion



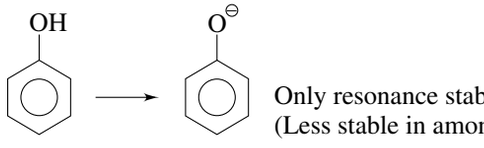
2 equal contributor



3 equal contributor



Aromatic stable



Only resonance stable
(Less stable in among)

27. [3]

Electron deficient molecules are electrophile

28. [2]

Acidic strength ∝ stability of anion

Thus carboxylic acid is more acidic than alcohol due to formation of equal contributor canonical form of carboxylate ion.

Further in same group

$$\text{Acidic strength} \propto -M, -I \propto \frac{1}{+M, +1}$$

$$\text{Acidic strength} \propto K_a \propto \frac{1}{pK_a}$$

Hence of pK_a is (II > I > III > IV)

29. [1]

Ease of hetrolysis ∝ Leaving ability of anion
∝ Acidic strength of conjugate acid of anion.

Leaving (anion) → $\overset{\ominus}{O}H$ $\overset{\ominus}{O}Ac$ $\overset{\ominus}{C}l$

Acidic strength order of conjugate acid → H_2O < ACOH < HCl

Hence order of case of hetralysis is (I) < (II) < (III)

30. [1]

α–NO_2 comes out of plane due to ortho effect,

So $\alpha(C - N) > \beta(C - N)$

(partial double bond character) in $\beta(C - N)$ due to resonance.

31. [2]

(i) Bond length (C=C bond) ∝ Resonance effect

(ii) Bond length (C=C bond) ∝ H-effect

C=C bond length is maximum in (III) because of resonance.

In (I) and (II) resonance is same but due to Hyperconjugation in (II) C=C bond length is higher than (I)

32. [4]

Bond dissociation energy

$$\propto \frac{1}{\text{stability of C – free radical}}$$ (refer solved example)

33. [4]

Stability of carbocation ∝ + H effect

+H power $CH_3 > CD_3 > CT_3$

34. [1]

Heat of hydrogenation ∝ reactivity

$$\text{Reactivity} \propto \frac{1}{\text{Stability of alkene}}$$ (Reoetivity)

Stability of alkene ∝ number of α – H(due to +H)

(P)	(Q)	(R)	(S)
1α–H	4α–H	10α–H	7α–H

35. [1]

No –M effect of $-NO_2$ work because of steric hindrance (ortho effect)

36. [1]

The more the s character, the more is the penetration effect of s orbital towards the nucleus, and hence more $\bar{e}$-withdrawing effect. So, sp(50% s) > sp^2(33% s) > sp^3(25% s).

37. [1]

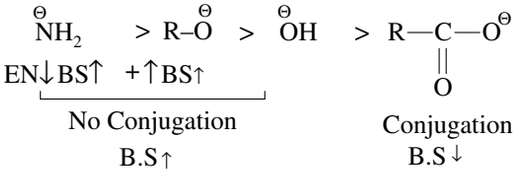
$FeCl_3 + Cl_2 \longrightarrow Cl^{\oplus} + FeCl_4^{\ominus}$

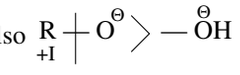
38. [1]

→ Nucleophilic strength predominantly depends upon size

→ N.S ∝ Size of nucleophilic site

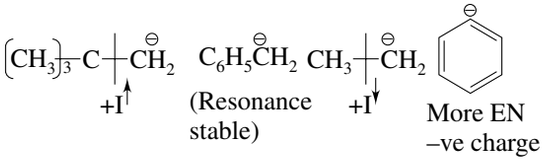
39. [2]



Also 

Base strength ∝ +I power

40. [4]



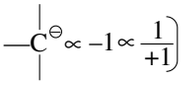
(II) > (I) , (III) , (IV)

E.N.↓ E.N.↑

($\overset{\ominus}{C}$ sp^3) ($\overset{\ominus}{C}$ sp^2)

(II) > (IV) > (I) , (III)

Same EN

(stability of  ∝ −1 ∝ $\frac{1}{+1}$)

(II) > (IV) > (III) > (I)

41. [4]

Acid strength ∝ Ka ∝ $\frac{1}{pKa}$ ∝ – I, M ∝ $\frac{1}{I, +M}$

Thus pKa ∝ +M, + I ∝ $\frac{1}{-M, -I}$

–M(–NO_2) > –M(–COOH)

42. [4]

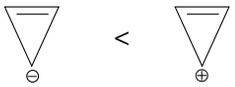
Reactivity of aromatic substance towards electrophile

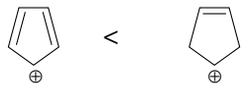
(Ar.SE) ∝ ERG ∝ $\frac{1}{EWG}$

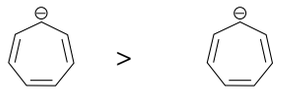
ERG($-O^{\ominus}$ > –NH–C(=O)–CH_3 > –O–C(=O)–CH_3 > –CH(CH_3)–CH_3)

(i) > (iii) > (ii) > (iv)

43. [4]

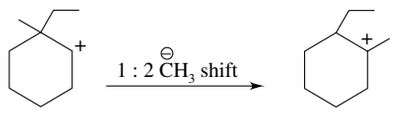
(I)  Anti aromatic < Aromatic

(II)  Anti aromatic < non Aromatic

(III)  Aromatic > Anti aromatic

44. [2]

- Such rearrangement in which carbocation gets stabilised is the most favorable

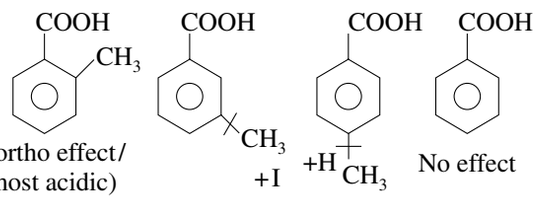


less stable more stable stable

45. [1]

In option 2, 3, 4 Equal contributed canonical form will exist hence same bond length between participating atom.

46. [4]



Acid strength $\propto$ – H, – I $\propto \frac{1}{+H, +I}$

(I) > (IV) > (II) > (III)

47. [2]

$CH_3–CH_2\overset{Lg}{|}Br + Na\overset{Nu}{|}I \rightarrow CH_3–CH_2–I + NaBr$

48. [2]

Acidity : HBr > MeOH > Me_2NH > Me_3CH

Basicity and nucleophilicity:

$Br^{\ominus} < MeO^{\ominus} < Me_2N^{\ominus} < Me_3C^{\ominus}$

i.e., IV > III > II > I

49. [4]

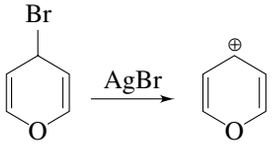
4n + 2 = 6

n = 1

aromatic

50. [2]

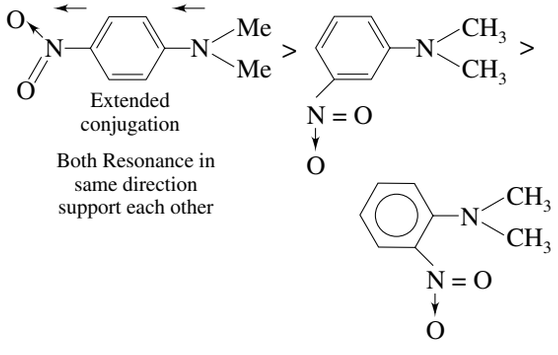
Reactivity of R–Br $\propto$ stability of $—C^{\oplus}$



Aromatic stable

EXERCISE # 2

1. [2]



Extended conjugation

Both Resonance in same direction support each other

Due to SIR effect Resonance is less

2. [2]

Bond strength $\propto$ E.N. $\propto$ % of S character

c > b > a.

3. [3]

lp delocalised — lp localised

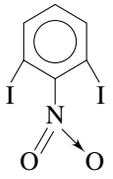
I: Less delocalised — II: More delocalised — III: E.N.↑ B.S.↓ — IV: E.N.↓ B.S.↑

Thus order is IV > III > > I > II

4. [4]

Basic strength $\propto$ – M, –I $\propto \frac{1}{+M, +I}$

5. [3]



$\rightarrow$ Due to presence of 2-bulky group at the ortho position of nitro group.

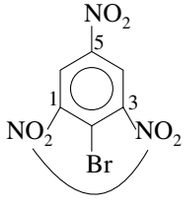
$\rightarrow$ $–NO_2$ comes out of plane, due to SIR effect (ortho effect).

6. [3]

Resonance $\propto$ Resonance energy

In (III), continuous conjugation Resonance energy

7. [3]



Out of plane (SIR Effect)

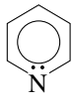
C_1—N & C_3—N out of plane due to SIR Effect

C_5—N present in resonance

Resonance $\propto \frac{1}{\text{BL of single bond}}$

Thus (C_1—N = C_3—N > C_5—N)

8. [1]

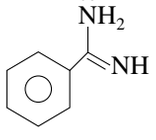


(I)

ℓp localised more basic

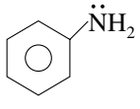
(II)

ℓp delocalised also participate in aromatisation more stable, least basic



(III)

Phenyl imidine most basic



(IV)

ℓp delocalised less basic

9. [4]

Acidity:

$H_3O^{\oplus} > \overset{\ominus}{E}tOH_2 >$MeCOOH > H_2O > EtOH

Basicity and nucleophilicity:

H_2O < MeOH < $MeCOO^{\ominus}$ < $\overset{\ominus}{O}H$ < $EtO^{\ominus}$

i.e. V > IV > III > II > I

10. [2]

$\alpha \rightarrow$ (double bond) in resonance

$\beta \rightarrow$ (single bond) in resonance

$\gamma \rightarrow$ pure single bond

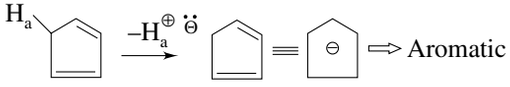
$\alpha < \beta < \gamma$

11. [4]

• positive charge at bridge head C cause unstability due to Bredt's rule

• 3° carbocation (carbonium) most stable

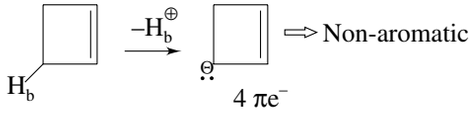
12. [1]

(I) 

Aromatic

$6\ \pi e^-$

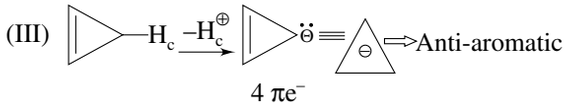
In delocalisation

(II) 

Non-aromatic

$4\ \pi e^-$

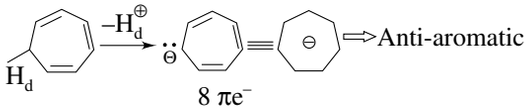
In delocalisation

(III) 

Anti-aromatic

$4\ \pi e^-$

In delocalisation

(IV) 

Anti-aromatic

$8\ \pi e^-$

In delocalisation

The order of Aromatic stability is:

Aromatic > Non-aromatic > Anti-aromatic

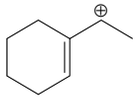
I > II > IV > III

IV has more resonating structures than III, and is therefore, more stable.

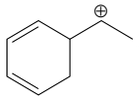
$\therefore$ H_a in I is more acidic since it will give $H^{\oplus}$ faster to become a stable aromatic anion. Thus least Pk_a value.

13. [1]

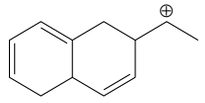
Due to resonance and hyperconjugation.

(1) 

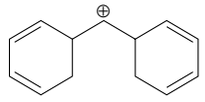
Resonance + 3α-H Most stable

(2) 

5α-H

(3) 

5α-H

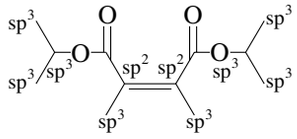
(4) 

2α-H

14. [2]

Due to higher extent of conjugation

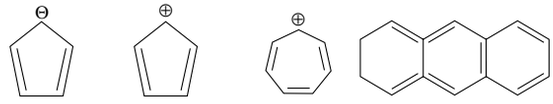
15. [1]



16. [1]

Nucleophilicity ∝ Attacking rate of anion

17. [2]



$4n + 2 = 5\pi e$	$4n + 2 = 4\pi e$	$4n + 2 = 6\pi e$	$4n + 2 = 14\pi e$
n = 1	n = 1	n = 1	n = 3
Aromatic	Anti Aromatic	Aromatic	Aromatic

18. [3]

In aqueous solution, amine basically follows the order

NH_3 < tertiary < primary < secondary

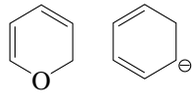
This is due to the combined effected of induction and stabilization of conjugate acid through H-bonding. Also, a cyclic amine is more basic (IV) than acyclic amine (II). If their degrees are same. Hence, the overall order is

K_b : III(3°) < I(1°) < II(2°, acyclic) < IV(2°, cyclic).

19. [2]

- Acidic strength ∝ ortho effect
- Ortho effect ∝ steric hindrance at ortho position

20. [1]

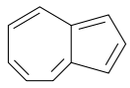


(I) (II)

Partial conjugation
non-planer
non-aromatic

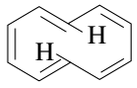
(III)

$4n + 2 = 2\pi e$
n = 1
Aromatic



(IV)

$4n + 2 = 10\pi e$
$n = 2$
Aromatic



(V)

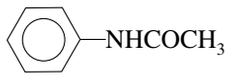
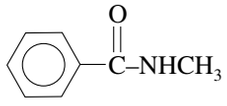
Non planer due to repulsion between adjacent H

21. [4]

Bond dissociation energy (B.D.E) $\propto \frac{1}{\text{Stability of C – free radical}}$

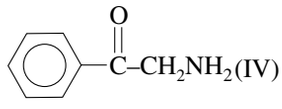
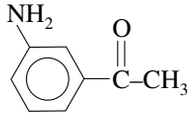
22. [4]

Rule 1 Base strength $\propto \frac{1}{\text{Delocalisation of } \ell p}$

(I)  (II) 

ℓp delocalised

In amide ℓp less delocalised

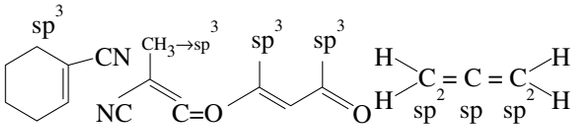
(III)  (IV) 

ℓp localised

ℓp delocalised

Rule 2 Base strength $\propto$ + M, +I $\propto \frac{1}{-M, I}$

23. [4]



24. [1]

$\rightarrow$ Ring expansion takes place

25. [2]

When nucleophilic centre is same then

Nucleophility $\propto$ basic strength $\propto$ +M, +I $\propto \frac{1}{-M, -I}$

26. [2]

27. [1]

Stability of  $\propto$ conjugation $\propto$ H-effect (α–H)

Note: positive charge at bridge head C de-stabilised carbocation due to Bredt's rule.

28. [4]

(I) Stable by resonance

(II) Stable by pπ – pπ bonding

(III) Stable by resonance

(IV) negative charge do not participate in resonance (less stable)

29. [1]

By the removal of $-Cl_{(C)}$, due formation of aromatic stable carbocation

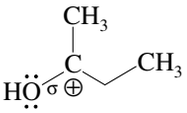
30. [1]

Base strength $\propto$ +M, +I $\propto \frac{1}{-M, -I}$

31. [4]

Theory based

32. [3]



- (positive)-ℓp conjugation
- most stable

33. [1]

(I) Acidic strength $\propto$ ortho effect

(II) Acidic strength $\propto$ –M, –I $\propto \frac{1}{+M, +I}$

34. [3]

Base strength $\propto$ +I $\propto \frac{1}{-I}$

Nucleophilic strength $\propto \frac{1}{\text{steric hindrance}}$

35. [2]

Bond length $\propto \frac{1}{\%S} \propto \frac{1}{EN}$

36. [1]

Leaving group ability $\propto$ acid strength of conjugate acid $\propto \frac{1}{\text{Base strength of (anion)}}$

37. [3]

Aromaticity $\propto$ resonance energy

38. [1]

39. [1]

Power of leaving group $\propto$ acid strength of conjugate acid $\propto \frac{1}{pK_a}$

$CH_3–COO^- \longrightarrow CH_3–COOH$ $\quad pK_a = 4.5$

$C_6H_5– \longrightarrow C_6H_5–OH$ $\quad pK_a = 10$

$C_6H_5– \longrightarrow C_6H_5–SO_3H$ $\quad pK_a = 2.6$

40. [1]

- Negative charged ions are better nucleophile
- NS $\propto$ size (dominating factor)
- NS $\propto$ base strength

EXERCISE # 3

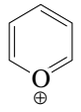
1. [1, 2, 3]

Due to H-bond and p-fluoro phenol exceptionally less acidic than p-chloro phenol

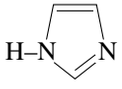
2. [2, 3, 4]

(1) 

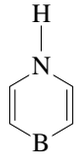
Non aromatic
non-planar

(2) 

4n + 2 = 6
n = 1
aromatic

(3) 

4n + 2 = 6
n = 1
aromatic

(4) 

4n + 2 = 6
n = 1
aromatic

3. [3]

Here, the negative charge of conjugate base is stabilized by electron withdrawing resonance effect of $-NO_2$ group.

4. [1, 4]

Both —NO_2 and —CHO exert electron withdrawing resonance effect but from ortho and para-positions so decreases basic strength, hence meta-isomer is more basic.

Both —Cl and —OCH_3 give electron donating resonance effect from ortho and para-positions, increases basic strength hence, their meta-isomer is less basic.

5. [1, 3]

(i) Stability of Carboanion ∝ Conjugation

(ii) Stability of Carboanion ∝ $-I \propto \frac{1}{+I}$

$$H_2N\text{–}\overset{\ominus}{C}H_2 < CH_3\text{–}\underset{\|}{\overset{}{C}}\text{–}\overset{\ominus}{C}H_2$$

conjugation

$$\overset{\ominus}{C}F_3 < \overset{\ominus}{C}Cl_3$$

$p\pi$–$d\pi$ conjugation

(1) $O_2N\text{–}\overset{\ominus}{C}H_2$ and $F\text{–}\overset{\ominus}{C}H_2$

$-I(-NO_2) > -I(-F)$

(2) $\overset{\ominus}{C}F_3$ and $\overset{\ominus}{C}Cl_3$

$p\pi$–$d\pi$ conjugation

(3) $F_3C\text{–}CH_2$ and $Cl_3C\text{–}CH_2$

$-I(CH_3) > -I(CCl_3)$

(4) $H_2N\text{–}\overset{\ominus}{C}H_2$ and $CH_3\text{–}\underset{\|}{\overset{O}{C}}\text{–}\overset{\ominus}{C}H_2$

conjugation

6. [1, 2, 3]

Theory based

7. [1, 2]

In same period

Nucleophilicity ∝ Base strength

In same group

Nucleophilicity ∝ Size (If Protic solvent, CH_3–OH)

So that $F^- > Cl^- > Br^- > I^-$ (incorrect)

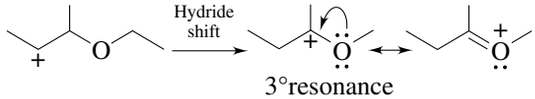
8. [2, 3, 4]

Reactive intermediates are formed for very small time, cannot be isolated practically. The most stable reactive intermediate is always formed in largest amount, hence from the major product. It is the reactive intermediates that leads to several products in a reaction

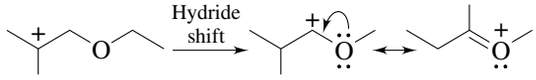
9. [3, 4]

In both option (3) and (4), less substituted, less stable alkene is being transformed into more stable alkene.

10. [1, 2]

(1) 

3°resonance
Stabilised
(more stable)

(2) 

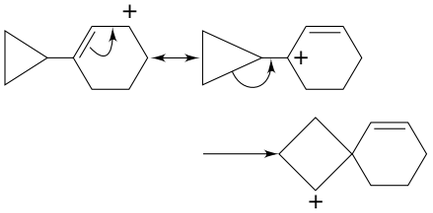
Stabilised by
Resonance
favourable shift

(3) 

I II

3° resonance
(stabilised more stable)

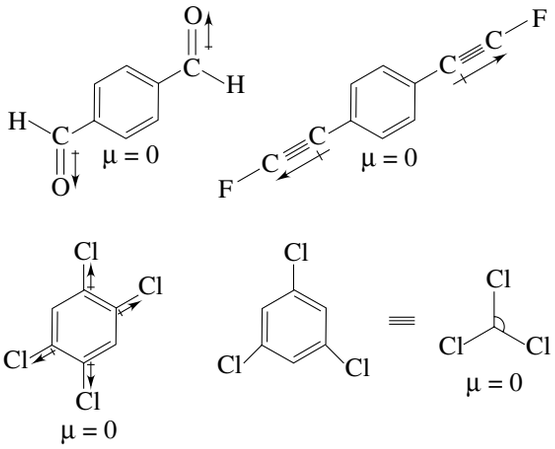
However, the above step is resonance delocalisation (I and II are canonical forms) not the required rearrangement.

(4) 

Less stable than the
Previous carbonation

Although the above ring expansion increases stability of cyclopropyl ring but decreases overall stability because of loss of resonance.

11. [1, 2, 3, 4]



12. [2, 3, 4]

Among amines, the order of basic strength in gas phase is 1° < 2° < 3°. Therefore, the order of K_b will also be the same Since, $pK_b = -\log K_b$, the order of pK_b would be reverse of the order of K_b, i.e. pK_b 3° < 2° < 1°.

13. [2, 4]

(2) $CH_3—\overset{O}{\overset{\|}{C}}—\overset{\ominus}{O} \longleftrightarrow CH_3—\overset{\ominus O}{\overset{|}{C}} = O^-$

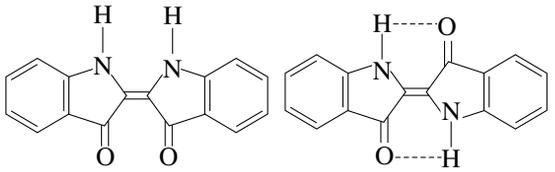
Equivalent resonance structures

(4) $\overset{\ominus}{O}—N=O \longleftrightarrow O=N—O^-$

Equivalent resonance

In option 1, 3, unequal contributor is formate other de-localisation

14. [1, 3, 4]



cis *trnas*

(Intramolecular H-bonding)

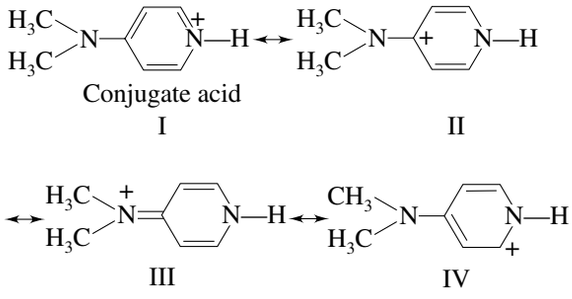
trans-isomer shown above is slightly more stable due to presence of intramolecular H-boding forming six membered ring. The molecule is planar, no enantiomerism is possible. It's *cis*-isomer has greater relative solubility in water due to free $\rangle C=O$ and $\rangle N—H$ groups capable of intermolecular H-bonding with water. Also, the molecular is planar and highly conjugated, has high resonance stabilisation energy.

15. [1, 2, 4]

All acidic groups, $—SO_3H$, —COOH and —OH would be neutralised by NaOH Sulphonic acid is most acidic, would be neutralised first, With $NaHCO_3$, $—SO_3H$ and —COOH groups would be neutralised requiring 3.0 moles of base. Electron withdrawing effect of $—SO_3H$ and —COOH increases acidity of one another.

16. [2, 3]

Nitrogen labelled-II is the most basic.



Conjugate acid

I II

III IV

Both I and III have complete valence shell of all the atoms. Also, $—CH_3O$, group at position-III of original base would increase the basic strength as it would stabilise the resonance structure IV by resonance effect.

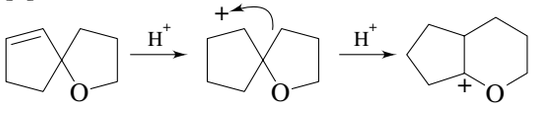
17. [1, 2, 3]

Dissociation of C—H (II) is the easiest as it produces a resonance stabilised free radical.

$CH_3—\overset{\bullet}{C}H—CH=CH_2 \longleftrightarrow CH_3—CH=CH—\overset{\bullet}{C}H_2$

Due to hyperconjugation, bond order of C—H (II) decreases on increasing bond length. C—H (I) involves the smaller on sp^2 hybridised orbital for sigma boding, shorter bond than on C—H (II) and C—H (III) which employs bigger sp^3 hybridised orbitals for bond formation.

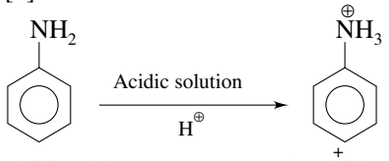
18. [4]



Most stability

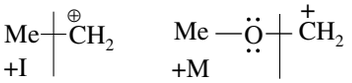
By resonance

19. [4]



$–NH_2$(+M) group changes in $–\overset{+}{N}H_3$ (–M) group which is least reactive towards $E^{\oplus}$

20. [3]

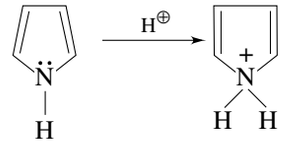


Due to resonance

21. [4]

: CCl_2 have vacant d-orbital so it is good electrophile

22. [3]



ℓp delocalised Anti aromatic

less basic

In pyrelle (I) ℓp-de localised so less basic them (II)

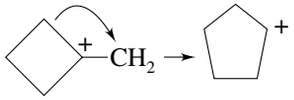
23. [1]

As distance of –I group increase from source, –I power decrease,

So that acid strength decrease.

24. [4]

It is generally true that a tertiary carbocation is more stable than primary one. However, this does not apply in the present case because it is less stable than I as II has greater angle strain. The favourable rearrangement here is ring expansion.



Primary Secondary

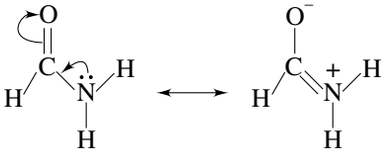
Less angle strain

25. [4]

26. [1]

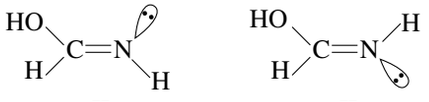
27. [2]

Sol. (25 to 27)



IV

I is obtained on protonation of formamide, hence conjugate acid. If has restricted rotation, show geometrical isomerism.



II cis II trans

28. [4]

29. [2]

30. [3]

Sol. (28 to 30)

In the given amino acid cation, –COOH α to $-\overset{+}{N}H_3$ is most acidic followed by the second –COOH group and $-\overset{+}{N}H_3$ least acidic. It is due to strong–ℓ-effect of $-\overset{+}{N}H_3$ on a-COOH

31. [4]

$$\underset{7}{\overset{sp^2}{CH_2}} = \underset{6}{\overset{sp}{C}} = \underset{5}{\overset{sp^2}{CH}} - \underset{4}{\overset{sp^3}{CH_2}} - \underset{3}{\overset{sp}{C}} \equiv \underset{2}{\overset{sp}{C}} - \underset{1}{\overset{sp^3}{CH_2}} - NH_2$$

$C_1 \longrightarrow sp^3$

$C_2 \longrightarrow sp$

$C_5 \longrightarrow sp^2$

$C_6 \longrightarrow sp$

32. [4]

(A) $\rightarrow B \longrightarrow A^+ + B^{\ominus}$

$A \rightarrow$ Heterolysis (q)

(B) $CH_3\text{–}\overset{+}{C}H\text{–}CH_3 \rightarrow$ carbocation (r)

(C) $A - A \longrightarrow A^{\bullet} + A^{\bullet}$

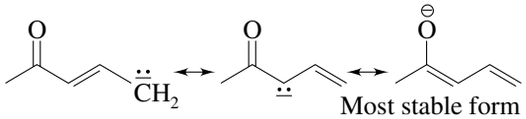
$\rightarrow$ Free radical (p)

(D) $CH_2N_2 \longrightarrow \ddot{C}H_2 + N_2$

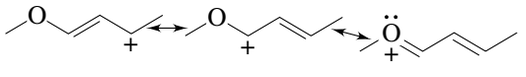
$D \longrightarrow$ carbene (t)

(E) $CH_3\text{–}\ddot{O}H \longrightarrow$ Nucleophile (s)

33. [4]

(i) 

Most stable form

(ii) 

Most stable form

This carbocation is also stabilised by hyperconjugation effect. Also the carbocation have deficiency of a pair of electron, act as a strong Lewis acid in chemical reaction

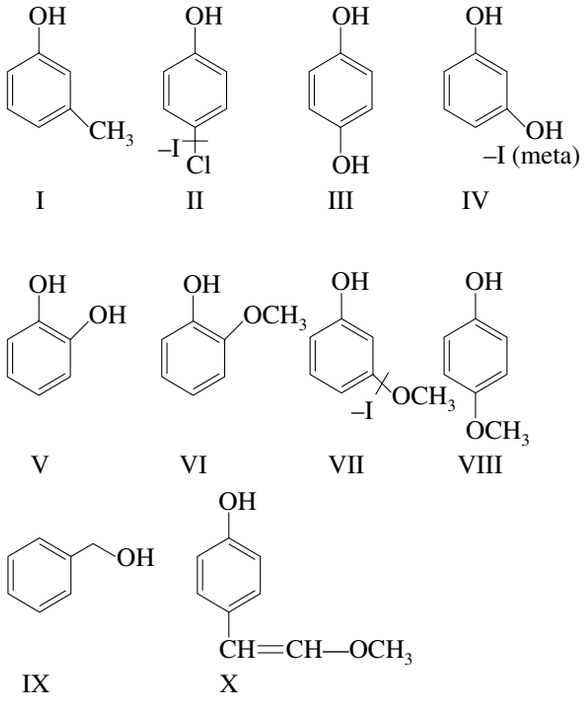
(iii) It is a free radical, therefore paramagnetic due to unpaired electron. It is also stabilised by hyperconjugation effect.

(iv) It is a carbene. It's triplet form is paramagnetic. It has deficiency of a pair of electron, acts as a strong Lewis acid during the reaction.

34. [3]

$$\text{Acidic strength} \propto -I, -M \propto \frac{1}{+I, +M}$$

Acids stronger than phenol are : II, IV, V, VII

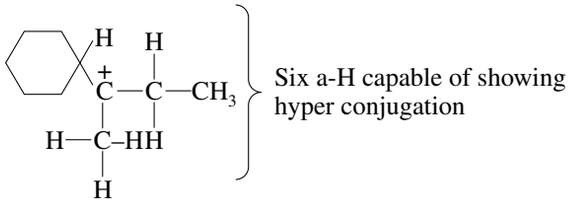


35. [5]

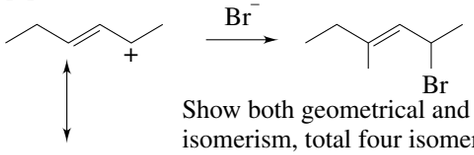
(i), (ii), (v), (i) and (vii) have conjugated C=O and resonance delocalisation decreases bond order of C=O less than 2, hence weaker bond than C—O bond in acetaldehyde

36. [6]

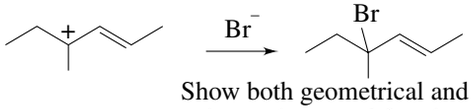
The given carbocation has six-H that can take part in hyperconjugation as:



37. [8]



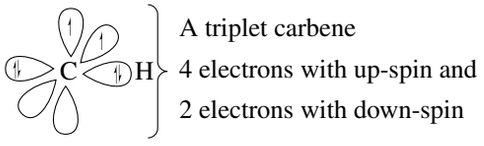
Show both geometrical and optical isomerism, total four isomers



Show both geometrical and optical isomerism, total four isomers.

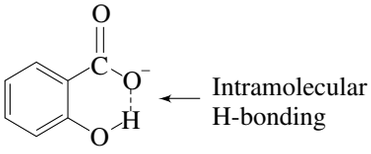
38. [4]

In carbene, there are a total of six valence electrons (2 bond pairs + 1 lone pair). In case of triplet carbine, there are four electrons having same spin direction.



39. [6]

Acids, I, III, IV, VII, VIII and IX are all stronger than benzoic acid. I is stronger because of stabilisation of conjugate base by intramolecular H-bonding.



III is stronger because from *meta* position, —OH exert only – I-effect, its electron donating resonance effect has no role on acidic strength.

IV is stronger acid due to loss of planarity of —COOH with phenyl ring, hence absence of electron donating resonance effect as phenyl rings on —COOH increases acidic strength.

VII is stronger because a sulphonic acid is stronger than a carboxylic acid.

VIII is stronger because electron withdrawing inductive effect of one —COOH over other increases acidic strength.

IX is stronger due to only – I-effect of methoxy group operate from *meta* position but not its electron donating resonance effect.

40. [3]

Antiaromatic substance are unstable at room temperature

EXERCISE #4

1. [1]

When R is attached with benzyl/allyl system + inductive effect occurred + I Power ∝ branching

2. [1]

As per NCERT result

In aq. solution (when R = $-CH_3$)

2° amine > 1° amine > NH_3 (basic strength)

3. [1]

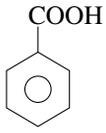
Rate of SN reaction ∝ Leaving tendency ∝ Acidic strength of conjugate acid

Since HCl is strongest acid so that Cl^- is best leaving group

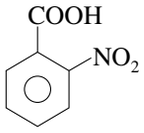
4. [4]

Acid strength $\propto$ M, –I (EWG)

$\propto \frac{1}{+M, +I}$ (ERG)



(a)



(b)

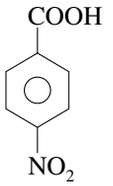
Effect → no effect

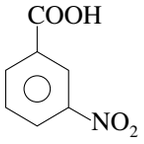
–M, –I

–I↑distance↓

Not effect → no effect

$(EWG)_1$





–M, –I

$(EWG)_2$

(c)

–I

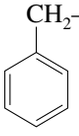
$(EWG)_3$

(d)

b > c > d > a

5. [4]

Base strength $\propto \frac{1}{\text{De. localisation of lp.}}$

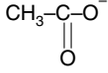
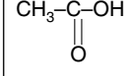
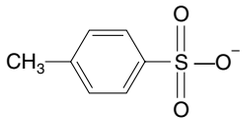
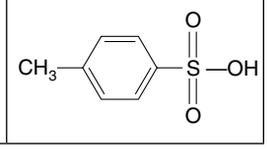


ℓp localised

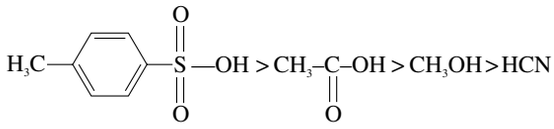
benzyl amine

6. [4]

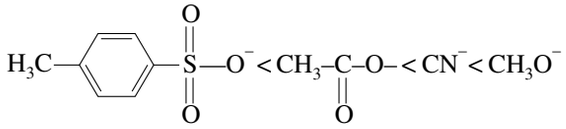
Weaker the acid, more stable is their conjugate base and greater is their nucleophilicity. Thus, nucleophilicity order of the conjugate bases is opposite to their acidic strength.

Conjugate bases	Acids
	
CH_3O^-	CH_3OH
CN^-	HCN
	

Since, alcohols and cyanides are weaker acid than sulphonic and carboxylic acids. Thus, the order of acidic strength of the given species are

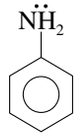


Hence, the decreasing order of nucleophilicity of the given nucleophiles is as follows



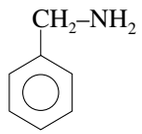
7. [2]

Base strength $\propto \frac{1}{\text{De. localisation of lp.}}$



Aniline

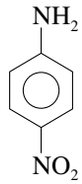
ℓp delocalised



Benzylamine

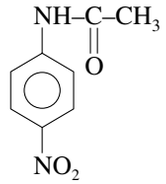
ℓp localised

most basic



p-nitroaniline

ℓp delocalised

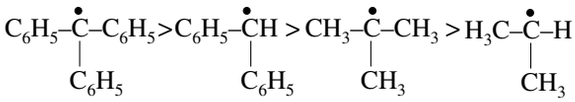


Acetanilide

ℓp delocalised

8. [4]

Free radicals stability

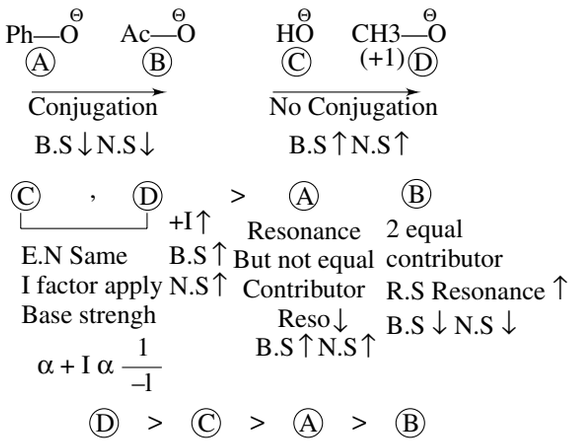


(Highly stable by delocalisation of 3 phenyl groups)

(9-hyperconjugative hydrogens and +/– effect of 3 alkyl groups)

9. [4]

When nucleophilic centre is same but category of anion is different, Then N.S α B.S

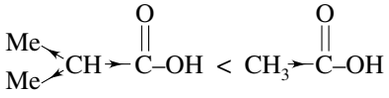


10. [4]

$pk_a = -\log K_a$, Hence, higher the value of K_a, smaller pK_a. K_a is the measure of acidic strength. It is highest for the strongest acid (d) in given case, therefore has lowest pK_a value.

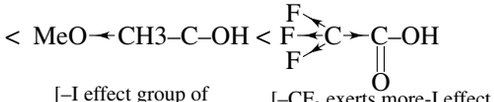
11. [3]

Acidic strength of the compound depends on the ease of release of proton –I effect exerting groups (e^- withdrawing increase the acidic strength while +I effect exerting group decreases the strength of an acid.



[2 + I effect exerting groups, increases e^- density of on O-atom, thus the release of ease of proton becomes difficult (least acidic)]

[+I effect group of $-CH_3$ group]



[–I effect group of $-OCH_3$ group]

[$-CF_3$ exerts more-I effect than MeO (most acidic)]

12. [3]

2° amine is more basic in aqueous solution CH_3–NH–CH_3

Dimethyl amine (2° amine)

13. [4]

$-NO_2$ group (e with drawing) de-crease e-density of benzene ring.

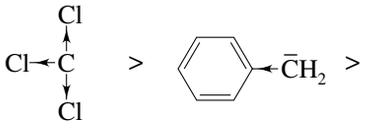
So it deactivates the benzene ring towards electrophilic substitution.

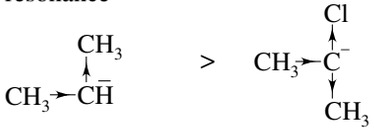
14. [2]

–/-effect (e^- withdrawing) exerting groups stabilises carbanion by the dispersal of their negative charge while +/-effect exerting (e^- releasing) groups destabilizes the carbanion by increasing electron density on them.

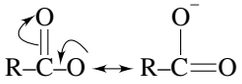
On the other hand, resonance stabilized carbanion are stable due to the involvement of their lone pair of electron with the delocalisation of π-electrons of attached phenyl group.

Thus





15. [4]



- In carboxylate ion, the negative charge is present on oxygen, is in conjugation with π bond thus it is resonance stabilised.
- $HC\equiv C^-$: Carbon is sp hybridised so its electronegativity is increased & higher relative to nitrogen.
- If negative charge atom belongs to same period
- $\overline{N}H_2$: Nitrogen is more electronegative than sp^3 hybridised C-atom. From the above discussion, it is clear that the order of the stability of conjugated bases is as

  $RCOO^- > HC \equiv \overline{C} > \overline{N}H_2 > \overline{R}$

  And higher is the stability of conjugated bases, lower will be basic character. Hence, the order of basic character is as

  $RCOO^- < HC \equiv \overline{C} - < \overline{N}H_2 < \overline{R}$

16. [1]

Nucleophilic strength $\propto$ size

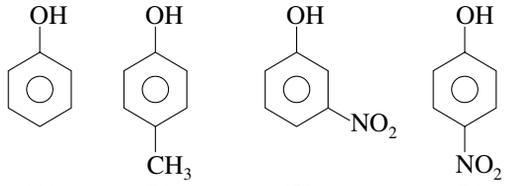
Basic strength $\propto \frac{1}{\text{size}}$

Thus $R–S^{\ominus}$ is less basic but more nuelophilic strength than $R–O^{\ominus}$

17. [1]

Acidic strength $\propto$ M, –I (EWG)

$\propto \frac{1}{+M,\ +I(ERG)}$



(A) (B) (C) (D)

No effect +H, +I (at meta position) –I –M, –I

Thus D > C > A > B

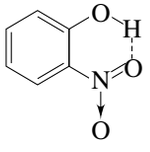
18. [4]

→ non-planar
Non aromatic

For aromatic substance molecule most be cyclic| planar conjugated and obey Huckle rule (4n + 2 = πe)

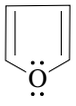
Rest other satisfied given condition so they are aromatic

19. [1]



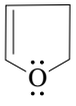
→ In tramolecular H-bond
→ Less bpt.
→ Less soluble
→ More volatile

20. [2]

(i)  planner, conjugated, 4n + 2 = 6, n = 1(aromatic)

(ii)  non-planar (non-aromatic)

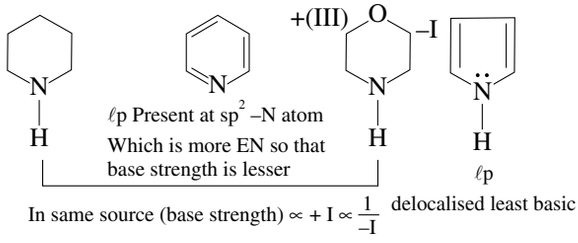
(iii)  non-planar (non-aromatic)

(iv)  non-planar (non-aromatic)

(v)  non-planar, conjugated, 4n = 4, n = 1 (Anti aromatic)

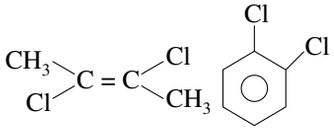
(vi)  planar, conjugated, 4n = 4, n = 1 (Anti aromatic)

21. [3]

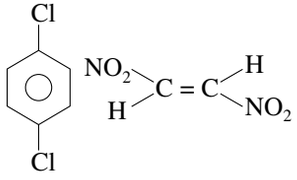


Thus I > III > II > IV

22. [2]

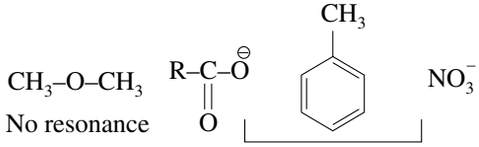


μ = 0 μ ≠ 0



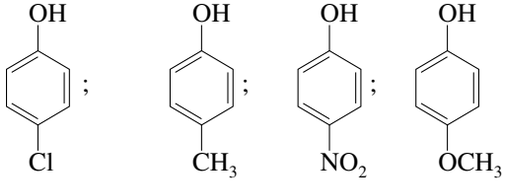
μ = 0 μ = 0

23. [1]



24. [1]

Acidic strength $\propto$ –M, –I $\propto \frac{1}{+M,\ +I}$



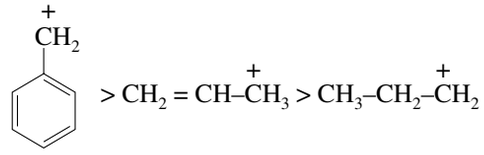
Over all +M < –I effect $(EWG)_2$ | +H, +I $(EWG)_2$ | –M, –I $(EWG)_1$ | +M > –I $(EWG)_1$

(I) (II) (III) (IV)

Thus III > I > II > IV

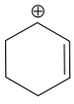
25. [2]

The order of stability of carbocation will be



(III) Benzyl carbocation (more resonance stabilised) | (I) Alyl carbocation (resonance stabilised) | (II) Propyl carbocation (stabilised by + I effect)

26. [3]



+ve charge present in conjugation with π-bond so it is most stablised.

27. [3]

Theory bosed

28. [2]

N.S. ∝ size

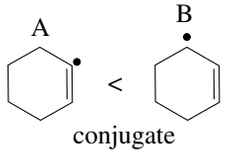
If solvent is not given then nucleophilic strength compared in polar solvent

29. [3]

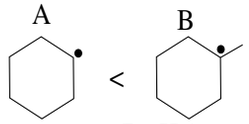
Stability of anion ∝ –I, –M ∝ $\frac{1}{+I,\ +M}$

$-CH_3$	$-OCH_3$	$-\overset{\overset{O}{\|}}{C}-CH_3$	$-CH_2-OH$
+H	+M	–M	+H

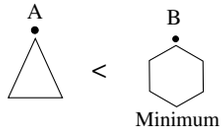
30. [4]

(1) 

conjugate

(2) 

4α-H 7α-H (more hyper conjugation)

(3) 

Minimum ring strain

(4) $\underset{\text{more resonance stabilised}}{\overset{A}{Ph_3C^{\bullet}}} > \underset{\text{only hyper conjugation stabilised}}{\overset{B}{(CH_3)_3C^{\bullet}}}$

31. [4]

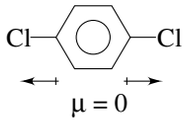
- $C_6H_5-\ddot{N}H_2$, Here ℓp de-localised so it is least basic

  As per NCERT
- In aq. solution, 2° > 1° > 3° (if R–CH_3)

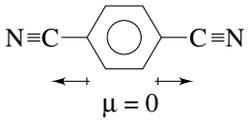
  Basic strength ↑K_b↑pK_b↓

32. [4]

In (iii) and (iv), the dipole vectors O–H and S–H are in tetrahedral plane, do not cancel, In (i) and (ii) dipole vectors cancel each other completely as:



μ = 0

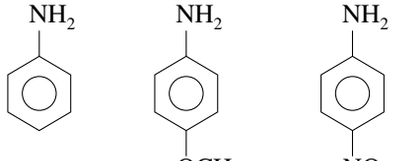


μ = 0

33. [2]

(i) in CH_3-NH_2, ℓp localised so that base strength highest

(ii) Base strength ∝ + M, + I ∝ $\frac{1}{-M,\ -I}$



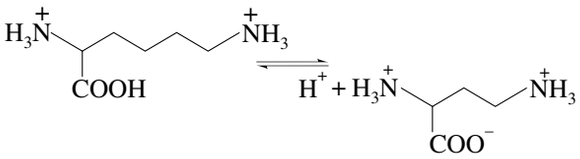
no effect | OCH_3 (+M > –I) | NO_2 (–M, –I)

34. [3]

2 moles of $NaNH_2$ would neutralise the first two more acidic groups. Here, —COOH is most acidic followed by hydroxyl group of the nitrophenol ring because —NO_2 has strong *–I* as well as –R-effect.

35. [4]

A carboxylic acid is more acidic than ammonium ion, hence X is most acidic. For 2nd most acidic group, we need Investigets the conjugate base of given ion formed after first deprotonation as:



Now in conjugate base I, COO^- is electron donating, decreases acidic strength of $-\overset{+}{N}H_3$ at α-position, hence Y is second most acidic followed by Z.

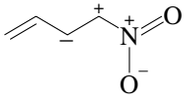
36. [3]

$CH_2=CH-\overset{\oplus}{C}H=\overset{\ominus}{C}H-O-CH_3$

Lone pair of oxygen is not the part of this mode of delocalisation.

37. [1]

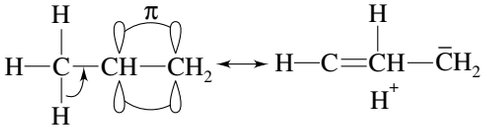
The following structure has like charge on adjacent atoms, therefore, least stable



38. [4]

Statement I is incorrect but Statement II is correct. Intramoelcular H-bonding in ortho-hydroxy benzoic acid lowers the boiling point.

39. [2]

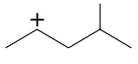


The σ-electrons of C—H bond is delocalised with p-orbitals of π-bond.

40. [4]

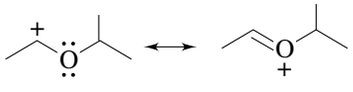
3°, has resonance stability

(I)



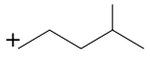
has no resonance stability but 2°

(II)



2°, has resonance stability

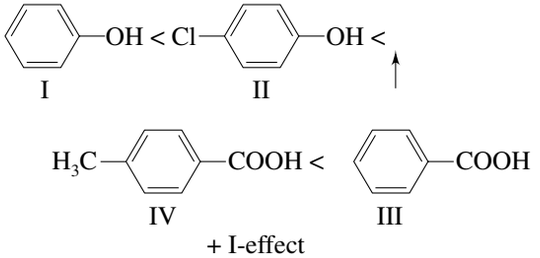
(III)



1°, has no resonance stability

(IV)

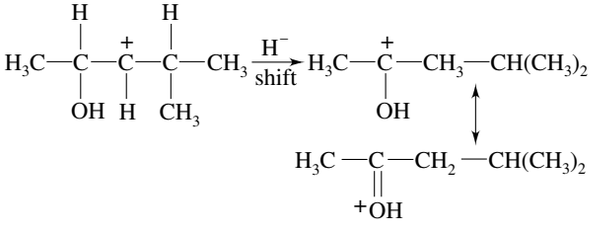
41. [1]



+ I-effect decreases acidic strength

42. [4]

H at C-2 will migrate giving resonance stabilised carbocation



43. [2]

I is most stable because it has more covalent bonds and negative charge on electronegative nitrogen, III is more stable than II and IV due to greater number of covalent bonds. Between II and IV, II is more stable since, it has negative charge on electronegative atom and positive charge on electropositive atom. Hence, overall stability order is

I > III > II > IV.

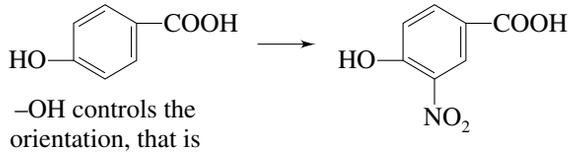
44. [2]

Lysine contains two basic groups, e.g., NH_2

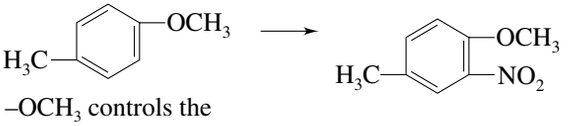
Biomolecules

Basic straight

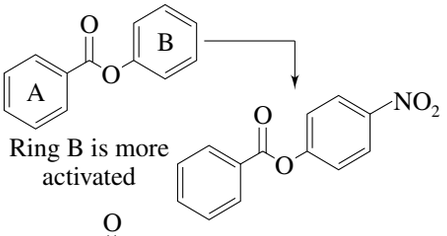
45. [3]



–OH controls the orientation, that is ortho-para directing



$-OCH_3$ controls the orientation (o/p-directing)

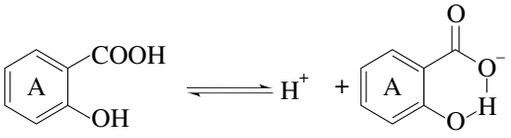


Ring B is more activated

and $-O-\overset{O}{\overset{\|}{C}}-Ph$ is (o/p-directing)

46. [3]

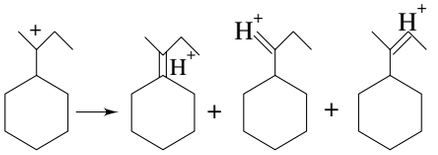
A monosubstituted benzoic acid is stronger than monosubstituted phenol as former being a carboxylic acid. Among the given substituted benzoic acid, ortho-hydroxy acid is strongest acid although —OH causes electron donation by resonance effect which tends to decrease acid strength. It is due to a very high strength of conjugate base by intramolecular H-bond which outweight the electron donating resonance effect of —OH.



The overall order of acid-strengthof given four acids is ortho-hydroxybenzoic acid (pK_a = 2.98) > Toluic acid pK_a = 4.37) > p-hydroxybenzoic acid (pK_a = 4.58) > p-nitrophenol (pK_a = 7.15)

47. [1]

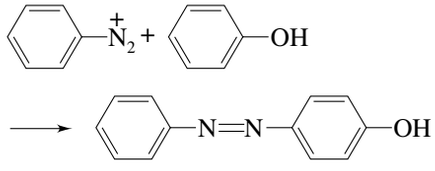
There are total 6 α-H attached to sp^2 carbon and they all can participate in hyperconjugation.



(Three structures) (Two structures)

48. [1]

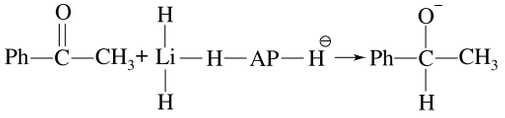
(i)



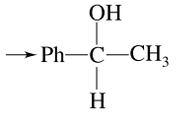
This is an example of electrophilic substitution at para position of phenol, giving a coupling product.

(ii) Pianacol-pinacolone rearrangement, occur

(iii)



Nucleophilic addition



(iv) Nucleophilic addition occur at sp^2 (planar) carbon, generating a chiral centre, hence product will be a racemic mixture.

49. [2, 3]

(1) Aromatic

(2) Anti aromatic

(3) Anti

(4) Aromatic

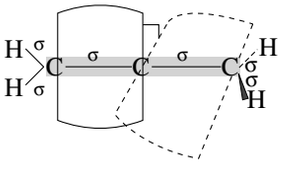
Anti aromatic substance also unstable

50. [2]

Allene is the name given to propdiene, $H_2C=C=CH_2$.

Hybridisation of an atom is determined by determining the number of hybrid orbitals at that atom which is equal to the number of sigma (s) bonds plus number of lone pairs at the concerned atom.

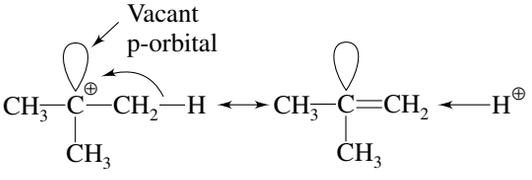
Pi(π) bonds are not formed by hybrid orbitals, therefore, not counted for hybridisation.



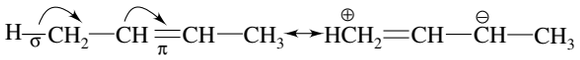
Here, the terminal carbons have only three sigma bonds associated with them, therefore, hybridisation of terminal carbons is sp^3. The central carbon has only two sigma bonds associated, hence hybridisation at central carbon is sp.

51. [1]

Spreading out charge by the overlap of an empty p-orbital with an adjacent σ bond is called hyperconjugation. This overlap (the hyperconjugation) delocalises the positive charge on the carbocation, spreading it over a larger volume, and this stabilises the carbocation.



tertiary butyl carbocation has one vacant p-orbital hence, it is stabilised by σ-p (empty) hyperconjugation.



In 2-butene, stabilisation is due to hyperconjugation between $\sigma - \pi^*$ electron delocalisation.

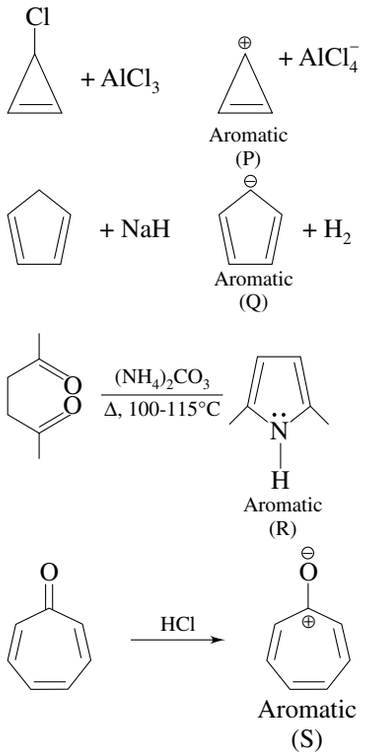
52. [1, 2, 3, 4]

A species is said to have aromatic character if

(a) ring is planar.

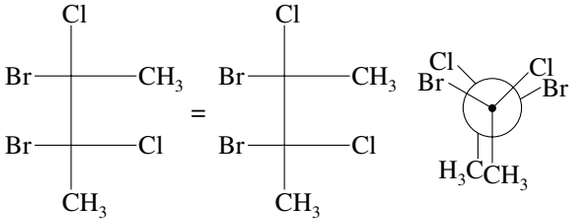
(b) there is complete delocalisation of p electrons.

(c) Huckel rule, i.e. (4n + 2) rule is followed. Where *n* is the number of rings (4n + 2) = π electron delocalised.

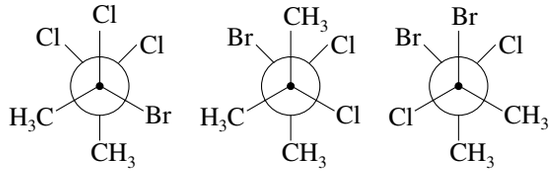


53. [3]

This problem can be solved by using concept of conformational analysis of given organic compound. To the question draw the stable conformational structures of organic compound and determine the net resultant dipole moment.



Stable conformer (with $\mu \neq 0$)



(Me-Me) gauche (Br-Me) gauche (Cl-Me) gauche

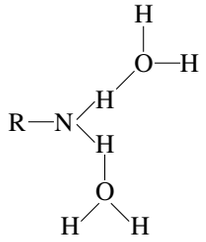
These three have non-zero dipole moment due to non-cancellation of all dipole moment created by C–Cl and C–Br bond.

54. [1, 2, 4]

This problem can be solved by using concept of H-bonding and applications of H-bonding.

(1) Ice floats in water due to the low density of ice as compare to water which is due to open cage like structure (formed by intermolecular H-bonding).

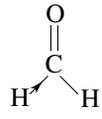
(2) Basic strength of $RNH_2 > R_3N$. It is also explained by hydrogen bonding.



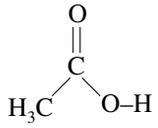
Two H-bonds are possible with water present in aqueous solution. (stabilise by solvation)

No H-bonding is possible with water present in aqueous solution. (stabilisation by salvation is very)

(3)

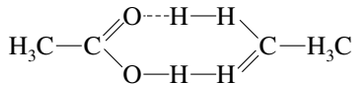


More acidic due to the presence of H. (Due to the absence of electron donating group)



Less acidic than HCOOH due to presence of CH_3 (Electron donating group)

(4) Dimerisation of acetic acid in benzene is due to intermolecular hydrogen bonding.



55. [1]

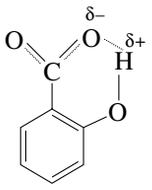
–OH group displays both kinds of effect:

An electron withdrawing acid-strengthening inductive effect from the meta-position and an electron-releasing acid weakening resonance effect from the para-position (at this position, resonance effect overweighs the inductive effect)

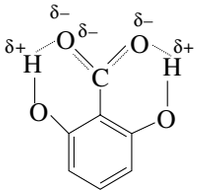
o-hydroxybenzoic acid (II) is far stronger than the corresponding meta and para isomers as the carboxylate ion it stabilised by intramolecular H-bonding

2,6-dihydroxybenzoic acid (I) forms carboxylate ion which is further stabilised by intramoleular H-bonding, Thus, correct order is

I > II > III > IV



II



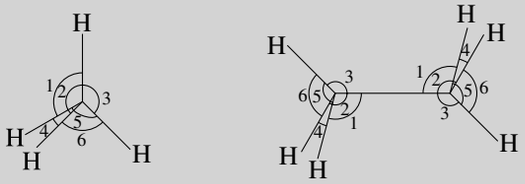
I
(most stable)

CHAPTER 4

Aliphatic Hydrocarbons (Alkanes)

INTRODUCTION

- These are the hydrocarbons in which carbon-carbon contains single bond. (saturated hydrocarbon).
- These are also called as **'Paraffins'** (Parum + Affinis i.e. less reactive).
- General reagents such as dil. and conc. HCl, dil. and conc. H_2SO_4, dil. and conc. HNO_3, acidic and basic $KMnO_4$ and $K_2Cr_2O_7$ usually does not react with alkane.
- General formula is C_nH_{2n+2}.(n = 1, 2, 3, 4 …….)
- Hybridisation state of carbon is sp^3
- Bond angle on sp^3 carbon is 109°28' and geometry is tetrahedral.
- Number of bond angles in methane are six, while in ethane they are twelve.



- Nature of bonding

Type of bond	Bond length	Bond energy
C–C	1.54 Å	84 Kcal/mole
C–H	1.12 Å	98 Kcal/mole

- Alkanes have following isomerisms with given minimum number of carbons.

Isomerism	Minimum Number of carbons
Chain isomerism	4
Position isomerism	6
Conformational isomerism	2
Optical isomerism	7

- In alkane if chiral carbon or unsymmetrical carbon is present, then it shows optical isomerism.

PHYSICAL PROPERTIES

(i) Alkanes are colourless, odourless and tasteless.

(ii) Physical state:
$C_1 \rightarrow C_4$ Gaseous state
$C_5 \rightarrow C_{17}$ Liquid state (except neo pentane)
C_{18} & above $\rightarrow$ solid like wax

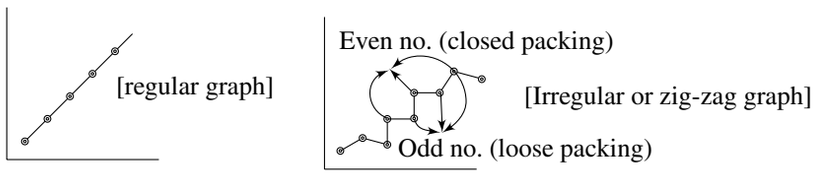
(iii) Alkanes are lighter than water, so they floats over water.

(iv) **Solubility: [Like dissolves like]**
Alkanes are non-polar or weakly polar compounds so these are soluble in non-polar solvents (benzene, ether, chloroform, carbon tetrachloride etc.)

(v) **Boiling point:**
For homologues boiling point $\propto$ Molecular weight
For isomeric alkanes

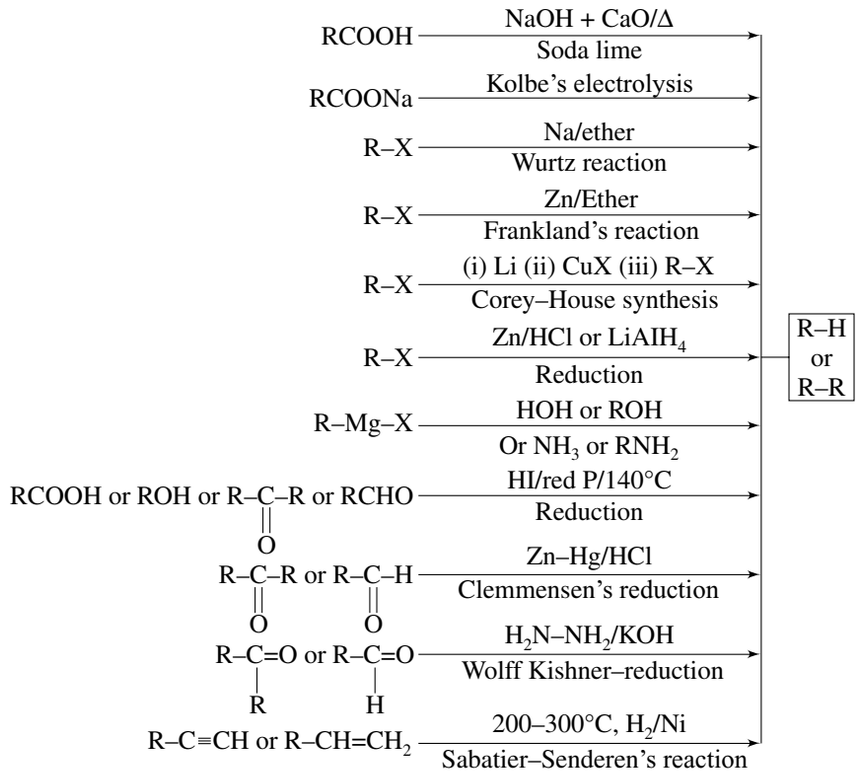
$$\text{boiling point} \propto \frac{1}{\text{Number of branches}}$$

(vi) **Melting point:**
The melting point of alkanes depends upon molecular weight as well as packing in crystal lattice



↑ M.P. (odd to even) > ↑ M.P. (even to odd)

METHODS OF PREPRATION OF ALKANE



CHEMICAL PROPERTIES OF ALKANES

1. Substitution Reaction:

(i) Halogination The characteristics reaction of alkanes are free radical substitution reaction (F.R.S.R)

$$R\text{–}H \xrightarrow[\text{or } X_2/\Delta]{X_2/h\nu} R\text{–}X + HX$$

(F.R.S.R)

Mechanism:

(1) Initiation step

$$X_2 \xrightarrow{h\nu} 2X^{\bullet}$$

(2) Propogation step

$$R - H + X^{\bullet} \longrightarrow R^{\bullet} + HX$$

$$R^{\bullet} + X - X \longrightarrow R - X + X^{\bullet}$$

(3) Termination step

$$R^{\bullet} + R^{\bullet} \longrightarrow R - R$$

$$X^{\bullet} + X^{\bullet} \longrightarrow X_2$$

$$R^{\bullet} + X^{\bullet} \longrightarrow R\text{–}X$$

Important Points

(i) It is 3-step process.

(ii) It is also known as chain reaction.

(iii) propagation step is rate determination step (r.d.s.).

(iv) Rate of radical substitution or rate of $H^{\bullet}$ radical abstraction $\propto$ stability of carbon-free radical.

(v) Bond dissociation energy (B.D.E) $\propto \dfrac{1}{\text{Stability of carbon free radical}}$

(vi) Reactivity of X_2

$F_2 > Cl_2 > Br_2 > I_2$

$10^{15} : 10^6 : 10^3 : 1$ (relative rate order)

(vii) Fluorination is very fast and explosive so carried out in dark.

$(CH_4 + F_2 \xrightarrow{\text{dark}} CH_3F + HF)$

(viii) Iodonation very slow and reversible so carried out in presence of strong oxidant like HNO_3, HgO, HIO_3 etc.

$CH_4 + I_2 \rightleftharpoons CH_3 - I + HI$

$2HI + HgO \longrightarrow HgI_2 + H_2O$

(ix) Relative rate for abstraction of per $H^{\bullet}$ by $Cl^{\bullet}/Br^{\bullet}$ is-

Radical	$1^{\bullet}_H$	$2^{\bullet}_H$	$3^{\bullet}_H$
Cl•	1	3.8	5.0
Br•	1	82	1600

% of product (p) $\propto$ number of similar type hydrogen atoms (n) $\times$ selectivity (s)

$$\frac{P_1}{P_2} = \frac{n_1}{n_2} \times \frac{s_1}{s_2}$$

(x) Regents:

For chlorination – Cl_2/hv, Cl_2/Δ, SO_2Cl_2/hv, $(CH_3)_3C\text{–}OCl$ etc.

For bromination – Br_2/hv, Br_2/Δ, – $(CH_3)_3C\text{–}OBr$

– N.B.S (N-bromo succinamide)

(xi) In excess of alkane mono halo product is major product.

(xii) In excess of halogen most halogenated product is major product.

(xiii) Number of monohalo products (structural isomers) = Type of H in alkane.

Note: For total mono halo isomer (including stereoisomer).

(ii) Nitration of alkanes:

Alkane on reactin with HNO_3 gives nitroalkane in vapor phase at 400° to 500°. In case of alkane containing more than one carbon atom, all possible mono nitroalkanes are formed.

$$R–H + HNO_3 \xrightarrow{\Delta} R–NO_2 + H_2O$$

$$CH_3–CH_2–CH_3 + HNO_3 \xrightarrow[\text{Vapour phase}]{400–500°C} CH_3–NO_2 + CH_3–CH_2–NO_2$$

$$CH_3–CH_2–CH_2–NO_2 + CH_3–\underset{\displaystyle NO_2}{\underset{|}{CH}}–CH_3$$

- In nitration breaking of C–C and C–H bond takes place at high temperature so all possible nitro alkane are formed

(iii) Sulphonation of Alkanes:

- For sulphonation n-Alkane must have minimum 6C
- *Reagent:* Fuming sulphuric acid (oleum)

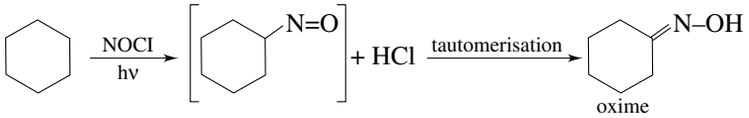
$$R–H + H_2SO_4 \xrightarrow[\text{High temp}]{\text{fuming}} R–SO_3H + H_2O$$

(iv) Chlorosulphonation of Alkanes (Reed reaction): The chlorosulphonation of organic compounds with chlorine and sulphur dioxide in called the Reed reaction.

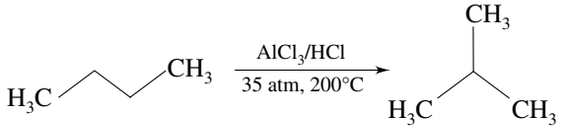
$$RH + SO_2 + Cl \xrightarrow{h\nu} RSO_2Cl$$

Na-salt of Sulphonic acid called as detergent.

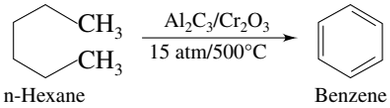
(v) Nitrososation: Alkane give free radical substitution reaction with nitrosyl chloride. The product of the reaction is nitroso compound. This compound, on tautomerisation, gives oxime.



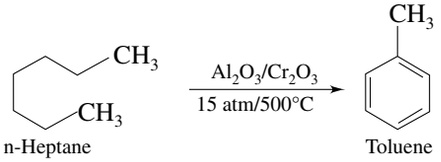
2. Isomerisation: Normal alkane when heated (200°C) in the presence of $AlCl_3$ and HCl gives branched alkanes



3. Aromatisation or Reforming or Hydroformation: n-Hexane and onwards on aromatisation in the presence of Cr_2O_3 or Al_2O_3 or MoO_3 at 500°C and 15 atm gives benzene and its derivatives.



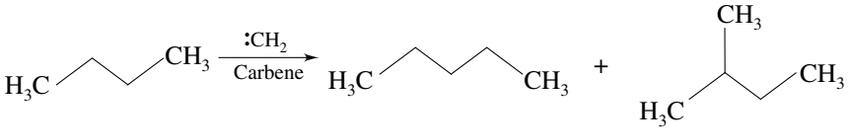
n-Hexane Benzene



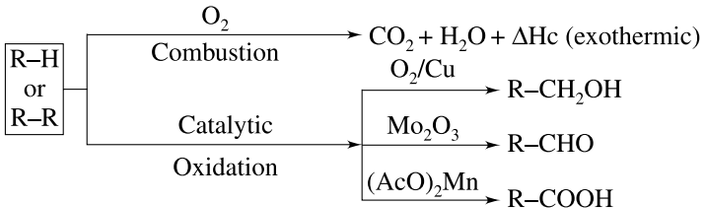
n-Heptane Toluene

4. Carbene Insertion:

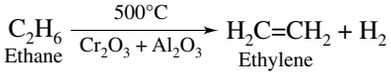
- The lower alkanes are converted into higher homologues.
- *Reagent:* diazomethane or ketene acts as insertion reagent.

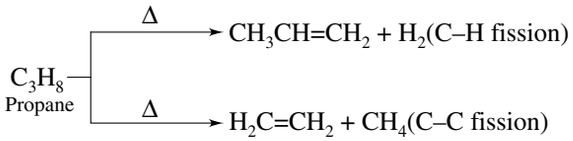


5. Oxidation



6. Pyrolysis or Cracking: The decomposition of a compound by heat is called pyrolysis. When pyrolysis occurs in alkanes, the process is termed cracking.





Special Points

- LPG is called as liquefied petroleum gas or kitchen gas which is a mixture of propane and butane.
- CNG (compressed natural Gas) mainly contains CH_4.
- A mixture of n-butane and isobutene is called as Calore gas.
- Methane reacts with ozone to make formaldehyde.
- When methane is heated (at about 1500°C) in presence of nickel it makes acetylene.
- Sabetier Senderen's reaction:

$$CO + 3H_2 \xrightarrow{Ni/200°C} CH_4 + H_2O$$

$$CO_2 + 3H_2 \xrightarrow{Ni/200°C} CH_4 + 2H_2O$$

- Preparation of synthesis gas:

$$CH_4 + H_2O \xrightarrow{Ni/1000°C} CO + 3H_2$$

- Methane can be prepared by aluminum carbide

$$Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3$$

SOLVED EXAMPLE

1. Which of following reagents does not give isobutane when reacted with isobutyl magnesium bromide?

(1) $CH_3–C\equiv CH$

(2) $CH_3–\overset{\overset{O}{\|}}{C}–CH_2–\overset{\overset{O}{\|}}{C}–O–CH_3$

(3) $CH_3–CH_2–OH$

(4) $PhOCH_3$

Sol. **[4]**

$Ph–O–CH_3 \rightarrow$ don't have acidic H

So can not be takes part in acid base reaction

$$CH_3–\underset{CH_3}{\underset{|}{CH}}–CH_2–MgBr \xrightarrow[\text{Acid Base reaction}]{\text{Acidic H}} CH_3–\underset{CH_3}{\underset{|}{CH}}–CH_3$$

2. Methane as well as ethane can be obtained in one step (in two separate reactions) from

(1) CH_3OH (2) C_2H_5OH

(3) CH_3I (4) CH_3CH_2I

Sol. **[3]**

$$CH_3–I \xrightarrow[Zn/H^+]{\text{reduction}} CH_4$$

$$\downarrow \text{Wurtz reaction (Na/ether)}$$

$$CH_3–CH_3$$

3. An alkane of molecular weight 86 gives on monochlorination two product. The alkane is

(1) 2-Methylbutane

(2) n-butane

(3) 2, 2-Dimethyl propane

(4) 2, 3-Dimethyl butane

Sol. **[4]**

$C_nH_{2n+2} = 86$

$12n + 2n+2 = 86$

$14n = 84$

$n = 6$

$m.f = C_6H_{14}$

for two monochloro product alkane must have 2-type H

$$\overset{1^\circ}{CH_3}–\underset{3^\circ}{\underset{|}{CH}}–\underset{3^\circ}{\underset{|}{CH}}–\overset{1^\circ}{CH_3}$$

Type of H = 2

2, 3-dimethyl butane

4. Which of the following alkanes will give a single product with a methylene insertion?

(1) Me_4C

(2) $CH_3CH_2CH_3$

(3) $Me_2CHCHMe_2$

(4) $MeCH_2C(Me)_2CH_2CH_3$

Sol. **[1]**

Number of methylene insertion product = Type of C–H

$$CH_3–\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}–CH_3$$

5. $C_5H_{10} \xrightarrow{H_2/Ni} (X) \xrightarrow{Cl_2/h\upsilon} 3$ monochloro structural isomers for compound C_5H_{10} how many pairs of geometrical isomers are possible?

(1) 1 (2) 2

(3) 3 (4) None

Sol. **[1]**

$$C_5H_{10} \xrightarrow{H_2/Ni} \underset{(X)}{C_5H_{12}} \xrightarrow{Cl_2/h\upsilon} 3\,\text{M.C.P.}$$

- (X) must have 3-type of H, so it is n-pentane

Possible structure of C_5H_{10} is

$CH_3–CH_2–CH_2–CH=CH_2$ no GI

$CH_3–CH=CH–CH_2–CH_3$ GI

Only one pair of GI is possible (cis/trans)

6. $(CH_3)_2CHBr \xrightarrow[(2)\,CuI,\,(3)\,(CH_3)_2CH(CH_2)_2Br]{(1)\,Li/ether} A$

This is Corey–House method of synthesis of A which is

(1) $(CH_3)_2CH(CH_2)_2CH(CH_3)_2$

(2) $(CH_3)_2CHCH_2CH_2CH_3$

(3) $(CH_3)_2CHCH_2CH_2CH_2CH_3$

(4) $(CH_3)_2–CH–CH_2–CH(CH_3)_2$

Sol. **[1]**

$$(CH_3)_2CH–Br \xrightarrow[CuI]{Li/ether} [(CH_3)_2CH]_2LiCu$$

$$(CH_3)_2–CH–(CH_2)_2–Br + [(CH_3)_2CH]_2LiCu \xrightarrow[SN_2]{} (CH_3)_2CH–(CH_2)_2–CH(CH_3)_2$$

7. An alkyl bromide reacts with sodium to form 4, 5-diethyloctane. The alkyl bromide is

(1) $CH_3(CH_2)_2CH_2Br$

(2) $CH_3(CH_2)_4CH_2Br$

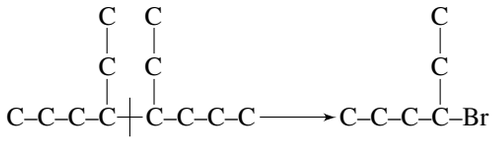
(3) $CH_3(CH_2)_3CHBrCH_3$

(4) $CH_3(CH_2)_2CHBrCH_2CH_3$

Sol. **[4]**

$$R–X \xrightarrow{Na/ether} R–R$$

so given alkane divided by half and gets corresponding alkyl halide as following:



4, 5-diethyloctane

8. Iodine practically does not react with ethane in the presence of light of heat because

(1) the dissociation of I_2 into iodine radicals is more difficult compared to that of F_2, Cl_2 or Br_2

(2) the reaction $CH_3^{\bullet} + I_2 \rightarrow CH_3I + I^{\bullet}$ is endothermic

(3) the hydrogen abstraction step ($I^{\bullet} + CH_4 \rightarrow CH_3^{\bullet} + HI$) is highly endothermic which makes the overall reaction also endothermic

(4) the reaction $CH_3^{\bullet} + I_2 \rightarrow CH_3I + I^{\bullet}$ is exothermic

Sol. **[3]**

$I^{\bullet} + CH_4 \longrightarrow HI + CH_3^{\bullet} \quad \Delta H° = +142$

$CH_3^{\bullet} + I_2 \longrightarrow CH_3I + I^{\bullet} \quad \Delta H° = -89$

Overall $\Delta H° = +53$ endothermic

9. Monochlorination of ethylbenzene ($PhCH_2CH_3$) with Cl_2 under heat produces

(1) $PhCH_2CH_2Cl$

(2) $PhCHClCH_3$

(3) both (1) and (2) in equal amounts

(4) more of (2) and less (1)

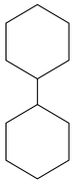
Sol. **[4]**

$$Ph–CH_2–CH_3 \xrightarrow{Cl^{\bullet}} \underset{\text{Resonance stable C-free radical}}{Ph–\dot{C}H–CH_3} + \underset{\text{Less stable}}{Ph–CH_2–\dot{C}H_2}$$

$$Ph–\dot{C}H–CH_3 \xrightarrow{Cl_2/\Delta} Ph–\underset{\underset{Cl}{|}}{CH}–CH_3 \quad \text{(major)}$$

$$Ph–CH_2–\dot{C}H_2 \xrightarrow{Cl_2/\Delta} Ph–CH_2–CH_2–Cl \quad \text{(Minor)}$$

10.  $\xrightarrow{Br_2}$ (A) $\xrightarrow[\text{Dry ether}]{Na}$ (B) Product B is:

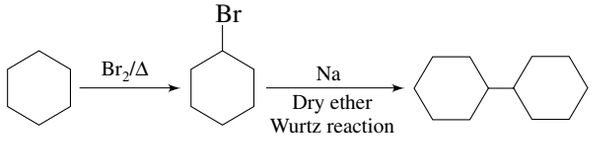
(1) 

(2) 

(3) 

(4) 

Sol. **[1]**



11. In the reaction $Br_2 + CH_3Br \xrightarrow{h\nu} CH_2Br_2 + HBr$ which of the following mechanism steps is productive, but relatively unlikely to occur?

(1) $Br^{\bullet} + CH_3Br \longrightarrow HBr + {}^{\bullet}CH_2Br$

(2) $Br^{\bullet} + {}^{\bullet}CH_2Br \longrightarrow CH_2Br_2$

(3) $Br^{\bullet} + Br_2 \longrightarrow Br_2 + Br^{\bullet}$

(4) $Br^{\bullet} + {}^{\bullet}CH_3 \longrightarrow CH_3Br$

Sol. **[3]**

Initiation step

$Br–Br \xrightarrow{h\nu} 2\ Br^{\bullet}$

Propogation step

(option 1) $CH_3–Br + Br^{\bullet} \longrightarrow \dot{C}H_2–Br + H – Br$

$\dot{C}H_2 – Br + Br \longrightarrow CH_2Br_2 + Br^{\bullet}$

Termination step

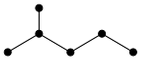
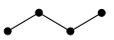
(option 2) $\dot{C}H_2 – Br + Br^{\bullet} \longrightarrow CH_2–Br_2$

$Br^{\bullet} + Br^{\bullet} \longrightarrow Br_2$

(option 3) $\dot{C}H_3 + Br^{\bullet} \longrightarrow CH_3–Br$

Thus option (3) $Br^{\bullet} + Br_2 \longrightarrow Br + Br^{\bullet}$ is relatively unlike.

12. Compare the heats of combustion of the following compounds:

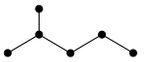
(i)  (ii)  (iii) 

(1) I > II > III (2) II > I > III

(3) III > I > II (4) II > III > I

Sol. **[2]**

Heat of combustion $\propto$ number of carbon

(i)  (ii)  (iii) 

no of C = 5 no of C = 6 no of C = 4

$\because$ (II) > (I) > (III)

13. (A) + $Cl_2 \xrightarrow{h\nu}$ monochloro product

To maximise the yield of monochloro product in the above reaction?

(1) Cl_2 must be added in excess

(2) Reactant (A) must be added in excess

(3) Reaction must be carried out in dark

(4) Reaction must be carried out with equimolar mixture of Cl_2 and A

Sol. **[2]**

Since intermediate is C-free radical so when alkane taken in excess then maximum collision between (A) and Cl radical takes place thus monochloro product obtained as major product

14. How much volume of oxygen will be needed for complete combustion of 10 lit. of ethane:

(1) 135 lit. (2) 35 lit.

(3) 175 lit. (4) 205 lit.

Sol. **[2]**

$$C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$$

Making mole equation

$$\text{Mole } C_2H_6 = \frac{2}{7}\text{mole } O_2$$

$$\text{vol } C_2H_6 = \frac{2}{7}\text{vol } O_2$$

$$10 = \frac{2}{7}\text{vol } O_2$$

vol of O_2 = 35 lit

15. The most volatile alkane is-

(1) n-pentane (2) isopentane

(3) neopentane (4) n-hexane

Sol. **[3]**

$$\text{volatile nature} \propto \frac{1}{\text{boiling point}}$$

$$\text{boiling point} \propto \text{molecular weight}$$

$$\propto \frac{1}{\text{branching (forisomer)}}$$

So neo pentane have least boiling point, thus most volatile

16. Arrange the following in the correct order of reactivity towards Cl_2/hv-

(A) CH_4 (B) CH_3CH_3

(C) $CH_3CH_2CH_3$ (D) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{CH}}}}-CH_3$

(1) A > > C > D (2) D > C > B > A

(3) B > C > A > D (4) C > B > D > A

Sol. **[2]**

Reactivity for radical substitution ∝ stability of C-free radical

(A) $CH_3-H \longrightarrow \dot{C}H_3$ 0α-H (least stable)

(B) $CH_3-CH_2-H \longrightarrow CH_3-\dot{C}H_2$ 3α-H

(C) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{CH}}}}-CH_3 \longrightarrow CH_3-\dot{C}H-CH_3$ 6α-H

(D) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-H \longrightarrow CH_3-\underset{\displaystyle \bullet}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3$ 9α-H (most stable)

Thus D > C > B > A

17. The best retrosynthetic set of reactant used for the preparation of 2-methyl butane by the Corey–House synthesis

(2) $CH_3-Br + (CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2)_2-LiCu$

(3) $CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-Br + (CH_3-CH_2)_2-LiCu$

(4) $CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-Br + (CH_3)_2-LiCu$

Sol. **[2]**

So that

$$CH_3-Br + (CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2)_2-LiCu \xrightarrow{SN_2} CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2+CH_3$$

since corey house synthesis taking place by SN_2 Reaction rate of SN_2 reaction

$$\propto \frac{1}{\text{steric hindrance of R}-\text{X}}$$

18. Which of the following reaction would be most exothermic?

(1) $H^{\bullet} + (CH_3)_3CH \longrightarrow H_2 + (CH_3)_3C^{\bullet}$

(2) $CH_3-CH_3 \longrightarrow 2\dot{C}H_3$

(3) $\dot{C}H_3 + CH_3-CH_3 \longrightarrow CH_4 + CH_3-\dot{C}H_2$

(4) $2CH_3\dot{C}H_2 \longrightarrow CH_3-CH_2-CH_2-CH_3$

Sol. **[4]**

It involves association of two free radicals without breaking any old bonds of reactant hence, highly exothermic

19. Which of the following reaction pairs constitutes the chain propagation step in chlorination of methyl chloride–

(1) $^{\bullet}CH_3 + Cl_2 \rightarrow CH_3Cl + {}^{\bullet}Cl$

$CH_3Cl + {}^{\bullet}Cl \rightarrow {}^{\bullet}CH_2Cl + HCl$

(2) $CH_3Cl + {}^{\bullet}Cl \rightarrow CH_2Cl + {}^{\bullet}H$

$^{\bullet}CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + {}^{\bullet}Cl$

(3) $CH_3Cl + {}^{\bullet}Cl \rightarrow {}^{\bullet}CH_2Cl + HCl$

$^{\bullet}CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + {}^{\bullet}Cl$

(4) $^{\bullet}CH_2Cl + {}^{\bullet}CH_2Cl \rightarrow CH_2Cl - CH_2Cl$

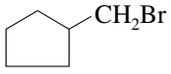
$^{\bullet}CH_2Cl + {}^{\bullet}Cl \rightarrow CH_2Cl_2$

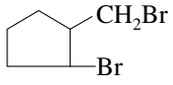
Sol. **[3]**

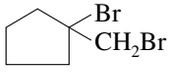
P_1 : $CH_3–Cl + \dot{C}l \rightarrow \dot{C}H_2–Cl + HCl$

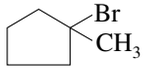
P_2 : $^{\bullet}CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + {}^{\bullet}Cl$

20. **[4]** The major product formed by monobromination of methylcyclopentane is

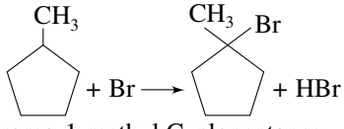
(1) 

(2) 

(3) 

(4) 

Sol. Relative reactivity for the abstraction on of different $H^{\bullet}$ by bromination is $3^{\circ}_{H} > 2^{\circ}_{H} > 1^{\circ}_{H}$



1-Bromo-1-methyl Cyclopentance

3. The Grignard reagent derived from an alkyl halide (A) forms propane on treatment with water. Which one among the following could be the structures of (A)?

(1) $CH_2=CHCH_2Br$ (2) $HC\equiv C—CH_2Br$

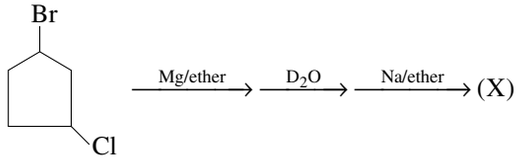
(3) 

(4) $CH_3CHBrCH_3$

4. Which product is obtained at the anode by the electrolysis of sodium butyrate:

(1) Butane + CO_2 (2) Pentane + CO_2

(3) Hexane + CO_2 (4) Hexane

5. 

The compound (X) is:

EXERCISE 1

1. In which of the following reactions, alkanes containing the same number of carbons as the substrate are obtained?

(a) $CH_3CH_2COOH \xrightarrow[\Delta]{\text{soda lime}}$

(b) $CH_3COOK \xrightarrow{\text{electrolysis}}$

(c) $(CH_3)_2CHCOOH \xrightarrow[\text{reduction}]{\text{HI/P}}$

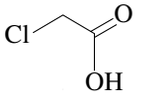
(d) $CH_3CH_2Br \xrightarrow[\text{EtoH}]{\text{Zn-Cu couple}}$

(e) $CH_3CH_2Br \xrightarrow[\text{dry ether}]{\text{Na and}}$

Code is:

(1) b, c, d (2) c, d, e

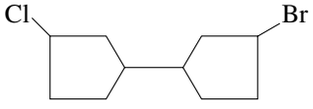
(3) a, d, e (4) a, e, c

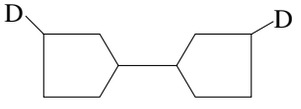
2. 

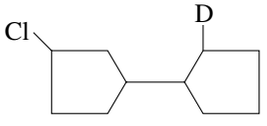
$\xrightarrow{Zn+DCl}$ (A) $\xrightarrow{NaOH}$? $\xrightarrow{NaOD+CaO}$ (B)

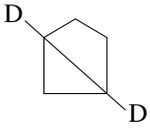
The compounds (A) and (B) in the equation given above are:

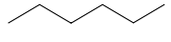
	(A)	**(B)**
(1)	CH_3COOH	CH_3CH_3
(2)	$DCH_2–COOD$	CH_4
(3)	$DCH_2–COOH$	CH_2D_2
(4)	$CH_3–COOD$	CH_3D

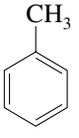
(1) 

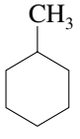
(2) 

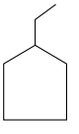
(3) 

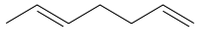
(4) 

6.  $\xrightarrow[600°C]{Cr_2O_3–Al_2O_3}$ Major product:

(1) 

(2) 

(3) 

(4) 

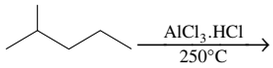
7. Nitration of propane with nitric acid vapour at about 430°C is expected to yield-

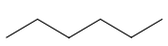
(1) $CH_3CH_2CH_2–NO_2$

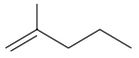
(2) $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH–NO_2$

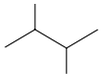
(3) $CH_3CH_2–NO_2$

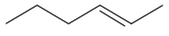
(4) A mixture of all the above

8.  Product is-

(1) 

(2) 

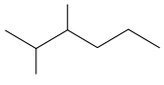
(3) 

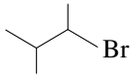
(4) 

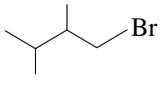
9. How many alkene react with H_2 in presence of platinum or nickel catalyst to yeild 2-methyl butane

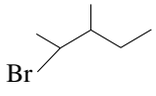
(1) Only one (2) Two

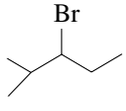
(3) Three (4) None of these

10. (A) $+(CH_3–CH_2)_2–CuLi \longrightarrow$  Deduce the strurure of A

(1) 

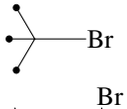
(2) 

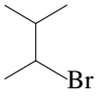
(3) 

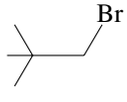
(4) 

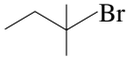
11. (A) $\xrightarrow{Zn/H^{\oplus}}$ neopentane

Suggest the most suitable structure of A.

(1) 

(2) 

(3) 

(4) 

12. $CH_3–\underset{\underset{OH}{|}}{CH}–COOH \xrightarrow{RedP/HI}$ Product looses its (B)

(A)

optical activity because of-

(1) chirality of the molecule destroyed

(2) Symmetry of molecule is destroyed

(3) Spatial arrangement is changed

(4) Racemic mixture is formed

13. An alkane C_5H_{12} is produced by the reaction of lithium di (2propyl) cuprate with ethyl bromide. The alkane is:

(1) n-pentane (2) 2-Ethylpropane

(3) 3-Methylbutane (4) 2-methyl butane

14. Which of the following compounds may be decarboxylated most easily?

(1) CH_3COOH

(2) $CH_3CH_2–COOH$

(3) Ph–COOH

(4) $HOOC–CH_2–COOH$

15. An organic compound A(C_4H_9Cl) on reaction with Na/ether gives a hydrocarbon which on monochlorination gives only one chloro derivative then A is

(1) t-butyl chloride (2) sec-butyl chloride

(3) iso butyl chloride (4) n-butyl chloride

16. Which of the following may yield racemic monochlorinated product?

(1) n-Butane

(2) 2, 2-Dimethylpropane

(3) Isobutane

(4) 2, 2, 3, 3-Tetramethylbutane

17. Monochlorination of monodeuterioethance (CH_3CH_2D) yields:

(1) chloroethane only

(2) monodeuteriochloroethance only

(3) equal amounts of (1) and (2)

(4) a large amount of (2) and a small amount of (1)

18. The addition of oxygen gas to a reaction mixture of methane and chlorine undergoing photochemical chlorination will:

(1) accelerate the reaction

(2) retard the reaction for some time

(3) rate of the reaction not effect

(4) accelerate or retard the rate of the reaction depending upon the amount of oxygen

19. Consider the following reaction:

$$CH_3–\underset{\underset{CH_3}{|}}{CH}–CH_3 + CCl_4 \xrightarrow[heat]{SO_2Cl_2}$$

The major products formed in this reaction are:

(1) $(CH_3)_3CCl$ and $CHCl_3$

(2) $(CH_3)_3COH$ and CH_3Cl

(3) $(CH_3)_3C–C(CH_3)_3$ and $(CH_3)_3COH$

(4) No reaction

20. Photochemical fluorination is explosive while iodination is too slow to occur. The reason for this is:

(1) Bond dissociation energy of I_2 is minimum

(2) Formation of $CH_3–F$ is most exothermic

(3) Formation of H–F is most exothermic while formation of HI is endothermic

(4) F_2 has lower bond dissociation energy than Cl_2 and Br_2

21. An alkane with the formula C_6H_{14} can be prepared by reduction with Zn^{2+} and H^+ of only two isomeric alkyl chloride ($C_6H_{13}Cl$) what is the systematic name of this alkane

(1) 2, 2-dimethyl butane (2) 2, 3-dimethyl butane

(3) 3-methyl pentane (4) 2-methyl pentane

22. An alkane will form a single monochloro derivative if

(1) it possesses only primary hydrogens

(2) it possesses only primary hydrogens which are all equivalent

(3) both (1) and (2) are correct

(4) both (1) and (4) are wrong

23. Consider the reaction

$CH_3CH_3 + (CH_3)_3C–O–Cl \xrightarrow{heat}$

The major products expected are

(1) CH_3CH_2OH and $(CH_3)_3C–Cl$

(2) $CH_3CH_2OC(CH_3)_3$ and HCl

(3) CH_3CH_2Cl and $(CH_3)_3C–OH$

(4) CH_3CH_2OCl and $(CH_3)_3CH$

24. Consider the following reaction

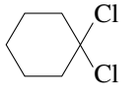
$$CH_3CH_2OH \xrightarrow[Et_3N]{CH_3SO_2Cl} A \xrightarrow{LiaAlH_4} B$$

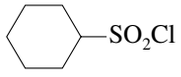
The end product (B) is

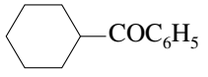
(1) $CH_3CH_2OSO_2CH_3$ (2) CH_3CH_3

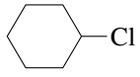
(3) $CH_3CH_2CH_3$ (4) CH_3CH_2Cl

25. A mixture of cyclohexane and sulphuryl chloride (3 : 1 molar ratio) is refluxed in the presence of a small amount of $(C_6H_5CO)_2O_2$. The major product obtained is

(1) 

(2) 

(3) 

(4) 

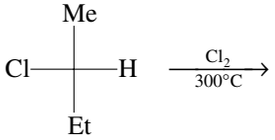
EXERCISE 2

1. Mono chlorination reaction of n-pentane takes place n-pentane $\xrightarrow{Cl_2/h\nu}$ (A) $\xrightarrow[Distillation]{fractional}$ (B). A and B are respectively:

(1) 3, 3 (2) 4, 3

(3) 3, 4 (4) 4, 4

2. Pick the correct statement for monochlorination of R-secbutyl chloride.

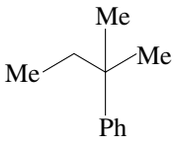


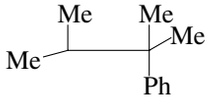
(1) There are four possible products; three are optically active one is optically inactive

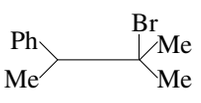
(2) There are five possible products; three are optically inactive & two are optically active

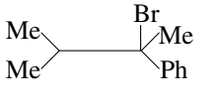
(3) There are five possible products; two are optically inactive & three are optically active

(4) There are four possible products; two are optically inactive & two are optically inactive

3.  $\xrightarrow{Br_2 + h\nu}$ (A). (A) is:

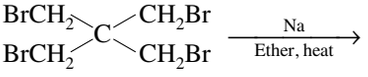
(1) 

(2) 

(3) 

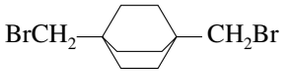
(4) All

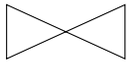
4. The product formed in the reaction is:

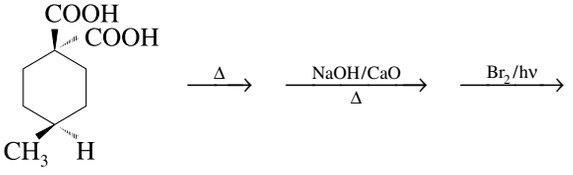


(1) $(BrCH_2)_3CCH_2CH_2C(CH_2Br)_3$

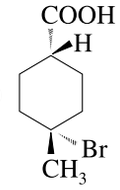
(2) 

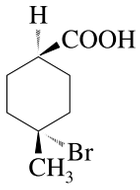
(3) 

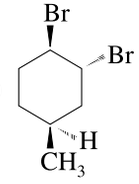
(4) 

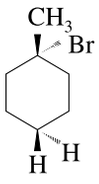
5. 

P (Major)

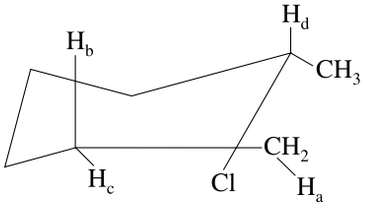
(1) 

(2) 

(3) 

(4) 

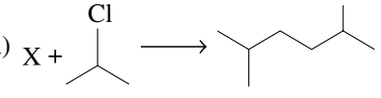
6. In the following halogen substituted hydrocarbon, the hydrogen atom that can be eliminated most readily is:

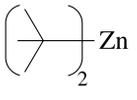


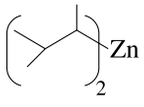
(1) H_a (2) H_b

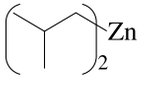
(3) H_c (4) H_d

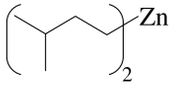
7. Select the starting material for following reactions

(A) 

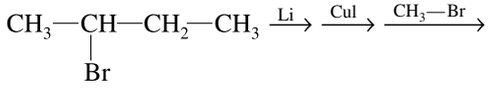
(1) 

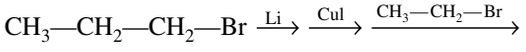
(2) 

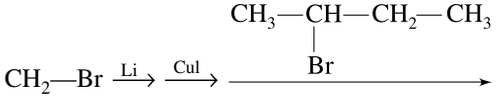
(3) 

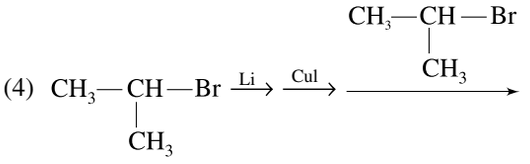
(4) 

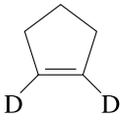
8. Which of the following is the best way to prepare isopentane?

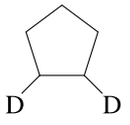
(1) 

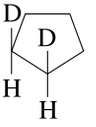
(2) 

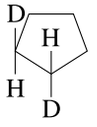
(3) 

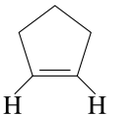
(4) 

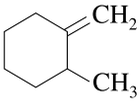
9.  Product is:

(1) 

(2) 

(3) 

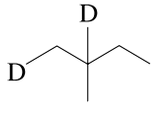
(4) 

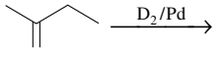
10.  Products of the above reaction will be:

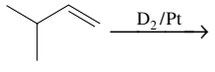
(1) racemic mixture (2) diastereomers

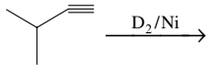
(3) meso (4) structural isomer

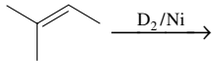
11. Choose the correct option to obtain the given product

Reactant 

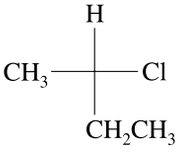
(1) 

(2) 

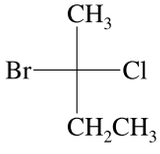
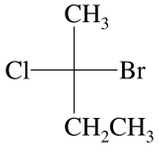
(3) 

(4) 

12. A sample of (R)-2-chlorobutane,



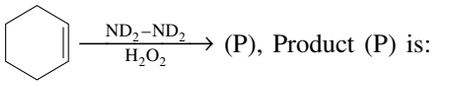
reacts with Br_2 in the presence of light, and all the products having the formula C_4H_8BrCl were isolated. Two possible isomers are shown below:

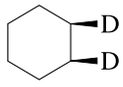
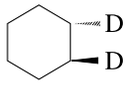
 and 

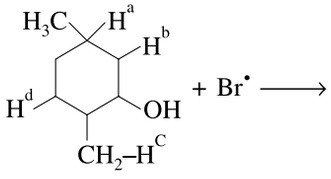
(I) (II)

of these:

(1) only I was formed
(2) both I and II were formed in equal amounts
(3) both I and II were formed in unequal amounts
(4) only II was formed

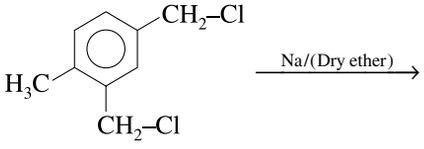
13.  (P), Product (P) is:

(1) 
(2) 
(3) 
(4) both (2) and (3)

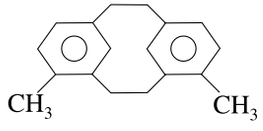
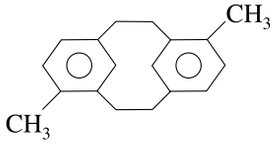
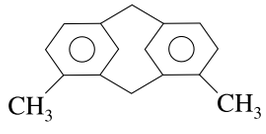
14. 

$Br^{\bullet}$ will abstract which of the hydrogen most readily?

(1) a
(2) b
(3) c
(4) d

15. 

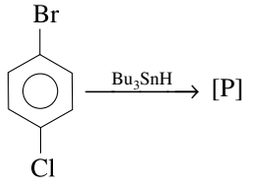
Products obtained in above Wurtz reaction is:

(1) 
(2) 
(3) 
(4) Both (1) and (2)

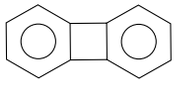
16. Isobutane on monochlorination with Cl_2 in the presence of UV light gives t-butyl chloride (36%) and isobutyl chloride (64%) (based on the total yield of monochlorinated product). On the basis of this data, relative reactivity of tertiary and primary hydrogens on a per-hydrogen basis is expected to be

(1) 3.2 : 1
(2) 5.1 : 1
(3) 2.5 : 1
(4) 4.5 : 1

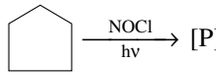
17. In the given reaction

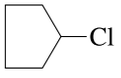
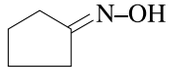
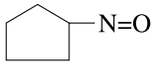
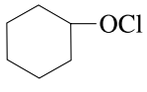


[P] will be:

(1) H_6H_5–Br
(2) C_6H_5–Cl
(3) 
(4) Mixture of (1), (2) and (3)

18. In the given reaction (P) will be



(1) 
(2) 
(3) 
(4) 

19. Consider the following statements:

(i) In free radical substitution reactions both propagation steps should be exothermic
(ii) Reaction intermediate is carbon free radical
(iii) Termination step is always exothermic
(iv) Initiation step is always exothermic, Select the correct statements and give the answer from the codes given below

Code:

(1) i, ii and iii
(2) i, ii and iv
(3) ii and iii
(4) i, ii, iii and iv

20. Chlorination of methane may proceed according to one of the two alternative mechanism.

Mechanism A: $Cl^{\bullet} + CH_4 \longrightarrow HCl + \dot{C}H_3$

$\dot{C}H_3 + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$

Mechanism B: $Cl^{\bullet} + CH_4 \longrightarrow CH_3Cl + H^{\bullet}$

$H^{\bullet} + Cl_2 \longrightarrow HCl + Cl^{\bullet}$

Which statement about these mechanism is correct?

(1) Mechanism A is preferred because none of the steps is strongly endothermic
(2) Mechanism A is preferred because step-II is strongly exothermic

(3) Mechanism B is preferred because none of the steps is strongly endothermic

(4) Mechanism B is preferred because step-II is strongly exothermic

EXERCISE 3

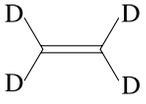
One and More Than One Option Correct Type Question

1. Select **correct** statement:

(1) Methane cannot be prepared by catalytic hydrogenation of alkene

(2) All isomers of the formula C_6H_{14} can be prepared by catalytic hydrogenation of alkene

(3) All isomers of the formula C_5H_{12} can be prepared by catalytic hydrogenation of alkene

(4)  product obtained show now optical rotation

2. Which statement is **correct**?

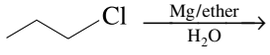
(1) C_2H_6 can be prepared by Wurtz reaction

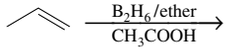
(2) CO_2 gas liberates at anode in Kolbe electrolytes of aqueous CH_3COOK

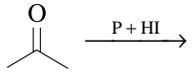
(3) Benzene liberates at anode on Kolbe electrolysis of aqueous Ph–COONa

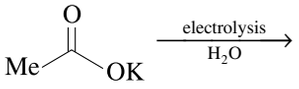
(4) Anhydrous ether should be used in Wurtz reaction

3. Which of the following reactions will give propane?

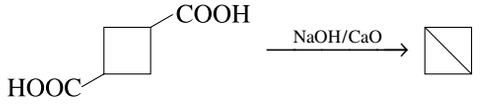
(1) 

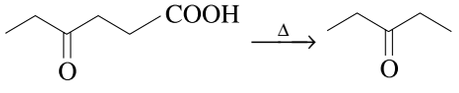
(2) 

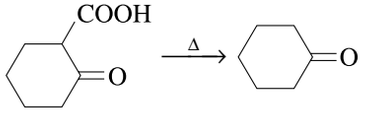
(3) 

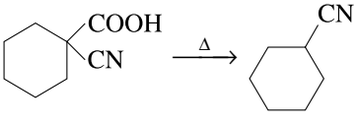
(4) 

4. Which of the following decarboxylation reaction and their product is/are incorrectly matched?

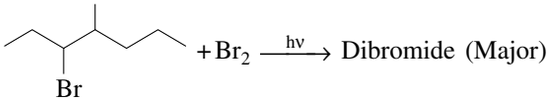
(1) 

(2) 

(3) 

(4) 

5. Consider the following bromination reaction



If a pure enantiomer of reactant is taken in the above reaction, the correct statement concerning product bromination is/are

(1) A racemic mixture is formed

(2) Two optically active isomers are formed

(3) A pair of diastereomers in equal amount is formed

(4) A pair of enantiomers but in unequal amounts is formed

6. $C_6H_{14(n\text{–hexane})} \xrightarrow{Al_2O_3/\Delta} (A) \xrightarrow{(CO+HCl)/AlCl_3} (B)$

Select the correct statement among following:

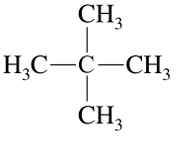
(1) Compound 'B' form silver mirror on reaction with $[Ag(NH_3)_2]OH$

(2) Molecularity of reaction during conversion from 'A' to 'B' is '3'

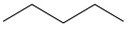
(3) Compound 'A' can also be synthesised by reaction of benzene diazonium chloride with H_3PO_2

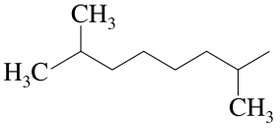
(4) Compound 'B' give grey colour with aq. $HgCl_2$ solution

7. Which of the following can't be produced as the single alkene in Wurtz's reaction?

(1) 

(2) 

(3) 

(4) 

Assertion and Reason Type Question

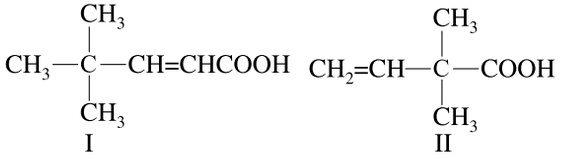
(1) If both (A) and (R) are correct and (R) is the correct explanation for (A)

(2) If both (A) and (R) are correct and (R) is not the correct explanation

(3) If (A) is correct and (R) is incorrect

(4) If (A) is incorrect and (R) is correct

8. Statement-1:



Acid (II) will decarboxylate more readily on heating.

Statement-2: Acid (II) is a β–γ unsaturated acid and will decarboxylate easily on heating by a mechanism involving cyclic transition state.

9. Statement-1: iso-butyl bromide, on reaction with sodium in the presence of dry ether, gives 2, 5-dimethylhexane.

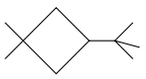
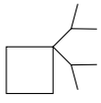
Statement-2: In Wurtz reaction, alkyl halides yield hydrocarbon containing double the number of carbon atoms present in the halide.

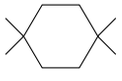
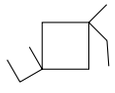
Comprehension Type Question

Passage (Q. 10–12)

A hydrocarbon with molecular formula $C_{10}H_{18}$, upon catalytic hydrogenation gives $C_{10}H_{20}$(X). X on free radical chlorination gives two monochloro derivatives with their molecular formula $C_{10}H_{19}Cl$ that are constitutional isomers.

10. Which of the following satisfy the criteria of X?

(1)  (2) 

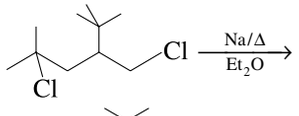
(3)  (4) 

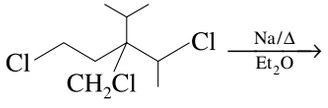
11. How many different alkenes on hydrogenation, can gives X?

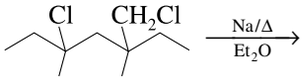
(1) 1 (2) 2

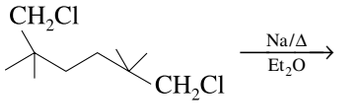
(3) 3 (4) 4

12. Which of the following reactions can synthesise X?

(1) 

(2) 

(3) 

(4) 

Comprehension (Q. 13–15)

Deutrium (D) is the hydrogen isotope of mass number 2, with a proton and neutron in its nucleus. The chemistry of deuterium is nearly identical to the chemistry of hydrogen, except that the C—D bond is slightly stronger than the C—H bond by 5.0 kJ mol (1.2 kcal mol). Reaction rates tend to be slower if a C—H bond (as opposed to C—H bond) is broken in a rate limiting step.

This effect, called a kinetic isotope effect, is clearly seen in the chlorination of methane, Methane undergoes free radical chlorination 12 times as fast as tetra-deuteriomethane (CD_4)

Faster: $CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$, Relative rate = 12

Slower: $CD_4 + Cl_2 \longrightarrow CD_3Cl + DCl$, Relative rate = 1

13. What is true regarding transition state for the rate determining step in the monochlorination of CH_4 and CD_4?

(1) Transition states have same potential energies for both CH_4 and CD_4

(2) Transition state has greater potential energy for CH_4 than for CD_4

(3) Transition state has greater potential energy for CD_4 than for CH_4

(4) The byproduct HCl is is more stable than DCl

14. Monochlorination of deuterioethane (C_2H_5D) leads to a mixture containing 93% (C_2H_4DCl) and 7% (C_2H_5Cl). Based on these percentages, what is the relative rate of abstraction per hydrogen with respect to D?

(1) 93 times greater (2) 18.6 times greater

(3) 13.3 times greater (4) 2.7 times greater

15. Consider the thermodynamics of the rate determining step in the chlorinatin of methane and the chlorination of ethane,

$CH_4 + \dot{Cl} \longrightarrow \dot{C}H_3 + HCl$; $\Delta H = 4$ kJ/mol

$CH_3CH_3 + \dot{Cl} \longrightarrow \dot{C}H_2–CH_3 + HCl$; $\Delta H = -21$kJ/mol

The correct statement is

(1) Methane shows greater kinetic isotopic effect than ethane

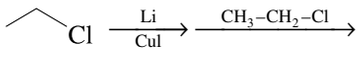
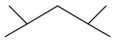
(2) Ethane shows greater kinetic isotopic effect thane methane

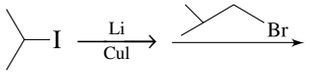
(3) Both sow the same kinetic isotopic effect

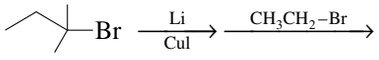
(4) Kinetic isotopic effect cannot be compared in the above two reactions

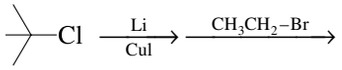
Column Matching Type Question

16. **Column-(I)** **Column-(II)**

(a)  (P) 

(b)  (Q) 

(c)  (R) 

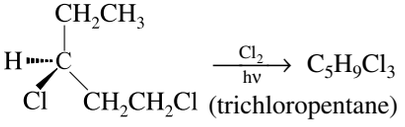
(d)  (S) 

(1) a → Q; b → P; c → S; d → R
(2) a → Q; b → P; c → R; d → S
(3) a → P; b → Q; c → S; d → R
(4) a → Q; b → P; c → R; d → S

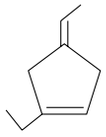
Single Digit Integer Type Question

17. How many different dichlorides, including stereoisomers by Wurtz coupling reaction with ethereal solution of sodium, can give 1,4-dimethyl cyclohexane?

18. If a pure enantiomers of 1, 3-dichloropentane, shown below, is subjected to free radical chlorination to obtain trichloropentane, how many different isomers would be formed?



19. If the following compound is treated with Pd/C in excess of H_2 gas, how many stereoisomers of the product will be obtained?



20. Haw many type of acids can be used to obtained isopentane by decarboxylation?

EXERCISE 4

1. On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloroalkane. This alkane could be- **[AIEEE-2003]**

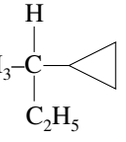
(1) Isopentane (2) Neopentane
(3) Propane (4) Penetane

2. Butene-1 may be converted to butane by reaction with- **[AIEEE-2003]**

(1) Zn–Hg (2) Pd/H_2
(3) Zn–HCl (4) Sn–HCl

3. Amongst the following compounds the optically acitive alkane having lowest molecular mass is- **[AIEEE-2004]**

(1) $CH_3–CH_2–CH_2–CH_3$ (2) $CH_3–CH_2–\underset{\displaystyle CH_3}{\underset{|}{C}}H–CH_3$

(3)  (4) $CH_3–CH_2–C\equiv CH$

4. Alkyl halides react with dialkyl copper reagents to give **[AIEEE-2005]**

(1) Alkyl copper halides (2) alkenes
(3) alkenyl halides (4) alkanes

5. Phenyl magnesium bromide reacts with methanol to give- **[AIEEE-2006]**

(1) a mixture of benzene and Mg(OMe)Br
(2) a mixture of toluene and Mg(OH)Br
(3) a mixture of phenol and Mg(Me)Br
(4) a mixture of anisole and Mg(OH)Br

6. The treatment of CH_3MgX with $CH_3C{\equiv}C{-}H$ produces **[AIEEE-2008]**

(1) $CH_3C{\equiv}C{-}CH_3$ (2) $CH_3{-}CH_2{-}\underset{\displaystyle CH}{\underset{|}{C}}H{-}CH_3$

(3) CH_4 (4) $CH_3{-}CH{=}CH_2$

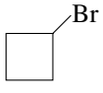
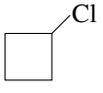
7. Which branched chain isomer of the hydrocarbon with molecular mass 72 u gives only one isomer of mono substituted alkyl halide? **[AIEEE-2012]**

(1) Neopentane
(2) Isohexane
(3) Neohexane
(4) Tertiary butyl chloride

8. The major product obtained in the photo catalysed bromination of 2-methylbutane is:
[JEE Main Online-2012, 2014]

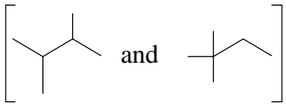
(1) 1-bromo-2-methylbutane
(2) 1-bromo-3-methylbutane
(3) 2-bromo-3-methylbutane
(4) 2-bromo-2-methylbutane

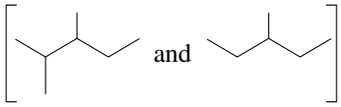
9. 1-Bromo-3-chloro cyclobutane on reaction with 2-equivalent of sodium in ether gives
[IIT Screening-2005]

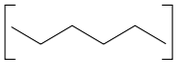
(1)  (2) 

(3)  (4) 

10. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure. (on the basis of bpt)
[JEE Advance-2014]

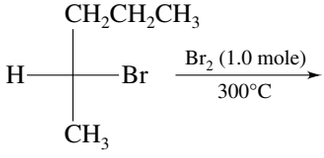
(I) 

(II) 

(III) 

(1) I > II > III (2) III > II > I
(3) II > II (4) III > I > II

11. In the following monobromination reaction, the number of possible chiral product(s) is (are) _____
[JEE Advance-2016]



(1.0 mole) (Enantiomerically pure)

ANSWER KEY

EXERCISE # 1

1. (1)	2. (3)	3. (4)	4. (3)	5. (2)
6. (1)	7. (4)	8. (3)	9. (3)	10. (2)
11. (3)	12. (1)	13. (4)	14. (4)	15. (1)
16. (1)	17. (4)	18. (2)	19. (1)	20. (3)
21. (2)	22. (2)	23. (3)	24. (2)	25. (4)

EXERCISE # 2

1. (2)	2. (3)	3. (3)	4. (4)	5. (4)
6. (4)	7. (4)	8. (1)	9. (2)	10. (2)
11. (1)	12. (2)	13. (2)	14. (1)	15. (4)
16. (2)	17. (3)	18. (2)	19. (1)	20. (1)

EXERCISE # 3

1. (1,2,4)	2. (1,2,4)	3. (1,2,3)	4. (1,2)	5. (2,3)
6. (1,3,4)	7. (1,3)	8. (1)	9. (1)	10. (3)
11. (1)	12. (4)	13. (3)	14. (14)	15. (1)
16. (1)	17. (7)	18. (7)	19. (2)	20. (4)

EXERCISE # 4

1. (2)	2. (2)	3. (2)	4. (4)	5. (2)
6. (3)	7. (1)	8. (4)	9. (4)	10. (2)
11. (5)				

HINT AND SOLUTION

EXERCISE # 1

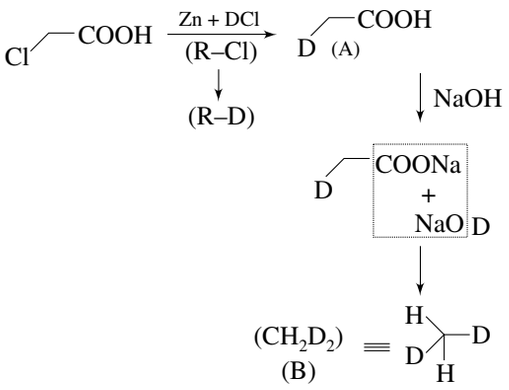
1. [1]

(b) $CH_3 - COOK \xrightarrow{\text{electrolysis}} CH_3 - CH_3 + CO_2$

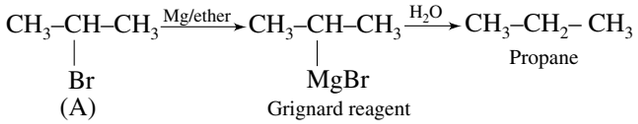
(c) $(CH_3)_2CHCOOH \xrightarrow[\text{reduction}]{HI/P} (CH_3)_2CH{-}CH_3$

(d) $CH_3 - CH_2 - Br \xrightarrow[EtoH]{Zn-Cu\ couple} CH_3 - CH_3$

2. [3]



3. [4]



4. [3]

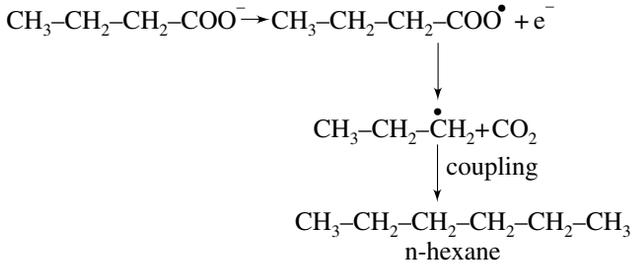
sodium butyrate $CH_3{-}CH_2{-}CH_2{-}COONa$

$\xrightarrow{\text{electrolysis}} CH_3{-}CH_2{-}CH_2{-}COO^- + Na^+$

At cathode $Na^+ + e^- \longrightarrow Na$

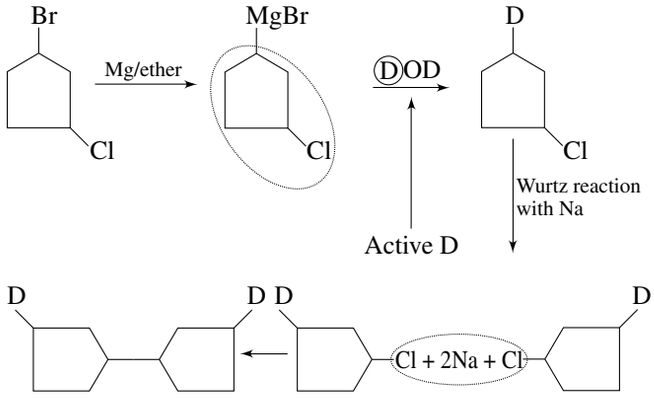
$2Na + 2H_2O \longrightarrow 2NaOH + H_2$

At Anode

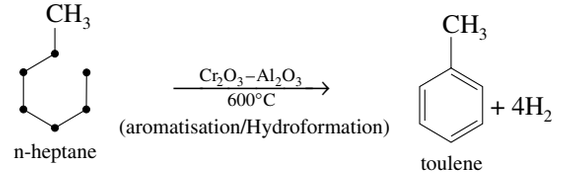


5. [2]

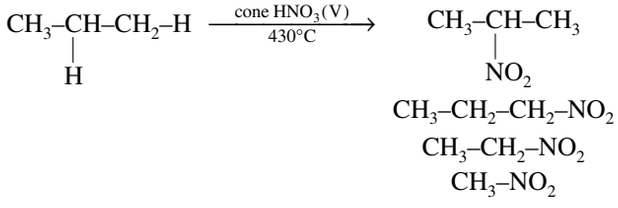
(C–Br) bond is weaker than (C – Cl) bond, Grignard reagent is formed more predominantly with (C – Br)



6. [1]

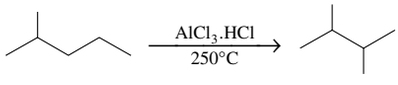


7. [4] At high temprature breaking of both C–C & C–H bond takes place, thus.



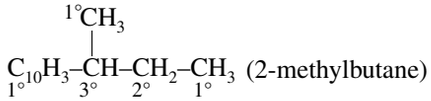
Breaking of C–H and C–C bond takes place

8. [3]



It is isomerisation reaction so that branching takes place.

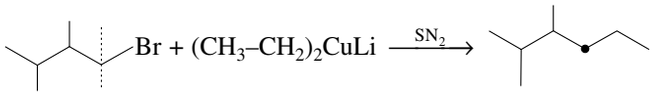
9. [3]



number of alkene = type of C – C having H in alkane

Type of C – C $\longrightarrow$ 1° and 3°
$\longrightarrow$ 2° and 3° } = 3 type
$\longrightarrow$ 1° and 2°

10. [2]



Corey–House synthesis

11. [3]

$Zn/H^{\oplus} \Rightarrow$ Reducing agent

(1) $CH_3-CH(CH_3)-C(CH_3)_2-Br \xrightarrow{Zn/H^+} CH_3-CH(CH_3)-CH(CH_3)_2$

(2) $CH_3-CH(CH_3)-CH(Br)-CH_3 \xrightarrow{Zn/H^+} CH_3-CH(CH_3)-CH_2-CH_3$

(3) $CH_3-C(CH_3)_2-CH_2-Br \xrightarrow{Zn/H^+} CH_3-C(CH_3)_2-CH_3$ (neo pentane)

(4) $CH_3-CH_2-C(CH_3)_2-Br \xrightarrow{Zn/H^+} CH_3-CH_2-CH(CH_3)-CH_3$

12. [1]

$CH_3-CH(OH)-COOH \xrightarrow{Red\ P/HI} CH_3-CH(H)-CH_3$

Chiral C = 1 Chiral C = 0

13. [4]

$CH_3-CH_2-Br + (CH_3-CH(CH_3)-)_2CuLi$

Corey–House synthesis, SN_2

$CH_3-CH_2-CH(CH_3)-CH_3$

2-methyl butane

14. [4]

Reate of de-corboxylation $\propto$ stability of carboanion

15. [1]

$(CH_3)_3C-Cl \xrightarrow[\text{Wurtz reaction}]{Na/ether} (CH_3)_3C-C(CH_3)_3$

t-butyl chloride (type of H = l)

$\xrightarrow{Cl_2/h\nu} CH_3-C(CH_3)_2-C(CH_3)_2-CH_2-Cl$

(only single product)

16. [1]

$CH_3-CH_2-CH_2-CH_3 \xrightarrow{Cl_2/h\nu} CH_3-CH_2-\overset{*}{C}H(Cl)-CH_3$

$\rightarrow$ 1 C chiral

$\rightarrow$ Mixture of *d* and *l* isomer possible

$\rightarrow$ Racemic mixture

17. [4]

$CH_3-CH_2-D \xrightarrow{Cl_2/h\nu} CH_3-CH_2-Cl + CH_3-CH(Cl)-D$

Minor Major

B.E (C – H) < B.E(C–D)

18. [2]

$CH_4 \xrightarrow{Cl_2/h\nu} \dot{C}H_3$

$\dot{C}H_3 \xrightarrow{O_2} CH_3-O-O^{\bullet}$

Due to formation of methyl peroxide, rate of reaction retards

19. [1]

$CH_3-CH(CH_3)-CH_3 + CCl_4 \xrightarrow{SO_2Cl_2} CH_3-C(Cl)(CH_3)-CH_3 + CHCl_3$

Radical substitution

20. [3]

$F^{\bullet} + CH_4 \longrightarrow HF + CH_3^{\bullet}$ $\quad \Delta H^\circ = -130$

$CH_3^{\bullet} + F_2 \longrightarrow CH_3F + F^{\bullet}$ $\quad \Delta H^\circ = \underline{-302}$

Overall $\Delta H^\circ = -432$

A Large amount at heat released so that flourination is explosive.

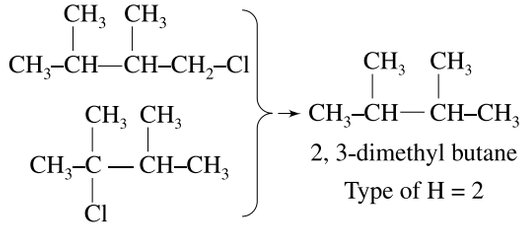
$I^{\bullet} + CH_4 \longrightarrow HI + CH_3^{\bullet}$ $\quad \Delta H^\circ = +142$

$CH_3^{\bullet} + I_2 \longrightarrow CH_3I + I^{\bullet}$ $\quad \Delta H^\circ = \underline{-89}$

Overall $\Delta H^\circ = +53$

Heat absorbed so that iodonation is very slow.

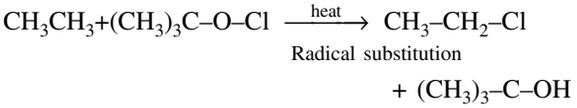
21. [2]



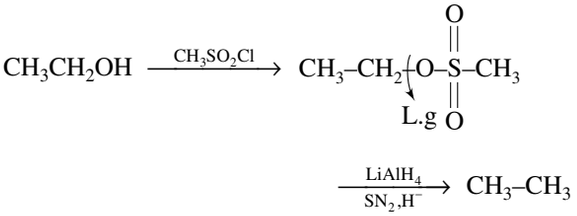
Thus the forming alkane prepared by only two isomeric alkyl halide

22. [2]

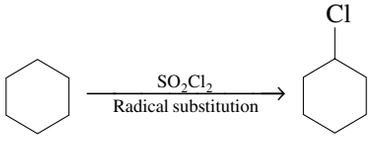
23. [3]



24. [2]

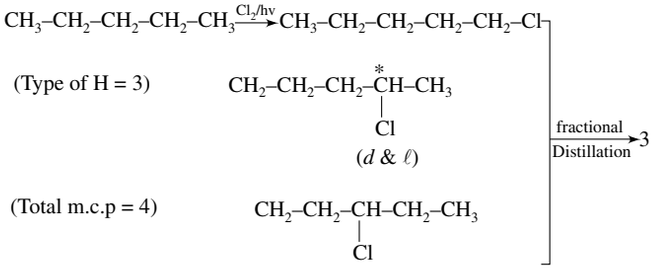


25. [4]



EXERCISE # 2

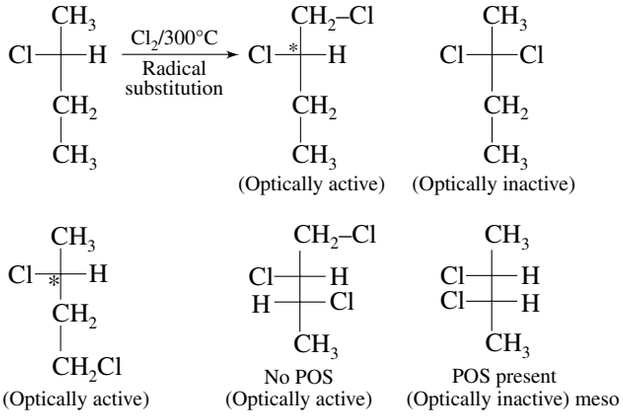
1. [2]



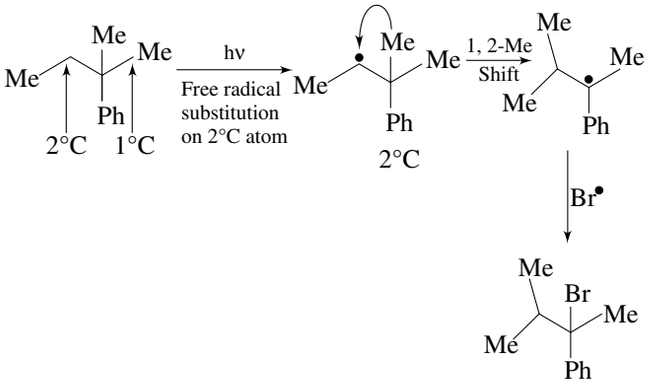
Total monochloro product = 4

Note: Separation of enantiomeric pair do not takes place by fractional distillation

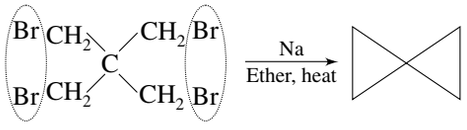
2. [3]



3. [3]

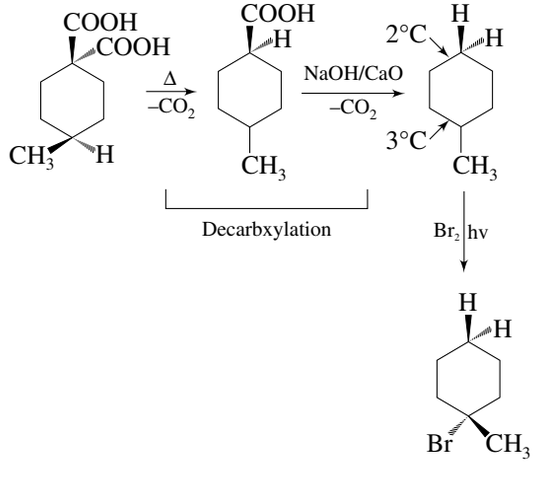


4. [4]



Intramolecular Wurtz reaction

5. [4]



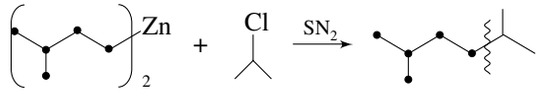
6. [4]

→ Rate of H elimination for halogenation

$\propto$ stability of $-\dot{C}<$

→ Removal of H_d gives 3°C radical

7. [4]



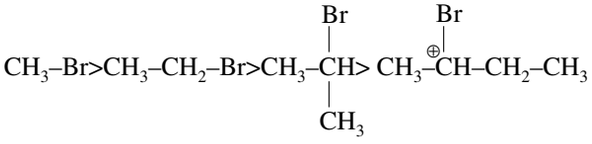
Frankland reaction

8. [1]

All above reaction final step completed by SN_2 mechanism

$$\text{Rate of } SN_2 \propto \frac{1}{\text{Steric hindrance of RX}}$$

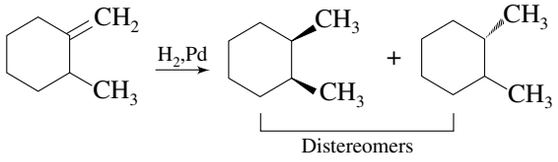
Rate of SN_2



9. [2]

Syn addition takes place so that meso isomer obtained as major product.

10. [2]



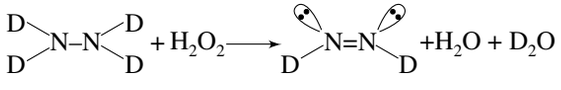
Distereomers

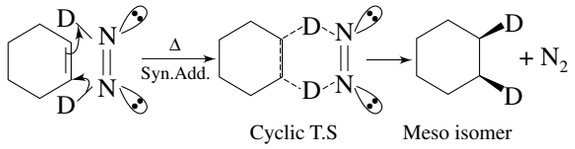
11. [1]

12. [2]

Since intermediate is radical which is planner so $Br^{\bullet}$ radical attacks from both side.

13. [2]

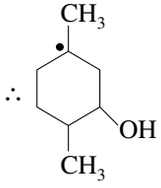




Cyclic T.S Meso isomer

14. [1]

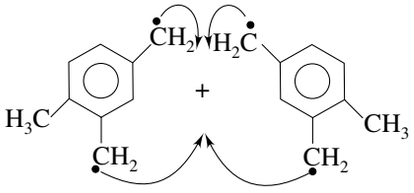
→ $B\dot{r}$ ∴ abstract that hydrogen which forms stable free-radical

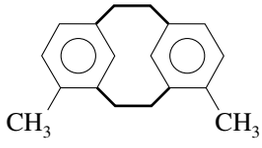


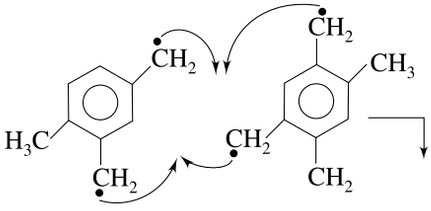
∴ (3° free-radical) is most stable

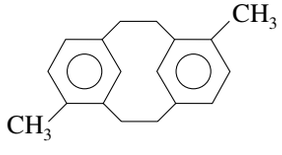
15. [4]

Wurtz reaction:

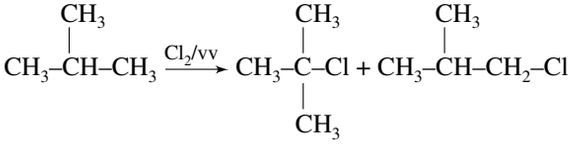








16. [2]



$1^{\bullet}_{H} = 9$

$2^{\bullet}_{H} = 1$

t-butyl chloride (36%) Isobutyl chloride (64%)

Let relative reactivity of $1^{\bullet}_{H}$ and $3^{\bullet}_{H}$ is n_1 and n_2

Contribution of 1° halide = $9 \times n_1$

Contribution of 3° halide = $1 \times n_2$

$$\% \text{ of } 1° \text{ halide} = \frac{9n_1}{9n_1 + n_2} = 64 \quad ...(1)$$

$$\% \text{ of } 3° \text{ halide} = \frac{n_2}{9n_1 + n_2} = 36 \quad ...(2)$$

Divide equation (2) by equation (1)

$$\frac{36}{64} = \frac{n_2}{9n_1}$$

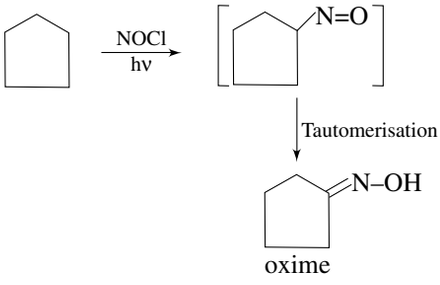
$$\because \quad \frac{n_2}{n_1} = \frac{9 \times 36}{64} = \frac{81}{16} = 5.1 : 1$$

17. [3]

Bu_3SnH is is specific reducing agent

The relative rates of abstraction of halogen by Bu_3Sn radical depend upon the halogen in the order I > Br > Cl > F.

18. [2]



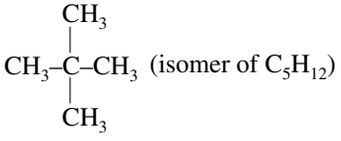
19. [1]

20. [1]

$H^{\bullet}$ radical is very less stable than $Cl^{\bullet}$

EXERCISE # 3

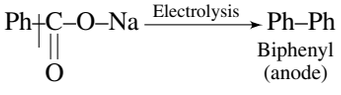
1. [1,2,4]



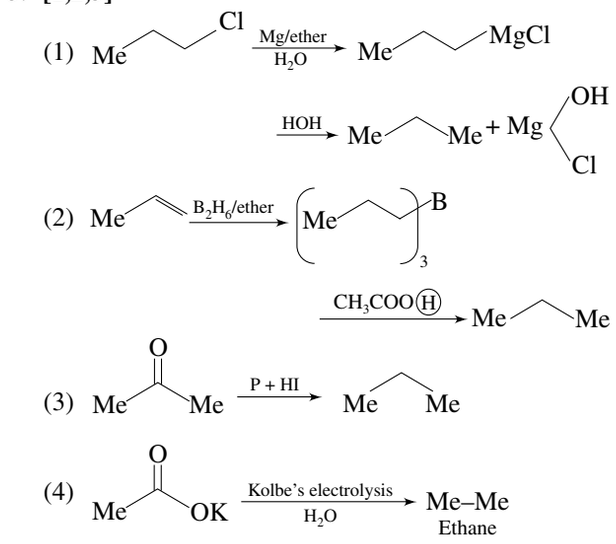
(isomer of C_5H_{12})

It is not prepared by hydrogenation of alkene

2. [1,2,4]



3. [1,2,3]



4. [1,2]

(1) No such new C–C bond is formed in decarboxylation.

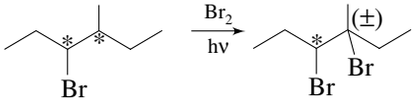
(2) It is not a β-keto acid, does not undergo decarboxylation on simple heating.

(3) It is a β-keto acid

(4) Like β-keto acid, it also forms a resonance stabilised carbanion.

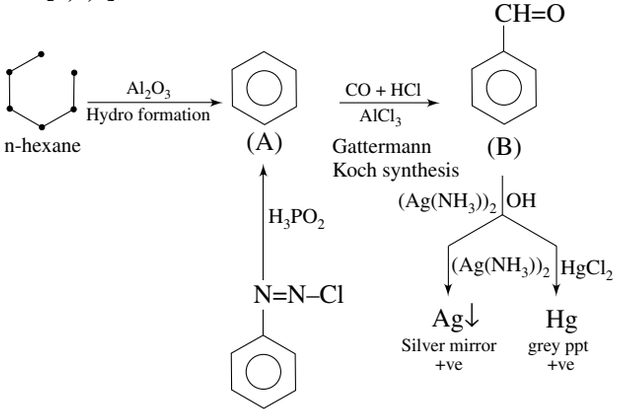
5. [2,3]

Reactant has two chiral carbons but reaction occur at only one chiral carbon leaving configuration at other chiral carbon intact.



The product also has two chiral carbons. If configuration at one chiral carbon in the above product in altered leaving configuration at other chiral carbon intact, diastereomers would result. Hence, the two products formed above the diastereomers and in equal amounts.

6. [1,3,4]



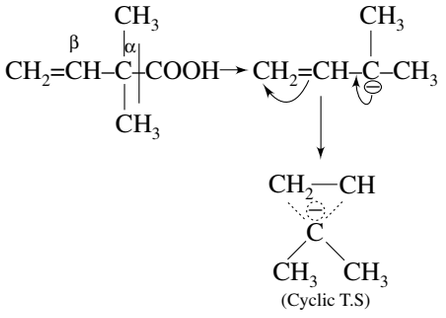
7. [1, 3]

Unsymmetrical alkane can't produced by wurtz reaction as single product.

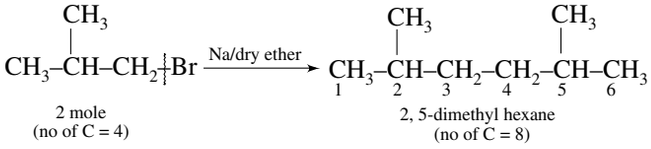
Both require reactions of two different alkyl halides. In such situation, multiple products (via self and cross coupling) are always formed.

8. [1]

Rate of decarboxylation ∝ stability of carboanion

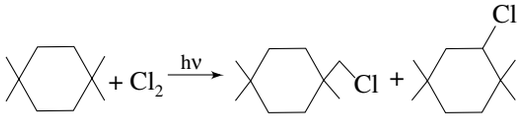


9. [1]



10. [3]

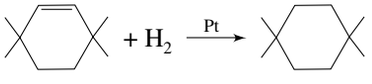
This compound gives only two monochlorination products as



All other gives more than two monochlorination products.

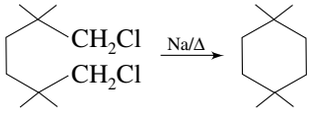
11. [1]

There is only one position available for double bond in X.



12. [4]

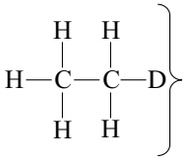
All of the above reaction are Wurtz Coupling reaction. Only reaction (4) can give the expected product as



13. [3]

Since, C—D bond is slightly stronger than C—H bond, hence transition state leading to C—D bond has greater maximum height than the same of C—H bond.

14. [4]



Let x and y be the reactivity of C—D and C—H bonds in chlorination reaction

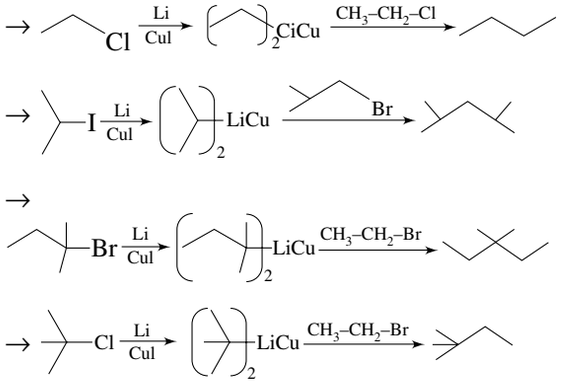
x = 7 and 5y = 93, i.e., y = 93/5 = 18.6

$$\frac{y}{x} = \frac{18.6}{7} = 2.7$$

15. [1]

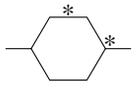
In methane, product is closer to transition state and there is very small difference in potential energies between reactant and product for the rate determining step. Hence, change of C—H by C—D bond will have greater effect on rate here. In ethane, product is much more stable, rate will not be as much affected by change of C—H to C—D bond.

16. [1]

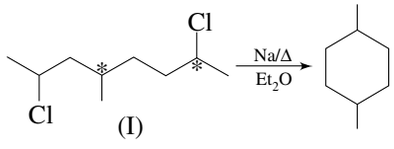


17. [7]

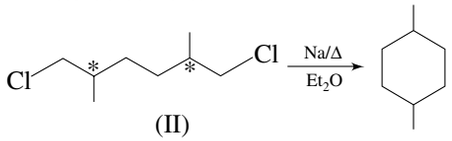
In 1-4-dimethyl cyclohexane, the following indicated bonds can be formed in the given reaction condition



Therefore, following dichlorides can be used for this purpose



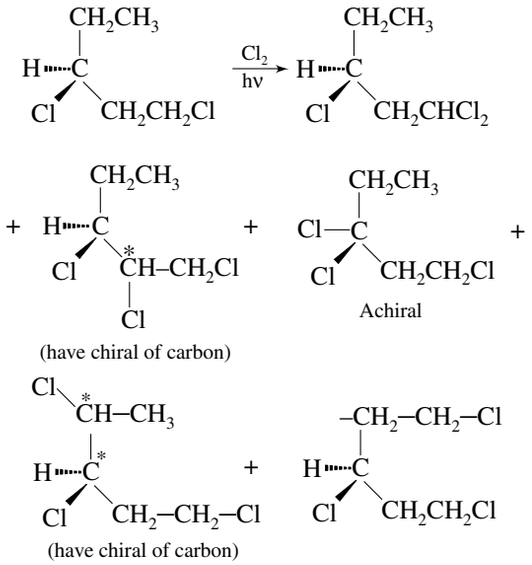
(I) has two chiral carbons, hence it has four stereoisomers.



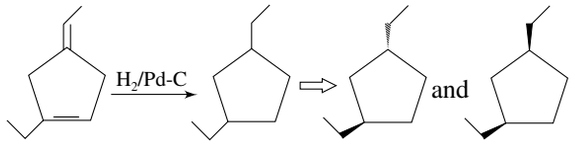
(II)

(II) Also has two chiral carbons but there are only three stereoismers as one of them is meso.

18. [7]

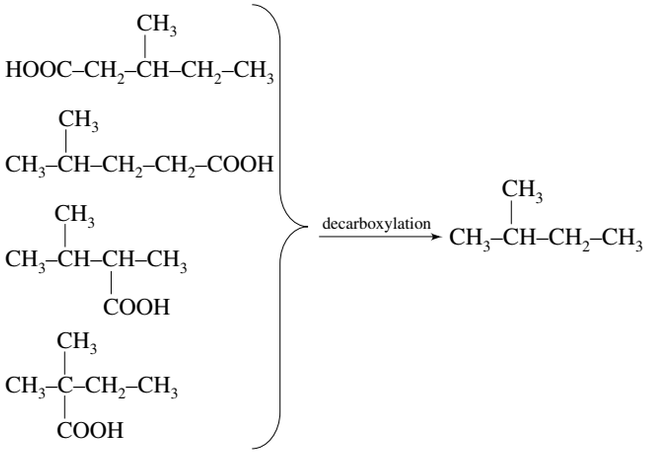


19. [2]



No of stereoisomer = 2

20. [4]



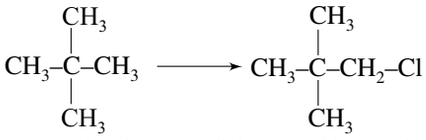
Type of H = 4

Thus 4 type of acid are used to obtained is pentane

EXERCISE #4

1. [2]

No of monochloro product = Type of H

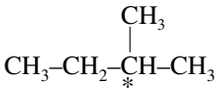


(type of H = 1) Only mono chloro product

2. [2]

3. [2]

For optical octivity, molecule must have is chiral, thus

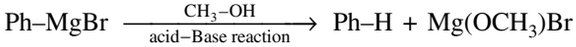


(chiral carbon present)

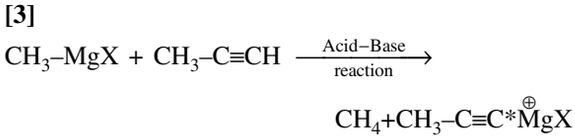
So it is optically active

4. [4]

5. [1]



6. [3]



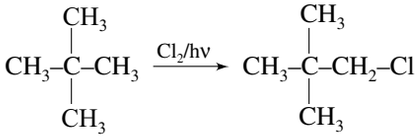
7. [1]

$C_nH_{2n+2} = 72$

$12n + 2n + 2 = 72$

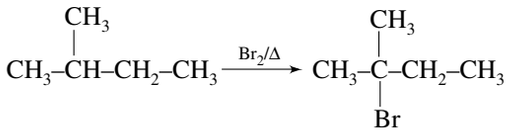
$n = 5$

$\because$ M.F = C_5H_{12}



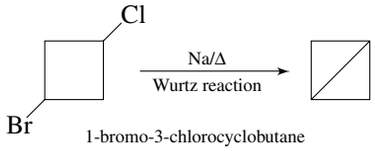
Neo pentane Single monochloro product

8. [4]



2-bromo-2-methyl butane

9. [4]

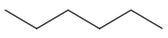


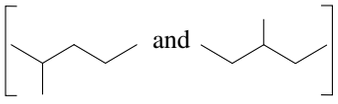
1-bromo-3-chlorocyclobutane

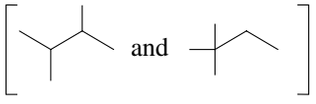
10. [2]

This problem is based on boiling point of isomeric alkanes.

As we know more the branching in an alkane, lesser will be its surface area and lesser will be the boiling point.

(III) 

(II) 

(I) 

One moving left to right (III to I)

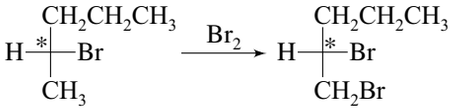
- branching increase
- surface area decreases
- boiling point decreases

Hence the correct choice is (2)

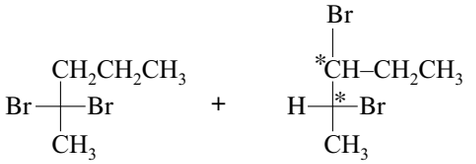
11. [5]

Given compound undergoes free-radical bromination under given conditions, replacing H by Br.

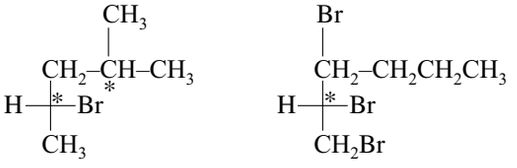
C* is chiral carbon.



I. Chiral

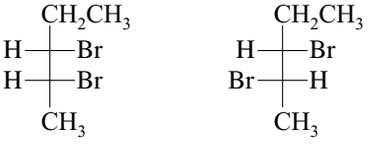


(II) Achiral (III) Chiral



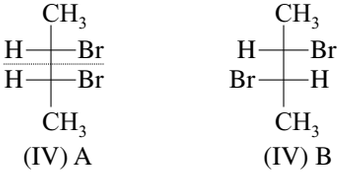
IV V. Chiral

(III) has two chiral centres and can have two structures.



(III) A (III) B

(IV) has also two chiral centres and can have two structures.



(IV) A (IV) B

It has plane of symmetry thus, achiral. Thus, chiral compounds are five. I, III A, III B, IV B and V.

CHAPTER 5

Aliphatic Hydrocarbons (Alkenes)

INTRODUCTION

- Alkenes are the acyclic hydrocarbons in which the unsaturation is double bond between carbon atoms (C=C)
- Alkenes are also known as olefins (i.e., oleum, oil + fines, forming) because lower alkene react with halogens to form dihalides which are oily substance.
- General formula of alkenes is C_nH_{2n} (n = 2, 3, 4, 5, ...).
- Hybridisation of unsaturated carbon is sp^2.
- Bond angle of sp^2 carbon is 120° and geometry is trigonal planar.
- Nature of bonding

Bond	Bond length	Bond energy
C=C	1.34 Å	142 kcal/mole
=C–H	1.10 Å	106 kcal/mole

- The following table gives the types of isomerism alkenes show with the minimum number of carbon required for that isomerism.

Isomerism	Minimum number carbon
Chain isomerism	4
Position isomerism	4
Functional isomerism	3
Ring chain isomerism	3
Geometrical isomers	4
Optical isomerism	6

- Cumulated polyene having even number of double bonds that has $=C\begin{matrix}a\\b\end{matrix}$ system at both ends can exhibit optical isomerism but cannot exhibit geometrical isomerism.
- Cumulated polyene having odd number double bonds that has $=C\begin{matrix}a\\b\end{matrix}$ system at both ends can exhibit geometrical isomerism but cannot exhibit optical isomerism

PHYSICAL PROPERTIES

- Alkenes are colourless and odourless.
- Alkenes are insoluble in water and soluble in organic solvents.
- Physical state:

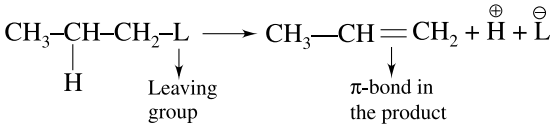
  C_2–C_4 ⟶ gaseous

  C_5–C_{15} ⟶ liquid

  C_{16} and above ⟶ solid like wax
- Boiling point and Melting point ∝ Molecular weight
- B.P. and M.P. decrease with increase in branches in alkene
- Melting points of *cis* isomers are lower than *trans* isomers, because *cis* isomer is less symmetrical than *trans*, and therefore *trans* isomer packs more tightly in the crystal lattice and hence have a higher melting point.
- Boiling points of *cis* isomers are higher than *trans* isomers because *cis*-alkenes has greater polarity (Dipole moment) than trans one.
- Alkenes are lighter than water.

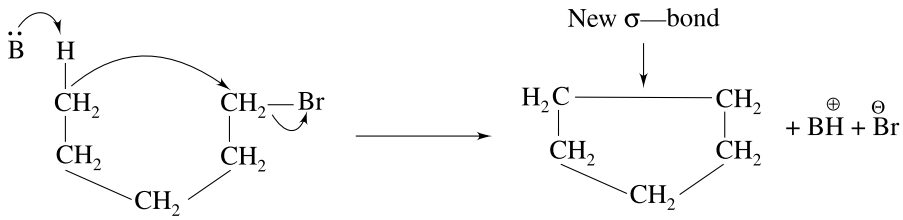
ELIMINATION REACTIONS

The most common type of elimination reaction is one in which two fragments are removed from a substrate to produce a modified substrate and two small units. One of these fragments is usually the leaving group of the substrate. Elimination usually produces a new pi-bond in the modified substrate (1).



...(1)

In some elimination reactions (but very uncommon) a new sigma-bond is produced instead of a pi-bond.

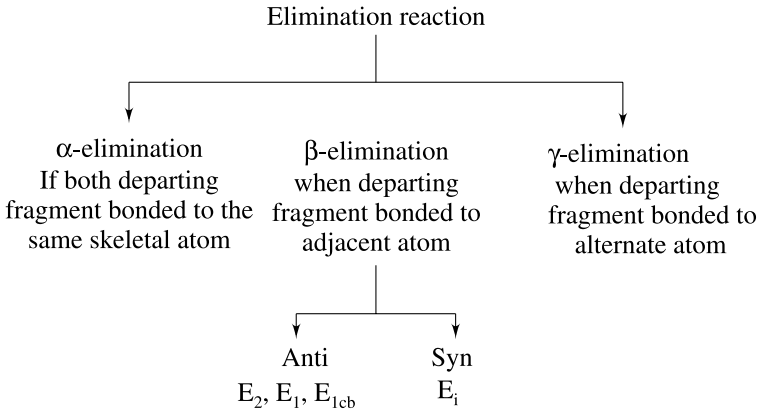


...(2)

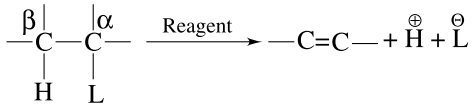
Elimination reactions occur when the compounds have nucleophilic group as a leaving group. The leaving groups responsible for elimination reaction are:

Leaving groups are X, OH, OR, $\overset{\oplus}{N}_2$, N_3, $H_2\overset{\oplus}{O}$, $\overset{\oplus}{N}R_3$ and $\overset{\oplus}{S}R_2$

Classification of elimination reaction:

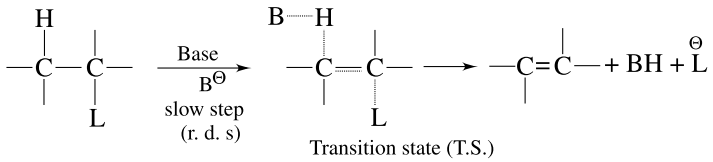


β elimination: Such elimination reaction is which removal of one fragment (leaving group) from α. Carbon & other fragment (mostly H-atom) from β Carbon is known as β-elimination reaction

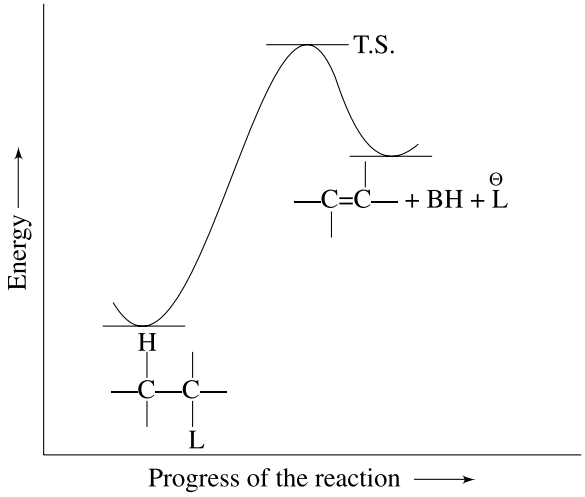


Types of β-elimination

(i) **E_2 (bi molecular elimination reaction)**



Energy Profile

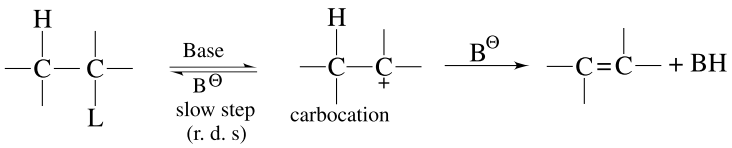


Important Points

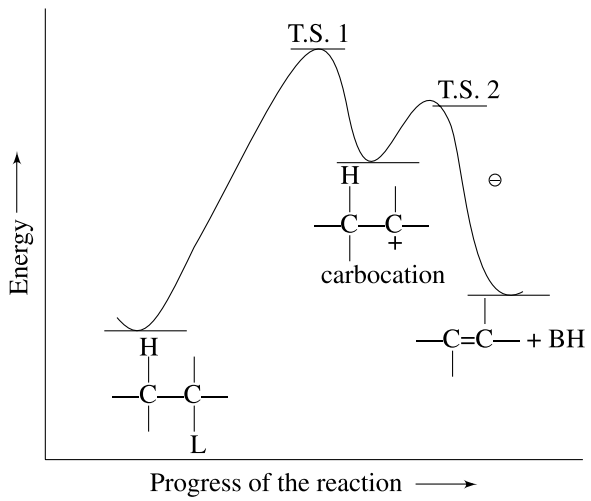
1. One-step reaction
2. No intermediate forms, product formation taking place by formation of TS
3. Strong base needed to remove hydrogen as proton from β carbon
4. Follows the second order kinetics: Rate = K [Substrate] [base]

5. In most of cases major product is Saytzeff and in few cases the major product is Hofmann
6. Stereospecific and stereoselective
7. Reactivity order 3° > 2° > 1°
8. Branching at α and β-carbons and the presence of electron-withdrawing group on the carbon increases the rate of reaction
9. In a polar solvent the rate decreases
10. With increasing concentration and basicity of the added base, the rate increases
11. As the temperature increases, the rate increases
12. E_2 reactions compete with SN_2 reactions

E_1 (Unimolecular elimination reaction)



Energy Profile

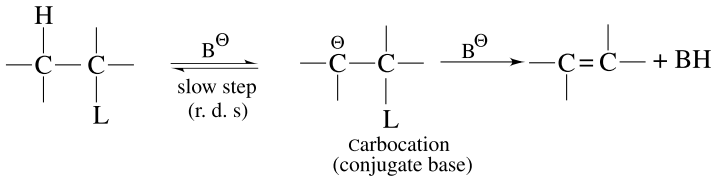


Important Points:

1. Two-step reaction
2. Carbocation as reaction intermediate
3. In the second step the hydrogen leaves as proton from the carbocation
4. Weak base is needed in second step to remove hydrogen as proton
5. Follows the first order kinetics: Rate = K [Substrate]
6. Major product of the reaction is Saytzeff product
7. Non-stereospecific and non-stereoselective
8. Reactivity order 3° > 2° > 1°
9. Any structural feature that stabilises the carbocation will increase the rate; thus, branching at α and β-carbons increases the rate
10. Polar protic solvents increase rate
11. The concentration and the basicity of the solvent have no effect on the rate
12. As the temperature increases, the rate increases
13. E_1 reactions compete with SN_1 reactions

E1cb (Unimolecular elimination reaction with respect to conjugate base)

Elcb mechanism is limited to substrates that can stabilise the carbanion intermediate, i.e., β-carbon should contain carbonyl, nitro, cyano, sulphonyl, or other carbanion stabilising group.



Important Points:

1. Two-step reaction
2. Carbanion as reaction intermediate
3. The leaving group leaves the carbanion either as an anion or as a neutral group
4. Strong base is needed to remove hydrogen as proton in the first step
5. Follows the second order kinetics: Rate = K [Substrate] [Base]
6. Major product of reaction obtain by Hofmann elimination
7. Non-stereospecific and non-stereoselective
8. Reactivity order 3° > 2° > 1°
9. Any structural feature that stabilises the intermediate carbanion will increase the rate; presence of an α-aryl group shifts a β-elimination toward Elcb pathway
10. Polar aprotic solvent increases the rate
11. With increasing concentration and basicity of the added base, the rate increases
12. As the temperature increases, the rate increases

Direction of Elimination

- When all β-hydrogens are not equal, more than one type of alkenes is formed.
- Elimination, in which the most substituted alkene is the major product, is known as Saytzeff elimination and the rule is known as **Saytzeff rule**.
- Elimination, in which the least substituted alkene is the major product, is known as Hofmann elimination and the rule is known as **Hofmann rule**.

Hofmann elimination reaction takes place in the following four cases.

(i) When the base is bulky
(ii) When the leaving group is a poor leaving group, such as F, $\overset{\oplus}{N}R_3$ and $\overset{\oplus}{S}R_2$
(iii) When the alkyl halide contains one or more double bonds at β-carbon
(iv) Steric hindrance at γ-carbon

Trick - In terms of β-hydrogen, saytzeff rule **Poorer became poorer**

Stereochemistry of Elimination Reaction:

Optically active substrates, in which α and β carbons are chiral, give stereoselective as well as stereospecific products. Geometry of alkene depends on the configuration of the substrate, as described in the following section.

Stereochemistry of elimination can be remember by the following two words:

(I) CAR where
C means *cis* (or *Z*) alkene
A means *anti* elimination
R means racemic mixture (or threo form)
(i) Erythro form (or meso form) gives *E* or *trans* alkene, upon *anti* eliminations
(ii) Threo form (or d or *l* form) gives *Z* or *cis* alkene, upon *anti* eliminations

(II) CSM where

C means *cis* alkene

S means *syn* elimination

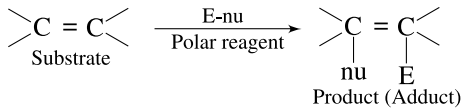
M means meso form (or erythro form)

(i) Erythro form (or meso form) gives *Z* or *cis* alkene, upon *syn* elimination

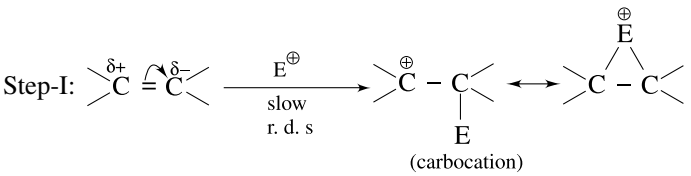
(ii) Threo form (or *d* or *l* form) gives E or *trans* alkene, upon *syn* elimination

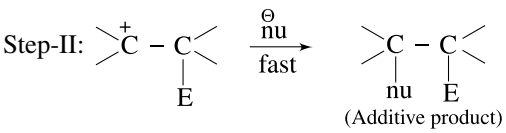
ELECTROPHILIC ADDITION REACTION TO CARBON–CARBON DOUBLE BOND:

- To introduce the mechanism of electrophilic addition, let us consider the following general reaction.



Mechanism





Important Points

- It is a two-step process
- Breaking of π-bond of carbon–carbon double bond is achieved by electrophile (E^+) in slow step; so it is known as electrophilic addition reaction (E.A.R)
- Intermediate is carbocation so re-arrangement, ring expansion, etc., takes place
- Rate law:

$$\frac{dx}{dt} = k[\text{Alkene}][E^+]$$

- It is a second order reaction
- Rate of E.A.R ∝ stability of carbocation
- It is a stereospecific reaction
- Major product given by Markovnikov's rule

Markovnikov's rule

Markovnikov's rule can be used in those alkenes which fulfil the following conditions:

(i) Both alkene and reagent must be unsymmetrical

(ii) Substituent(s) present on doubly bonded carbon(s) should only be +I group(s)

(iii) If phenyl group is present on doubly bonded carbon, then both doubly bonded carbons should be substituted by phenyl group

This rule states that electrophilic part of an unsymmetrical reagent attaches itself to that double bonded carbon atom which has more number of hydrogen atoms and negative part goes to that doubly bonded carbon which bears less number of hydrogen atoms.

Or

In terms of hydrogen Markovnikov's rule is: '**Richer becomes richer**'

Advanced Markovnikov's Rule:

Formation of a more stable carbocation takes place by the addition of the electrophilic part of unsymmetrical reagent on unsymmetrical alkene.

Note:

(i) A reaction in which two or more constitutional isomers could be obtained as product but one of them predominates, is called a **regioselective reaction.** Thus, ionic addition of unsymmetrical reagents to unsymmetrical alkenes is a regioselective reaction.

(ii) It is important to remember that whenever a reaction leads to the formation of a carbocation you must check its structure for the possibility of rearrangement etc.

Stereochemistry of Addition Reactions

Stereochemistry of addition reaction depends upon two factors:

(i) Whether both electrophile and the nucleophile will join themselves of the two double bonded carbons from the same side (*syn* addition) of the double bond or from the opposite sides (*anti* addition).

(ii) The geometrical orientation of the two parts of the addendum $\overset{\oplus}{E}$ and $\overset{\oplus}{N}$ to each other.

Selection of stereoisomer

Profile 1: When both alkene and reagent are symmetrical

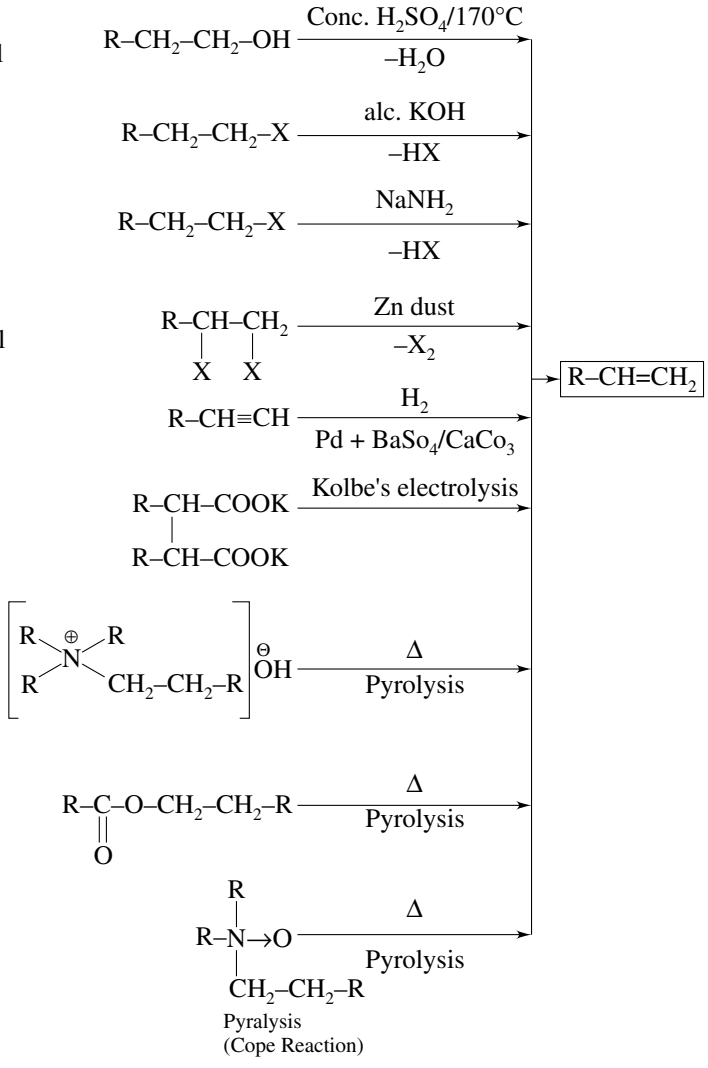
Alkene	Reagent	Major addition product
Cis	*Syn*	Meso
Cis	*Anti*	Racemic mix
Trans	*Syn*	Racemic mix
Trans	*Anti*	Meso

Profile 2: Either alkene or reagent or both unsymmetrical

Alkene	Reagent	Major addition product
Cis	*Syn*	Erythro
Cis	*Anti*	Threo
Trans	*Syn*	Threo
Trans	*Anti*	Erythro

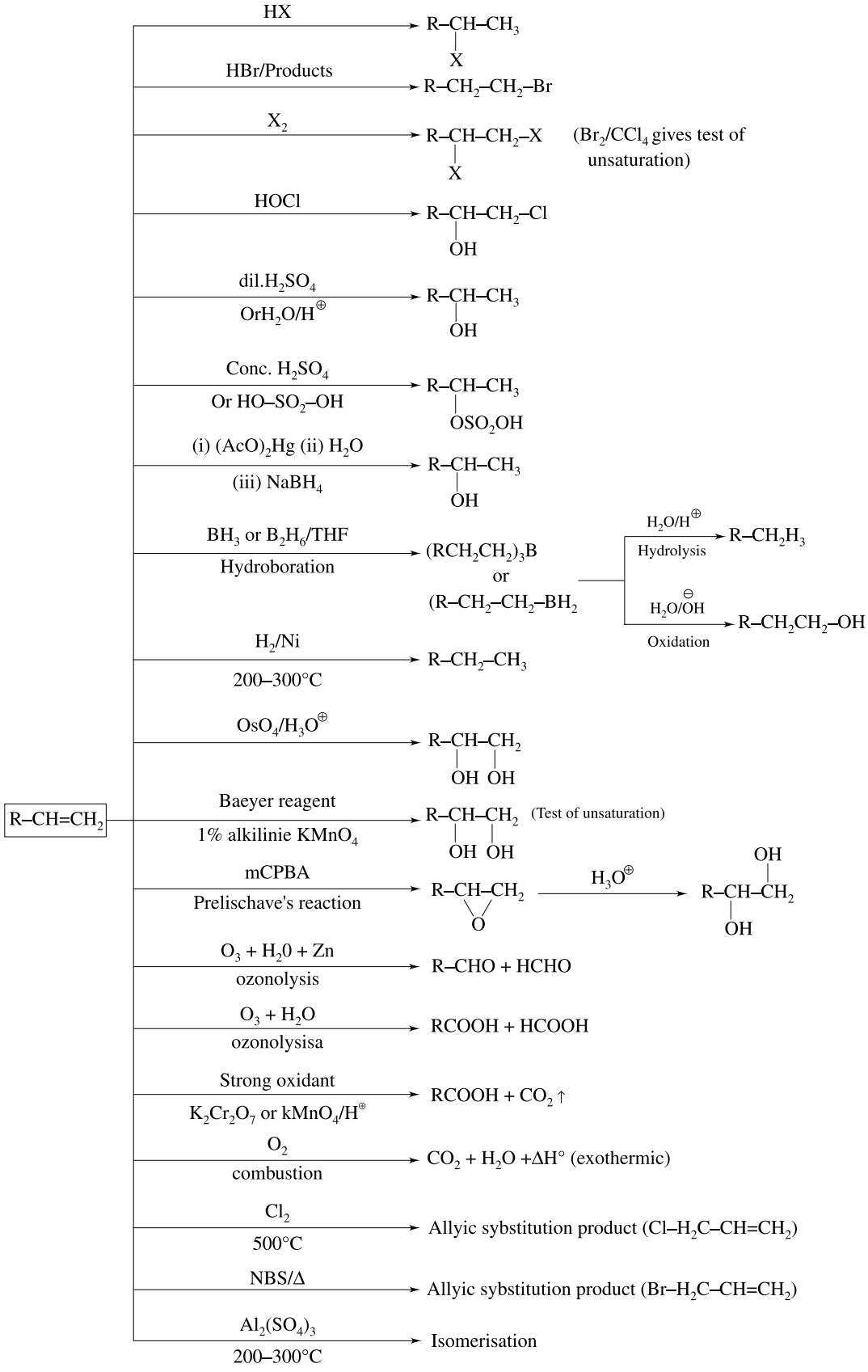
Note: From left to right → Major addition product

From right to left → Major β-elimination product



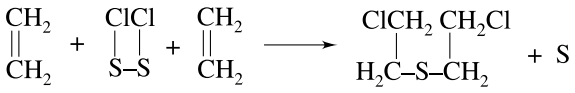
METHOD OF PREPARATION

CHEMICAL PROPERTIES OF ALKENES

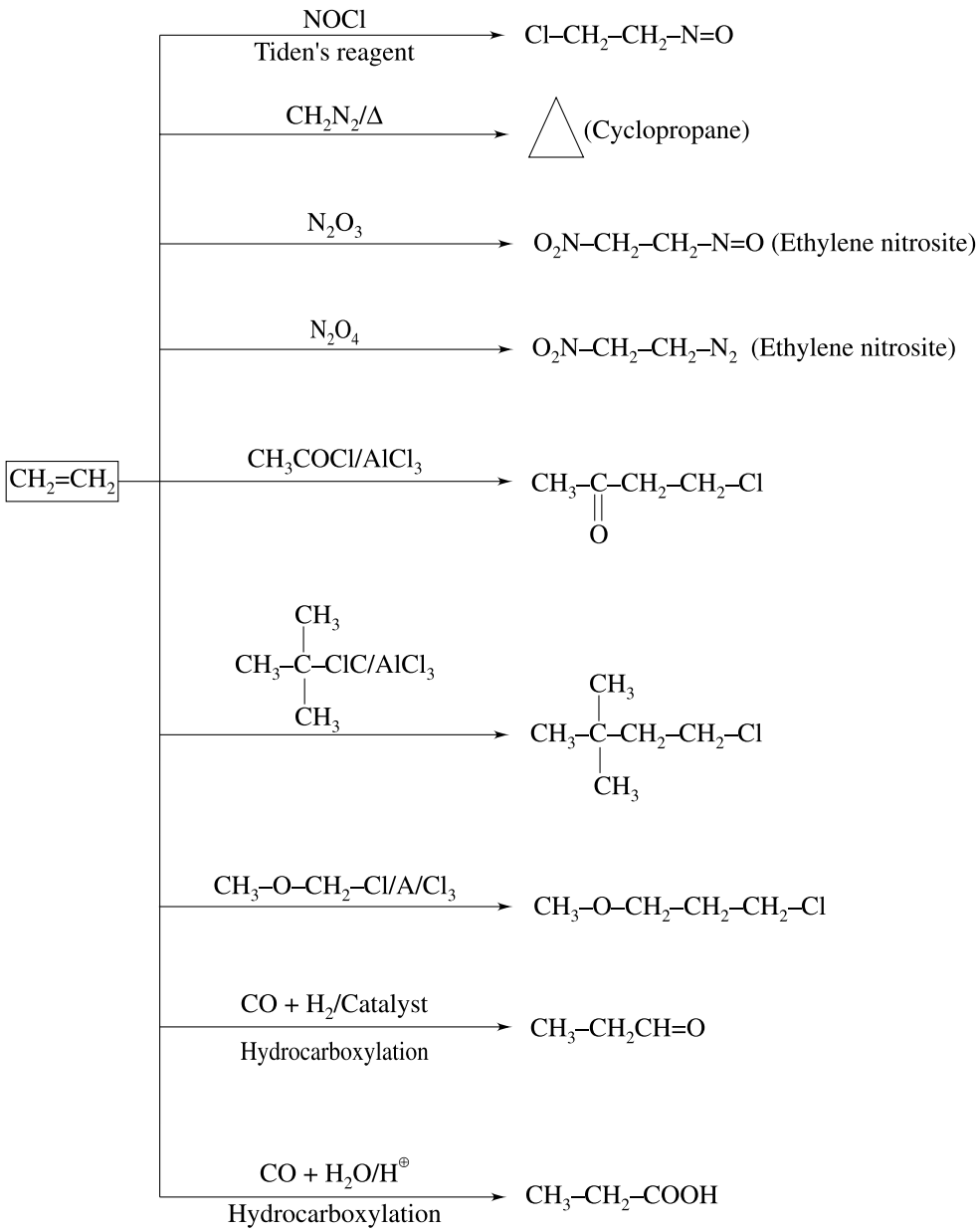


SPECIAL POINTS:

- Ethene is used in the artificial ripening of fruits
- Water solution of sodium or potassium salt of succinic acid on electrolysis gives ethane at anode
- Ethene reacts with sulphur monochloride (S_2Cl_2) to form poisonous mustard gas (β, β-dichloro diethyl sulphide), gas is used a war gas (Used in the World War I)

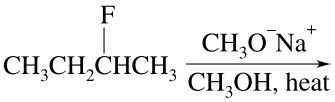


- Some other reactions of ethene are:



SOLVED EXAMPLE

1. In the reaction



the major product formed is

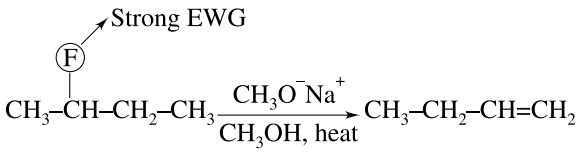
(1) $CH_3CH_2CH(OCH_3)CH_3$

(2) $CH_3CH{=}CHCH_3$

(3) $CH_3CH_2CH{=}CH_2$

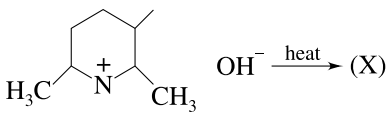
(4) $CH_3CH_2CH_2OCH_3$

Sol. **[3]**

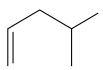


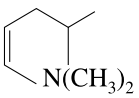
→ It is E_1cb reaction thus major product obtained by Hoffmann elimination hence1-butene (major)

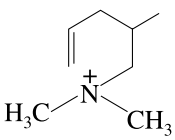
2. In the reaction



the organic product (X) is

(1) 

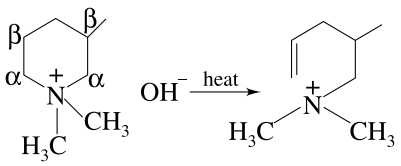
(2) 

(3) 

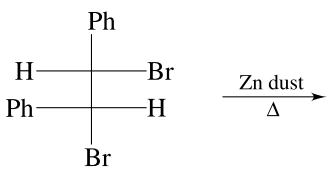
(4) 

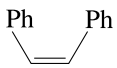
Sol. **[3]**

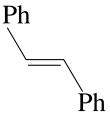
Pyrolysis of Quaternary ammonium hydroxide takes place according to Hoffman rule.



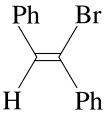
Hoffmann elimination

3. 

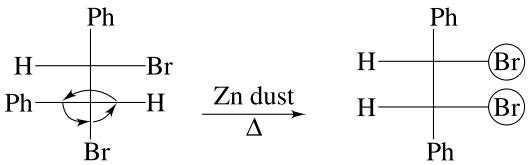
(1) 

(2) 

(3) 

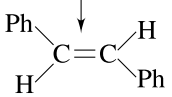
(4) 

Sol. **[2]**



Meso form

Anti elimination Zn/dust

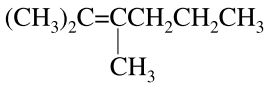


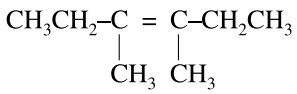
Concept form *Trans* form

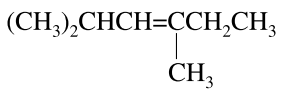
Meso upon *anti* elimination gives *trans* isomer as the major product (refer key concept).

4. A hydrocarbon C_8H_{16} on oxidation with a hot acidified solution of $KMnO_4$ forms 2-butanone and isobutyric acid. The hydrocarbon is

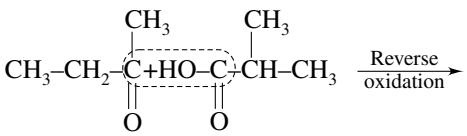
(1) $(CH_3)_2C{=}C(CH_2CH_3)_2$

(2) 

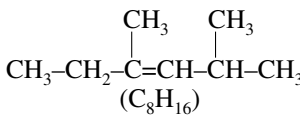
(3) 

(4) 

Sol. **[4]**



2-butanone reverse iso butyric acid



5. An unsaturated hydrocarbon on reductive ozonolysis gives two molecules of propanedial $[CH_2(CHO)_2]$ and no other carbon compound. The hydrocarbon is

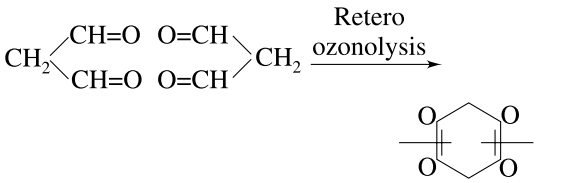
(1) hexa-2,4-diene

(2) cyclohexa-1,3-diene

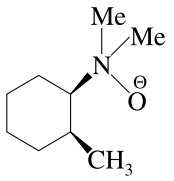
(3) cyclohexa-1-4-diene

(4) 1,2-dimethylcyclobutene

Sol. **[3]**



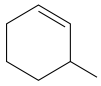
Cyclohexa-1,4-diene

6. 

$\xrightarrow{\Delta}$ Major product

(1) 

(2) 

(3) 

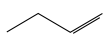
(4) None of these

Sol. **[3]**

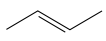
It's Cope reaction. Hoffmann elimination takes place.

7. $\begin{matrix}CH_3–CH–CO_2K\\ |\\ CH_3–CH–CO_2K\end{matrix} \xrightarrow{\text{Electrolysis}}$ A (Major)

Major product (A) of the above reaction

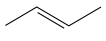
(1) 

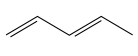
(2) 

(3) 

(4) 

Sol. **[3]**

 (trans will be major) by Kolbe electrolysis

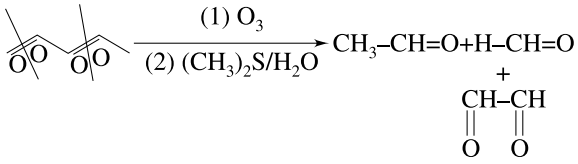
8.  $\xrightarrow[(2)\ (CH_3)_2S/H_2O]{(1)\ O_3}$

Which of the following is not formed in the above reaction?

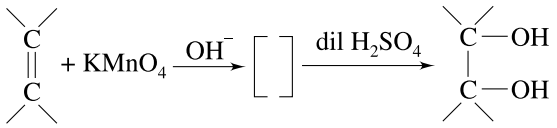
(1) HCHO (2) CH_3CHO

(3) Glyoxal (4) CH_3CH_2CHO

Sol. **[4]**



9. In the oxidation of alkenes with a dilute $KMnO_4$ solution followed by acidification with dilute H_2SO_4 to give diol

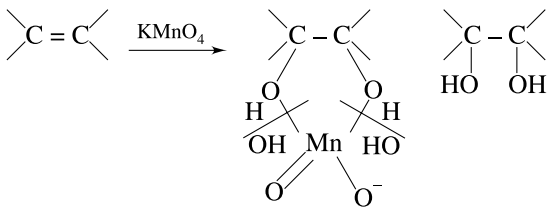


The OH group comes from

(1) NaOH (2) H_2O

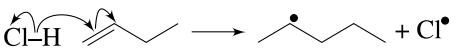
(3) $KMnO_4$ (4) H_2SO_4

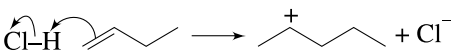
Sol. **[3]**

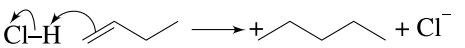


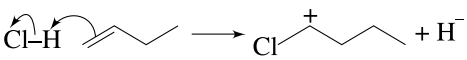
This mechanism indicates that OH group came from $KMnO_4$.

10. Which of the following most accurately describes the first step in the reaction of hydrogen chloride with 1-butene?

(1) 

(2) 

(3) 

(4) 

Sol. **[2]**

Attack on alkene by H–Cl takes place in such a way that most stable carbocation is formed as reaction intermediate.

11. In the addition reaction

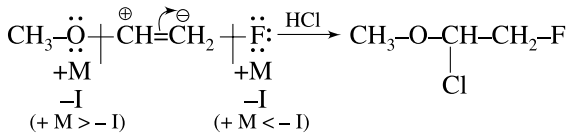
$CH_3OCH = CHF + HCl \longrightarrow$

the major product obtained is

(1) CH_3OCH_2CHClF (2) $CH_3OCH(Cl)CH_2F$

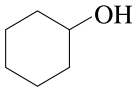
(3) $ClCH = CHF$ (4) $CH_2–\overset{+}{O}(H)–CH=CHFCl^-$

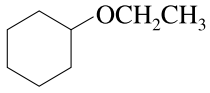
Sol. **[2]**

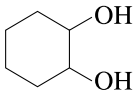


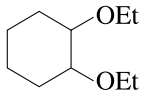
12.  $\xrightarrow[(2)\ NaBH_4,\ HO^-]{(1)\ (CF_3CO_2)_2Hg,\ CH_3CH_2OH}$ (P) (100%) ; product (P) is

Cyclohexene

(1) 

(2) 

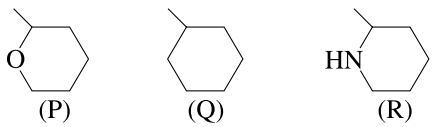
(3) 

(4) 

Sol. **[2]**

Alkoxymercuration–De-mercuration reaction according to Markownikoff rule.

13. Rank the following in the increasing order of rate of reaction with HBr.

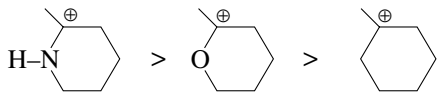


(1) R > P > Q (2) R > Q > P

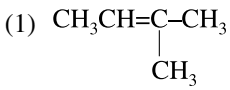
(3) P > R > S (4) P > S > R

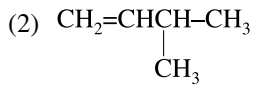
Sol. **[1]**

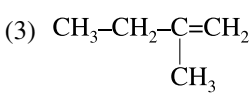
Formation of carbocation is the rate determining step. Thus Rate of E.A.R. ∝ Stability of carbocation

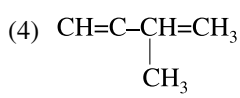


14. A hydrocarbon reacts with HI to give (X) which on reacting with aqueous KOH forms (Y). Oxidation of (Y) gives 3-methyl-2-butanone. The hydrocarbon is

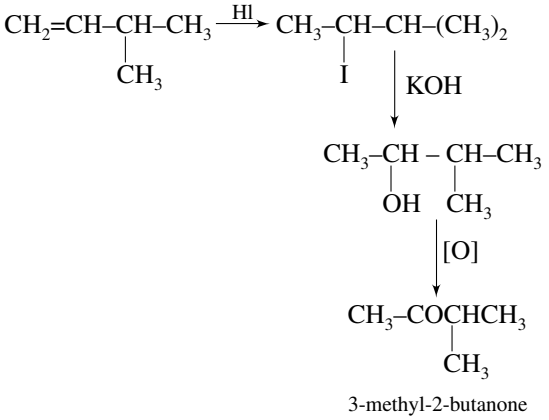
(1) 

(2) 

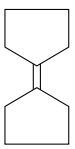
(3) 

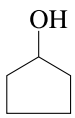
(4) 

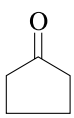
Sol. **[2]**



3-methyl-2-butanone

15.  $\xrightarrow{O_3}$ A $\xrightarrow[\text{or } LiAlH_4]{H_2/NI}$ B $\xrightarrow[\Delta]{H^+}$ C; product (C) of the reaction is

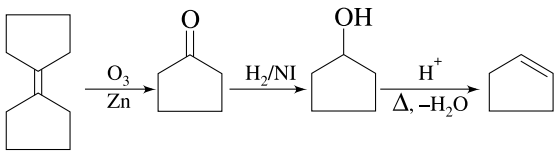
(1) 

(2) 

(3) 

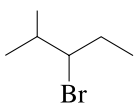
(4) 

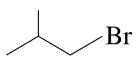
Sol. **[3]**

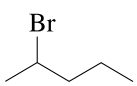


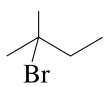
EXERCISE 1

1. Which alkyl bromide will yield only one alkene upon E_2 elimination?

(1) 

(2) 

(3) 

(4) 

2. Consider the following conversion

$C_6H_5CH_2CH_3 \xrightarrow{(P)}$ Product $\xrightarrow{(Q)} C_6H_5CH{=}CH_2$

Ethylbenzene Styrene

The reagents (P) and (Q) that should be employed are respectively

(1) $SOCl_2$ and H_2O

(2) SO_2Cl_2 and KOH/C_2H_5OH

(3) Cl_2, hv and H_2O|KOH

(4) $SOCl_2$ and KOH/C_2H_5OH

3. $CH_3CH_2Cl \xrightarrow[KOH]{alc.} [B] \xrightarrow{HCl} [C] \xrightarrow[KOH]{aq.} C_3H_8O$
[A] [D]

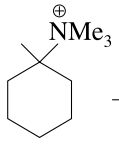
[A] will be

(1) 1-chloro propane

(2) 2-chloro propane

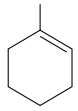
(3) Both of these

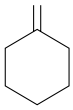
(4) None of these

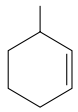
4. 

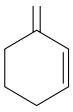
$\xrightarrow[\Delta]{HO^-}$ A (Major)

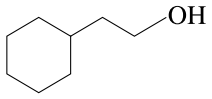
Major product is:

(1) 

(2) 

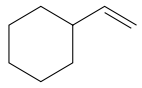
(3) 

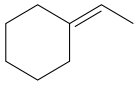
(4) 

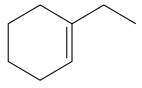
5. 

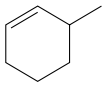
$\xrightarrow[\Delta]{H^+}$ A is the major product,

So A is:

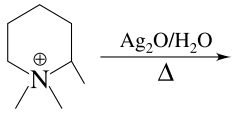
(1) 

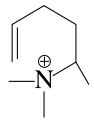
(2) 

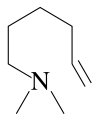
(3) 

(4) 

6. Which of the following is correct for the given reaction?



(1) Major product of reaction is 

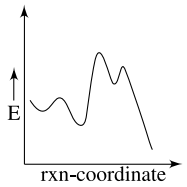
(2) Major product of reaction is 

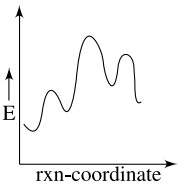
(3) Syatzeff alkene is the major product of the reaction

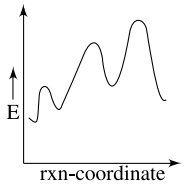
(4) Reaction is unimolecular

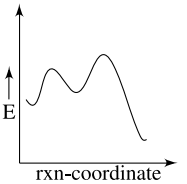
7. The energy profile of the given reaction

$CH_3–\underset{\underset{OH}{|}}{CH}–CH_3 \xrightarrow[\Delta]{H^\oplus} CH_3–CH=CH_2$

(1) 

(2) 

(3) 

(4) 

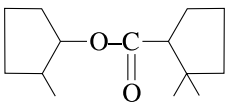
8. Which of the following will give the best yield of 2-pentene on reaction with C_2H_5ONa/C_2H_5OH?

(1) 2-Iodopentane

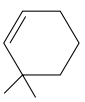
(2) 2-Bromopentane

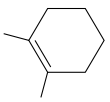
(3) 3-Iodopentane

(4) All equally satisfactorily

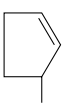
9. 

$\xrightarrow{\Delta}$ An alkene (major)

(1) 

(2) 

(3) 

(4) 

10. Consider the following reactions

$Ph_3P^+CH_3CH_2Br \longrightarrow A$

$A + C_2H_5ONa \longrightarrow B$

$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C = O + B \longrightarrow C$

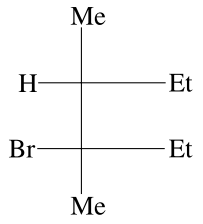
The final product is

(1) $Ph_3P^+CH_2CH_3Br^-$

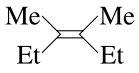
(2) $Ph_3P = CH - CH_3$

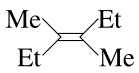
(3) $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C = CH - CH_3$

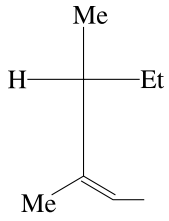
(4) $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH - CH = CH_2$

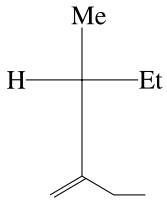
11. 

$\xrightarrow[\Delta]{\text{alc. KOH}}$ ma

(1) 

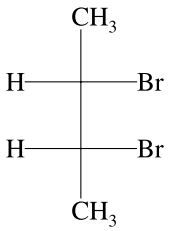
(2) 

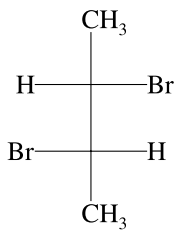
(3) 

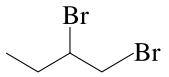
(4) 

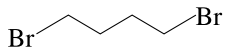
12. (p) $\xrightarrow{\text{Zn–dust}}$ 

Compound (p) is:

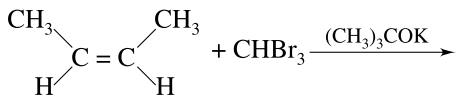
(1) 

(2) 

(3) 

(4) 

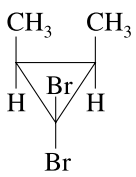
13. Consider the following reaction

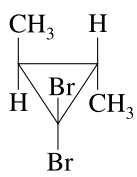


The product obtained in the reaction is

(1) $CH_3CH_2–CHCBr_3$ with CH_3 below CH

(2) $CH_3CHBr–CHCHBr_2$ with CH_3 below CH

(3) 

(4) 

14. Ethylene on reaction with Br_2 in methanol forms

(1) 1,2-dimethoxyethane

(2) 1-bromo-2-methoxyethane

(3) 1, 2-dibromoethane

(4) a mixture of (2) and (3)

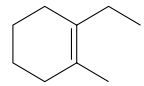
15. Cis-2, 3-Diphenyl-2-butene is allowed to react with H_2 in the presence of palladium catalyst. The major product will be

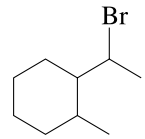
(1) meso-2, 3-diphenylbutane

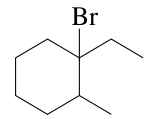
(2) (+)-2, 3-diphenylbutane

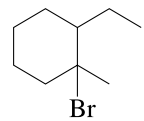
(3) (–)-2, 3-diphenylbutane

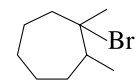
(4) (±)-2, 3-diphenylbutane

16.  $\xrightarrow{\text{HBr}}$ Major product. Major product is:

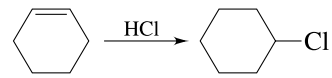
(1) 

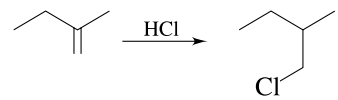
(2) 

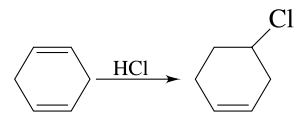
(3) 

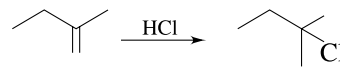
(4) 

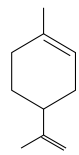
17. Which reaction will occur at the fastest rate?

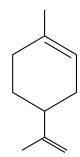
(1) 

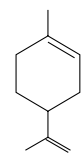
(2) 

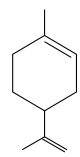
(3) 

(4) 

18.  $\xrightarrow[\text{(1 Mole)}]{H_2, Ni}$ Product–

(1) 

(2) 

(3) 

(4) No reaction

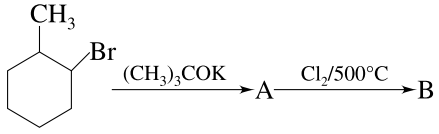
19. 3-Phenylpropene ($C_6H_5CH_2CH = CH_2$) when subjected to oxymercuration–demercuration process produces

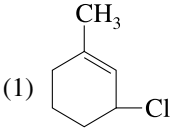
(1) $C_6H_5CH_2CHOCHCH_2OH$

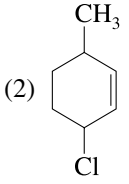
(2) $C_6H_5CH_2CH_2CH_2OH$

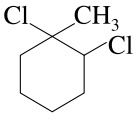
(3) $C_6H_5CHOHCH = CH_2$

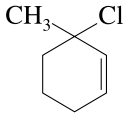
(4) $C_6H_5CH_2CHOHCH_3$

20. 

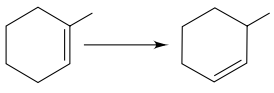
(1) 

(2) 

(3) 

(4) 

21. Which reagent is best to perform the following transformation?



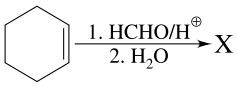
(1) HBr, NaOH, $\overset{\ominus}{C}OK^{\oplus}$

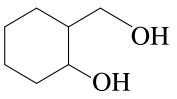
(2) HBr, R–O–O–R, hν, OH–(alc)

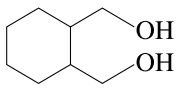
(3) BH_3.THF, NaOH – H_2O_2, ThO_2

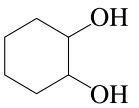
(4) Br_2, NaOH

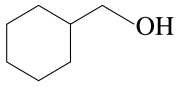
22. In the given reaction



(1) 

(2) 

(3) 

(4) 

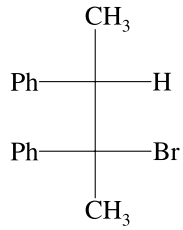
23. The major product in the reaction

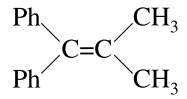
$CH_2 = CHCl + HOCl \longrightarrow$

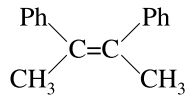
is

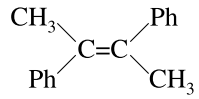
(1) $HOCH_2–CHCl_2$ (2) $CH_2Cl–CH(Cl)OH$

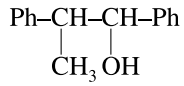
(3) CH_2ClCHO (4) $ClOCH_2–CH_2Cl$

24.  Major product of the reaction is:

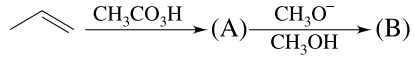
(1) 

(2) 

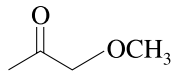
(3) 

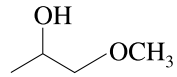
(4) 

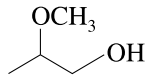
25. Consider the following sequence of reaction.

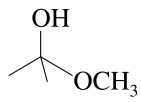


The product (B) is

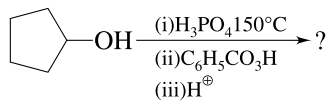
(1) 

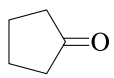
(2) 

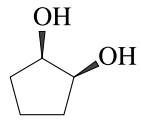
(3) 

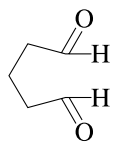
(4) 

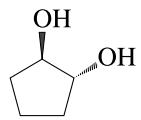
26. What will be the chief product from the following reaction sequence?

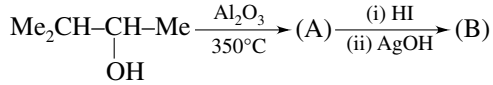


(1) 

(2) 

(3) 

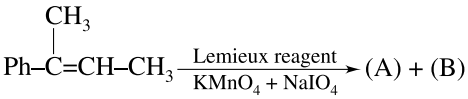
(4) 

27. 

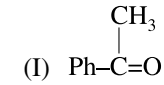
Product (B) of above reaction:

(1) $Me_2C(OH)CH_2Me$ (2) $Me_2CH–\underset{\underset{OH}{|}}{CH}–Me$

(3) $Me_2–\underset{\underset{OH}{|}}{CH}–CMe_3$ (4) $HO–CH_2–(CH_2)Me$

28. 

Which of the following compounds are (A) and (B) in this order?



(II) $CH_3CH=O$

(III) $CH_3–COOH$

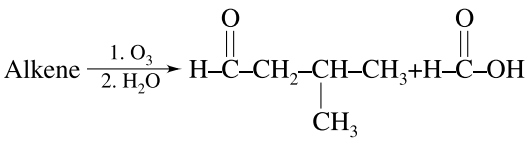
(V) CH_3CH_2OH

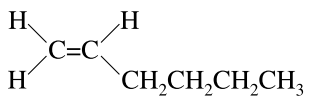
(VI) PhCOOH

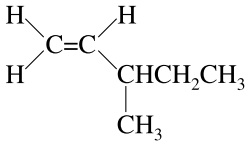
(1) I, II (2) I, III

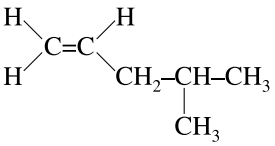
(3) III, VI (4) IV, V

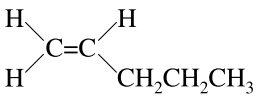
29. Which alkene will undergo the following reaction?



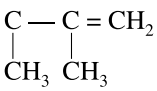
(1) 

(2) 

(3) 

(4) 

30. One mole of a hydrocarbon on ozonolysis yields one mole of glyoxal and two moles of formaldehyde. The hydrocarbon is

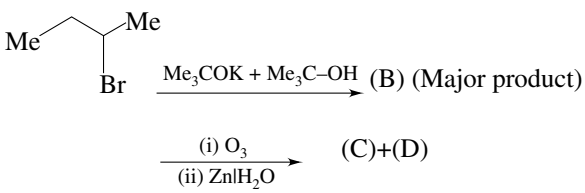
(1) 

(2) $CH_2 = CH - CH = CH_2$

(3) $CH_2 = CH - CH_2 - CH = CH_2$

(4) $CH_3CH = C = CH_2$

EXERCISE 2

1. 

The products (C) and (D) are:

(1) Methanal + Propanal

(2) Propanoic acid + CO_2

(3) 2 mol ethanoic acid

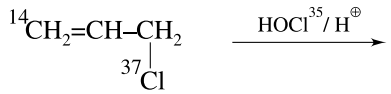
(4) 2 mol ethanal

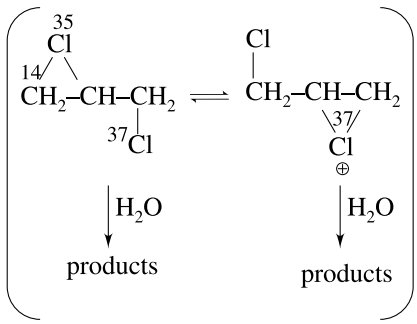
2. The racemic-2-3-dibromopentane on reaction with KI in acetone gives:

(1) *E*-Pent-2-ene (2) *Z*-Pent-2-ene

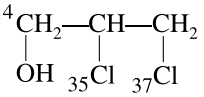
(3) Both (1) and (2) (4) None of these

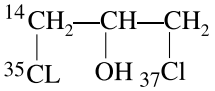
3. Observe the following reaction

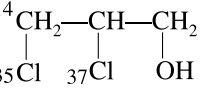


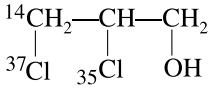


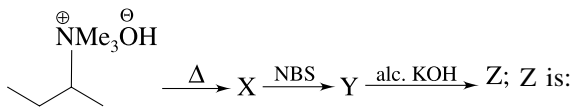
Which of the following cannot be the product?

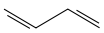
(1) 

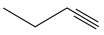
(2) 

(3) 

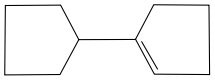
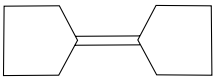
(4) 

4. 

(1)  (2) 

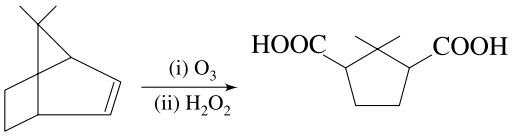
(3)  (4) 

5.  (A) $\xrightarrow{\text{Conc. } H_2SO_4}$ (B) Product (B) is:

(1)  (2) 

(3) Both (1) and (2) (4) None of these

6. Consider the following ozonolysis reaction



The correct statement about the above product formed is:

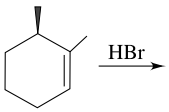
(1) it is a racemic mixture

(2) a pure enantiomer

(3) it is meso form of isomer

(4) it has a pseudochiral carbon

7. The products(s) of the following reaction can best be described as:

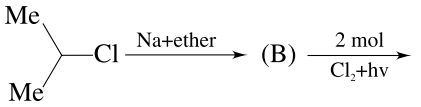


(1) A racemic mixture

(2) A single enantiomer

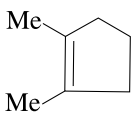
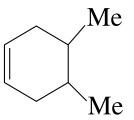
(3) A pair of diastereomers

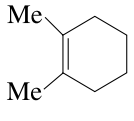
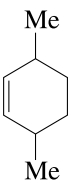
(4) An achiral molecule

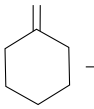
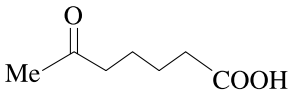
8.  (B) $\xrightarrow{2 \text{ mol } Cl_2+hv}$

(C) $\xrightarrow[\text{Alc. KOH}]{2 \text{ mol}}$ (D) $\xrightarrow[\Delta]{CH_2=CH_2}$ (E)

The final product (E) is:

(1)  (2) 

(3)  (4) 

9.  (A) $\longrightarrow$  (B)

The above conversion can be carried out by which process?

(1) **i.** HBr + Peroxide
ii. Me_3CO, Δ
iii. O_3/H_2O

(2) **i.** HBr
ii. C_2H_5O, Δ
iii. O_3/H_2O

(3) **i.** HI
ii. MeO, Δ
iii. O_3/Zn-acid

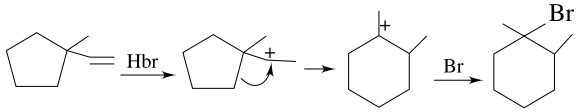
(4) **i.** HCl + Peroxide
ii. Aq. KOH
iii. O_3/Zn-H_2O

10.  $\xrightarrow[\text{1 mole}]{H_2/Hi}$ Major Product is:

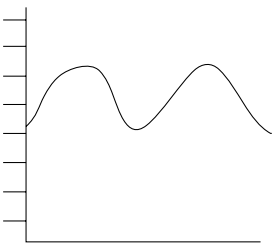
(1)  (2) 

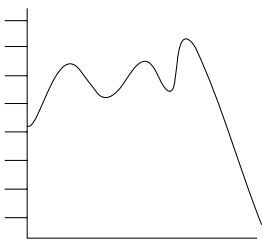
(3)  (4) 

11. Consider the following rearrangement reaction:

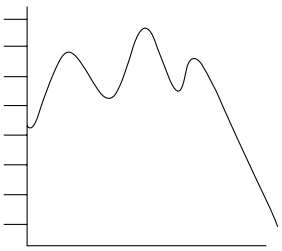


Which of the following reaction coordinates best represents the overall reaction? (Note: the units are arbitrary)

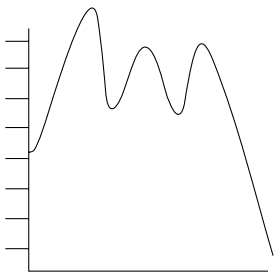
(1) 

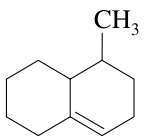
(2) 

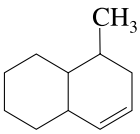
(3)

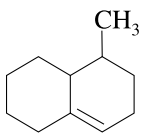


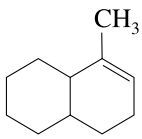
(4)

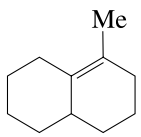


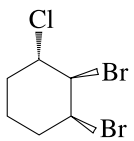
12.  $\xrightarrow[2.\ H_2O_2/OH^{\ominus}]{1.\ BH_3/THF}$ (A) 5 $\xrightarrow[\Delta]{H^{\oplus}}$ (B) The product (B) is:

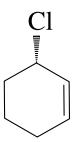
(1) 

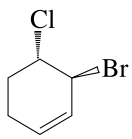
(2) 

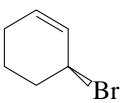
(3) 

(4) 

13.  $\xrightarrow{Zn,\ \Delta}$ Major product:

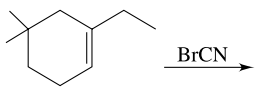
(1) 

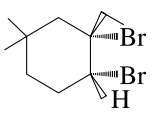
(2) 

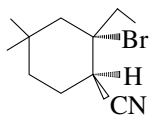
(3) 

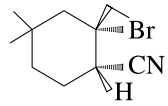
(4) None of these

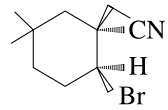
14. Give the major product of the following reaction

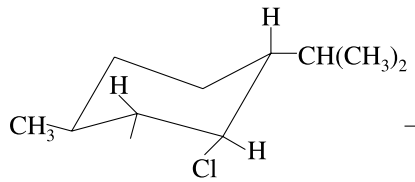


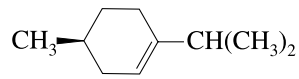
(1) 

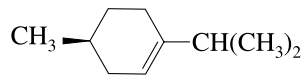
(2) 

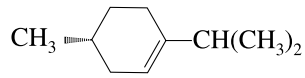
(3) 

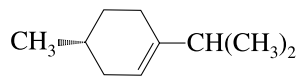
(4) 

15. 

(I) 

(II) 

(III) 

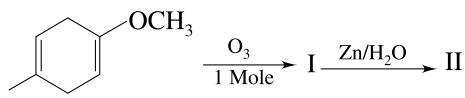
(IV) 

Correct code of Answer is

(1) A → I, B → II (2) A → I, B → III

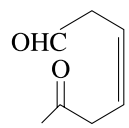
(3) A → III, B → IV (4) A → III, B → II

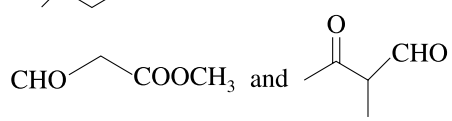
16. In the reaction

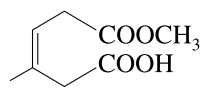


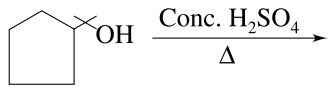
The final product (II) formed in major amount is

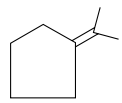
(1) 

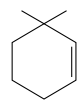
(2) 

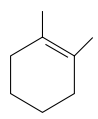
(3) 

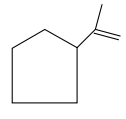
(4) 

17. 

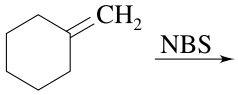
(1) 

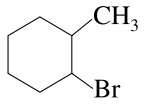
(2) 

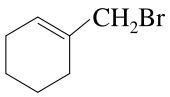
(3) 

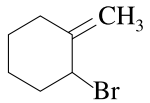
(4) 

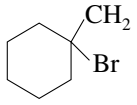
18. The major product formed in the following reaction is:



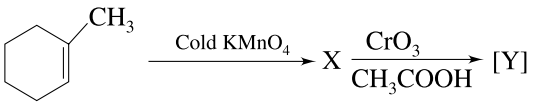
(1) 

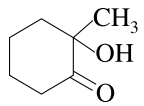
(2) 

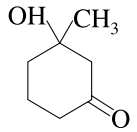
(3) 

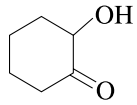
(4) 

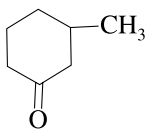
19. What is the compound 'Y' in the following sequence of reactions?

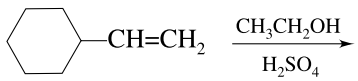


(1) 

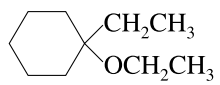
(2) 

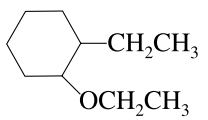
(3) 

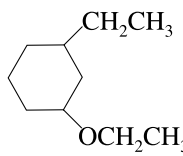
(4) 

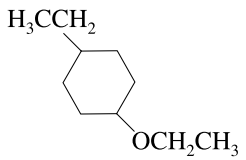
20. 

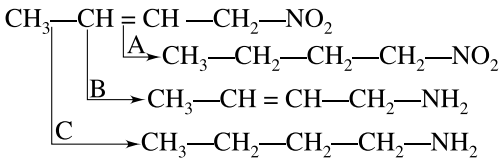
Identify the product

(1) 

(2) 

(3) 

(4) 

21. 

A, B and C are respectively–

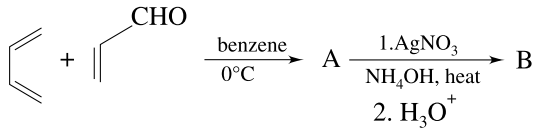
(1) A = Raney Ni, H_2, B = Sn/HCl, C = NH_2-NH_2, H_2O_2

(2) A = NH_2-NH_2, H_2O_2, B = Sn/HCl, C = Raney Ni, H_2

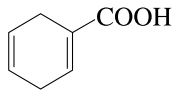
(3) A = Sn/HCl, B = Raney Ni, H_2 , C = NH_2-NH_2, H_2O_2

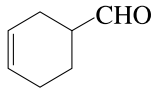
(4) A = NH_2-NH_2, H_2O_2, B = Raney Ni, C = Sn/HCl

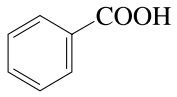
22. Consider the following sequence of reaction

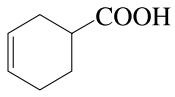


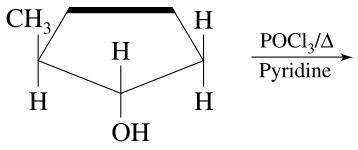
The structure of the end product (B) is:

(1) 

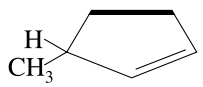
(2) 

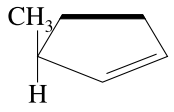
(3) 

(4) 

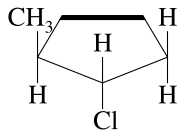
23. 

Major product of the reaction is:

(1) 

(2) 

(3) 

(4) 

24. In the reaction

Cis-CH_2=$CH(CH_2)_2CH$=CH–$COOCH_3$ + Br_2(1 mole) $\xrightarrow{CCl_4}$

The major product obtained is:

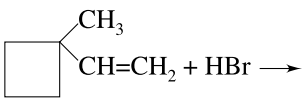
(1) meso-CH_2=$CH(CH_2)_2CHBrCHBrCOOCH_3$

(2) (±) cis-$CH_2BrCHBr(CH_2)_2CH$=$CHCOOCH_3$

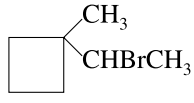
(3) (±)-CH_2=$CH(CH_2)_2CHBrCHBrCOOCH_3$

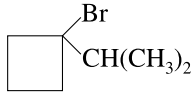
(4) (±)-cis-CH_2=CH–CH–CH–CH=$CHCOOCH_3$ (Br, Br)

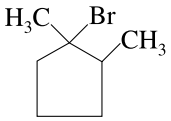
25. In the reaction

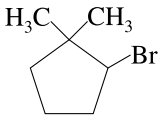


the major product formed is:

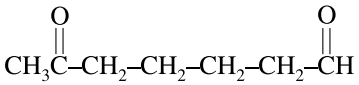
(1) 

(2) 

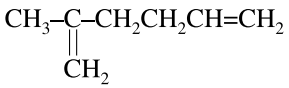
(3) 

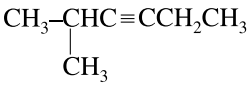
(4) 

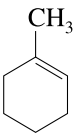
26. On catalytic hydrogenation, an organic compound X(C_7H_{12}) absorbs 1 mol of hydrogen and yields a compound C_7H_{14}. On ozonolysis and subsequent treatment with Zn/H_2O, the compound

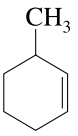


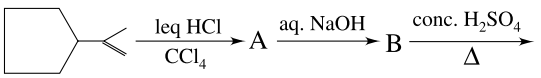
is obtained. The structure of X is

(1) 

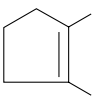
(2) 

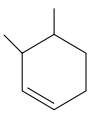
(3) 

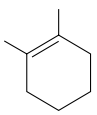
(4) 

27.  C;

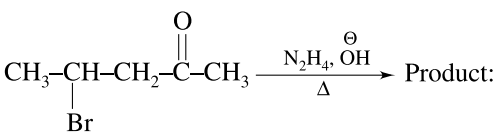
C is:

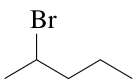
(1) 

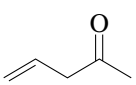
(2) 

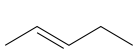
(3) 

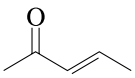
(4) 

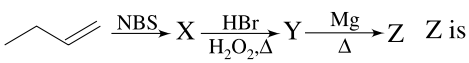
28.  Product:

(1) 

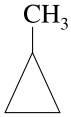
(2) 

(3) 

(4) 

29.  Z is

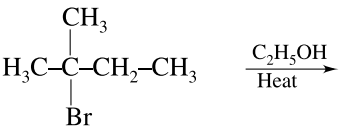
(1) 

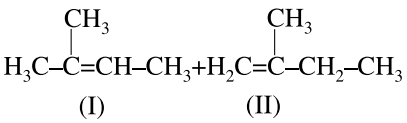
(2) 

(3) 

(4) 

30. Consider the following reaction,





(I) (II)

The correct statement concerning I and II is

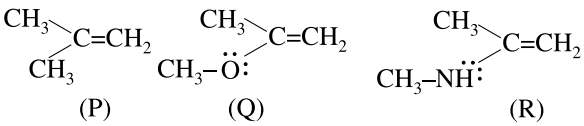
(1) I is the major product as it is formed at faster rate than II

(2) II is the major product as it is formed at faster rate than I

(3) I is major product as it is more stable than II

(4) I and II are formed in comparable amounts

31. Arrange the following reactions in decreasing order of electrophilic addition reaction towards HCl:

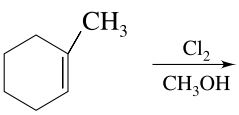


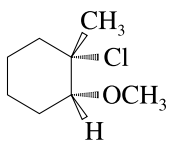
(P) (Q) (R)

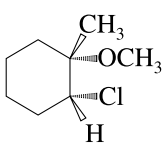
(1) P > Q > R (2) Q > R > P

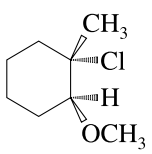
(3) R > Q > P (4) P = Q = R

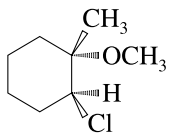
32. Which of the following is major product of reaction shown below?



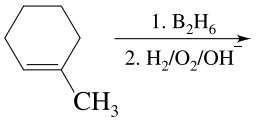
(1) 

(2) 

(3) 

(4) 

33. 1-Methylcyclohexene is allowed to react with B_2H_6. The product is hen treated with H_2O_2 and NaOH. The reaction is



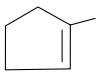
The product formed is

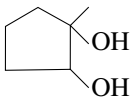
(1) 1-methylcyclohexanol

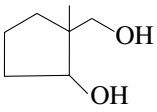
(2) 2-methylcyclohexanol

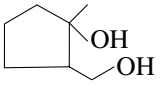
(3) (±) trans-2-methylcyclohexanol

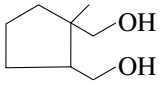
(4) (±) cis-2-methylcyclohexanol

34.  $\xrightarrow[H_2O]{HCHO.H^{\oplus}}$ Major product:

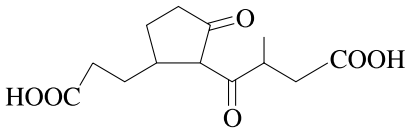
(1) 

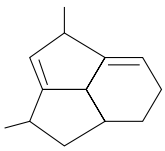
(2) 

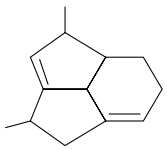
(3) 

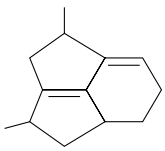
(4) 

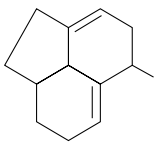
35. Which molecule will give the following dicarboxylic acid upon treatment with acidic solution of $KMnO_4$?



(1) 

(2) 

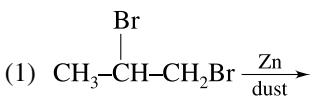
(3) 

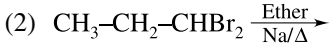
(4) 

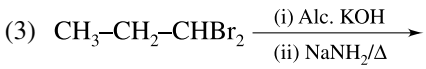
EXERCISE 3

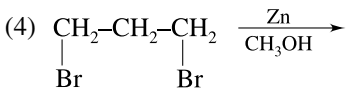
One and More Than One Option Correct Type Questions

1. Which of the following reactions result in formation of an alkene?

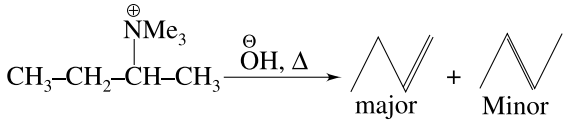
(1) 

(2) 

(3) 

(4) 

2. For the reaction



choose the correct statements:

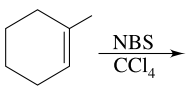
(1) The reaction is E_2

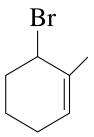
(2) Hoffmann product is major product

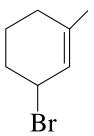
(3) Transition state has carbanion like character

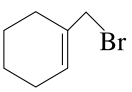
(4) Transition state has carbocation like character

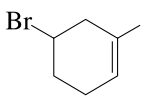
3. Which of the following are formed in the given reaction?



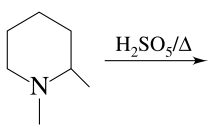
(1) 

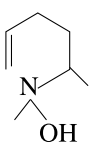
(2) 

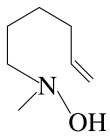
(3) 

(4) 

4. Which of the following statements are correct for the given reaction?



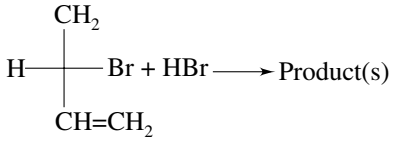
(1) Major product of reaction is 

(2) Major product of reaction is 

(3) Syatzeff alkene is major product of reaction

(4) Reaction is intramolecular elimination

5. Consider the following addition reaction on a pure enantiomer of the shown bromoalkene.



What is/are true regarding products of the above reaction?

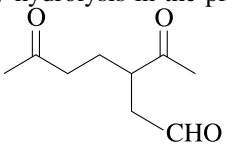
(1) Four stereoisomers of products are formed

(2) A pair of enantiomers and a meso-dibromide is formed

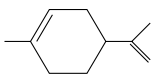
(3) Only a pair of diastereomers is formed

(4) One of the products is meso-dibromide

6. A hydrocarbon X ($C_{10}H_{16}$) upon catalytic hydrogenation gives 4-methyl-1-isopropyl cyclohexane. Also X upon ozonisation followed by hydrolysis in the presence of Zn gives CH_2O and



The correct statement(s) concerning X is/are

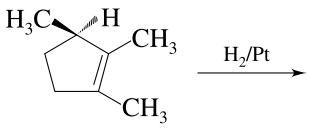
(1) Structure of X is 

(2) X has two chiral carbons

(3) X has one chiral carbon

(4) With excess of HCl, X gives racemic dichloride

7. The compound given below is chiral. What would be the outcome of catalytic hydrogenation of a pure enantiomer of this compound?



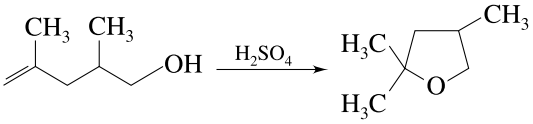
(1) A pair of enantiomers in equal amount would be produced

(2) A pair of diastereomers in unequal amounts would be produced

(3) A pair of enantiomers in unequal amounts would be produced

(4) A pair of diastereomers in equal amount would be produced

8. Consider the following reaction



Which of the following is/are true statement/s?

(1) Reaction initiates by protonation of –OH followed by formation of carbocation

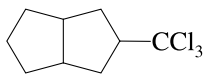
(2) Reaction is initiated at C=C forming a tertiary carbocation

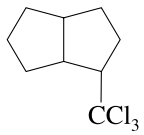
(3) Here intramolecular reaction is favoured by entropy of reaction

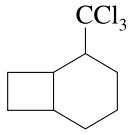
(4) The same reaction can also be accomplished using NaOH as catalyst

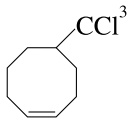
9. What products are expected in the following reaction?

1.0 equivalent

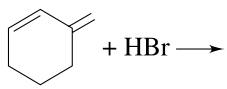
(1) 

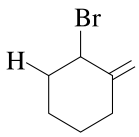
(2) 

(3) 

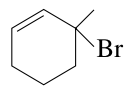
(4) 

10. Predict the product(s) in the following reaction

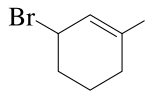


(1) 

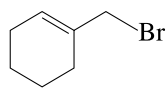
Kinetic

(2) 

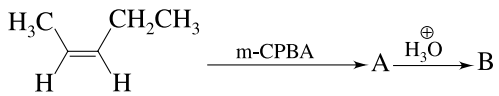
Kinetic

(3) 

Thermodynamic

(4) 

Thermodynamic

11. 

Choose the correct statements regarding above reaction

(1) Product A is optically active

(2) The conversion of alkene to product B is a stereospecific reaction

(3) Product B has achiral molecules

(4) Formation of 'A' is *syn* addition reaction

Assertion and Reason Type Question

(1) If both (A) and (R) are correct and (R) is the correct explanation for (A)

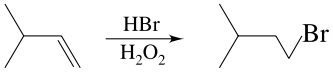
(2) If both (A) and (R) are correct and (R) is not the correct explanation

(3) If (A) is correct and (R) is incorrect

(4) If (A) is incorrect and (R) is correct

12. **Statement-I:** cis-2-butene with cold, dilute, alkaline $KMnO_4$ gives meso-2,3-butanediol.

Statement-II: In alkaline solution, under cold condition, $KMnO_4$ acts as a mild oxidising agent.

13. **Statement-1:** 

Statement-2: Reaction completes via free radical mechanism and initially ·Br attach with alkene to form more stable free radical.

14. **Statement-I:** 2-bromobutane with $(CH_3)_3COK$ in tertiary butanol gives 1-butene as major product.

Statement-II: Very strong base $(CH_3)_3COK$ in tertiary butanol brings about E2 elimination reaction.

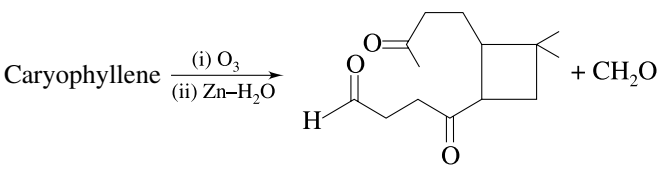
15. **Statement-I:** In reductive ozonolysis, dimethylsulphide is better reducing reagent than Zn-H_2O.

Statement-II: $(CH_3)_2S$ bring about homogeneous catalysis

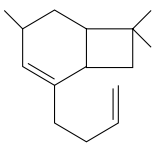
Comprehension Type Question

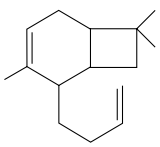
Comprehension (Q. 16 and 17)

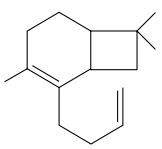
Caryophyllene ($C_{15}H_{24}$) contains a six membered ring and on ozonolysis gives the following product.

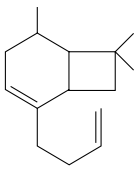


16. The structure of caryophyllene is

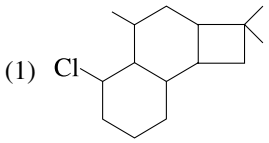
(1) 

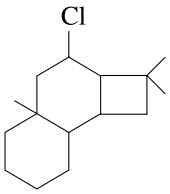
(2) 

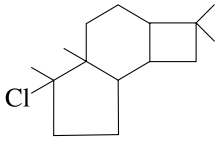
(3) 

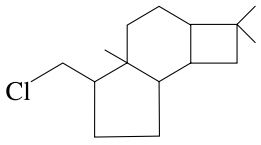
(4) 

17. If caryophyllene is treated with 1.0 mole of HCl, a ring closure reaction takes place to form monochloride. What is the most likely product of this reaction?

(1) 

(2) 

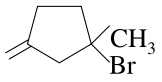
(3) 

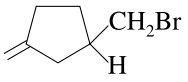
(4) 

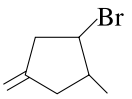
Comprehension (Q. 18–20)

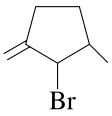
An organic compound X ($C_7H_{11}Br$) shows optical isomerism as well as decolourises brown colour of bromine water solution. X on treatment with HBr in the absence of a peroxide forms a pair of diastereomers, both of them are optically active. Also, X with C_2H_5ONa in C_2H_5OH gives a single product Y (C_7H_{10}). Y on treatment with ozone followed by reduction with $(CH_3)_2S$ given 1, 3,-cyclopentanedione as one product.

18. The structure of compound X is

(1) 

(2) 

(3) 

(4) 

19. The correct statement regarding product(s) formed by the reaction of X with HBr in the presence of H_2O_2 is

(1) Only a pair of enantiomers is formed

(2) Only a pair of diastereomers is formed

(3) Two pairs of enantiomers are formed

(4) A meso product is formed

20. The correct statement concerning product(s) formed when Y is treated with excess of HCl is

(1) A pair of enantiomers is formed in equal amount

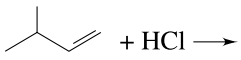
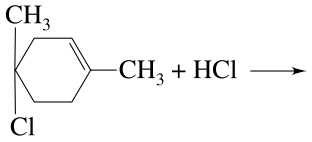
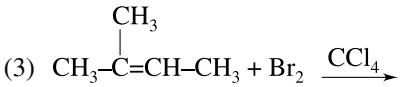
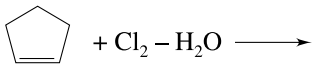
(2) Two pairs of diastereomers are formed

(3) Only a meso-dichloride is formed

(4) Only one pair of diastereomers is formed

Column Matching Type Question

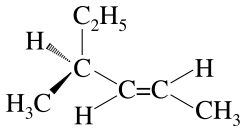
21. Consider the reaction in Column-I and match with the properties of products form Column-II

Column-I	**Column-II**
(1) 	(P) Racemic mixture of products
(2) 	(Q) Pair of stereoisomers
(3) 	(R) Involve a 2° carbocation
(4) 	(S) Involve a 3° carbocation

Codes

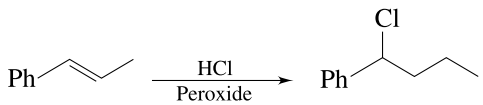
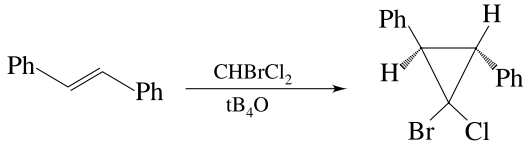
	A	**B**	**C**	**D**
(1)	P, Q, R, S	Q, S	P, Q	P, Q
(2)	S	R, S	Q	P, Q
(3)	S	R, S	P, Q, R	Q, R
(4)	R, S	P, S	Q, S	P

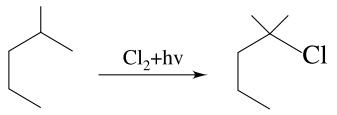
22. Match the alkenes in Column-I with the stereochemistry of addition product(s) obtained with Br_2/CCl_4 in presence of $FeBr_3$ in Column-II.

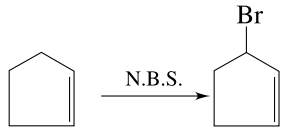
Column-I	**Column-II**
(A) *cis*-2-butene	(P) Racemic mixture of products
(B) *trans*-2-butene	(Q) Meso product
(C) *cis*-2-pentene	(R) Meso cyclic bromonium ion
(D) 	(S) Pair of diastereomers of product

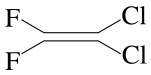
	A	**B**	**C**	**D**
(1)	P	Q, R	R	S
(2)	P, R	Q	P	S
(3)	S	R	P	Q, S
(4)	R, S	S	Q, R	P

23.

Column-I (Reactant, reagent, and product)	**Column-II (Intermediate involved)**
(a) 	(p) Carbene
(b) 	(q) Free radical

(c) 

(d) 

(e) $F_3C–CHCl_2 \xrightarrow{\text{Et ONa + EtOH}}$ 

(r) Carbanion

(s) Carbocation

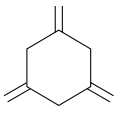
(1) a → s; b → p; c → q; d → q; e → r
(2) a → p; b → r; c → q; d → p; e → s
(3) a → p; b → s; c → r; d → p; e → q
(4) a → s; b → q; c → r; d → s; e → p

Single Digit Integer Type Question

24. If 3-bromo-4-methyl hexane is treated with ethanolic KOH solution, how many different alkenes would be formed?

25. If a racemic mixture of 3-methyl-1-pentene is treated with HCl, how many different chloropentane (important products only) would be formed?

26. Consider the following reaction

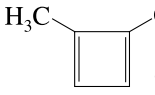
 + HBr (excess) $\xrightarrow{H_2O_2}$

How many different products would be formed?

27. A mixture containing all the stereoisomers of 3, 4, 5-trimethyl cyclopentene is treated with O_3 followed by Zn-hydrolysis, how many different isomers of products would result?

28. Cyclobutene when refluxed in presence of potassium metal, evolve hydrogen gas and an aromatic system is formed. How many pi-electrons are involved in the above formed aromatic system?

29. Consider the following reaction

 + HBr (excess) $\xrightarrow{\text{Peroxide}}$

How many different products (including stereoisomers) would be formed?

30. Alkene(s) + $O_3 \xrightarrow[H_2O]{Zn}$ $CH_3–CHO$ +
X

$CH_3–CH_2–\underset{\displaystyle O}{\underset{\|}{CH}}–\underset{\displaystyle O}{\underset{\|}{C}}–CH_3 + CH_3–\underset{\displaystyle O}{\underset{\|}{C}}–CH_2–CHO$

How many different isomers of alkene (X) can give the above reaction?

EXERCISE 4

1. The compound $H_3C–\underset{\displaystyle CH_3}{\underset{|}{C}}=CH–CH_2–CH_3$ $\xrightarrow{\text{Vigorous oxidation}}$ product, here product is **[AIEEE-2002]**

(1) CH_3COOH & $CH_3–\underset{\displaystyle O}{\underset{\|}{C}}–CH_3$

(2) $CH_3–CH_2–COOH$ & $CH_3–\underset{\displaystyle CH_3}{\underset{|}{C}}=O$

(3) $CH_3–CH_2–COOH$ only

(4) HCOOH & $CH_3–\underset{\displaystyle O}{\underset{\|}{C}}=CH_3$

2. During dehydration of alcohols to alkenes by heating with conc. H_2SO_4 the initiation step is **[AIEEE-2003]**

(1) elimination of water
(2) formation of an ester
(3) protonation of alcohol molecule
(4) formation of carbocation

3. Which one of the following has the minimum boiling point? **[AIEEE-2004]**

(1) n-Butane (2) 1-Butyne
(3) 1-Butene (4) Isobutane

4. Reaction of one molecule of HBr with one molecule of 1, 3-butadiene at 40°C given predominantly **[AIEEE-2005]**

(1) 1-bromo-2-butene thermodynamically controlled conditions
(2) 3-bromobutene under kinetically controlled conditions
(3) 1-bromo-2-butene under kinetically controlled conditions
(4) 3-bromobutene thermodynamically controlled conditions

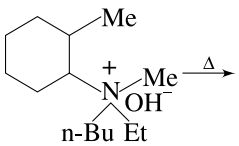
5. Acid catalysed hydration of alkenes except ethane leads to the formation of– **[AIEEE-2005]**

(1) secondary or tertiary alcohol
(2) primary alcohol
(3) mixture of secondary and tertiary alcohols
(4) mixture of primary and secondary alcohols

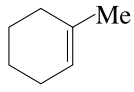
6. Elimination of bromine from 2-bromobutane results in the formation of **[AIEEE-2005]**

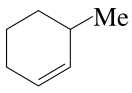
(1) predominantly 2-butene
(2) equimolar mixture of 1 and 2-butene
(3) predominantly 2-butyne
(4) predominantly1-butene

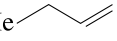
7.



The alkene formed as a major product in the above elimination reaction is **[AIEEE-2006]**

(1) $CH_2 = CH_2$ (2) 

(3) 

(4) 

8. In the following sequence of reactions, the alkene affords the compound 'B'

$CH_3CH = CHCH_3 \xrightarrow{O_3} A \xrightarrow[Zn]{H_2O} B$. The compound B is **[AIEEE-2008]**

(1) CH_3COCH_3 (2) $CH_3CH_2COCH_3$
(3) CH_3CHO (4) CH_3CH_2CHO

9. Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of **[AIEEE-2011]**

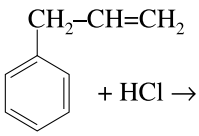
(1) two ethylenic double bonds
(2) vinyl group
(3) an isopropyl group
(4) an acetylenic triple bond

10. Ozonolysis of an organic compound 'A' produces acetone and propionaldehyde in equimolar mixture. Identify 'A' from the following compounds: **[AIEEE-2011]**

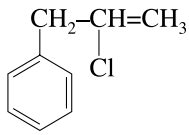
(1) 1-Pentene (2) 2-penetene
(3) 2-Methyl-2-pentene (4) 2-Methyl-1-pentene

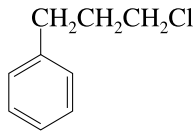
11. 2-Hexyne gives trans-2-hexene on treatment with– **[AIEEE-2012]**

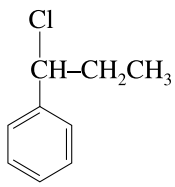
(1) Li/NH_3 (2) $Pd/BaSO_4$
(3) $LiAlH_4$ (4) Pt/H_2

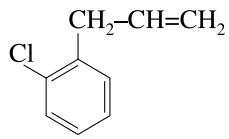
12. Given 

$+ HCl \rightarrow X$, X is **[JEE Main Online-2013]**

(1) 

(2) 

(3) 

(4) 

13. The addition of HI in the presence of peroxide catalyst does not follow anti Markovnikov's rule because **[JEE main Online-2013]**

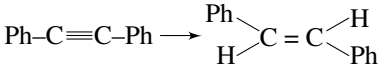
(1) HI is a strong reducing agent
(2) HI bond is too strong to be broken homolytically
(3) I atom combines with H atom so give back HI
(4) iodine atom is not reactive enough to add across a double bond

14. In the hydroboration–oxidation reaction of propene with diborane, H_2O_2 and NaOH, the organic compound formed is: **[JEE Main Online-2014]**

(1) CH_3CH_2OH (2) $CH_3CHOHCH_3$
(3) $CH_3CH_2CH_2OH$ (4) $(CH_3)_3COH$

15. The reagent needed for converting

[JEE Main Online-2014]



(1) Cat. Hydrogenation (2) H_2/Lindlar Cat.

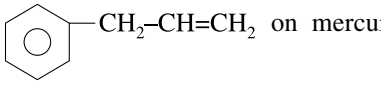
(3) Li/NH_3 (4) $LiAlH_4$

16. The gas liberated by the electrolysis of Dipotassium succinate solution is

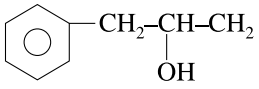
[JEE Main Online-2014]

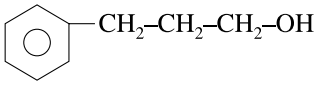
(1) Ethane (2) Ethyne

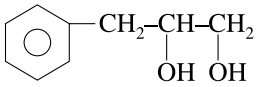
(3) Ethene (4) Propene

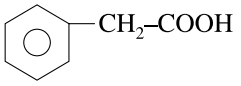
17.  on mercuration–demercuration produces the major product

[JEE Main Online-2014]

(1) 

(2) 

(3) 

(4) 

18. In the presence of peroxide, HCl and HI do not give anti-Markownikoff's addition to alkenes because

[JEE Main Online -2014]

(1) One of the steps is endothermic in HCl and HI

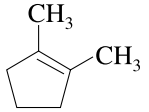
(2) Both HCl and HI are strong acids

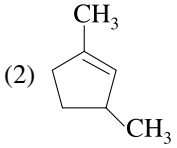
(3) HCl is oxidising and the HI is reducing

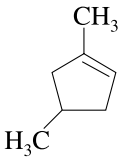
(4) All the steps are exothermic in HCl and HI

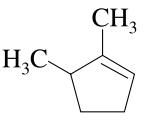
19. Which compound would give 5-Keto-2-methyl hexanal upon ozonolysis?

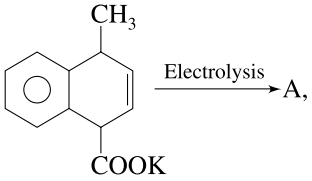
[JEE Main-2015]

(1) 

(2) 

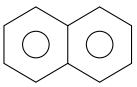
(3) 

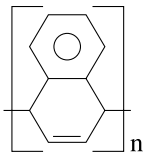
(4) 

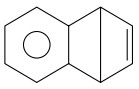
20. 

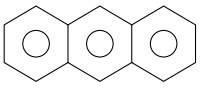
[JEE Main Online-2015]

A is:

(1) 

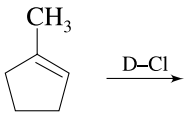
(2) 

(3) 

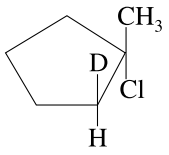
(4) 

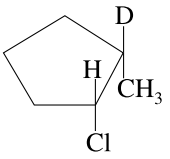
21. What is the major product expected from the following reaction?

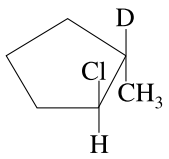
[JEE main Online-2015]

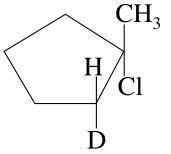


where D is an isotope of hydrogen.

(1) 

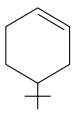
(2) 

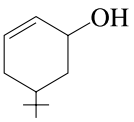
(3) 

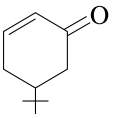
(4) 

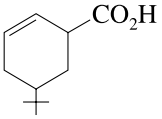
22. The product of the reaction given below is:

[JEE main-2016]

(1) 

(2) 

(3) 

(4) 

23. The reaction of propene with HOCl (Cl_2 + H_2O) proceeds through the intermediate:

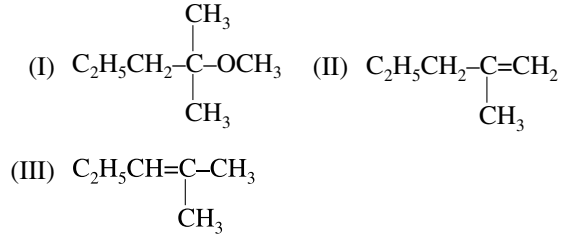
[JEE Main-2016]

(1) $HC_3–CH^+–CH_2–OH$ (2) $CH_3–CH^+–CH_2–Cl$

(3) $CH_3–CH(OH)–H_2^+$ (4) $CH_3–CHCl–H_2^+$

24. 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields

[JEE Main-2016]



(1) Both I and III (2) Only III
(3) Both I and II (4) All of these

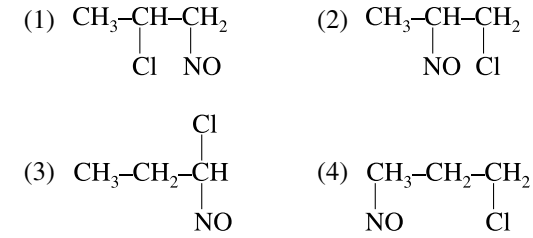
25. Cyclohexene is best prepared from cyclohexanol by which of the following?

[IIT-2005]

(1) conc. H_3PO_4 (2) conc. HCl/$ZnCl_2$
(3) conc. HCl (4) conc.HBr

26. $CH_3–CH=CH_2 + NOCl \longrightarrow P$; Identity the adduct.

[IIT-2006]



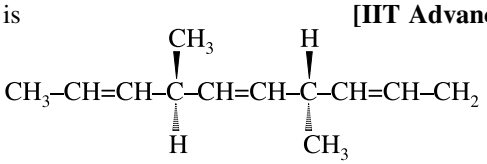
27. The number of stereoisomers obtained by bromination of trans-2-butene is

[IIT-2007]

(1) 1 (2) 2
(3) 3 (4) 4

28. The number of optically active products obtained from the complete ozonolysis of the given compound, is

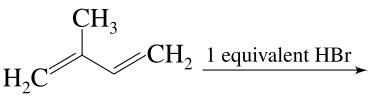
[IIT Advance-2012]

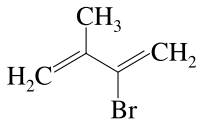
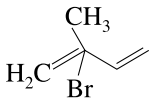
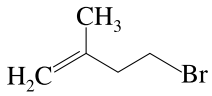
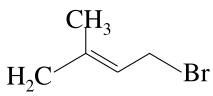


(1) 0 (2) 1
(3) 2 (4) 4

29. In the following reaction, the major product is

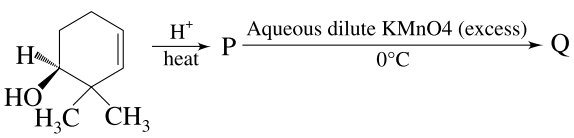
[JEE Advance-2015]



(1) 
(2) 
(3) 
(4) 

30. The number of hydroxyl group(s) in Q is

[JEE Advance-2015]



ANSWER KEY

EXERCISE # 1

1. (2)	2. (2)	3. (3)	4. (2)	5. (3)
6. (2)	7. (2)	8. (3)	9. (4)	10. (3)
11. (2)	12. (1)	13. (3)	14. (4)	15. (1)
16. (3)	17. (4)	18. (3)	19. (4)	20. (4)
21. (3)	22. (1)	23. (2)	24. (3)	25. (2)
26. (4)	27. (1)	28. (1)	29. (3)	30. (2)

EXERCISE # 2

1. (1)	2. (3)	3. (4)	4. (2)	5. (3)
6. (3)	7. (3)	8. (3)	9. (2)	10. (2)
11. (4)	12. (3)	13. (3)	14. (2)	15. (1)
16. (1)	17. (3)	18. (2)	19. (1)	20. (1)
21. (2)	22. (4)	23. (2)	24. (2)	25. (3)
26. (3)	27. (3)	28. (3)	29. (2)	30. (3)
31. (3)	32. (3)	33. (3)	34. (3)	35. (4)

EXERCISE # 3

1. (1,2)	2. (1,2,3)	3. (1,2,3)	4. (2,4)	5. (3,4)
6. (1,3,4)	7. (2)	8. (2,3)	9. (2,3,4)	10. (2,3)
11. (1,2,4)	12. (2)	13. (1)	14. (2)	15. (3)
16. (3)	17. (1)	18. (2)	19. (4)	20. (2)
21. (1)	22. (2)	23. (1)	24. (6)	25. (5)
26. (3)	27. (4)	28. (6)	29. (8)	30. (8)

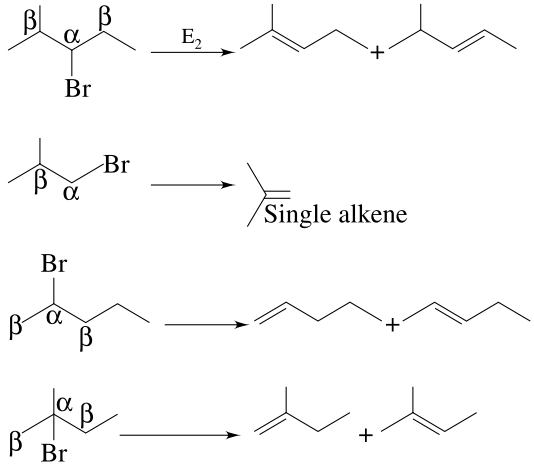
EXERCISE # 4

1. (2)	2. (3)	3. (4)	4. (1)	5. (1)
6. (1)	7. (1)	8. (3)	9. (2)	10. (3)
11. (1)	12. (3)	13. (4)	14. (3)	15. (3)
16. (3)	17. (1)	18. (1)	19. (2)	20. (1)
21. (1)	22. (2)	23. (2)	24. (4)	25. (1)
26. (1)	27. (1)	28. (1)	29. (4)	30. (4)

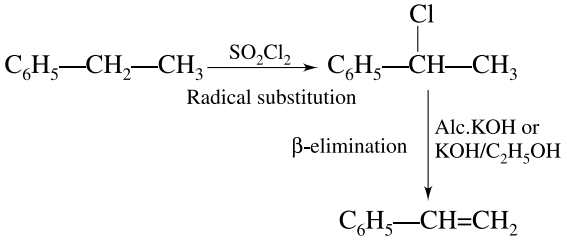
HINT AND SOLUTION

EXERCISE # 1

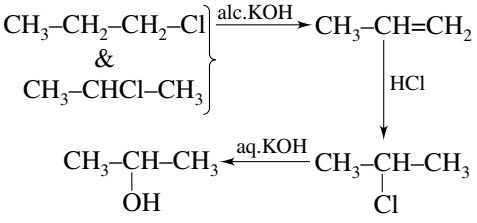
1. [2]



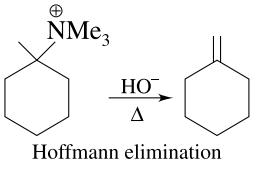
2. [2]



3. [3]

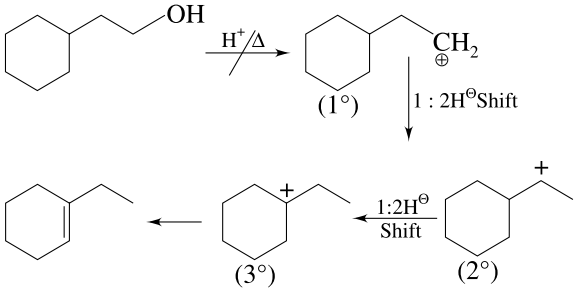


4. [2]

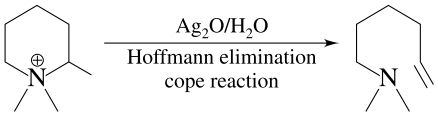


Pyrolysis of QAH takes place by Hoffmann rule

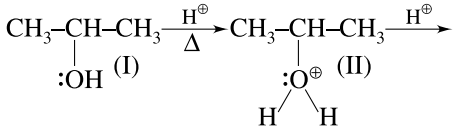
5. [3]

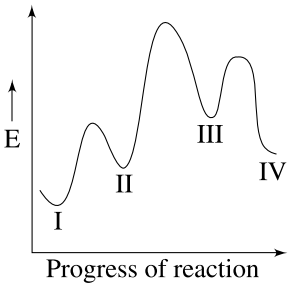


6. [2]



7. [2]

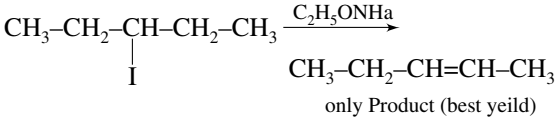


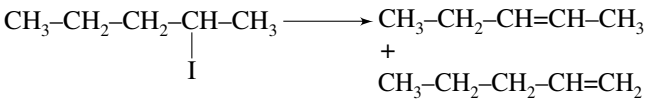


8. [3]

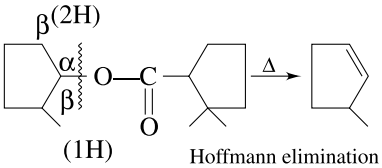
(i) Reactivity of β-elimination in alkyl halide
R – I > R – Br > R – Cl

(ii) If halide same
Reactivity ∝ stability of alkene

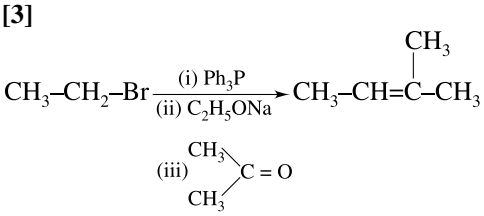




9. [4]

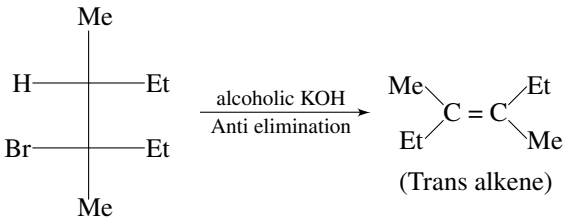


10. [3]



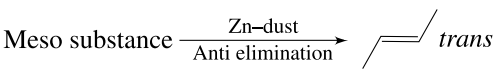
Witting reaction

11. [2]

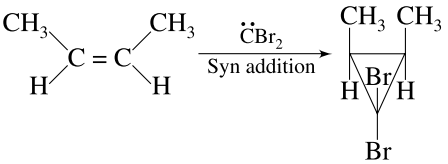


Erythero [EAT] (refer key concept)

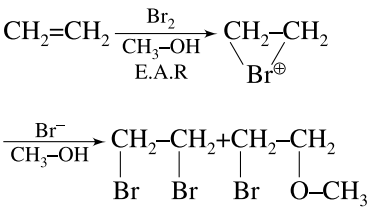
12. [1]



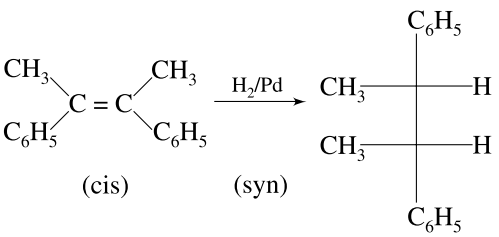
13. [3]



14. [4]



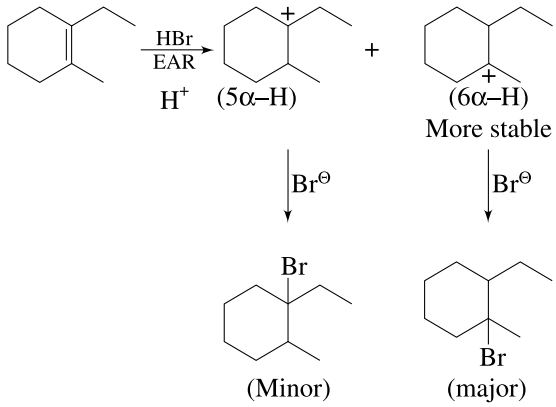
15. [1]



(cis) (syn)

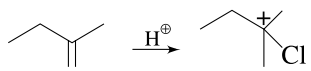
2, 3 diphenyl butane (Meso)

16. [3]



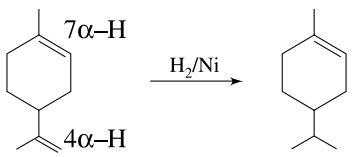
17. [4]

Rate of E.A.R α Stability of carbocation



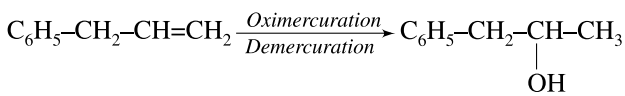
3° carbocation (most stable)

18. [3]



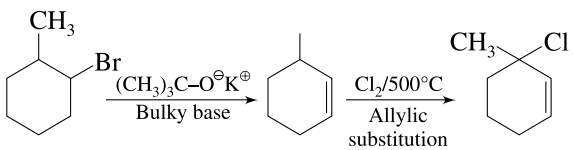
$$\text{Reactivity of alkene} \propto \frac{1}{\text{stability of alkene}} \propto \frac{1}{\alpha - H}$$

19. [4]

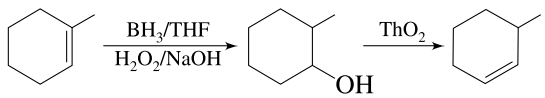


Overall OMDM is Hydration, according to Markownikoff rule

20. [4]

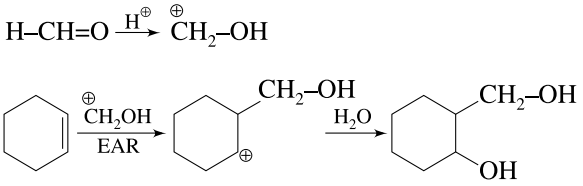


21. [3]

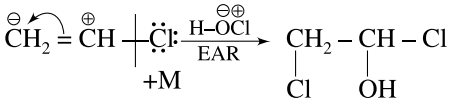


Hydration via anti-Markownikoff addition

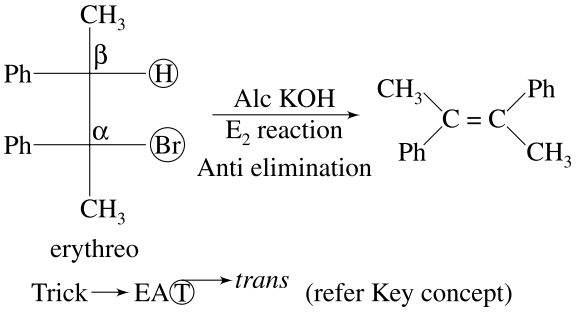
22. [1]



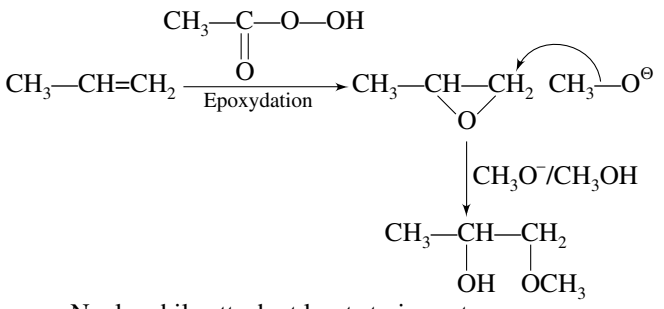
23. [2]



24. [3]

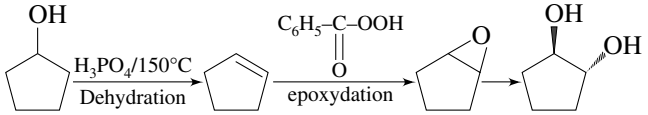


25. [2]

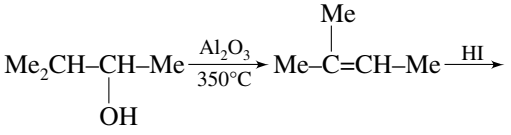


Nucleophile attach at least steric centre

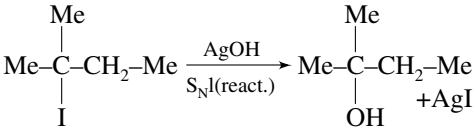
26. [4]



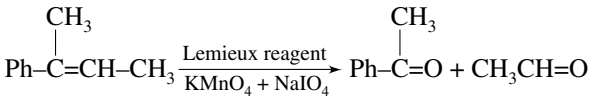
27. [1]



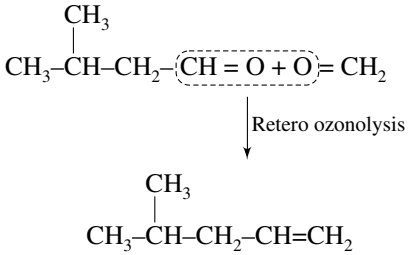
Al_2O_3 is dehydrating agent.



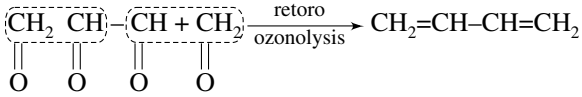
28. [1]



29. [3]

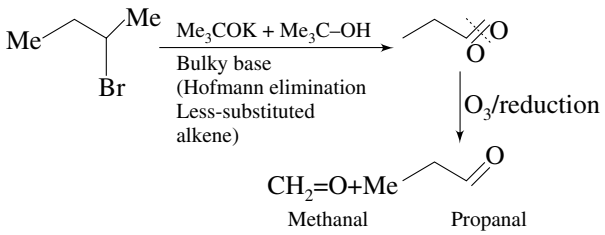


30. [2]



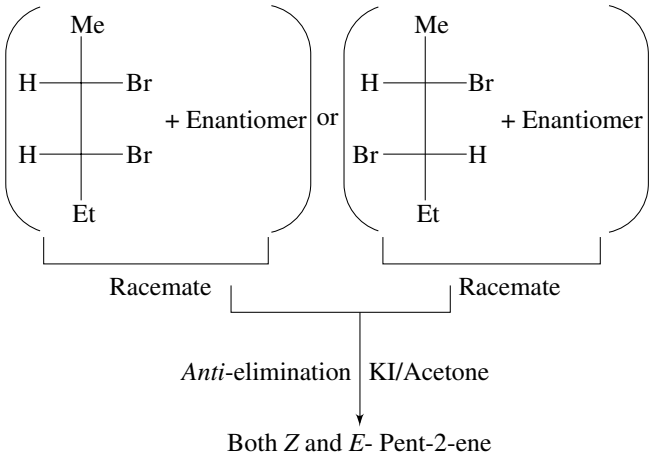
EXERCISE # 2

1. [1]

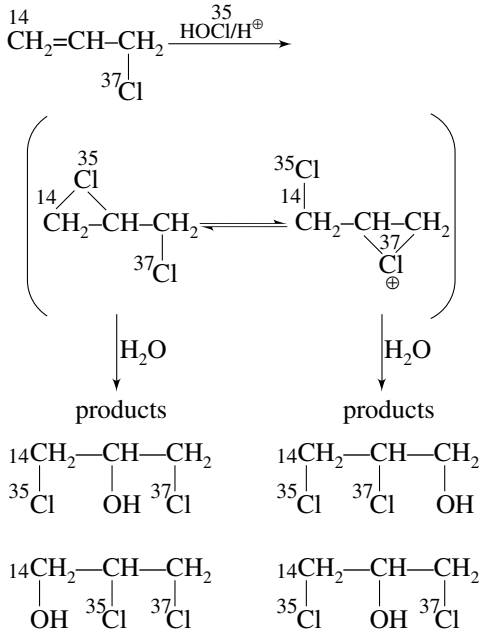


2. [3]

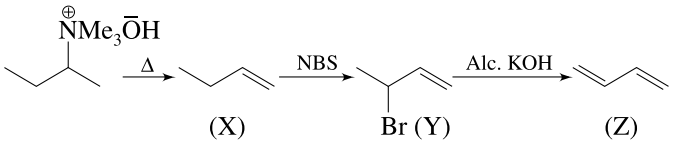
2, 3-dibromopentane, meso isomer is not possible, since two terminal groups are different.



3. [4]

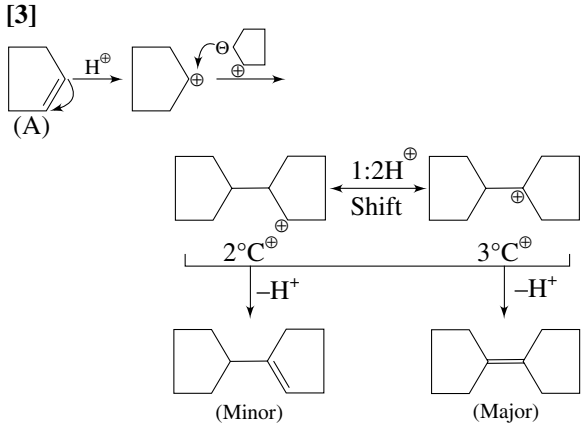


4. [2]



Hoffmann elimination

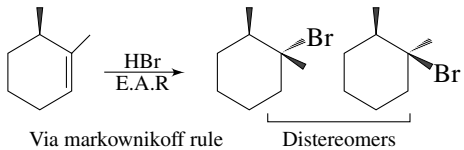
5. [3]



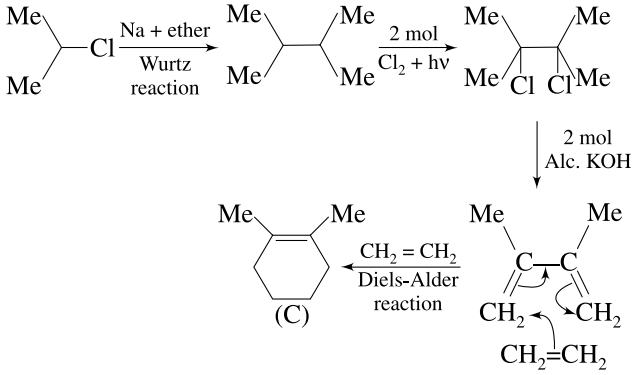
6. [3]

Product has 2 chiral C but POS present and also the two–COOH will come on the same side giving meso form of diacid

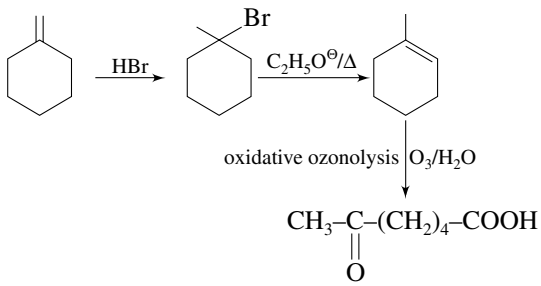
7. [3]



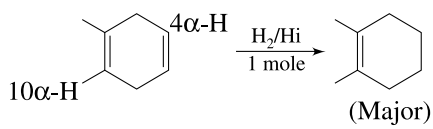
8. [3]



9. [2]

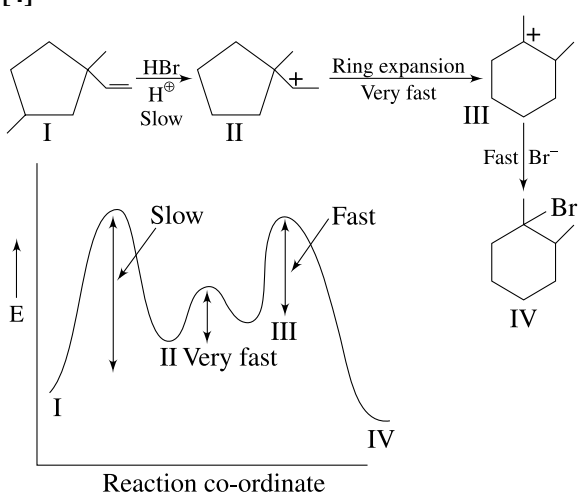


10. [2]

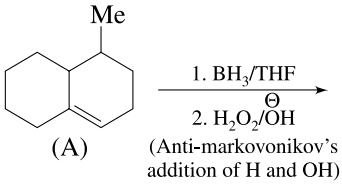


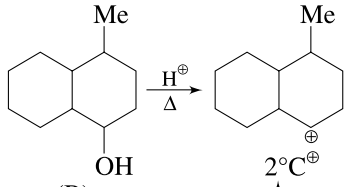
$$\text{Reactivity of alkene} \quad \frac{1}{\text{stability of alkene}} \propto \frac{1}{\alpha - H}$$

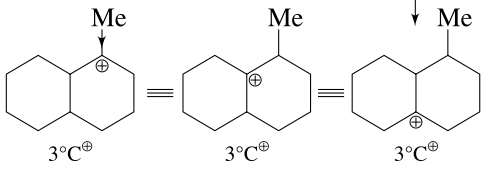
11. [4]



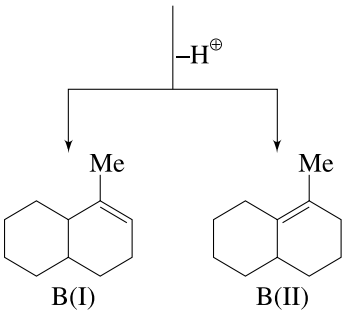
12. [3]







(More stable $3°C^{\oplus}$ due to +I effect of Me group)

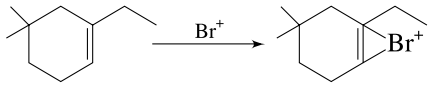


Out of B(I) and B(II), B(I) is more likely to be formed because in B(II) double bond is joined to two rings (exocyclic bond) and, hence, is not so stable.

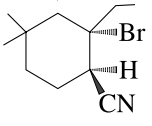
13. [3]

Anti-elimination takes place

14. [2]



Anti addition of CN^-
Via less strictly hindred site



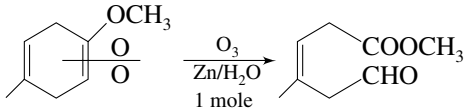
15. [1]

E_2-elelmation reaction takes place.

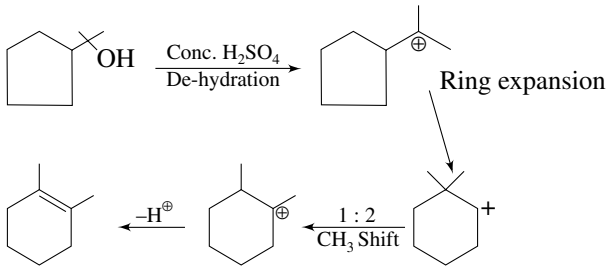
Syatzeff product obtained by anti-elimination

16. [1]

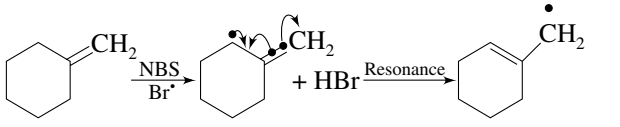
+M favours ozonolysis



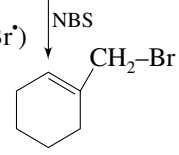
17. [3]



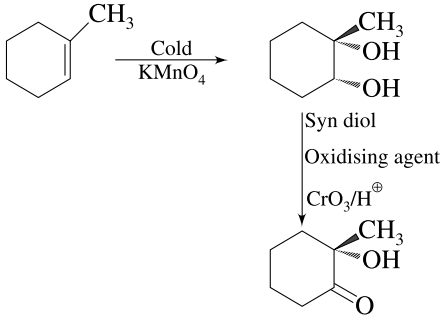
18. [2]



Radical substitution at Allylic position ($Br^{\bullet}$)



19. [1]



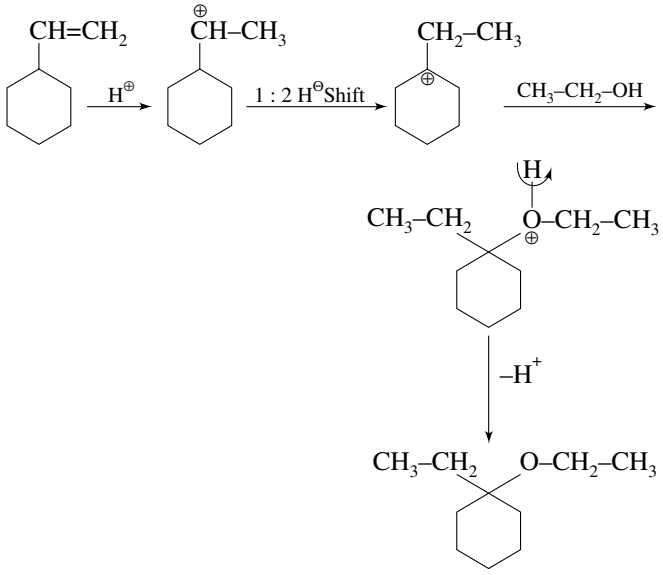
3° alcohol do not give oxidation reaction

20. [1]

→ E.A.R

→ Markownikoff rule applies

$H_2SO_4 \rightarrow H^{\oplus} + HSO_4^{\ominus}$



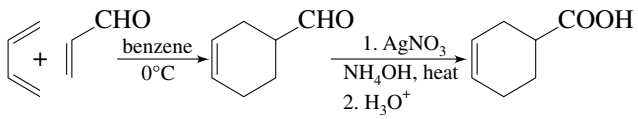
21. [2]

$NH_2–NH_2/H_2O_2$ only reduce C = C

Sn + HCl only reduce – NO_2

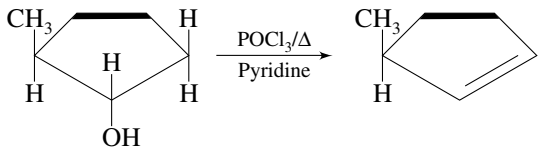
Raney Ni reduces C = C and – NO_2 Both

22. [4]



Diel's-Alder After reaction 1:4 addition

23. [2]

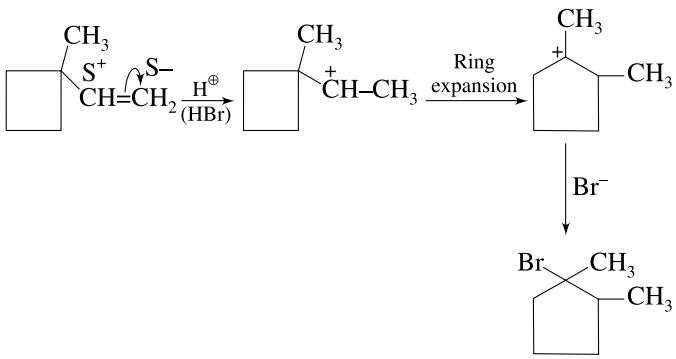


With bulky reagent Hoffmann elimination takes place.

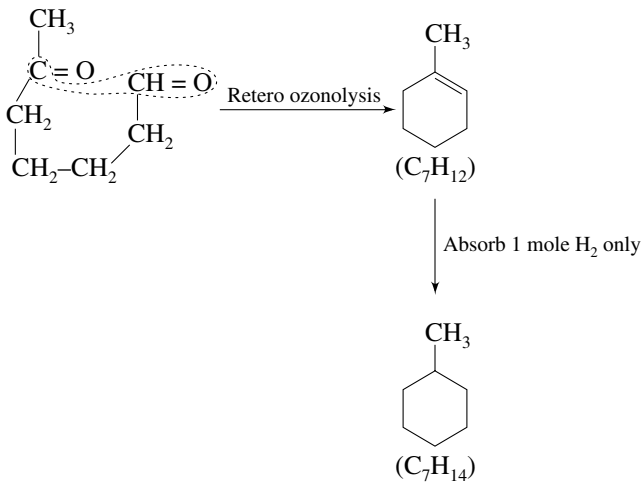
24. [2]

Cis alkene + *Anti* reagent ⇒ Racemic mixture

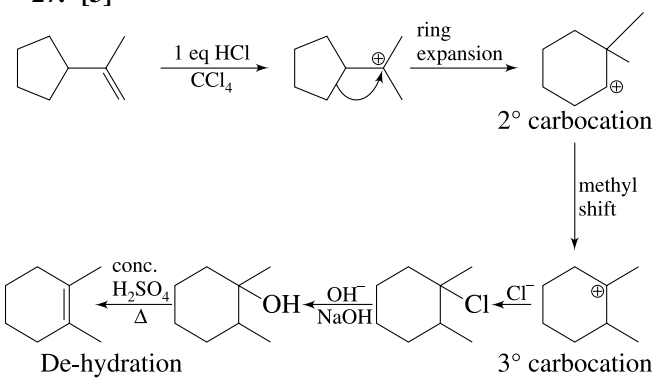
25. [3]



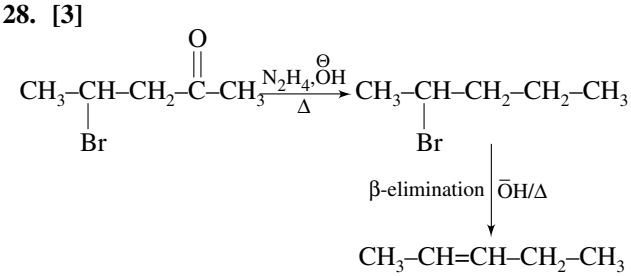
26. [3]



27. [3]

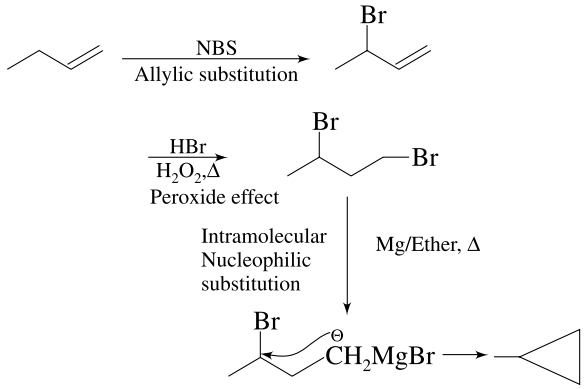


28. [3]



→ Wolf–Kishner reduction followed by β-elimination (De-hydrohalogenation) takes place simultaneously

29. [2]



30. [3]

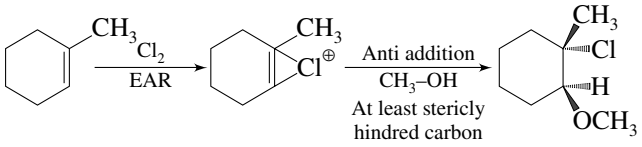
This is an example of E_1 reaction hence more stable alkene is obtained as major product. So that alkene (I) is formed as the major product because it is more substituted and thus more stable than alkene (II).

31. [3]

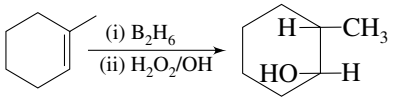
Rate of E.A.R $\propto$ stability of $-\overset{|}{\underset{|}{\overset{\oplus}{C}}}-$ $\propto$ ERG $\propto \frac{1}{\text{EWG}}$

$-NH-CH_3 > -OCH_3 > -CH_3$(ERG$\downarrow$)
+M +M +M

32. [3]



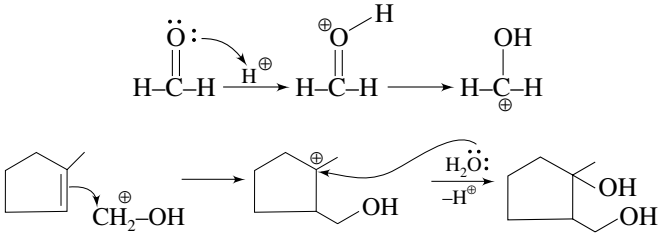
33. [3]



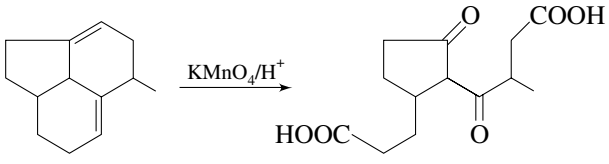
(±) *trans*-2-methylcyclohexanol

Syn addition via Anti-Markownikoff addition

34. [3]



35. [4]



EXERCISE # 3

1. [1, 2]

(1) $CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2Br \xrightarrow{\text{Zn-dust}} CH_3-CH=CH_2$

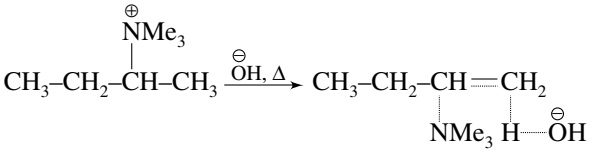
(2) $CH_3-CH_2-CHBr_2 + Na \xrightarrow[\Delta]{Et_2O}$

$CH_3-CH_2-CH=CH-CH_2-CH_3$

(3) $CH_3-CH_2-CHBr_2 \xrightarrow[\text{(ii) } NaNH_2/\Delta]{\text{(i) Alc. KOH}} CH_3-C\equiv CH$

(4) $CH_2(Br)-CH_2-CH_2(Br) \xrightarrow[CH_2OH]{Zn}$

2. [1, 2, 3]



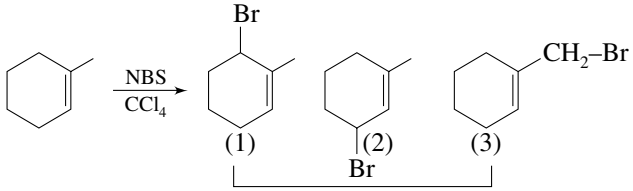
(Transition state have carbonion like character)

$\downarrow E_2$

$CH_3-CH_2-CH=CH_2 + Me_3N + H_2O$

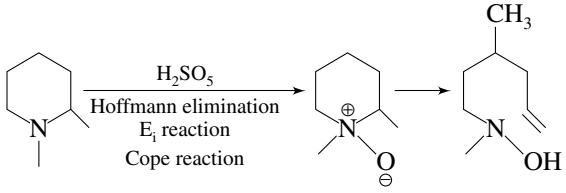
Hoffmann prouct

3. [1, 2, 3]



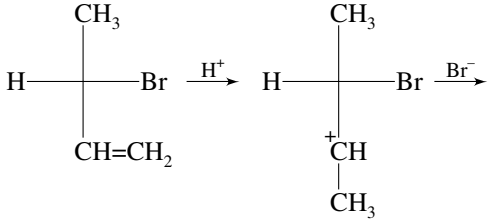
Allylic substituted product

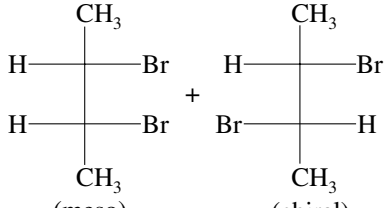
4. [2, 4]



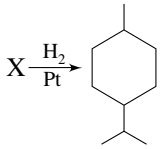
t-amine oxide Major product

5. [3, 4]



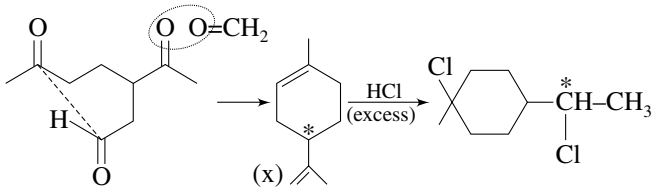


6. [1, 3, 4]



Therefore, X has a six membered ring.]

Connecting ozonolysis product to form a six membered ring gives structure of X as



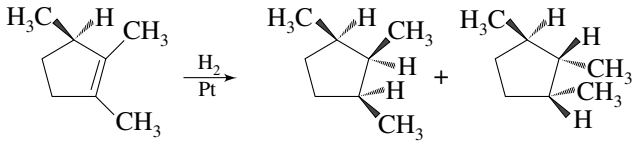
It has a chiral carbon

It has one chiral carbon (racemic mix)

Chiral carbon is produced through carbocation and racemic mixture would be formed

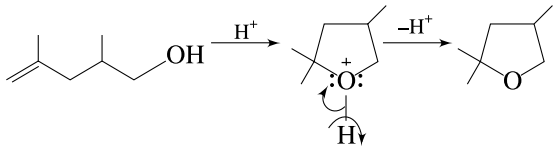
7. [2]

Catalytic hydrogenation occur with *syn*-orientation in the present case hydrogenation would be slightly more favoured from the side opposite to the methyl group at chiral carbon.

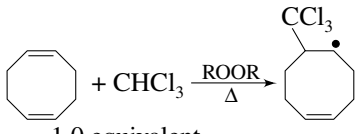


More favoured

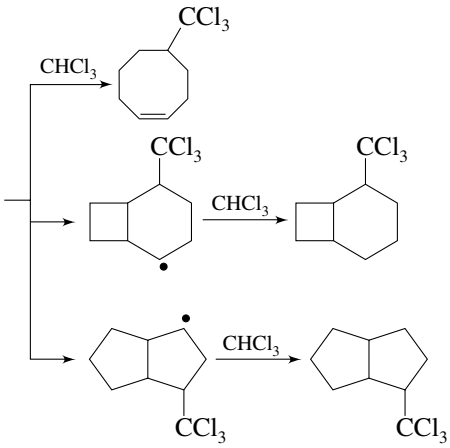
8. [2, 3]



9. [2, 3, 4]

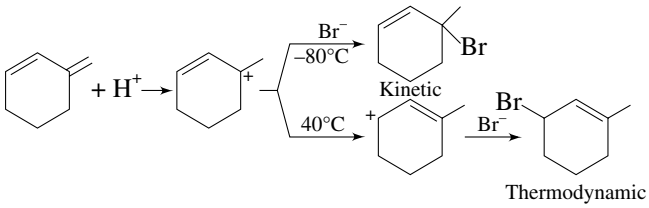


1.0 equivalent

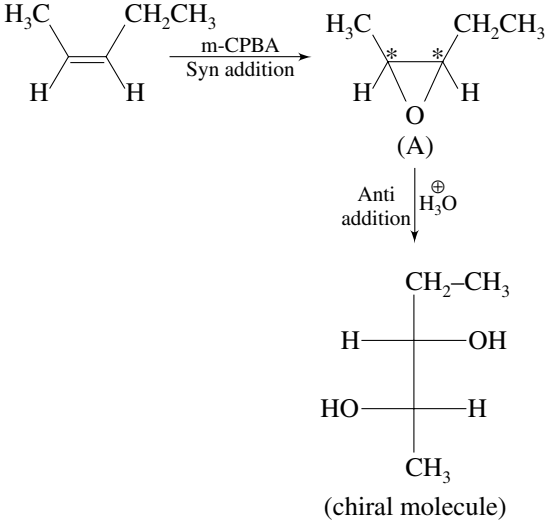


10. [2, 3]

Electrophilic addition occur at 1,2-position under kinetically controlled condition while at 1, 4-position under thermodynamically controlled condition



11. [1, 2, 4]

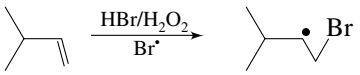


(chiral molecule)

12. [2]

It is true that in cold, alkaline condition, KMnO4 acts as mild oxidising agent but the reason for the formation of meso diol is syn hydroxylation via a cyclic intermediate.

13. [1]



2° radical
(more stable)

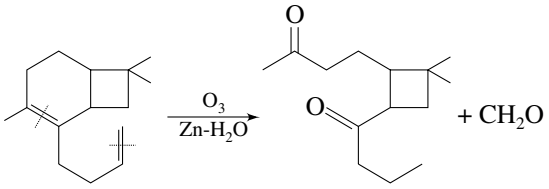
14. [2]

The bulky base $(CH_3)_3COK$ brings about E-2 elimination by abstracting hydrogen from less hindered β-carbon giving less substituted alkene as major product.

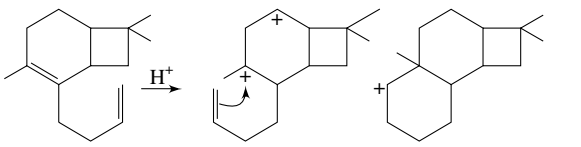
15. [3]

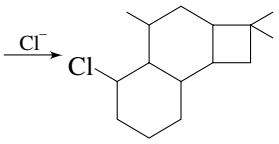
$(CH_3)_2S$ is better reducing agent, reduces ozonide to corresponding carbonyls and itself oxidised into $(CH_3)_2SO$ which is a common organic solvent. It does not reduce carbonyls products further.

16. [3]



17. [1]

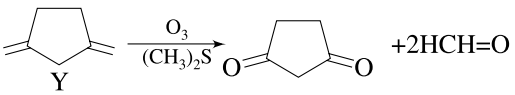




18. [2] **19. [4]** **20. [2]**

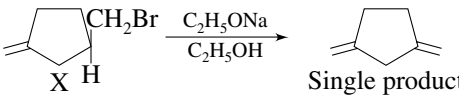
[18–20]

Y upon ozonolysis followed by work-up with $(CH_3)_2S$ gives 1,3-cyclopentanedione, it must be



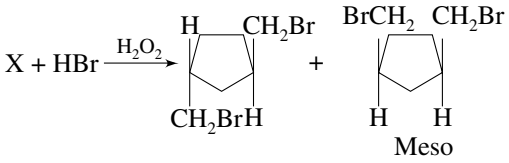
Y

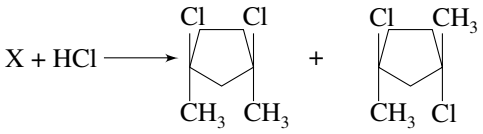
Y is obtained as single dehydrobromination product, X must be



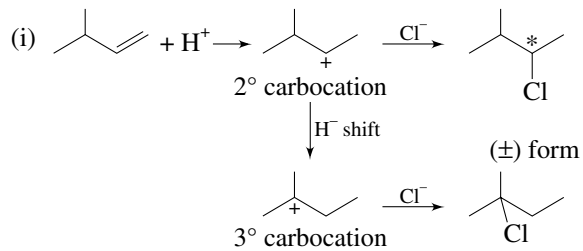
Single product

Also,

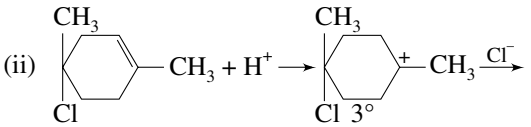


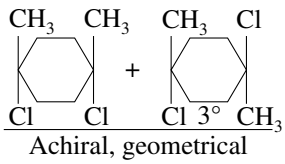


21. [1]



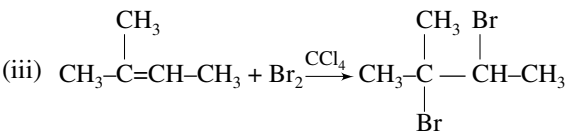
(i) → (P,Q,R,S)





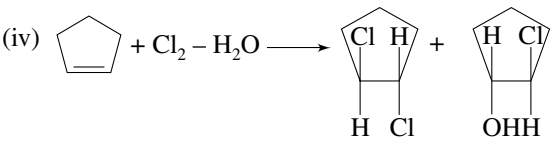
Achiral, geometrical

(ii) → (P,S)



(Chiral = racemic mixture)

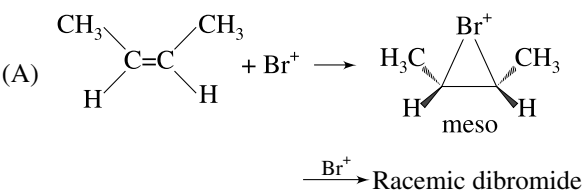
(iii) → (P,Q)

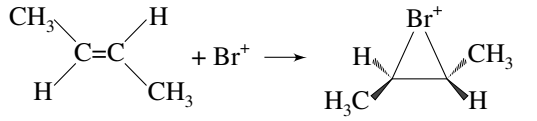


(iv) → (P,Q)

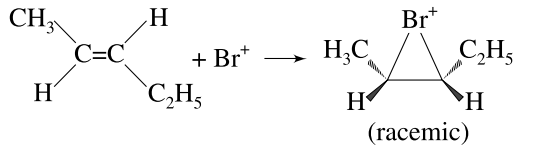
(Racemic mixture)

22. [2]



(B) 

meso

(C) 

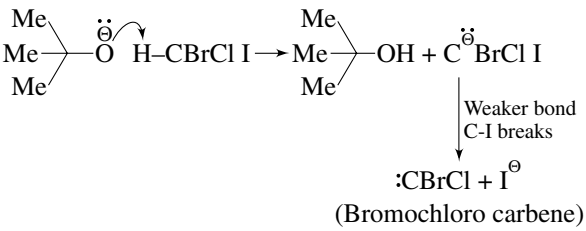
(racemic)

(D) Two *anti*-dibromides are formed in equal amounts but presence of an additional chiral carbon makes the two products diastereomers.

23. [1]

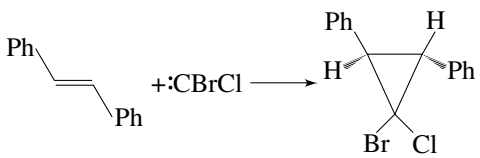
(a → s) HCl with peroxide does not undergo anti-Markovnikov's addition unlike HBr + peroxide, so reaction does not proceed by free-radical mechanism but by carbocation.

(b → p) Proceed via carbene mechanism.



(Bromochloro carbene)

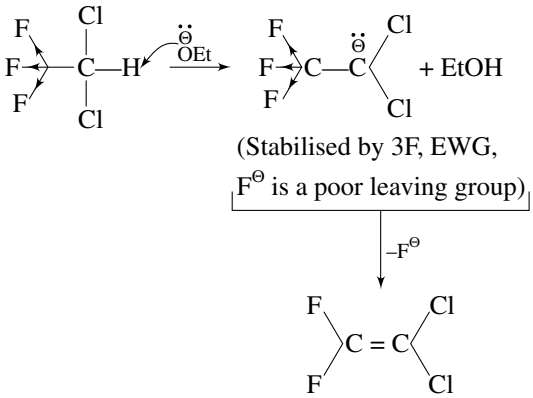
It is a stereospecific and stereoselective reaction; trans reactant gives trans product.



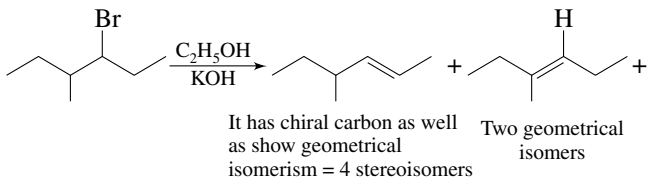
(c → q) Proceeds via free-radical mechanism.

(d → q) proceeds via free-radical mechanism.

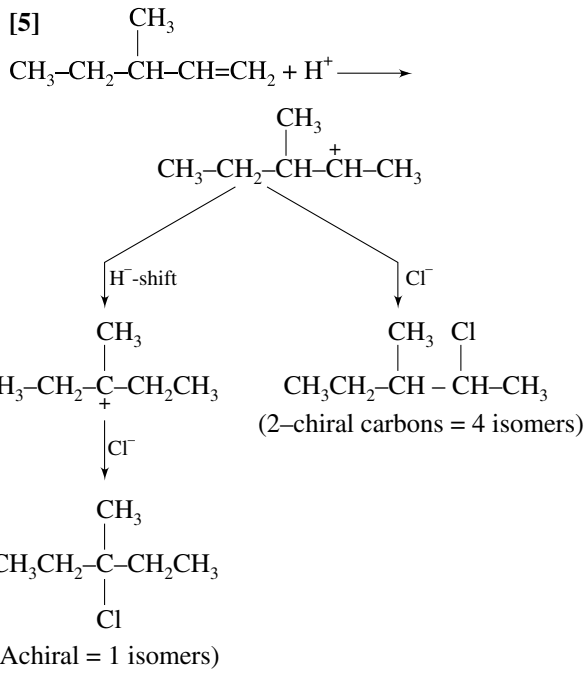
(e → r) It is an example of E_1 CB (elimination unimolecular via conjugate base) and proceeds via carbanion mechanism. EWG (electron-withdrawing group) and poor leaving, three F atoms stabilise the carbanion.



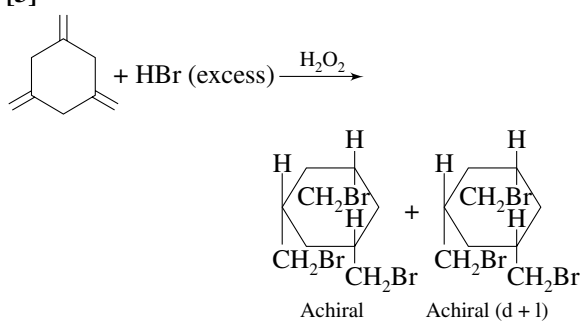
24. [6]



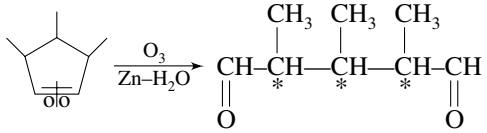
25. [5]

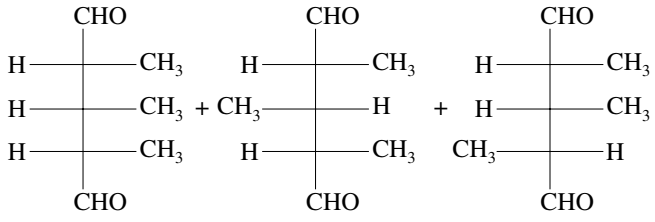


26. [3]

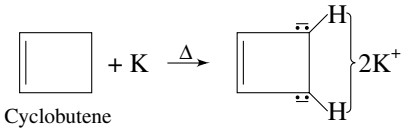


27. [4]

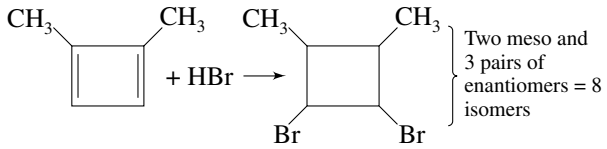




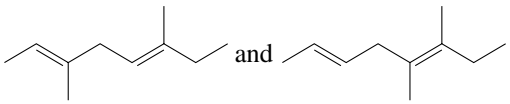
28. [6]



29. [8]



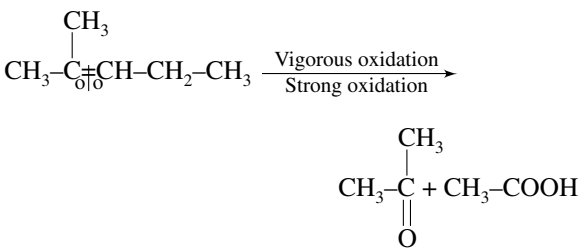
30. [8]



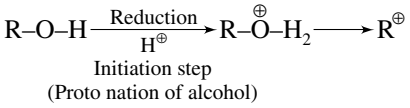
Both of the above dienes are capable of showing geometrical isomerism at both of their double bonds. Therefore, four stereoisomers exist for each of them.

EXERCISE # 4

1. [2]



2. [3]



3. [4]

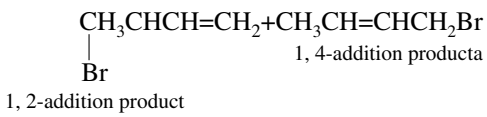
boiling point ∝ polarity

- Since alkanes are less polar, they have lesser boiling point than alkene and alkyne.
- In isomeric alkane (b. pt.) $\propto \frac{1}{\text{branching}}$

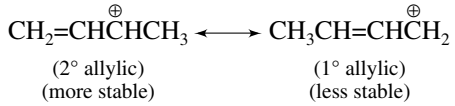
Thus isobutane has least boiling point

4. [1]

$CH_2=CHCH=CH_2 + HBr \longrightarrow$



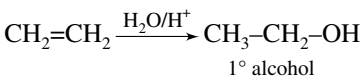
Addition is through the formation of allylic carbocation,

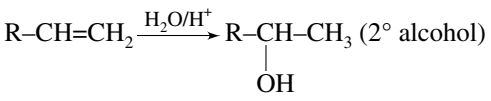


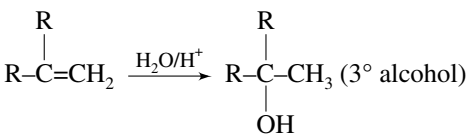
Under mild conditions (temperature = – 80°C) kinetic product is the 1, 2-addition product and under vigorous conditions, (temperature = 40°C) thermodynamic product is the 1, 4-addition product.

Thus, 1-bromo-2-butene is the product under given condition.

5. [1]

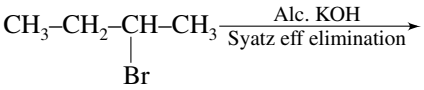


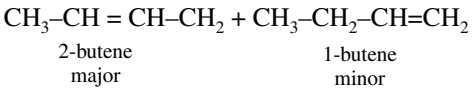




Except ethene other alkene will give secondary or tertiary alcohol

6. [1]

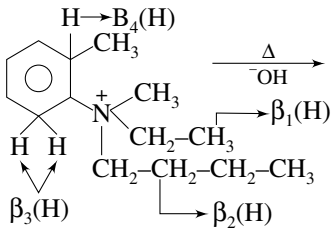


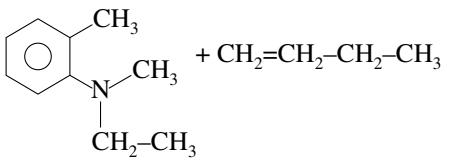


7. [1]

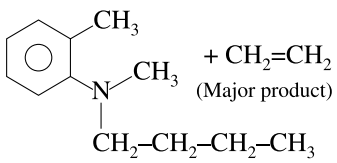
Compounds bearing a quaternary nitrogen atom bonded to four alkyl groups when heated in the presence of base like OH^- undergo E_2 elimination with the formation of less substituted alkene as a major product with the loss of β-H atom.

This type of elimination is called Hofmann elimination.



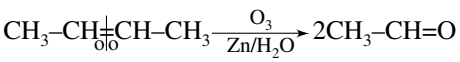


(Minor product)



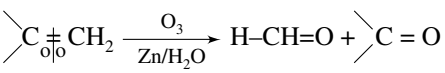
Hence, $CH_2=CH_2$ will be a major product.

8. [3]

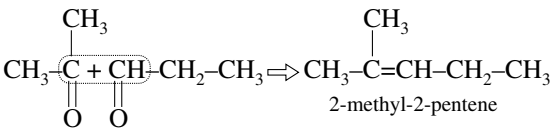


(Ozonolysis)

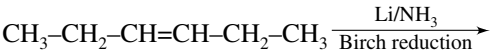
9. [2]

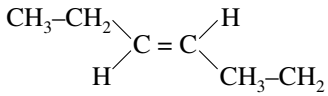


10. [3]



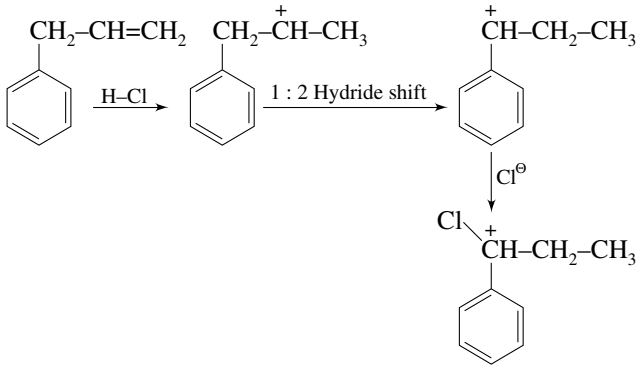
11. [1]





Trans-2-hexene

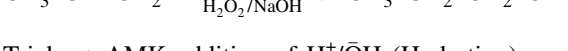
12. [3]



13. [4]

Factual

14. [3]

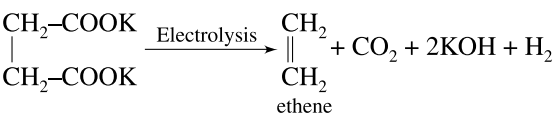


Trick → AMK addition of $H^+/\bar{O}H$ (Hydration)

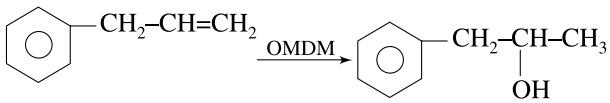
15. [3]

Li/NH_3 (Birch reduction) achieved vig., anti addition.

16. [3]



17. [1]

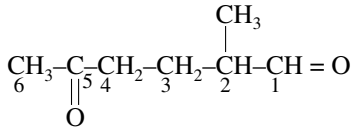


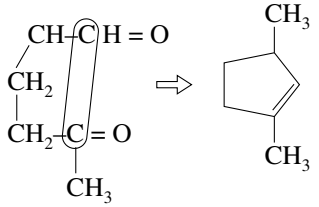
Hydration according to M.K rule

18. [1]

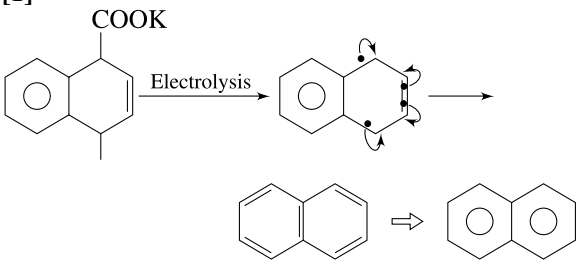
Factual

19. [2]

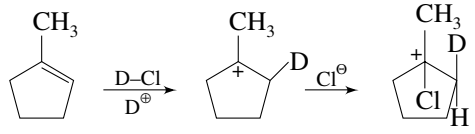




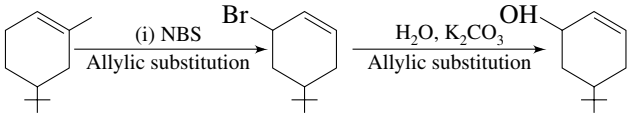
20. [1]



21. [1]



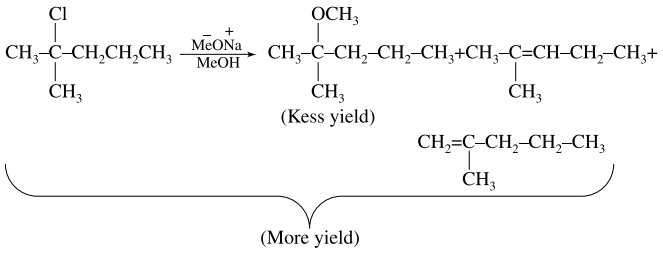
22. [2]



23. [2]

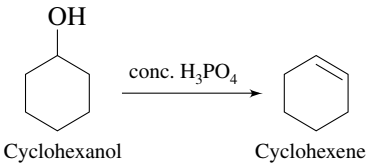
24. [4]

($\bar{O}$Me) in polar solvent (MeOH) gives elimination products over substitution products but all products are possible in different yields.



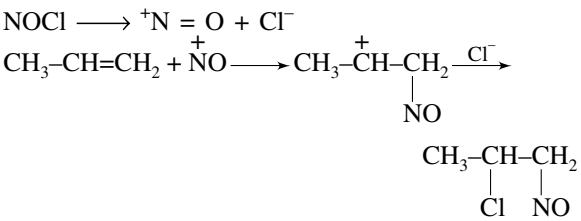
25. [1]

Cyclohexanol, on treatment with concentrated H_3PO_4 undergo acid catalysed dehydration giving cyclohexene.



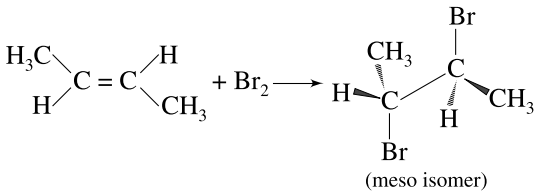
26. [1]

NOCl undergoes electrophilic addition on alkene as



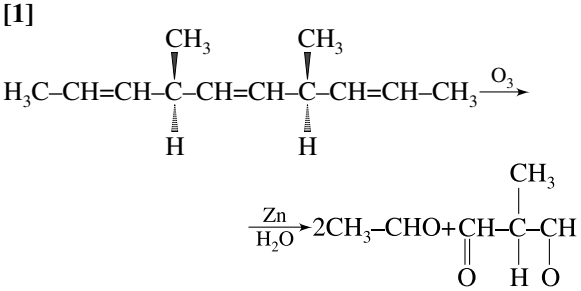
27. [1]

Br_2 undergoes *anti* addition on C = C bonds as:



Trick→TAM (refer Key concept)

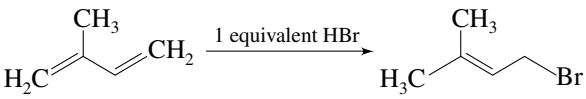
28. [1]



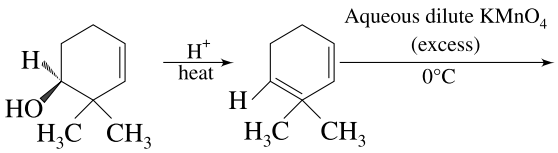
Since, none of the above dial is chiral, no optically active product is obtained.

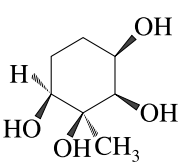
29. [4]

1:4 addition takes place



30. [4]





CHAPTER 6

Aliphatic Hydrocarbons (Alkynes)

INTRODUCTION

- ✦ Alkynes are the acyclic hydrocarbons in which the unsaturation between carbon atoms is triple bond (C≡C)
- ✦ Hybridisation of triple bonded carbon in alkyne is sp
- ✦ Geometry of unsaturated carbon is linear in alkynes
- ✦ Bond angle in alkyne on sp carbon atom is 180°
- ✦ The general formula is C_nH_{2n-2} (n = 2, 3, 4, 5, ...)
- ✦ Nature of bonding

Bond	Bond length	Bond energy
C≡C	1.20 Å	200 kcal/mole
≡C–H	1.08 Å	121 kcal/mole

- Alkynes show the following isomerism and in the table below each isomerism is given with minimum number of carbon atoms required for the isomerism

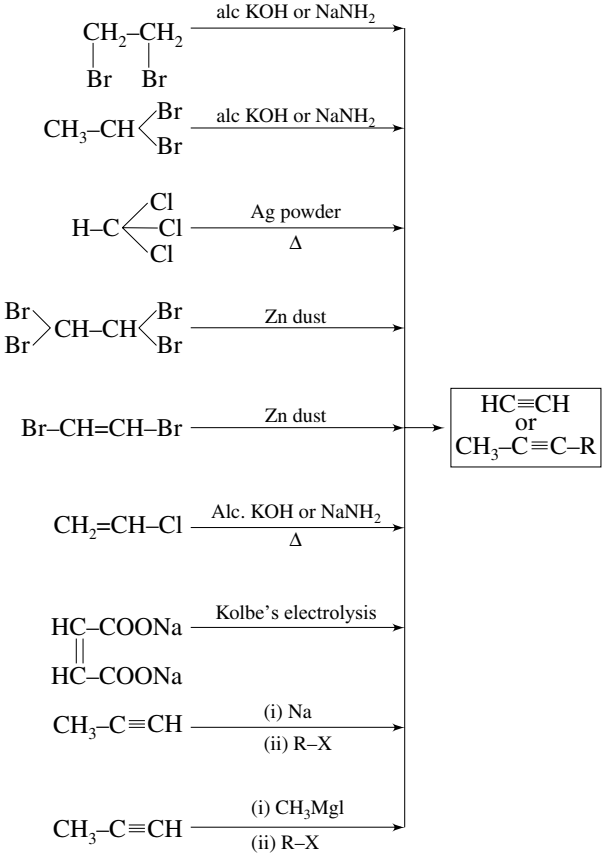
Isomerism	Minimum number carbon
Chain isomerism	5
Position isomerism	4
Functional isomerism	3
Ring chain isomerism	3
Optical isomerism	6

PHYSICAL PROPERTIES

- **Physical state:**
  C_2–C_4 → Gaseous C_5–C_{11} → Liquid C_{12} and above → Solid
- Alkynes are colourless, odourless and tasteless
- Lower alkynes are partially soluble in H_2O (It is due to its polarisability)
- Higher alkynes are insoluble in water due to more % of covalent character
- Completely soluble in organic solvents
- Melting point and Boiling point increases with molecular mass and decreases with number of branches

$$\text{Boiling point (B.P.) and Melting point (M.P.)} \propto \text{Molecular weight} \propto \frac{1}{\text{Number of branches}}$$

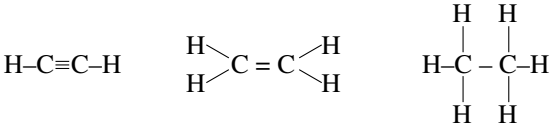
METHOD OF PREPRATION



CHEMICAL PROPERTIES OF ALKYNES

1. Acidic Nature of Terminal Alkynes

The hydrogen atoms of ethyne are considerably more acidic than those of ethane or ethene



$pK_a = 25$ $pK_a = 44$ $pK_a = 50$

The order of basicities of the anions is opposite the relative acidity of the hydrocarbons. The ethanide ions is the most basic and the ethynide ion is the least basic.

Relative Basicity

$$CH_3CH_2{:}^- > CH_2 = CH{:}^- > HC{\equiv}C{:}^-$$

What we have said about ethyne and ethynide ions is true of any terminal alkyne (RC≡CH) and any alkynide ion ($RC{\equiv}C{:}^-$).

If we include other hydrogen compounds of the first-row elements of the periodic table, we can write the following orders of relative acidities and basicities.

Relative Acidity

$$H{-}\ddot{O}H > H - \ddot{O}R > H - C{\equiv}CR > H{-}\dot{N}H_2 > H - CH = CH_2 > H{-}CH_2CH_3$$

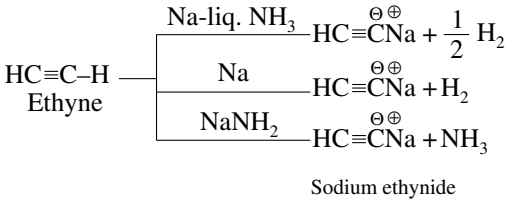
pK_a	15.7	16-17	25	38	44	50

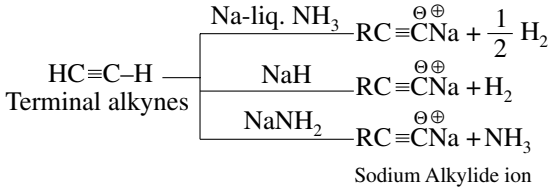
Relative Basicity

$$\overset{\ominus}{O}H < \overset{\ominus}{O}R < \overset{\ominus}{C} \equiv CR < \overset{\ominus}{N}H_2 < \overset{\ominus}{C}H = CH_2 < \overset{\ominus}{C}H_2CH_3$$

We see from the order just given that while terminal alkynes are more acidic than ammonia, they are less acidic than alcohols and are less acidic than water.

(I) Formation of sodium alkylide: Sodium ethynide and other sodium alkynides can be prepared as given below





Hence, ethyne and other terminal alkynes (1-alkynes) are weakly acidic in character. During these reaction, the acetylenic hydrogen is removed as a proton to form stable carbanions (acetylide ions)

Note: Ethyne and terminal alkynes do not give acid-base reaction with NaOH.

$$RC \equiv CH + NaOH \not\longrightarrow RC \equiv \overset{\ominus\,\oplus}{C}Na + H_2O$$

This reaction is not feasible because water (H_2O) is more acidic than ethyne and terminal alkynes

(II) Reaction with Grignard reagent: (Alkylation of acetylene and terminal alkynes).

$$HC \equiv CH + CH_3MgI \longrightarrow CH_4 + CH \equiv C\text{–}MgI$$

$$HC \equiv C\text{–}MgI + ICH_3 \longrightarrow \underset{\text{Propyne}}{CH \equiv C\text{–}CH_3} + MgI_2$$

(III) Reaction with X_2 + Aqueous alkali: Electrophilic substitution reaction takes place.

$$HC \equiv CH + 2Cl_2 + 2NaOH \longrightarrow Cl\text{–}C \equiv C\text{–}Cl + 2NaCl + 2H_2O$$

$$HC \equiv CH + I_2 + 2NH_4OH \longrightarrow I\text{–}C \equiv C\text{–}I + 2NH_3 + 2H_2O$$

(IV) Test of terminal alkynes:

(i) With ammonical solution of silver nitrate (Tollens' reagent).

$$\begin{matrix} CH \\ \| \\ CH \end{matrix} + 2AgNO_3 + 2NH_4OH \longrightarrow \underset{\text{Silver acetylide (White ppt.)}}{\begin{matrix} CH \\ \| \\ CH \end{matrix}} + 2NH_4NO_3 + 2H_4O$$

$$\underset{\text{(Terminal alkyne)}}{R\text{–}C \equiv CH} + \underset{\text{Tollens's reagent}}{[Ag(NH_3)_2]^+\overline{OH}} \longrightarrow \underset{\text{Silver alkynide (White ppt.)}}{R\text{–}C \equiv C\text{–}Ag} + H_2O + 2NH_3$$

(ii) With ammonical solution of cuprous chloride

$$\underset{\text{Acetylene}}{\overset{CH}{\overset{\|}{CH}}} + Cu_2Cl_2 + 2NH_4OH \longrightarrow \underset{\text{Cuprous acetylide (Red ppt.)}}{\overset{C-Cu}{\overset{\|}{C-Cu}}} + 2NH_4Cl + 2H_4O$$

$$\underset{\text{(Terminal alkyne)}}{R-C\equiv CH} + [Cu(NH_3)_2]^+ \overline{O}H \longrightarrow \underset{\text{Copper alkynide (Red ppt.)}}{R-C\equiv C-Cu} + H_2O + 2NH_3$$

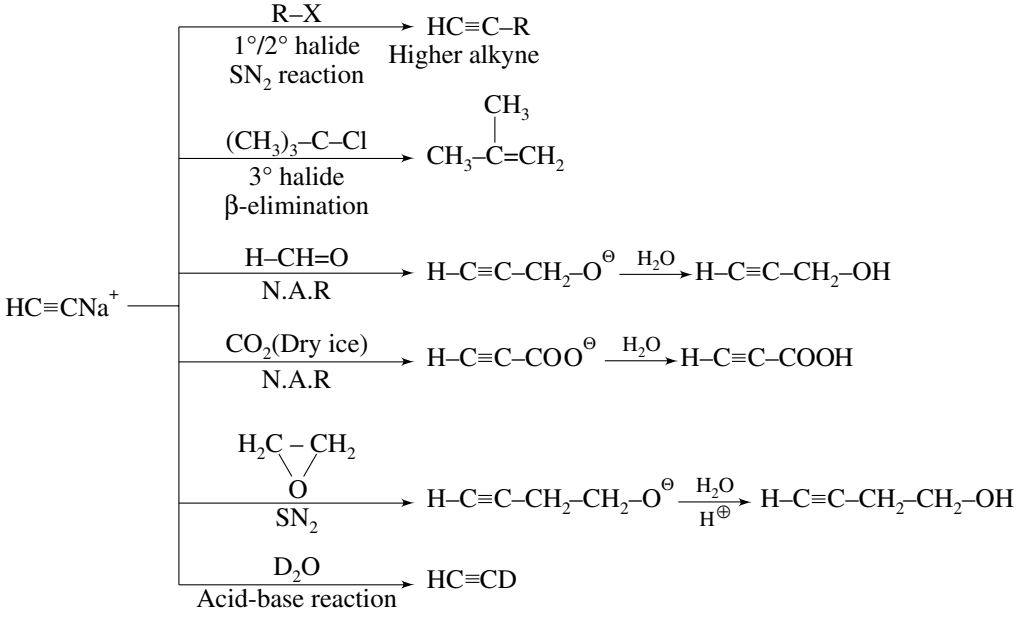
Note: Copper and silver acetylides are very sensitive to shock when dry and may explode violently. However, these can be decomposed by acids to regenerate acetylene.

$$\underset{\text{Cuprous acetylide}}{Cu-C\equiv C-Cu} + 2HCl\ (dil.) \longrightarrow \underset{\text{Acetylene}}{CH\equiv CH} + 2CuCl\downarrow\ \downarrow$$

$$\underset{\text{Silver acetylide}}{Ag-C\equiv C-Ag} + 2HNO_3\ (dil.) \longrightarrow \underset{\text{Acetylene}}{CH\equiv CH} + 2AgNO_3$$

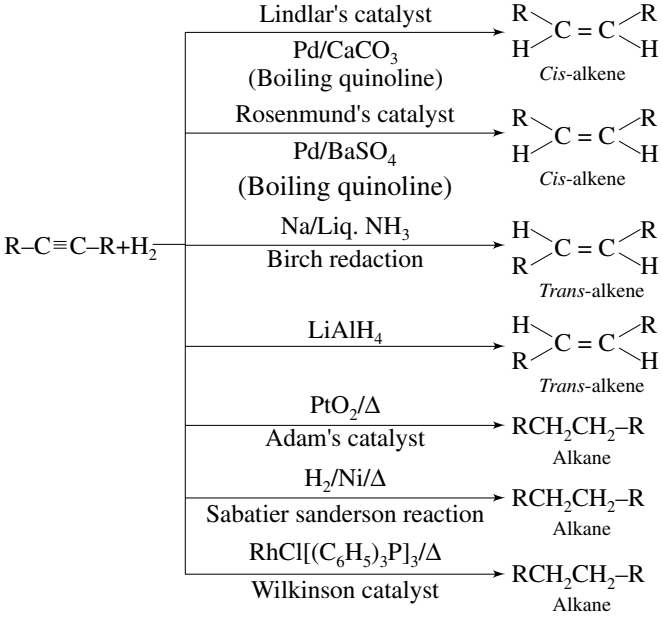
Hence, these reactions can be utilised for the separation of acetylene from a mixture containing ethane, ethylene and acetylene.

(V) Reaction of Sodium Alkynides: Sodium alkynides are useful intermediates for the synthesis of other higher alkynes and also gives many more other reaction.

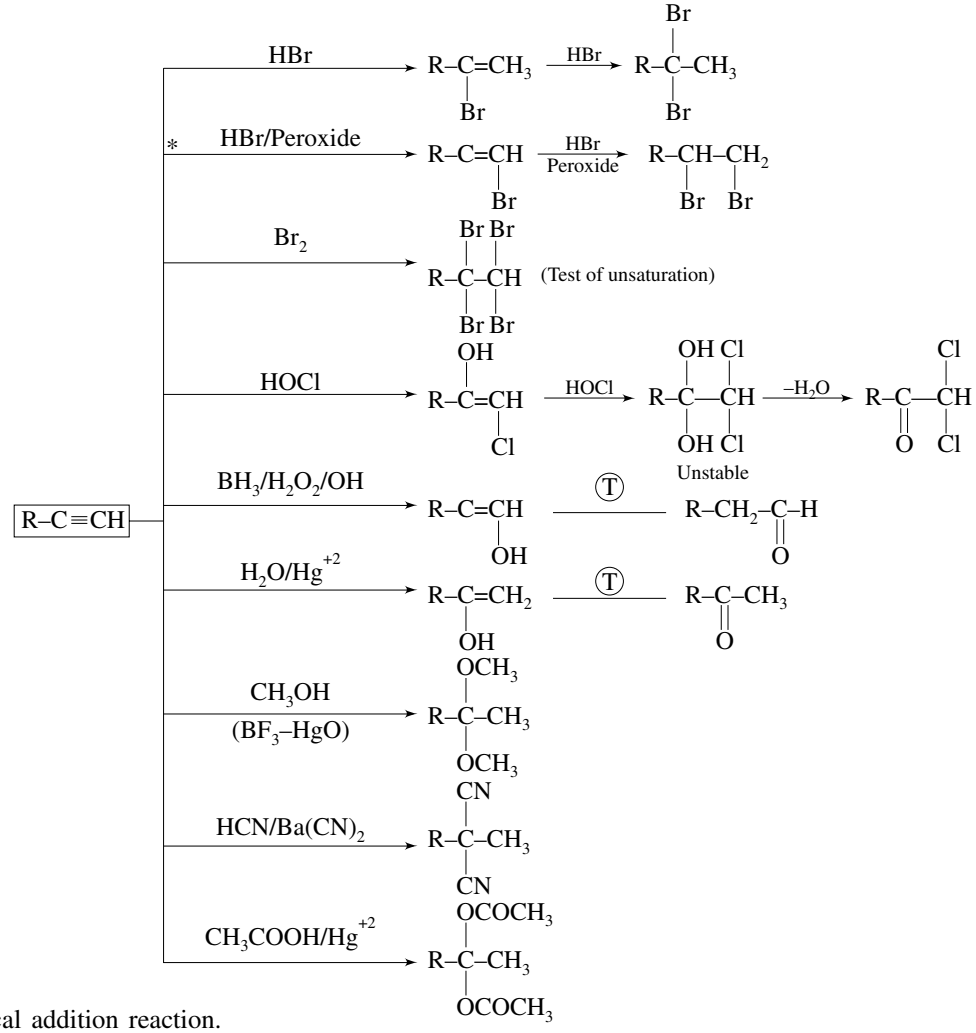


2. Addition Reactions

(i) Addition of hydrogen (Hydrogenation):

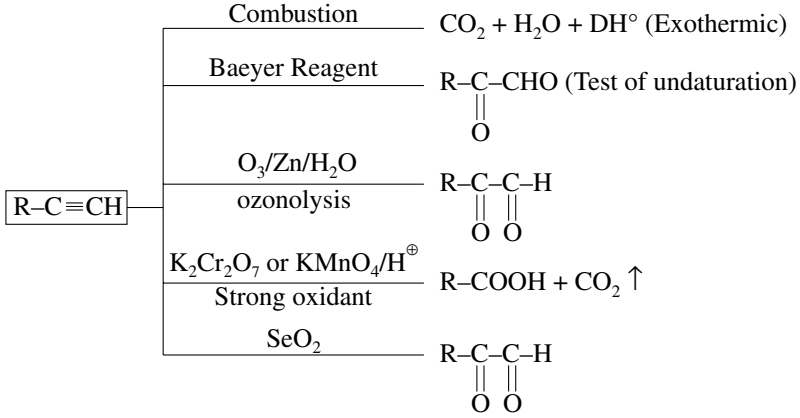


(ii) Ionic addition reaction:



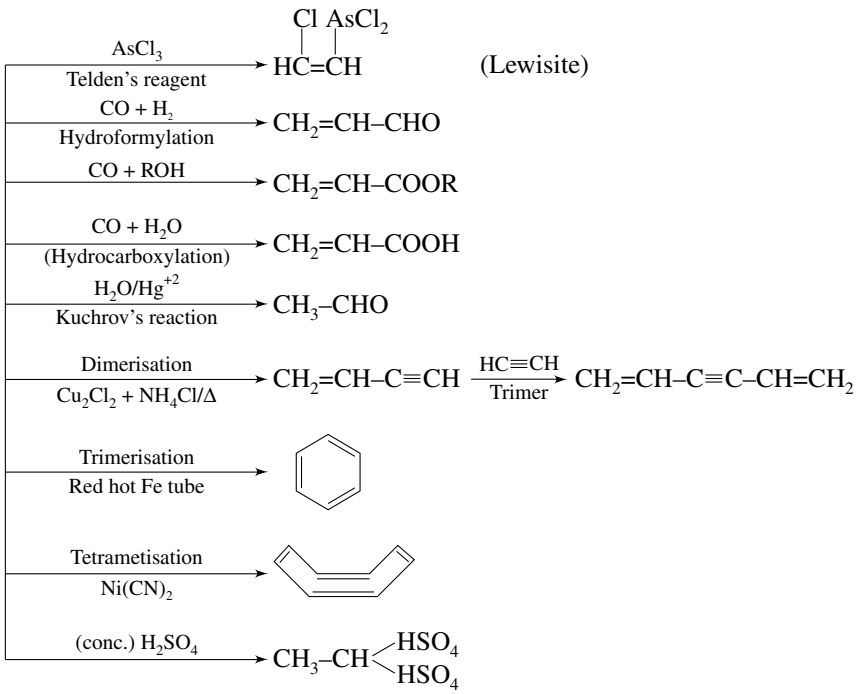
* It is free radical addition reaction.

3. Oxidation Reactions:



Special Points:

- Ethyne is used in oxy-acetylene flame (2800–3200°C) which is used for cutting and welding of metals
- Ethyne is used in carbide lamps for lighting (is an illuminating agent in hawker's lamp)
- When hydrogen is passed in atmosphere of electric arc between carbon electrode, a mixture of H_2 and ethyne is formed **(Berthelot Method)**
- Mixture of ethyne and nitrogen in electric spark converts into HCN
- Ethyne burns with sooty flame due to presence of high percentage of carbon
- Acetylene is used in artificial ripening of fruits
- Pure acetylene **(NARCYLENE)** is odourless and impure acetylene has odour like garlic. It is due to impurities of arsene (AsH_3) and phosphine (PH_3)
- Acetylene and 1-alkyne are acidic in nature. It is due to greater electronegativity of sp hybridised carbon
- Acetylene has two acidic hydrogen atoms. It can neutralise two equivalents of base at the same time. So it is also called as dibasic acid. But the base should be very stronger as $\overset{\ominus}{N}H_2$ or $\overset{\ominus}{C}H_2$, etc.
- Some other reactions of acetylene are:



- **Lewisite** is highly explosive which was used in the World War II. **British anti-Lewisite (B.A.L.)** is an organic compound whose structure is $\underset{OH}{CH_2}\text{–}\underset{SH}{CH}\text{–}\underset{SH}{CH_2}$

- Hydrolysis of metal carbides gives following hydrocarbons:

$Al_4C_3 + 12\ H_2O \longrightarrow 3CH_4 + 4\ Al(OH)_3$

$Be_2C + 4H_2O \longrightarrow CH_4 + 2\ Be\ (OH)_2$

$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$

$Mg_2C_3 + 4H_2O \longrightarrow C_3H_4 + 2\ Mg(OH)_2$

SOLVED EXAMPLE

1. Acetylene and propyne are separately treated with warm aqueous H_2SO_4 (30%) in the presence of $HgSO_4$ as catalyst. The products formed in these two experiments are, respectively

(1) acetone and acetaldehyde

(2) acetaldehyde and propionaldehyde

(3) acetone and propionaldehyde

(4) acetaldehyde and acetone

Sol. **[4]**

$$CH{\equiv}CH \xrightarrow[\text{Hydration}]{HgSO_4/H_2SO_4} CH_2{=}CH{-}O(H) \xrightarrow{\text{tautomerise}} CH_3{-}CH{=}O$$

$$CH_3{-}C{\equiv}CH \xrightarrow[\text{Hydration}]{HgSO_4/H_2SO_4} CH_3{-}\underset{OH}{C}{=}CH_2 \xrightarrow{\text{tautomerise}} CH_3{-}\underset{O}{\overset{\|}{C}}{-}CH_3$$

2. Consider the following two reactions.

$CH_3C \equiv CCH_3 \xrightarrow[\text{quinoline}]{H_2, Pd/BaSO_4}$ (A);

$CH_3C \equiv CCH_3 \xrightarrow{Na/NH_3(l)}$ (B)

The products (A) and (B) are

(1) *trans*-but-2-ene and *cis*-but-2-ene, respectively

(2) *cis*-but-2-ene and *trans*-but-2-ene, respectively

(3) both *cis*-but-2-ene

(4) both *trans*-but-2-ene

Sol. **[2]**

$$CH_3{-}C{\equiv}C{-}CH_3 \xrightarrow[\text{quinoline}]{H_2, Pd/BaSO_4} \underset{\text{Syn addition}}{CH_3{-}\underset{H}{C}{=}\underset{H}{C}{-}CH_3}$$

cis-2-butene

$$CH_3{-}C{\equiv}C{-}CH_3 \xrightarrow{Na\text{–}liqNH_3} \underset{\text{Anti addition}}{CH_3{-}\overset{H}{\overset{|}{C}}{=}\underset{H}{\overset{|}{C}}{-}CH_3}$$

trans-2-butene

3. Two gases P and Q both decolourise aqueous bromine but only one of them gives white ppt. with Tollens' reagent. P and Q are likely to be:

(1) $H_2C = CH_2$ and $CH_3 - C \equiv C - CH_3$

(2) $HC \equiv CH$ and $CH_3 - CH_2 - C \equiv CH$

(3) $HC \equiv CH$ and $CH_3 - C \equiv CH$

(4) $CH_3{-}CH_2{-}C \equiv CH$ and $CH_3{-}C \equiv C{-}CH_3$

Sol. **[4]**

$$\underset{(P)}{CH_3{-}CH_2{-}C{\equiv}CH} \xrightarrow[T.R]{Br_2 - \text{water}} \begin{matrix} + \text{ve test} \\ + \text{ve test} \end{matrix}$$

$$\underset{(Q)}{CH_3{-}C{\equiv}C{-}CH_3} \xrightarrow[T.R]{Br_2 - \text{water}} \begin{matrix} + \text{ve test} \\ - \text{ve test} \end{matrix}$$

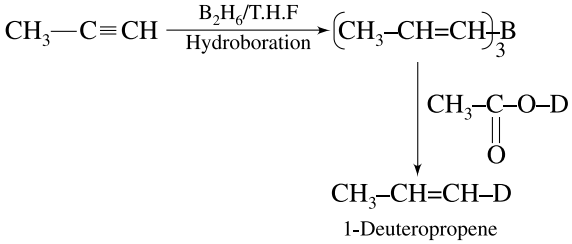
Only terminal alkynes (having acidic H) give white ppt. with Tollens' reagent

4. Propyne is allowed to react with B_2H_6 and the product is subsequently treated with CH_3COOD. The final product formed is

(1) 1-deuteriopropane (2) 2-deuteriopropane

(3) 1-deuteriopropene (4) 2-deuteriopropene

Sol. **[3]**



5. 1-Buten-3-yne, $CH_2=CH-C\equiv CH$, reacts with HCl (one mole) at a low temperature to form mainly:

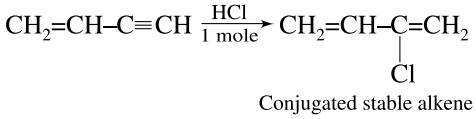
(1) $CH_2=CH-\underset{\displaystyle Cl}{\underset{|}{C}}=CH_2$

(2) $CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-C\equiv CH$

(3) $CH_2=C=CH-CH_2-Cl$

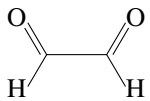
(4) $CH_3CH=C=CHCl$

Sol. **[1]**

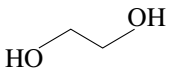


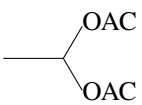
6. $H-\underset{(x)}{\equiv}-H \xrightarrow[(i)\ H_2O/Zn]{(i)\ O_3} (A) \xrightarrow{Zn/CH_3COOH} (B)$

Compound (B):

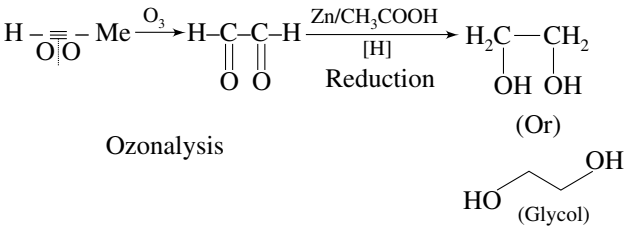
(1) 

(2) Me–COOH

(3) 

(4) 

Sol. **[3]**



7. In which of the following conditions does the reaction take place?

$CH \equiv CH + CH_3OH \longrightarrow CH_3O-CH=CH_2$

(1) $CH \equiv CH + CH_3OH \xrightarrow[160-200°C]{KOMe}$

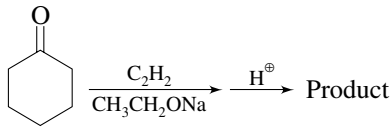
(2) $CH \equiv CH + CH_3OH \xrightarrow{Conc.H_2SO_4}$

(3) $CH \equiv CH + CH_3OH \xrightarrow{anhyd.\ ZnCl_2}$

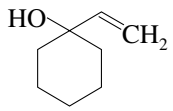
(4) $CH \equiv CH + CH_3OH \xrightarrow[ClHC=CHCl]{dil.HCl}$

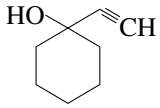
Sol. **[1]**

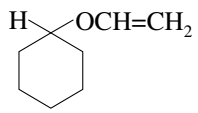
$$CH \equiv CH + CH_3OH \xrightarrow[160-200°C]{KOMe} CH_3-O-CH=CH_2$$

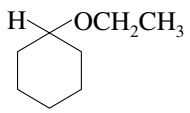
8. 

The Major product is:

(1) 

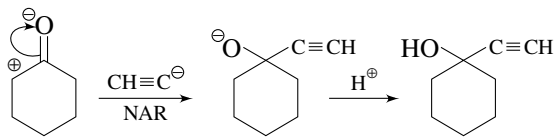
(2) 

(3) 

(4) 

Sol. **[2]**

$$CH{\equiv}CH \xrightarrow{C_2H_5ONa} CH{\equiv}C^{\ominus}(nu^{\ominus})$$



9. Which 2, 3-dibromobutane is treated with KOH in ethanol, 2-bromo-2-butene is formed which does not undergo further dehydrobromination to form 2-butyne under similar condition because

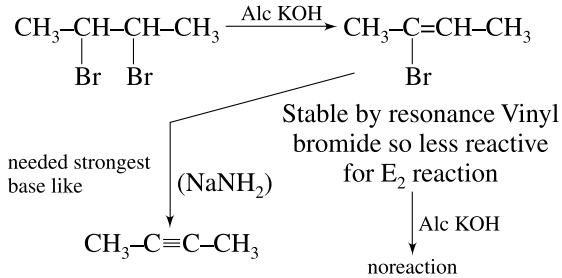
(1) H and Br are not *trans*

(2) There is no further B-H available

(3) Vinyl bromide is very less reactive in E_2 elimination reaction

(4) Reactant is more stable than product

Sol. **[3]**



10. $X \xrightarrow{Na} \xrightarrow{CH_3Br} Y \xrightarrow{Na} \xrightarrow{C_3H_7Br}$ 2-Hexyne.
X and Y are respectively:
(1) $CH_2{=}CH_2$, $CH_3{-}C{\equiv}CH$
(2) $CH{\equiv}CH$, $CH_3{-}C{\equiv}CH$
(3) $CH{\equiv}CH$, $CH_3{-}CH{=}CH_2$
(4) $CH{\equiv}CH$, $HC{\equiv}C{-}CH_2Br$

Sol. **[2]**

$$CH{\equiv}CH \xrightarrow{Na} CH{\equiv}C^{\ominus} \xrightarrow{CH_3-Br} CH_3{-}C{\equiv}CH\ (Y)$$
(X)

$$\xrightarrow{Na} CH_3{-}C{\equiv}C^{\ominus}Na^{\oplus} \xrightarrow{C_3H_7Br} CH_3{-}CH_2{-}CH_2{-}C{\equiv}C{-}CH_3$$
2-hexyne

EXERCISE 1

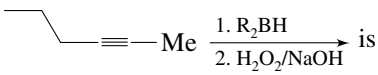
1. Consider the following reaction.

$$CH_3C{\equiv}CCH_3 \xrightarrow{Na/NH_3(l)} (X);$$

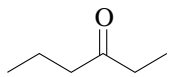
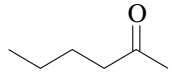
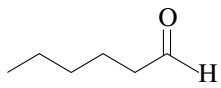
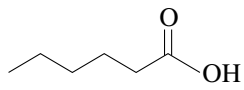
$$CH_3C{\equiv}CCH_3 \xrightarrow[2.CH_3COOH]{1.BH_3} (Y)$$

The products (X) and (Y) are, respectively
(1) (E)-but-2-ene and butan-2-one
(2) (Z)-but-2-ene and (E)-but-2-ene
(3) (*E*)-but-2-ene and (*Z*)-but-2-ene
(4) Both (*E*)-but-2-ene

2. The product of the reaction



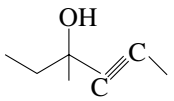
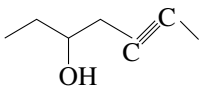
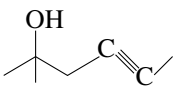
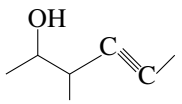
is

(1) 
(2) 
(3) 
(4) 

3. $H_3C - C \equiv C{-}OCH_3 \xrightarrow{Hg^{2+}/H^+/H_2O}$ Product
Major product of the reaction will be:

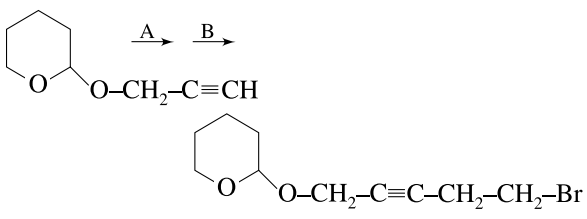
(1) $H_3C{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}OCH_3$
(2) $H_3C{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}OCH_3$
(3) $H_3C{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}OCH_3$
(4) $H_3C{-}CH_2{-}\underset{\underset{OH}{|}}{CH_2}{-}OCH_3$

4. $CH_3CH_2{-}\overset{\overset{O}{\|}}{C}{-}CH_3 + CH_3{-}C{\equiv}CH \xrightarrow[(ii)\ H^+]{(i)\ Na,\ NH_3(l)}$

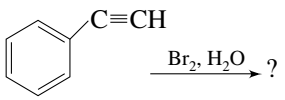
(1) 
(2) 
(3) 
(4) 

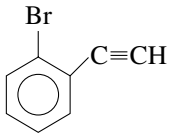
5. Which of the following statements is true for ethane, ethane and acetylene?
(1) Acetylene is the weakest acid and has the longest C–H bond distance
(2) Acetylene is the strongest acid and has the shortest C–H bond distance
(3) Ethane is the strongest acid and has the longest C–H bond distance
(4) Ethane is the strongest acid and has the shortest C–H bond distance

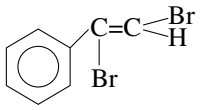
6.

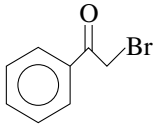


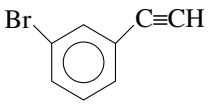
To carry out above conversion, (A) and (B) respectively, are:
(1) $NaNH_2$, $Cl - CH_2 - CH_2 - Br$
(2) $NaNH_2$, $F - CH_2 - CH_2 - Br$
(3) $NaNH_2$, $I - CH_2 - CH_2 - Br$
(4) $NaNH_2$, $I - CH_2 - CH_2 - I$

7. 

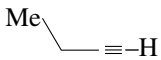
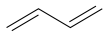
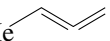
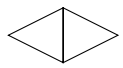
(1) 

(2) 

(3) 

(4) 

8. An organic compound (A) (C_4H_6) forms a precipitate with Tollens' and Fehling's reagents. (A) has an isomer (B). (B) reacts with 1 mol of Br_2 to form 1,4-dibromo-2-butene. (A) and (B) are:

	A		B
(1)		&	
(2)	Me – ≡–H	&	
(3)		&	
(4)	Me – ≡–Me	&	

9. Consider the following sequence of reactions:

$$CH_3C \equiv CH \xrightarrow[2.\ CH_3I]{1.\ NaNH_2} (A) \xrightarrow{Na/NH_3(l)} (B) \xrightarrow[heat]{CH_2N_2} (C)$$

The final product (C) is:

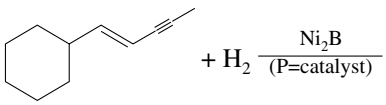
(1) but-2-yne

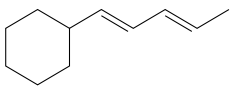
(2) *trans*-but-2-ene

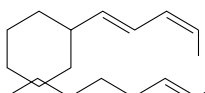
(3) *cis*-1, 2-dimethylcyclopropane

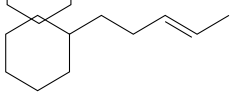
(4) (±)-*trans*-1, 2-dimethylcyclopropane

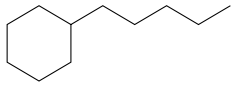
10. Which of the following products is expected in the reaction?

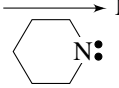


(1) 

(2) 

(3) 

(4) 

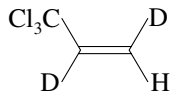
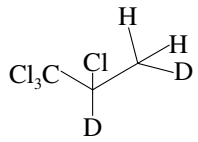
11. Ph – C≡C – H $\xrightarrow{I_2}$  Major product:

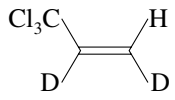
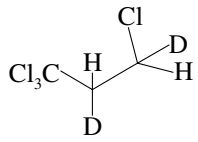
(1) Ph – C(I) = CH – I (2) Ph – CH(I) – CH_2 – I

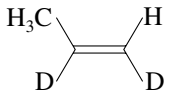
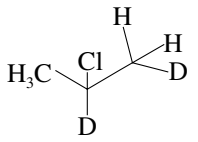
(3) Ph – C ≡ C – I (4) I – C ≡ C – H

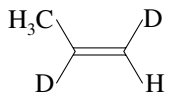
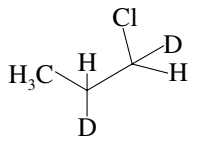
12. $\xrightarrow[D_2+P\text{-}2\text{catalyst}]{} (A) \xrightarrow{HCl} (B)$

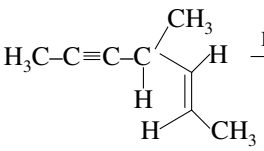
Compounds (A) and (B) are:

(1)  

(2)  

(3)  

(4)  

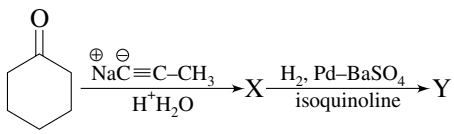
13.  Product:

(1) an optically active compound

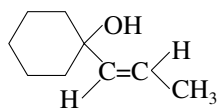
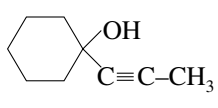
(2) an optically inactive compound

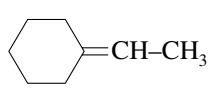
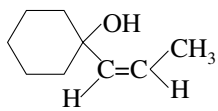
(3) a racemic mixture

(4) a diastereomeric mixture

14. 

Identify the structure of Y:

(1)  (2) 

(3)  (4) 

15. On catalytic hydrogenation, a compound X (C_7H_{12}) absorbs 2 mol of hydrogen and yields 2-methylhexane. On treatment with $Ag(NH_3)_2OH$, X gives a precipitate which contains silver and which regenerates X on treatment with dilute HNO_3. The structure of X is

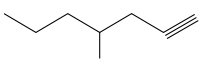
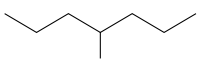
(1) $CH_3CH_2CH_2CH_2CH_2C{\equiv}CH$

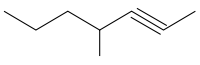
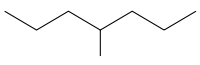
(2) $CH_2{=}CHCH{=}CHCH(CH_3)CH_3$

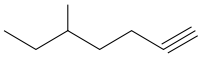
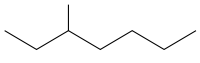
(3) $CH_2C{\equiv}CCH_2CH(CH_3)-CH_3$

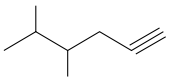
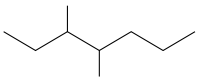
(4) $CH_3-CH(CH_3)CH_2CH_2C{\equiv}CH$

16. An optically active compound A has the molecular formula C_8H_{14}. The Compound gives a precipitate when treated with a solution containing $Ag(NH_3)_2OH$. On catalytic hydrogenation (A) yield B (C_8H_{18}). Compound (B) is optically inactive and cannot be resolved. Propose the structure of A and B.

(1)  and 

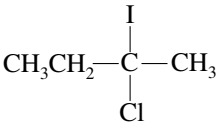
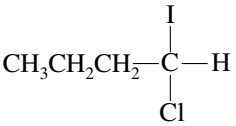
(2)  and 

(3)  and 

(4)  and 

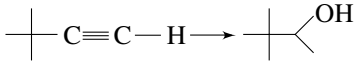
17. Consider the following sequence of reactions.

$CH_3-CH_2-C{\equiv}CH \xrightarrow{HCl} (A) \xrightarrow{HI} (B)$

(1)  (2) 

(3) $CH_3CH_2ClCH_2I$ (4) $CH_3CH_2CHICH_2Cl$

18. Select the reagent for following transformation:



(1) H_2-Pd, HCHO, H_2SO_4

(2) H_2, Pd-$BaSO_4$; $Hg(OAc)_2$, H_2O, $NaBH_4$, $\overset{\ominus}{O}H$

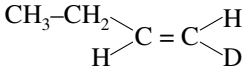
(3) BH_3, H_2O_2, $\overset{\ominus}{O}H$, Pd-C

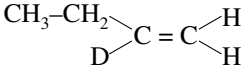
(4) Hg^{+2}, H_2SO_4, H_2, Pd-$BaSO_4$

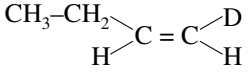
19. In the reaction

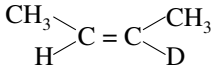
$CH_3CH_2C{\equiv}CH \xrightarrow[THF]{BH_3} I \xrightarrow{CH_3COOD} II$

the end product is

(1) 

(2) 

(3) 

(4) 

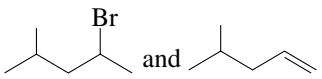
20. 1,1-Dichloropropane is treated with an excess of sodium amide in liquid ammonia. The reaction product is then treated with heavy water to give

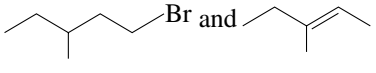
(1) $CH_3-CD{=}CH_2$ (2) $CH_3-CD{\equiv}CH$

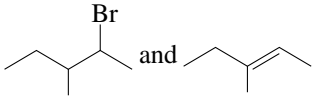
(3) $CH_3-C{\equiv}CH$ (4) $CH_3C \equiv CH-D$

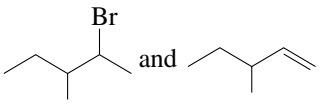
EXERCISE 2

1. An organic compound X ($C_6H_{13}Br$) is optically active. X on treatment with $(CH_3)_3COK$ in $(CH_3)_3COH$ gives Y (C_6H_{12}), a major product. Y on treatment with Br_2–CCl_4 in the presence of $FeBr_3$ gives a dibromide which on further treatment with $NaNH_2$ gives C_6H_{10} which is still optically active. Hence, X and Y. respectively, are

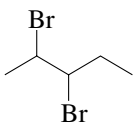
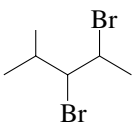
(1) 

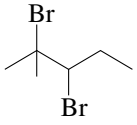
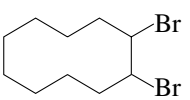
(2) 

(3) 

(4) 

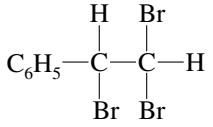
2. When vicinal dibromide is heated with KOH in ethanol (~ 200°C), double dehydrohalogenation takes place giving alkyne. Which of the following fails to give alkyne according to this procedure?

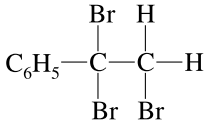
(1)  (2) 

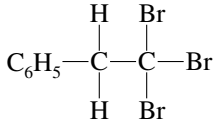
(3)  (4) 

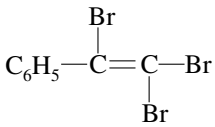
3. The major product of the following reactions is

$C_6H_5—C\equiv C—H + Br_2—H_2O \xrightarrow{HBr}$

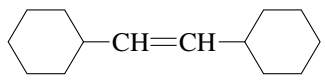
(1) 

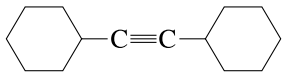
(2) 

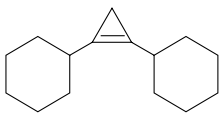
(3) 

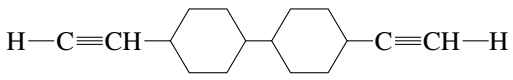
(4) 

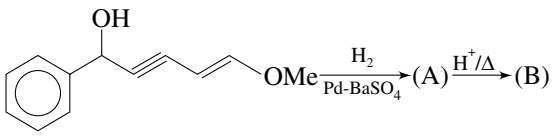
4. A hydrocarbon X ($C_{14}H_{22}$) on treatment with H_2/Pt gives $C_{14}H_{26}$. Also X on treatment with alkaline $KMnO_4$ followed by hydrolysis of products yields $C_7H_{12}O_2$ which on further heating with soda lime gives cyclohexane. Hence, X is

(1) 

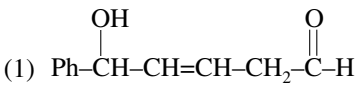
(2) 

(3) 

(4) 

5. 

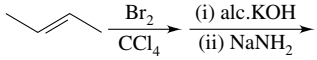
Product (B) is:

(1) 

(2) Ph–CH=CH–CHO

(3) Ph–$(CH=CH)_2$–CHO

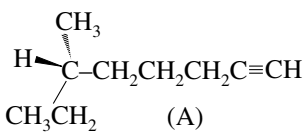
(4) Ph–$(CH = CH)_3$–CHO

6.  (A); Product (A) is:

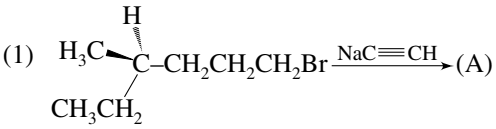
(1) $H_2C=CH–CH=CH_2$ (2) $CH_3–C\equiv C–CH_3$

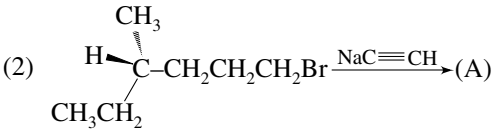
(3) $CH_3–CH_2–C\equiv CH$ (4) $CH_3–CH=C=CH_2$

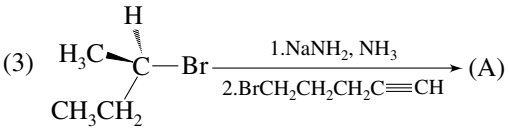
7. Which combination is best for preparation of the compound (A) shown below?

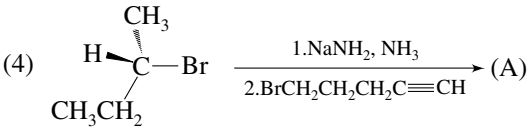


(A)

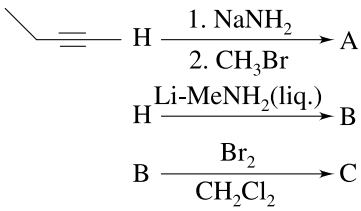
(1) 

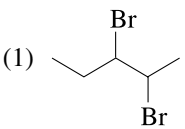
(2) 

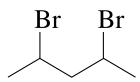
(3) 

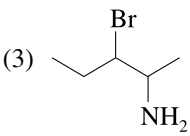
(4) 

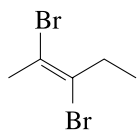
8. What is the final product, C, of the following reaction sequence?



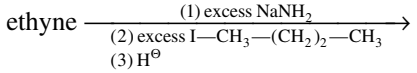
(1) 

(2) 

(3) 

(4) 

9. Predict the product of the following reaction sequence.



(1) 6-iodo-1-hexyne (2) 1-hexyne

(3) 5-decyne (4) 1-iodo-1-hexene

10. Choose the sequence of steps that describes the best synthesis of 1-butene from ethanol :

(1) (1) NaC ≡ CH; (2) H_2, Lindlar Pd

(2) (1) NaC ≡ CH; (2) Na, NH_3

(3) (1) HBr, heat; (2) NaC ≡ CH; (3) H_2, Lindlar Pd

(4) (1) HBr, heat; (2) $KOC(CH_3)_3$, DMSO; (3) H_2, Lindlar catalyst

11. Which of the following best describes what happens in the first step in the mechanism of reaction shown below?

$CH_3CH_2CH_2CHBr_2 + 3NaNH_2 \longrightarrow CH_3—CH_2—C\equiv CNa + 2NaBr + 3NH_3$

(1) $CH_3–CH_2–CH_2–CH(Br)–Br$

(2) $CH_3–CH_2–CH_2–CH(NH_2)–Br$

(3) $CH_3–CH_2–CH_2–CHBr_2$ with H and NH_2

(4) $CH_3–CH_2–CH(Br)–CH(Br)–Br$ with H and NH_2

12. In the following sequence of reactions, what is the end product (III)?

$$\text{C}_6\text{H}_5\text{–C(=O)–CH}_3 \xrightarrow[0°C]{PCl_5} \text{I} \xrightarrow[2.H_3O^+]{1.NaNH_2} \text{II} \xrightarrow[2.H_2O_2/OH^-]{1.B_2H_6} \text{III}$$

(1) $C_6H_5–C(=O)–CH_3$ (2) $C_6H_5–C\equiv CH$

(3) $C_6H_5–CH_2CHO$ (4) $C_6H_5–CH_2CH_2OH$

13. What is the major product of the following reaction?

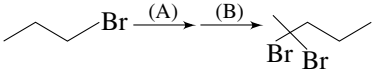
$CH_3C\equiv C–CH_2–CH_3 \xrightarrow[Cl_2]{1 \text{ mole of}}$

(1) $CH_3(Cl)C=C(Cl)CH_2CH_3$

(2) $CH_3CH_2–C(Cl)(Cl)–CH_2CH_3$

(3) $CH_3–C(Cl)(Cl)–CH_2CH_2CH_3$

(4) $CH_3(Cl)C=C(CH_2CH_3)Cl$

14. $CH\equiv CH +$  $\xrightarrow{(A)} \xrightarrow{(B)}$

Reagent A and B are, respectively,

(1) A = $NaNH_2$, B = HBr

(2) A $\Rightarrow$ $NaNH_2$, B = Br_2/CCl_4

(3) A $\Rightarrow$ NaOH, B = HBr

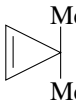
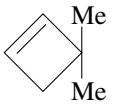
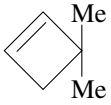
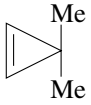
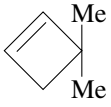
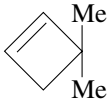
(4) A $\Rightarrow$ NaOH, B = Br_2/CCl_4

15. (A) $(C_5H_8) \xrightarrow[H_2+Pt]{1 \text{ mole}}$ (B) (C_5H_{10})

Resolvable Non-resolvable

(C) $(C_5H_8) \xrightarrow[H_2+Pt]{2 \text{ mole}}$ (D) (C_5H_{12})

Which statement is correct about (A) and (C)?

	(A)	(C)
(1)		
(2)		
(3)		MeHC = C = CHMe
(4)	MeHC = C = CHMe	

EXERCISE 3

One and More Than One Option Correct Type Question

1. Which of the following reactions will give $CH_2=C=CH_2$?

(1) $CH_2Br–CBr=CH_2 \xrightarrow{Zn/CH_3OH}$

(2) $HC\equiv C–CH_2CO_2H \xrightarrow[2. \text{ electrolysis}]{1. K_2CO_3(aq)}$

(3) $2CH_2=CHCH_2I \xrightarrow{2Na}$

(4) $CH_2(Br)–CH_2–CH_2(Br) \xrightarrow{Alc./KOH}$

2. Which of the following reagent(s) can be used to distinguish between 1-hexyne and 2-hexyne?

(1) Ammoniacal $AgNO_3$ solution

(2) Ammoniacal solution of Cu(II) tartarate

(3) Cold, dilute and alkaline $KMnO_4$

(4) $H_2SO_4/HgSO_4$

3. Which of the following sets of reagent when applied sequentially, on 2-butyne will produce a meso product?

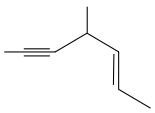
(1) CCl_4/CCl_2 then Br_2/CCl_4

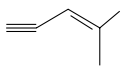
(2) $Na/NH_3(I)$ then Br_2/CCl_4

(3) $Pd/BaSO_4/H_2$ then Br_2–CCl_4

(4) $Pd/BaSO_4/H_2$ then $OsO_4/NaHSO_3$

4. Which would produce chiral molecule after treatment with Lindlar catalyst?

(1)  (2) 

(3)  (4) 

Assertion and Reason Type Question

(1) If both (A) and (R) are correct and (R) is the correct explanation for (A)

(2) If both (A) and (R) are correct and (R) is not the correct explanation

(3) If (A) is correct and (R) is incorrect

(4) If (A) is incorrect and (R) is correct

5. Statement I: Sodium alkynides ($RC\equiv\overset{\ominus}{C}\ \overset{\oplus}{Na}$) cannot be alkylated with $(CH_3)_3C$–Br to form R–C≡C–$C(CH_3)_3$.

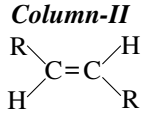
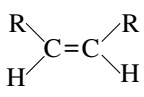
Statement II: The approach of the nucleophile $RC\equiv C^-$ from the opposite side of the C–Br of $(CH_3)_3CBr$ is hindered by the three bulky methyl groups.

6. Statement I: Treatment of either 1,2-dibromobutane or 2,2-dibromobutane with $NaNH_2$ gives the same 1-butyne.

Statement II: $NaNH_2$ forms salt with terminal alkyne which makes possible the above observation

Column Matching Type Question

10. Mach the following

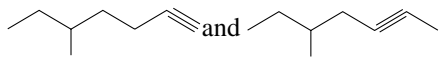
Column-I	*Column-II*
(A) $R–C\equiv C–R + Pd/C/H_2 \longrightarrow$	(p) 
(B) $R–C\equiv C–R + Li/NH_3 \longrightarrow$	(q) RCH_2CH_2R
(C) $R–C\equiv C–R + Pd/CaCO_3/PbO/H_2 \longrightarrow$	(r) 
(D) $R–C\equiv C–R + \dfrac{BH_3.THF}{CH_3COOH}$	(s) $RCH_2\overset{\overset{O}{\|}}{C}CH_3$

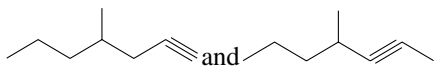
Comprehension Type Question

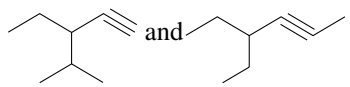
Comprehension (Q. 7–9)

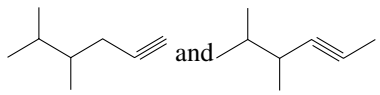
Two isomeric alkynes A and B have molecular formula C_8H_{14} A on treatment with ammoniacal $AgNO_3$ solution forms a white precipitate while B on similar treatment formed no precipitate. Also both A and B are chiral and hydrogenation of either A or B with H_2/Pt gives the same achiral hydrocarbon C (C_8H_{18}). Treatment of A with $HgSO_4/H_2SO_4$ (aq.) gives D ($C_8H_{16}O$) as major product, while on similar treatment of B, mixture of D and E in comparable amounts are formed.

7. The structures of A and B are respectively

(1) 

(2) 

(3) 

(4) 

8. The correct statement regarding A and B is

(1) A and B are chain isomers

(2) A and B are positional isomers

(3) A and B are stereoisomers

(4) Both A and B have only one methyl group

9. What is true regarding A and B?

(1) Both will evolve $H_2(g)$ on heating with Na metal

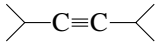
(2) A will give same product with either $HgSO_4/H_2SO_4$ or $B_2H_6/H_2O_2/NaOH$

(3) B will give same product with either $HgSO_4/H_2SO_4$ or $B_2H_6/H_2O_2/NaOH$

(4) Both will produce white ppt. with Tollens' reagent

(1) A → p; B → q; C → r; D → q
(2) A → q; B → p; C → r; D → q
(3) A → r; B → s; C → q; D → p
(4) A → q; B → r; C → p; D → s

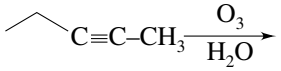
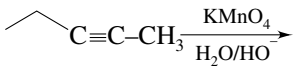
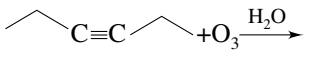
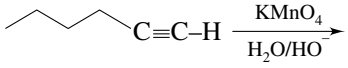
11. Column-I has some alkynes and Column-II has their corresponding reaction products. Match them appropriately.

Column-I	***Column-II***
(1) 1-pentyne	(P) Gives two carbonyls when treated with $H_2SO_4/HgSO_4$
(2) 2-pentyne	(Q) Gives a single carbonyls when treated with $H_2SO_4/HgSO_4$
(3) 	(R) Decolourises brown colour of Br_2–H_2O solution
(4) C_6H_5–C≡C–CH_3	(S) First on reaction with $Na/NH_3(l)$ the addition of Br_2 gives racemic dibromides

Code

	A	***B***	***C***	***D***
(1)	Q, R, S	P, R, S	Q, R	Q, R, S
(2)	S	R, S	Q	P
(3)	S	R	P, Q	Q, S
(4)	R, S	S	P, Q	P, Q, R

12. Column-I has some reaction and Column-II has the characteristics of reactions and products of Column-I. Match the appropriately.

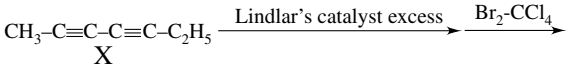
Column-I	***Column-II***
(A) 	(P) Gives only one type of carboxylic acid
(B) 	(Q) Gives more than one type of carboxylic acids
(C) 	(R) Gives off CO_2
(D) 	(S) Involve an *in situ* preparation of oxidizing agent

Code

	A	***B***	***C***	***D***
(1)	Q, S	Q	P, S	P, R
(2)	S	R	Q	P
(3)	S	R, S	P, Q	Q
(4)	R, S	S	P, Q	P

Single Digit Integer Type Question

13. In the reaction below:



how many different isomers of tetrabromides are formed?

14. One mole of 1,2-dibromopropane on treatment with X moles of $NaNH_2$ followed by treatment with ethyl bromide gave a pentyne. The value of X is

15. How many different isometric alkynes on catalytic hydrogenation can give 2, 3, 4-trimethyl heptane?

EXERCISE 4

1. Reaction **[AIEEE-2002]**

H–C≡C–H + HOCl ⟶ Product, here product will be

(1) $CHCl_2$–CHO (2) CHO–CHO
(3) CH–Cl≡CHCl (4) $CHCl_2$–$CHCl_2$

2. Acetylene does not react with **[AIEEE-2002]**

(1) $NaNH_2$ (2) NaOH
(3) Na metal (4) Ammonical $AgNO_3$

3. Which of the following reactions will yield 2, 2-dibromopropane? **[AIEEE-2007]**

(1) $CH_3–C\equiv CH + 2HBr \longrightarrow$

(2) $CH_3CH = CHBr + HBr \longrightarrow$

(3) $CH\equiv CH + 2HBr \longrightarrow$

(4) $CH_3–CH = CH_2 + HBr \longrightarrow$

4. The hydrocarbon which can react with sodium in liquid ammonia is **[AIEEE-2008]**

(1) $CH_3CH_2C\equiv CH$

(2) $CH_3CH=CHCH_3$

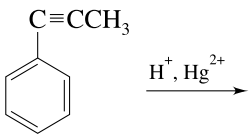
(3) $CH_3CH_2C\equiv CCH_2CH_3$

(4) $CH_3CH_2CH_2C\equiv CCH_2CH_2CH_3$

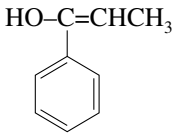
5. The hydration of propyne results in formation of **[JEE Main Online-2012]**

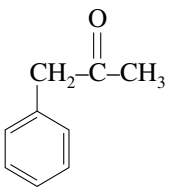
(1) Propanol-1 (2) Propanal

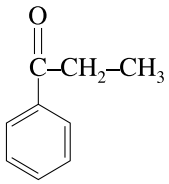
(3) Acetone (4) Propene

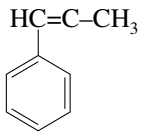
6. In the given reaction  The product 'A' is

[JEE Main Online-2012]

(1) 

(2) 

(3) 

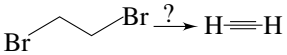
(4) 

7. The major organic compound formed by the reaction of 1, 1, 1–trichloroethane with silver powder is **[JEE Main Online-2014]**

(1) Ethene (2) 2-Butyne

(3) 2-Butene (4) Acetylene

8. The reagent(s) for the following conversion,

 is/are **[IIT Online-2007]**

(1) alcoholic KOH

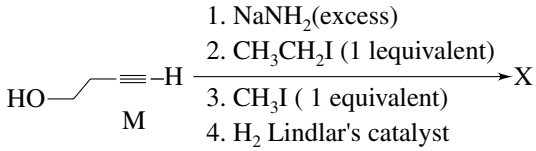
(2) alcoholic KOH followed by $NaNH_2$

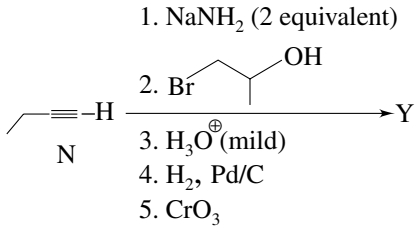
(3) aqueous KOH followed by $NaNH_2$

(4) Zn/CH_3OH

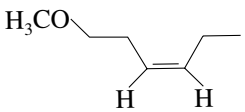
Passage: (9 and 10)

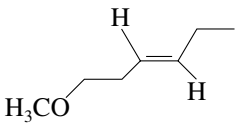
Schemes 1 and 2 describe sequential transformation of alkynes M and N. Consider only the major products formed in each step for both the schemes.

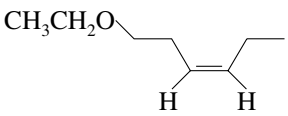


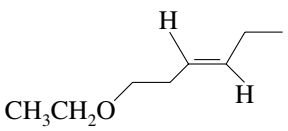


9. The product X is- **[JEE Adv.-2014]**

(1) 

(2) 

(3) 

(4) 

10. The correct statement with respect to product Y is **[JEE Adv.-2014]**

(1) It gives a positive Tollens' test and is a functional isomer of X

(2) It gives a positive Tollens' test and is a geometrical isomer of X

(3) It gives a positive iodoform test and is a functional isomer of X

(4) It gives a positive iodoform test and is a geometrical isomer of X

ANSWER KEY

EXERCISE # 1

1. (3)	2. (2)	3. (2)	4. (1)	5. (2)
6. (3)	7. (3)	8. (1)	9. (4)	10. (2)
11. (3)	12. (2)	13. (1)	14. (4)	15. (4)
16. (1)	17. (1)	18. (2)	19. (1)	20. (4)

EXERCISE # 2

1. (4)	2. (3)	3. (2)	4. (2)	5. (3)
6. (2)	7. (2)	8. (1)	9. (3)	10. (3)
11. (4)	12. (3)	13. (4)	14. (1)	15. (3)

EXERCISE # 3

1. (1,4)	2. (1,2)	3. (1,2,4)	4. (1,2,3)	5. (1)
6. (1)	7. (2)	8. (2)	9. (3)	10. (2)
11. (1)	12. (1)	13. (4)	14. (3)	15. (8)

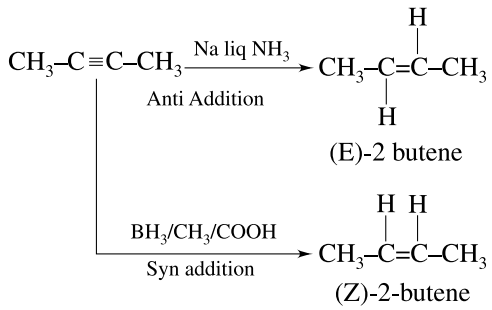
EXERCISE # 4

1. (1)	2. (2)	3. (1)	4. (1)	5. (3)
6. (3)	7. (2)	8. (2)	9. (1)	10. (3)

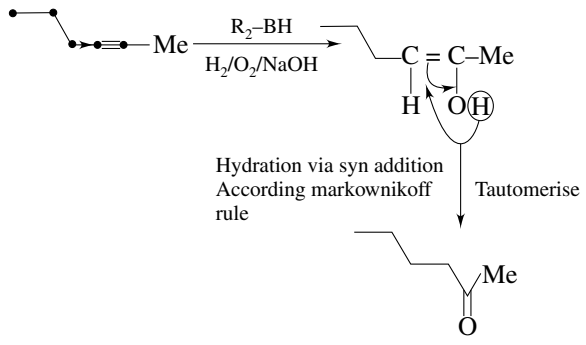
HINT AND SOLUTION

EXERCISE # 1

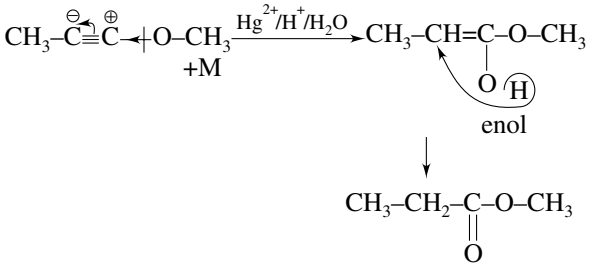
1. [3]



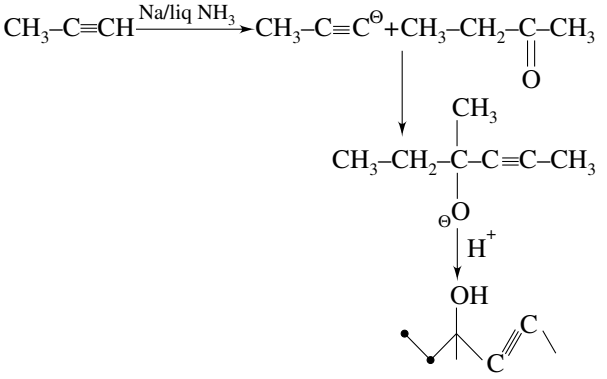
2. [2]



3. [2]

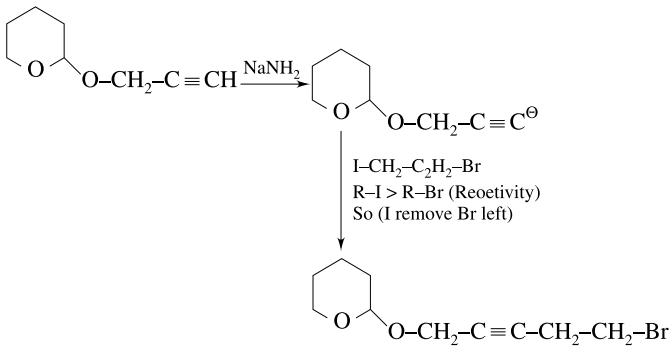


4. [1]

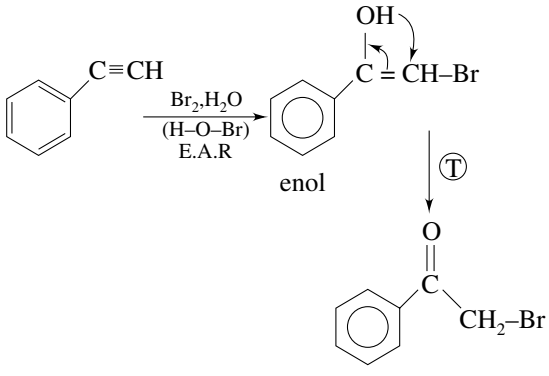


5. [2]

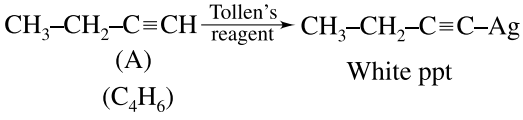
6. [3]

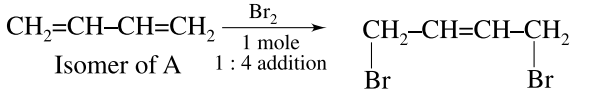


7. [3]



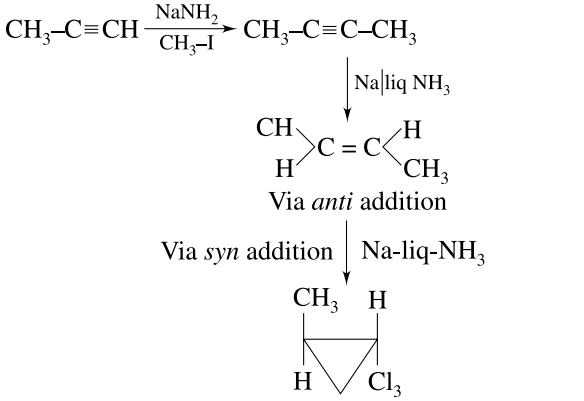
8. [1] A must be teminal alkyne



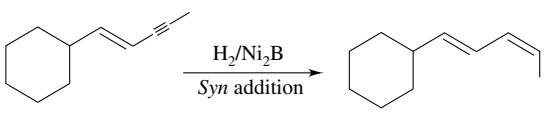


1, 4-dibromo-2-butene

9. [4]

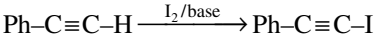


10. [2]

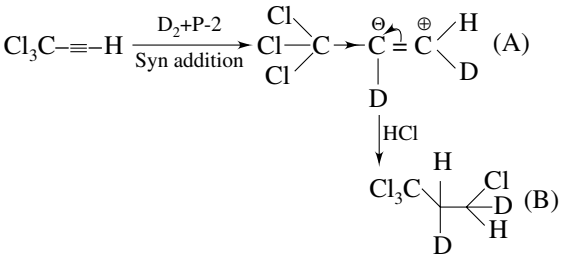


11. [3]

Electrophile substitution reaction takes place

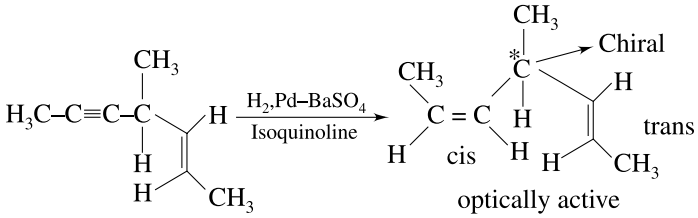


12. [2]

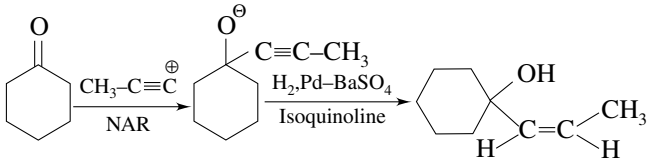


(Due to –I effect of three Cl atoms, electromeric effect takes place from C–1 to C–2)

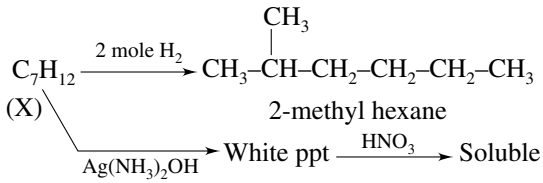
13. [1]



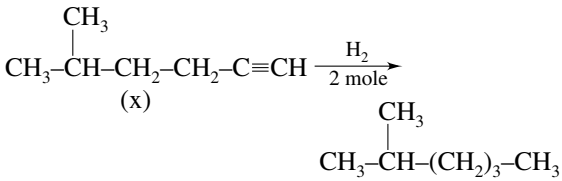
14. [4]



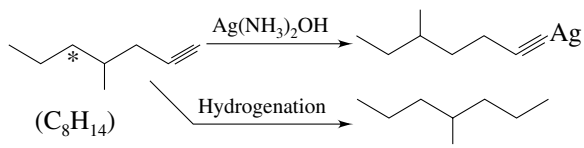
15. [4]



X → must be terminal alkyne having iso group



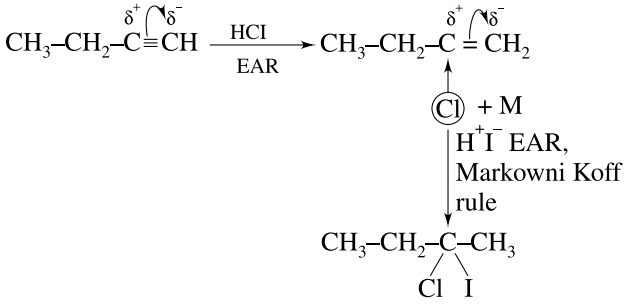
16. [1] A must be terminal alkyne



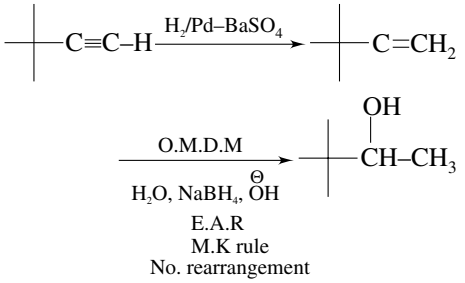
Optically active (A)

Optically inactive (B)

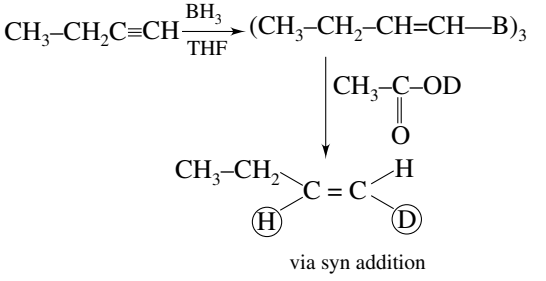
17. [1]



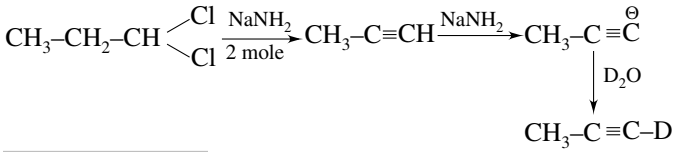
18. [2]



19. [1]



20. [4]

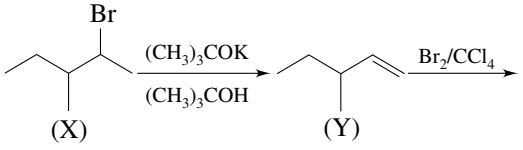


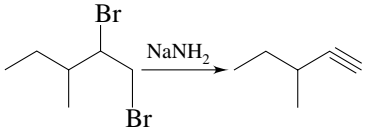
EXERCISE # 2

1. [4]

The last product formed after dehydrobromination (–2HBr) is an alkyne. The only optically active alkyne with six carbon atoms is 3-methly-1-pentene.

Hence, Y must be 3-methyl-1-pentene.

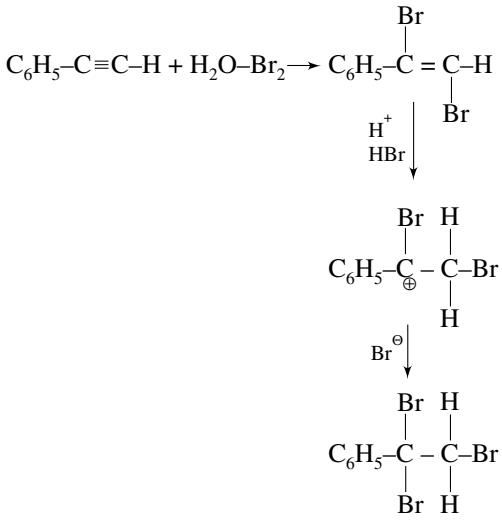




2. [3]

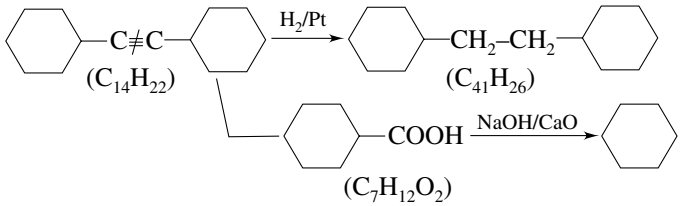
Triple bond cannot be formed in option 3 here between carbons bearing bromine atoms.

3. [2]

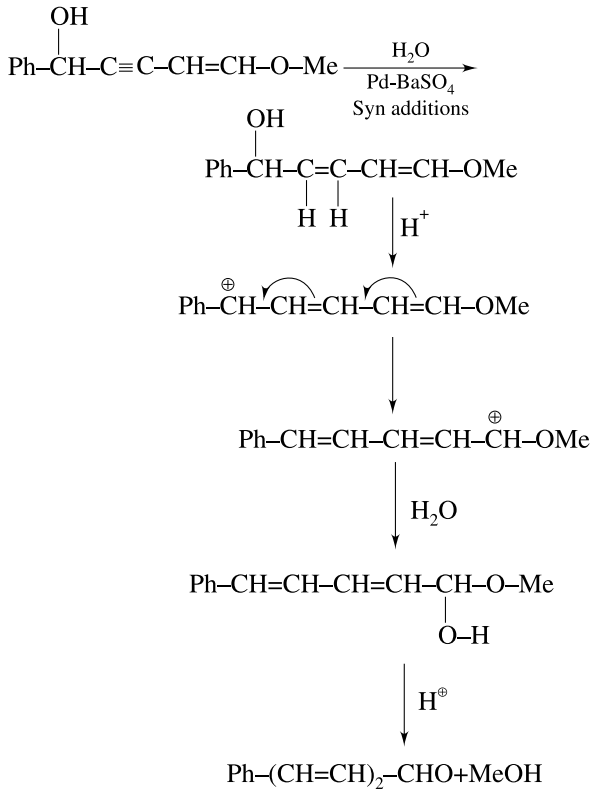


4. [2]

Decarboxylation reaction indicates that the acid is cyclohexane carboxylic acid. Hence, the alkyl must by dicyclohexyl ethyne.

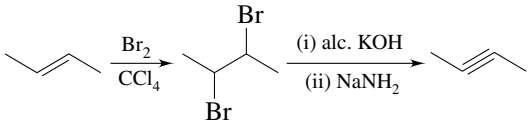


5. [3]

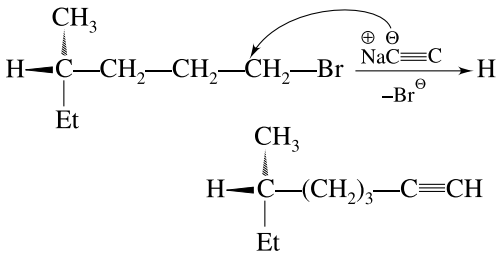


6. [2]

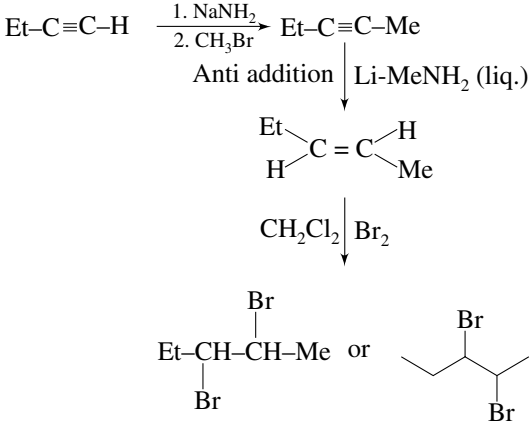
Formation of vicinal di-halide followed by two consecutive E_2 reaction.



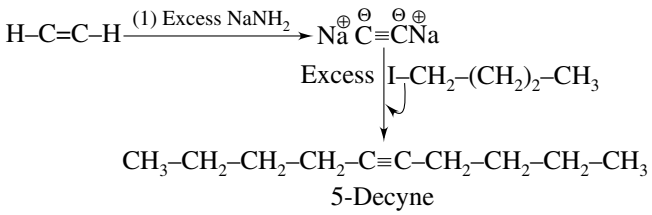
7. [2]



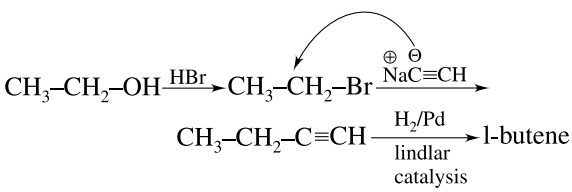
8. [1]



9. [3]



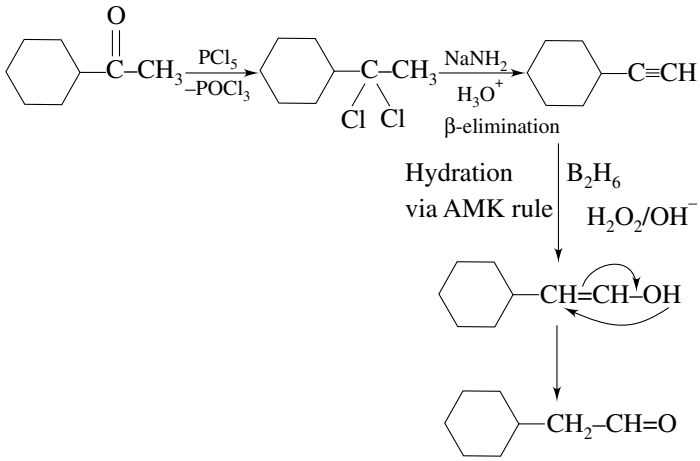
10. [3]



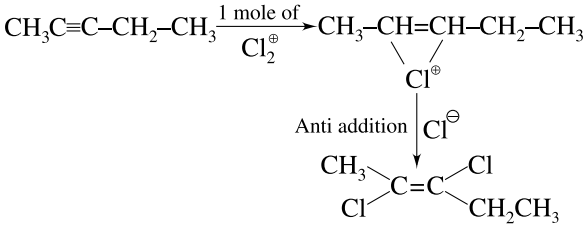
11. [4]

Strong base NH_2^- takes H from β-position.

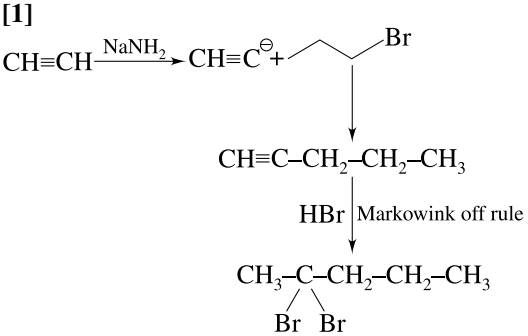
12. [3]



13. [4]



14. [1]

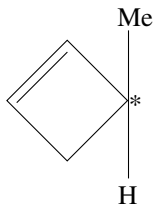


15. [3]

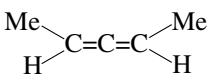
$$DU = (C + 1) - \left(\frac{H + X + N}{2}\right) = (5 + 1) - \frac{8}{2} = 2$$

D.U. of A is 2, it must have 3C, 4 C or 5C-ring, but 5C-ring alkene will not show optical isomerism

So structure of (A) ⇒

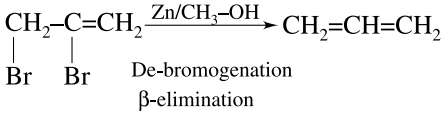


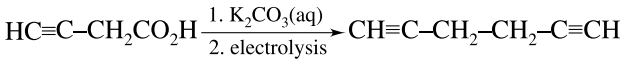
Similarly, D.U. of C is also 2, it must have two double bond, so that cannot have ring; therefore, only allenes with two different groups are resolvable. So the structure of (C) is:

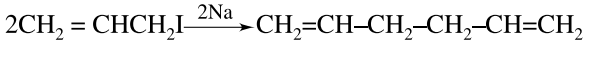


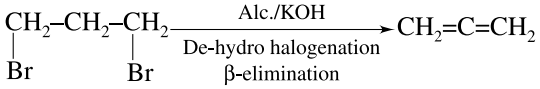
EXERCISE # 3

1. [1, 4]





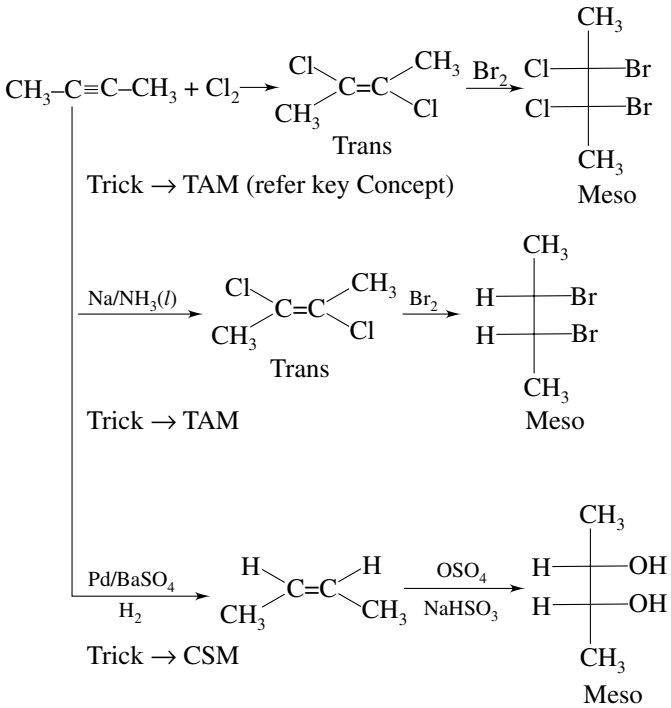




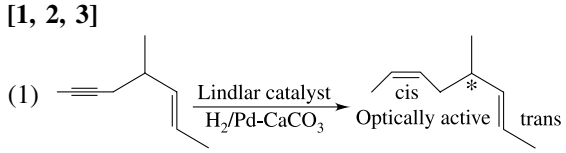
2. [1, 2]

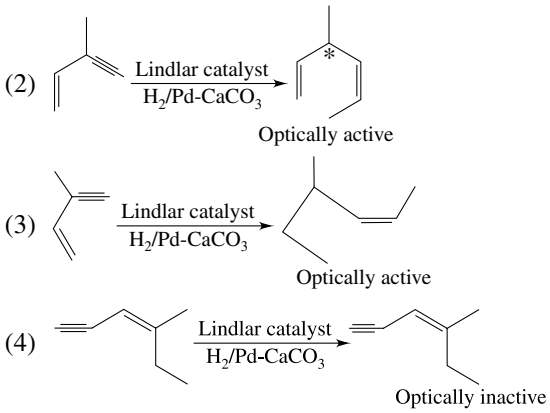
1-hexyne being terminal alkyne, has acidic hydrogen, forms silver and copper salt precipitate respectively while with internal alkyne, 2-hexyne, no such precipitate is formed. Cold, dilute and alkaline $KMnO_4$ (Baeyer's reagent) gives positive test with both terminal and internal alkynes, cannot be used for distinction between them.

3. [1, 2, 3]



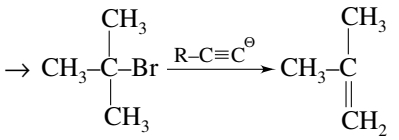
4. [1, 2, 3]





5. [1]

→ 3° halide will give β-elimination reaction predominantly with $R–C\equiv C^{\ominus}$

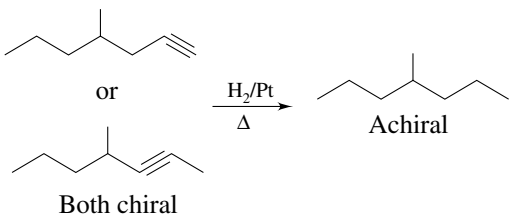


i.e., $nu^{\ominus}$ do not approach from opposite site

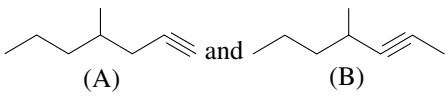
6. [1]

7. [9]

Since, both A and B giving achiral alkane 'C' on catalytic hydrogenation methyl group must be at the central carbon.



Since, A reacts with Tollens' reagent, B does not, A is terminal alkyne while B is internal alkyne Hence,



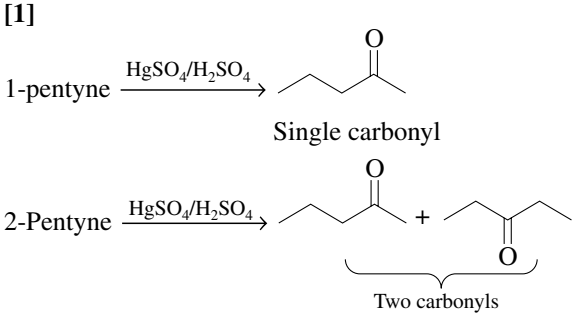
7. [2]

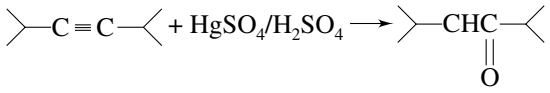
8. [2]

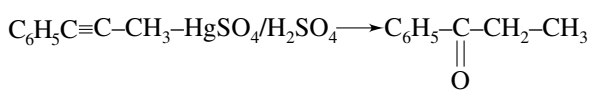
9. [3]

10. [2]

11. [1]







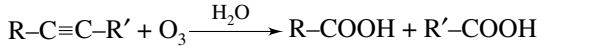
Single carbonyl (2)

All of the above decolourises brown Br_2–H_2O solution

(A) → Q, R, S; (B) → P, R, S; (C) → Q, R; (D) → Q, R, S

12. [1]

Ozonolysis of alkynes followed by hydrolysis result in formation of carboxylic acids as

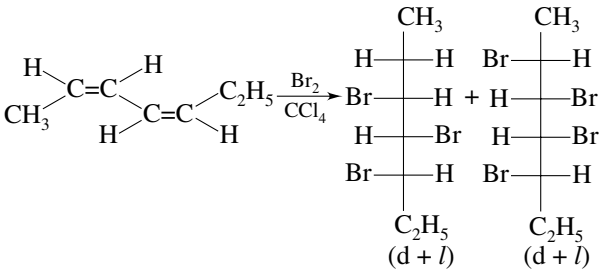


Here, hydrolysis of intermediate ozonide produces H_2O_2 which oxidizes the previously formed aldehydes into R–COOH

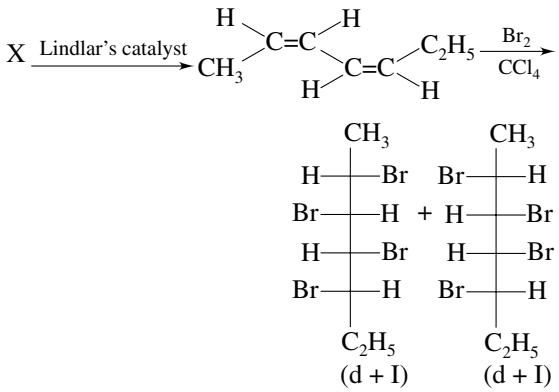
The aldehydes are oxidised further into carboxylic acid. With KMnO4, all internal or terminal alkynes are oxidised to acid

A → Q, S; B → Q; C → P, S; D → P, R

13. [4]

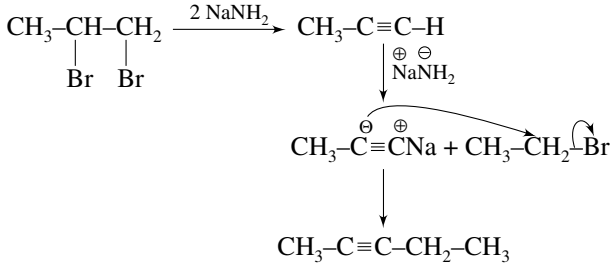


Only *anti*-dibromide at each double bond is formed.



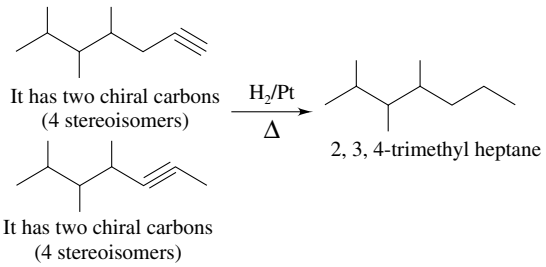
Only *anti*-dibromide at each double bond is formed.

14. [3]



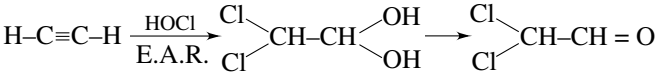
Total 3 moles of $NaNH_2$ are required.

15. [8]

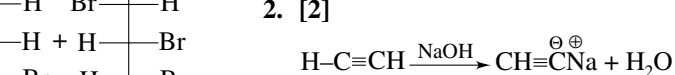


EXERCISE # 4

1. [1]



2. [2]

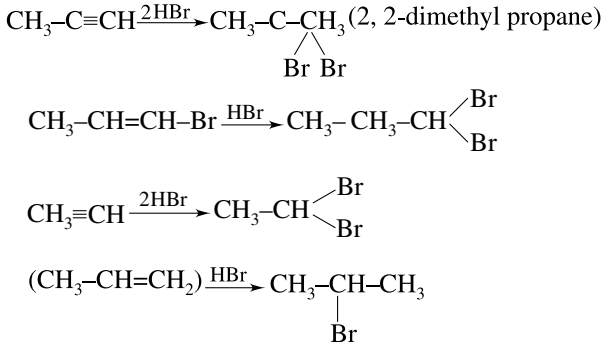


This reaction is not possible due to SAWB Theory

Acidic strength H–C≡CH < H_2O

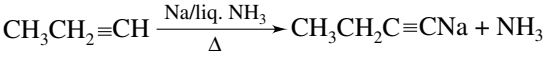
So that this reaction is not feasible.

3. [1]

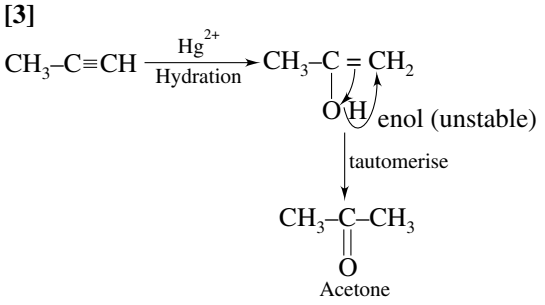


4. [1]

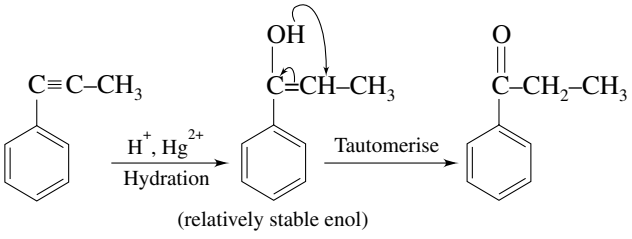
Only acidic H alkyne gives acid base reaction with Na/liq NH_3



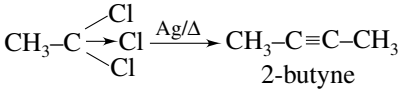
5. [3]



6. [3]

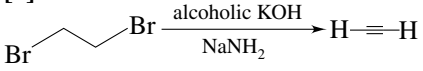


7. [2]



This reaction completed by methyl carbyne ($CH_3-\ddot{\ddot{C}}$) intermediate **

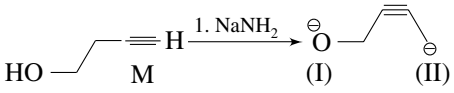
8. [2]



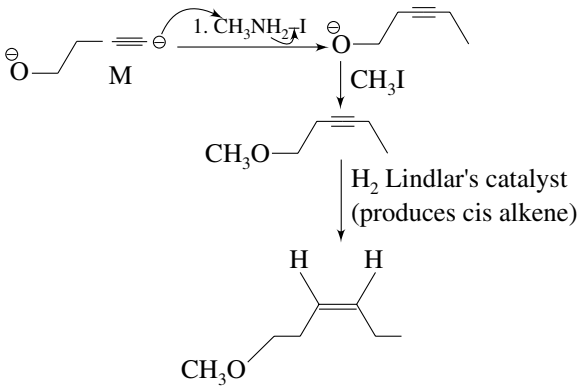
9. [1]

This problem can be solved by using the concept of nucleophilic substitution reaction, oxidation reaction and reduction reaction including strength of nucleophile and regioselectivity.

Reaction of Scheme 1 can be completed as



Among two nacked nucleophilic group I and II, II is more nucleophilic and then will react selectively as follows

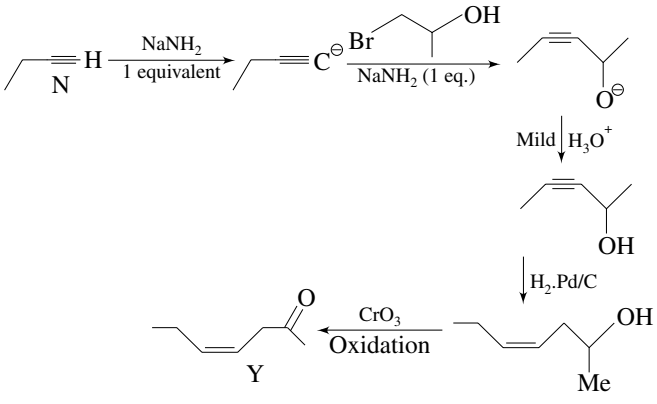


Hence, using the concept of regioselectivity we come on the conclusion that final product is correctly represented by structure (1).

10. [3]

This problem can be solved by using the concept of iodoform test and functional isomerism,

Iodoform test the compound containing $-COCH_3$ or –CH(OH) group will undergo iodoform test.



Thus, X and Y are function isomers of each other and Y Gives iodoform test due to the presence of CH_3CO group as indicated Hence, correct choice is (3)

CHAPTER 7

Aromatic Hydrocarbon (Arenes)

INTRODUCTION

- Aromatic hydrocarbons are also called arenes
- General formula of arenes is C_nH_{2n-6y} where y is the number of benzene ring in molecule
- Following reactions are important in the determination of the structure of benzene

(i) $C_6H_6 \xrightarrow[Pt]{H_2/\Delta}$ 

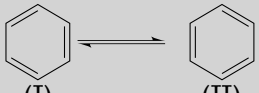
(ii) $C_6H_6 \xrightarrow[2.\ H_2O/Zn]{1.\ O_3}$ 

(iii) $C_6H_6 \xrightarrow[Cold\ \&\ dil.]{KMnO_4}$ No reaction (no decolourisation)

(iv) $C_6H_6 \xrightarrow{Br_2CCl_4}$ No reaction

(v) $C_6H_6 \xrightarrow{HCl}$ No reaction

On the basis of (i) and (ii) reactions Kekule in 1865 suggested that benzene is equilibrium mixture of cyclohexatrienes [(I) and (II)] as follows

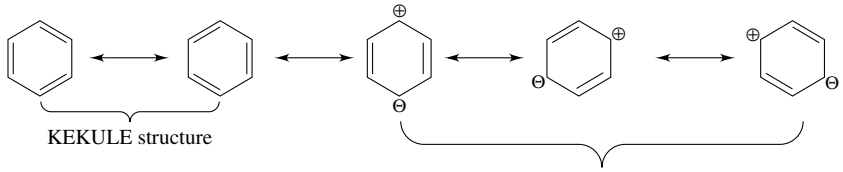


(I) (II)

But reaction (iii), (iv) and (v) cannot be explained by Kekule's structure.

THE RESONANCE HYBRID STRUCTURE

According to the resonance theory, benzene is a resonance hybrid of the following canonical forms.



Contribution: Total 80% Total 20%

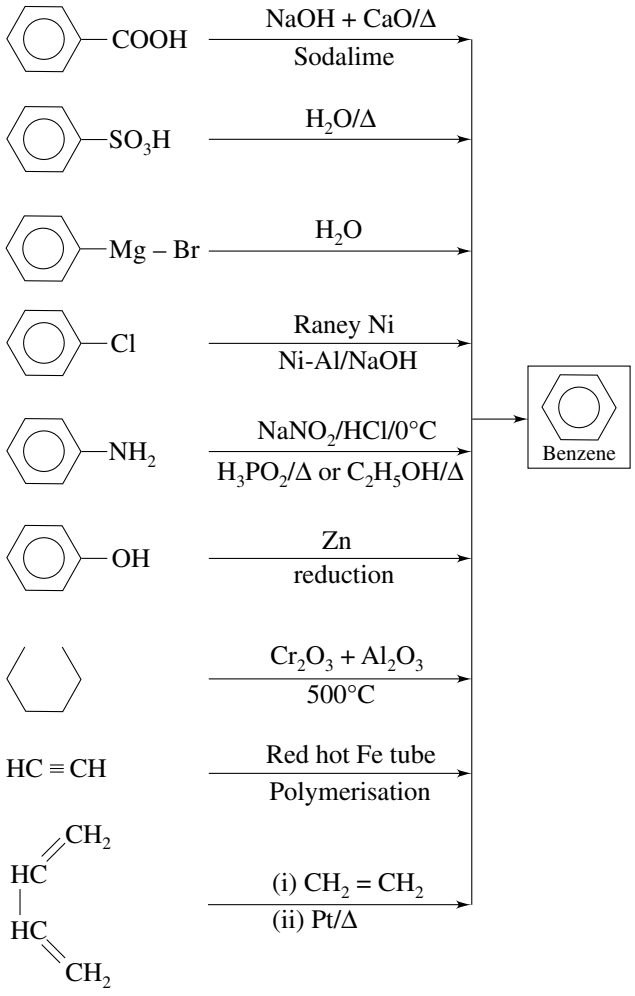
40% each i.e., $\frac{20}{3}$% contribution by each

It should be noted that the concept of resonance is imaginary and the canonical forms mentioned above actually do not exist. It is the hybrid structure which is a reality.

Physical Properties of Benzene

- Benzene is a colourless volatile liquid; it has characteristic smell
- Its boiling point is 80°C and freezing point is 5.5°C
- It is highly inflammable and burns with sooty flame
- It is lighter than water; its specific gravity at 20°C is 0.8788
- It is immiscible with water but miscible with organic solvents such as alcohol and ether
- It is a non-polar compound and its dipole moment is zero
- It is extremely poisonous substance. Inhalation of vapours or absorption though skin has a toxic effect.

METHODS OF PREPARATION OF BENZENE



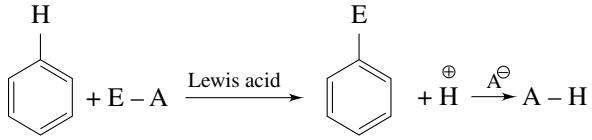
CHEMICAL PROPERTIES OF BENZENE

Aromatic Electrophilic Substitution Reactions

The most characteristic reactions of benzenoid arenes are the substitution reactions that occur when they react with electrophilic reagents.

The reactions in which one or more hydrogen atoms of the benzene ring are replaced by an electrophile are called electrophilic aromatic substitution reactions.

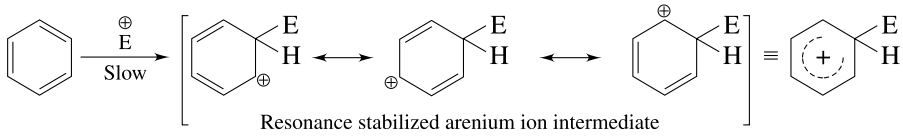
These reactions are of the general type shown below:



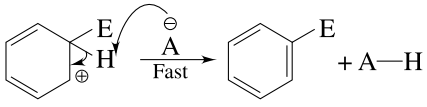
benzenoid arenes undergoes electrophilic substitution reactions because it has an electron rich system due to delocalized -electron.

General Mechanism

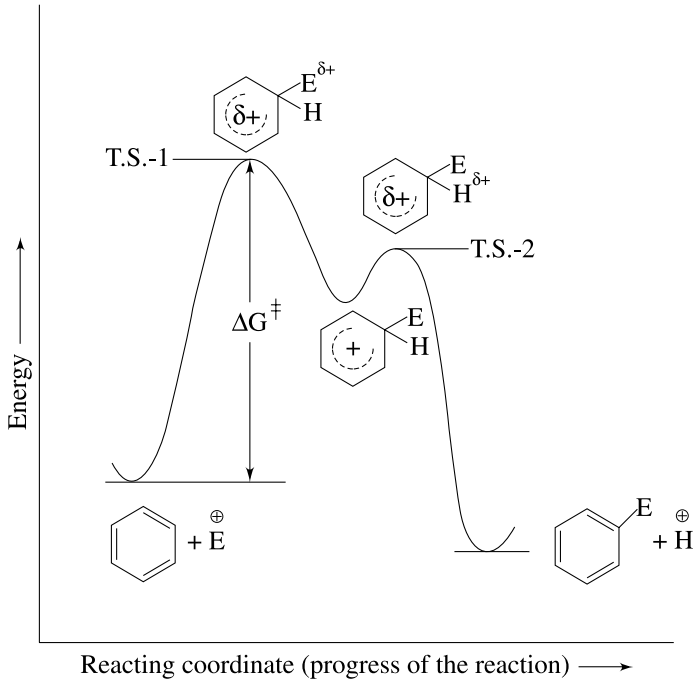
Step 1.



Step 2.



Energy profile for a typical aromatic electrophilic substitution reaction: A more detailed picture of the arenium ion mechanism may be represented by its energy profile.



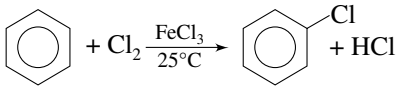
Important Points

- Benzene is a poor nucleophile because it losses its aromaticity
- First step is RDS where Wheeland intermediate or σ complex is formed
- σ complex has 4 e^- non-aromatic resonance stabilized carbocation
- Breaking of C–H bond takes place in fast step it means no isotopic effect thus rate of reaction is $C_6H_6 \approx C_6D_6 \approx C_6T_6$

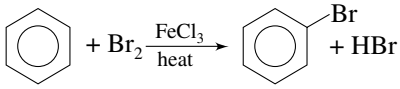
Note: In sulphonation and iodination isotopic effect considered because difference between TS_1 and TS_2 is very less.

Thus rate of reaction is $C_6H_6 > C_6D_6 > C_6T_6$

Halogenation of Benzene



Chlorobenzene (90%)

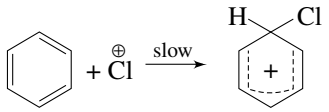


Bromobenzene (75%)

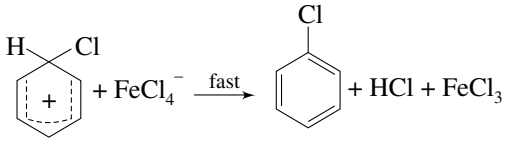
The mechanism for aromatic chlorination is as follows.

Step-1 $Cl–Cl + FeCl_3 \rightleftharpoons Cl^{\oplus} – Cl – \overset{\ominus}{F}eCl_3 \longrightarrow \overset{\oplus}{Cl} + \overset{\ominus}{F}eCl_4$

Step-2



Step-3



Some facts

(i) The function of Lewis acid is to convert weaker electophile (Cl_2) into stronger electrophile ($\overset{\oplus}{Cl}$)

(ii) The Lewis acids most commonly used to effect chlorination and bromination reactions are $FeCl_3$, $FeBr_3$, and $AlCl_3$ all in the anhydrous form.

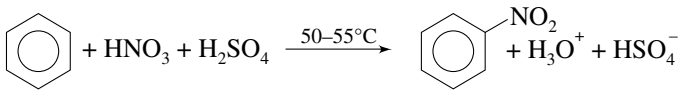
(iii) Ferric chloride and ferric bromide are usually generated in the reaction mixture by adding iron to it. The iron then reacts with halogen to produce the ferric halide.

$$2Fe + 3X_2 \rightarrow 2FeX_3$$

(iv) The Lewis acids behave as a halogen carrier.

Nitration of Benzene

A mixture of nitric acid and sulphuric acid is the nitrating reagent.



(85%)

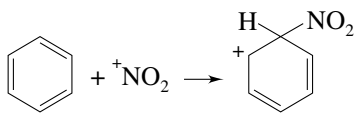
The steps involved in the mechanisms are as follows.

Step-1 Formation of nitronium ion

$$HONO_2 + 2H_2SO_4 \rightleftharpoons H_3O^+ + 2HSO_4^- + {}^+NO_2$$

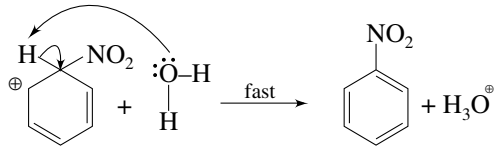
Nitronium ion

Step-2 Electrophilic attack by nitronium ion



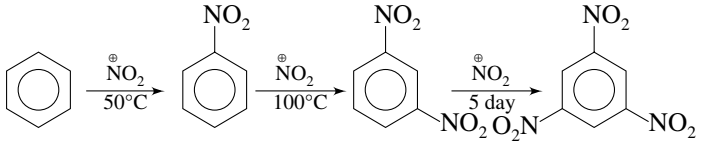
Arenium ion

Step-3 Removal of proton



Some facts

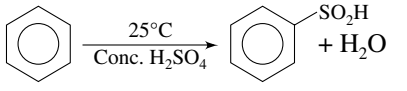
(i) In nitration HNO_3 behave as bronsted base and H_2SO_4 as a bronsted acid.
(ii) For formation of 1 mol NO_2^+ 2 : 1 ratio for H_2SO_4 and HNO_3 is used.
(iii) The rate determining step is the formation of carbocation (σ complex).
(iv) Breaking of C–H bond takes place in fast stape so that there is no isotopic effect.
(v) NO_2 is a deactivating group it means for further nitration, rate of reaction decreases.



1, 3, 5-tri nitro benzene (T.N.B)
(explosive)

Sulfonation of Benzene

Benzene reacts with fuming sulphuric acid at room temperature to produce benzene-sulfonic acid. Fuming sulphuric acid is sulphuric acid that contains added sulphur trioxide (SO_3). Sulfonation also takes place in concentrated sulphuric acid alone, but more slowly.

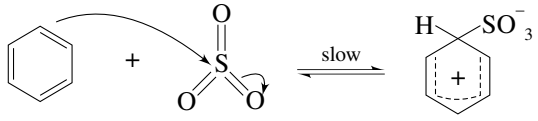


Benzenesulfonic acid
(56%)

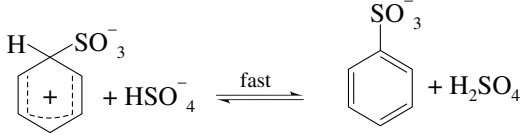
The steps involved in the mechanisms are as follows :

Step-1 $2H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- + SO_3$

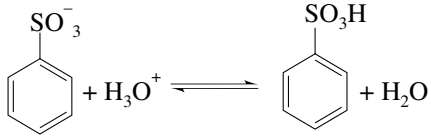
Step-2



Step-3



Step-4



Some Facts

(i) The entire sulphonation process is an equilibrium process

$$C_6H_6 + H_2SO_4 \overset{H^+}{\rightleftharpoons} C_6H_5SO_3H + H_2O$$

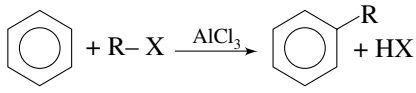
For sulphonation, we require excess of H_2SO_4 along with SO_3 and for desulphonation we use excess of H_2O along with heating (100–175°C).

(ii) Sulphonation is a reversible reaction because different between $T.S_1$ and $T.S_2$ is very less.

(iii) Order of reactivity in isotopic benzene is $C_6H_6 > C_6D_6 > C_6T_6$.

Friedel–Crafts Alkylation

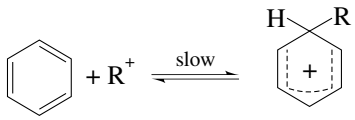
A general equation for a Friedel–Crafts alkylation reaction is the following:



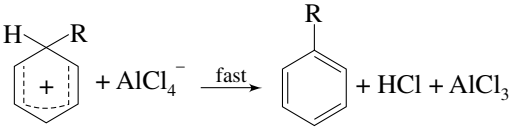
The steps involved in the mechanisms are as follows:

Step-1 $RCl + AlCl_3 \rightleftharpoons AlCl_4^- + R^+$

Step-2

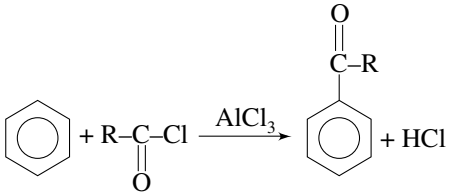


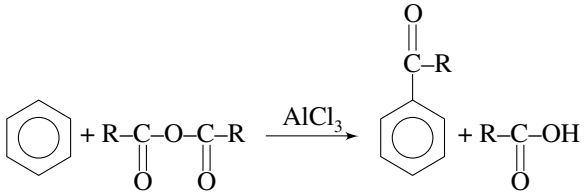
Step-3



Here $AlCl_3$ acts as a Lewis acid.

Friedel–Crafts Acylaction

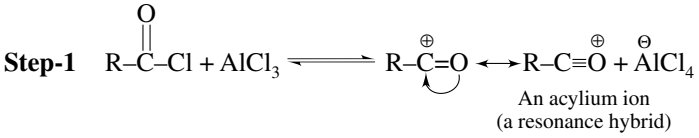




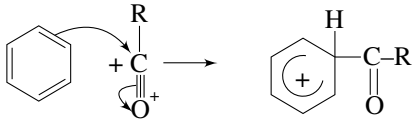
The steps involved in the mechanisms are as follows:

In most Friedel –Crafts acylation the electrophile appears to be an acylium ion formed from an acyl halide in the following ways:

Step-1

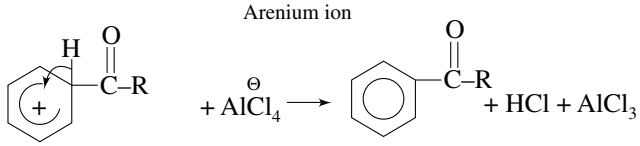


Step-2



Arenium ion

Step-3



Limitation of Friedel-Crafts Reactions:

(i) When the carbocation formed from an alkyl halide, alkene, or alcohol can rearrange to a more stable carbocation, it usually does so and the major product obtained from the reaction is usually the one from the more stable carbocation.

(ii) Vinyl halides and aryl halides do not react in Friedel-Crafts alkylation because carbocation derived from vinyl halide and aryl halide are highly unstable.

(iii) Friedel-Crafts reaction usually give poor (almost no yields) yields when powerful electron withdrawing groups are present on the aromatic ring due instability of σ complex.

(iv) When the ring bears an – NH_2, –NHR, or –NR_2 group, these groups are changed into powerful electron– withdrawing groups by the Lewis acids used to catalyze Friedel-Crafts reaction so that –NH_2, –NHR, and –NR_2 groups are not give Friedel-Crafts reaction.

(v) Another limitation of Friedel-Crafts alkylation arises because of polyalkylation as an alkyl substituted benzene is more reactive than benzene. However no Polyacylation takes place.

EFFECT OF SUBSTITUENTS ON REACTIVITY AND ORIENTATION

When substituted benzene undergo electrophilic attack, groups already on the ring affect both the rate of the reaction and the site of attack therefore substituent groups affect both reactivity and orientation in electrophilic aromatic substitutions.

We can divide substituent groups into two classes according to their influence on the reactivity of the ring. Those that cause the ring to be more reactive than benzene itself we call activating groups. Those that cause the ring to be less reactive than benzene we call deactivating groups.

Theory of Orientation

A group attached to benzene has a directing influence on the electrophilic substitution reaction. Two types of groups have been classified based on their orientation effects.

Activating Group

A group that releases electrons to benzene ring is an activating group. It directs the incoming electrophile to *ortho* or *para* position. Examples include

Strongly activating: –NH_2, –NHR, –NR_2, –OH, –OCH_3

Moderately activating: –$NHCOCH_3$, –$OCOCH_3$

Weakly activating: –CH_3, –$CH{=}CH_2$, –C_6H_5

Deactivating Group

A group that withdraws electrons from benzene is a deactivating group. It directs the incoming electrophile to *meta* position. Examples include

Strongly deactivating: –$\overset{+}{N}(CH_3)_3$,–NO_2, –CN, –SO_3H

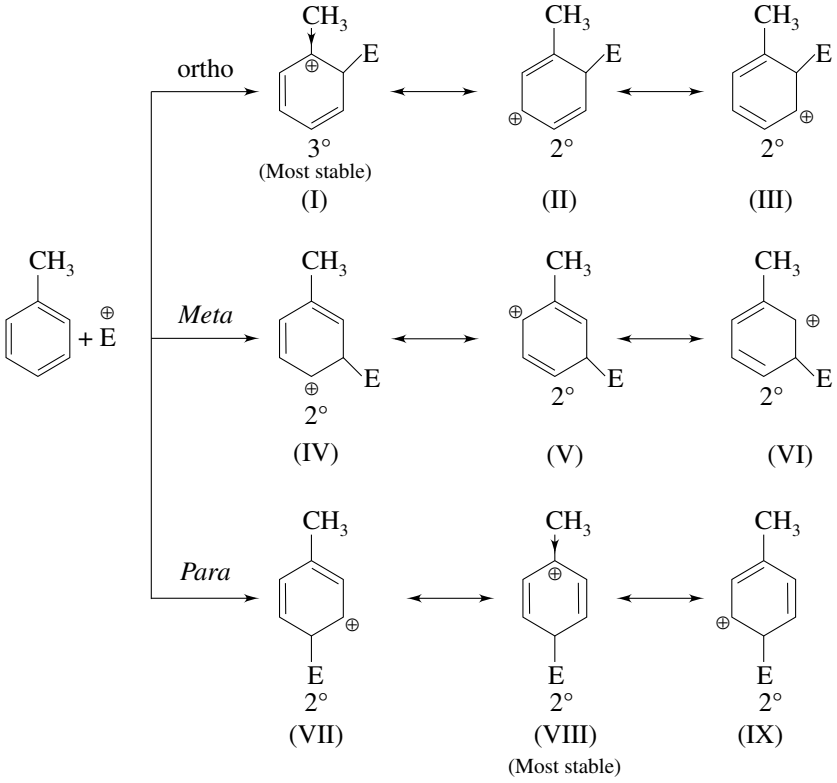
Moderately deactivating –CHO, –COR, –COOR, –COOH, –COCl

*Weakly deactivating: F, –Cl, –Br, –I (*o*/*p* director)

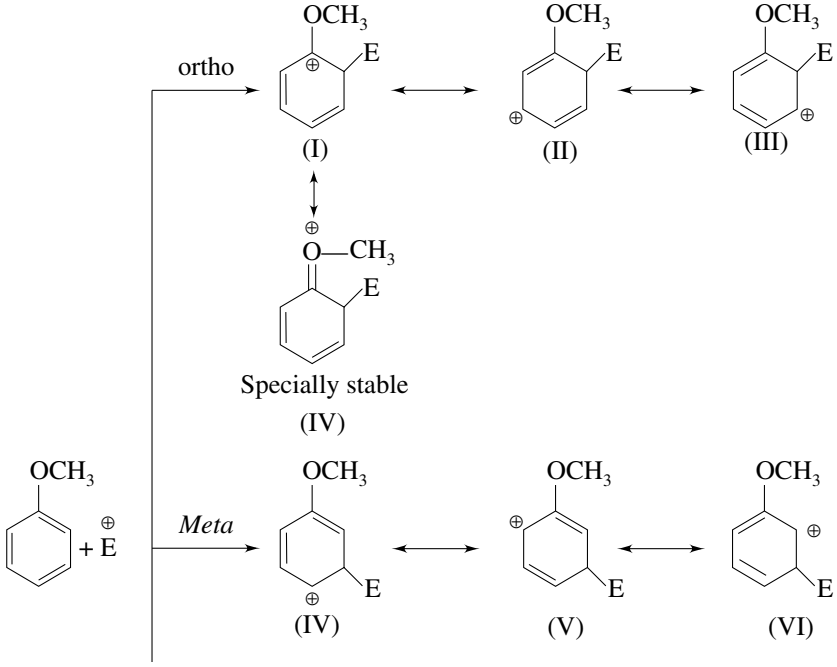
Orientation Based on Sigma Complex Stability

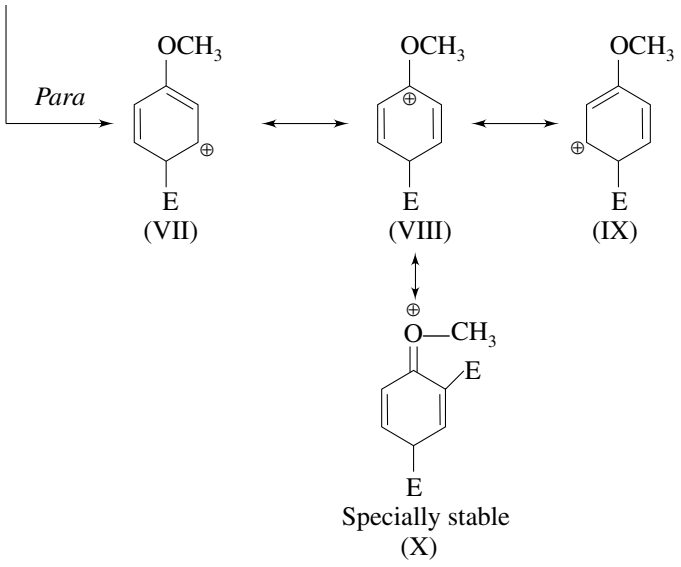
Case-I: Activating Groups : Ortho para Directors

(a) When group is +H/+I group only, i.e., Alkyl group: Structures of the carbocation intermediates formed from the reaction of an electrophile with toluene at the otrtho, at the ortho, meta and para position



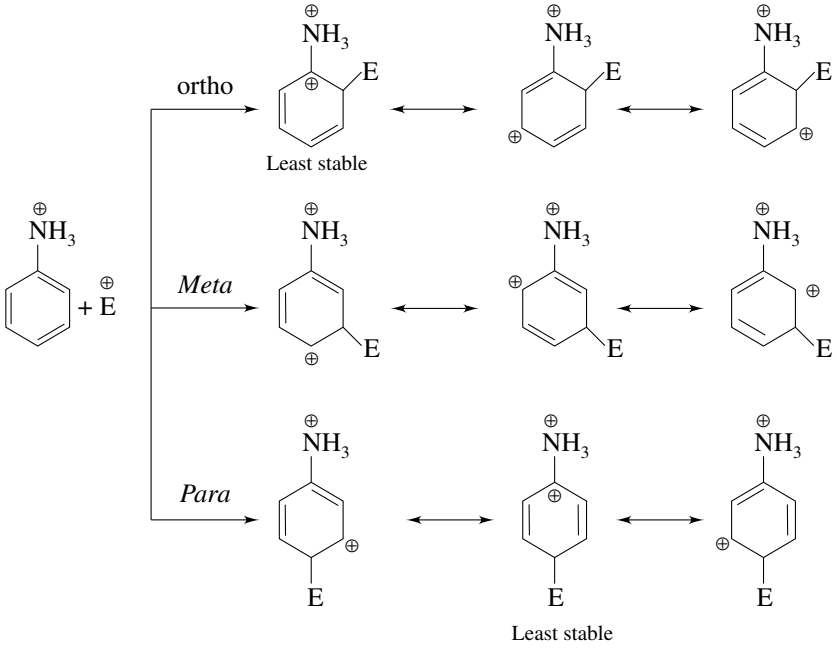
(b) When group +M/–I group: The structures of the carbocation intermediates formed from the reaction of an electrophile with anisole at the ortho, meta and para positions.



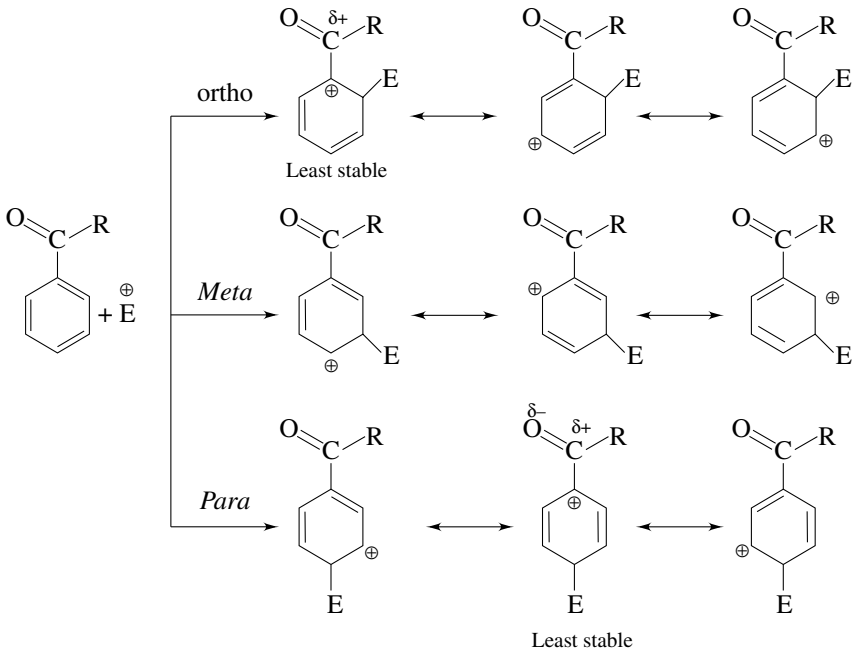


Case-II: Deactivating Groups : Meta Directors

(a) When group is –I group: Structure of the carbocatoin intermediates formed from the reaction of an electrophile with protonated aniline (–I group) at the ortho, meta and para positions

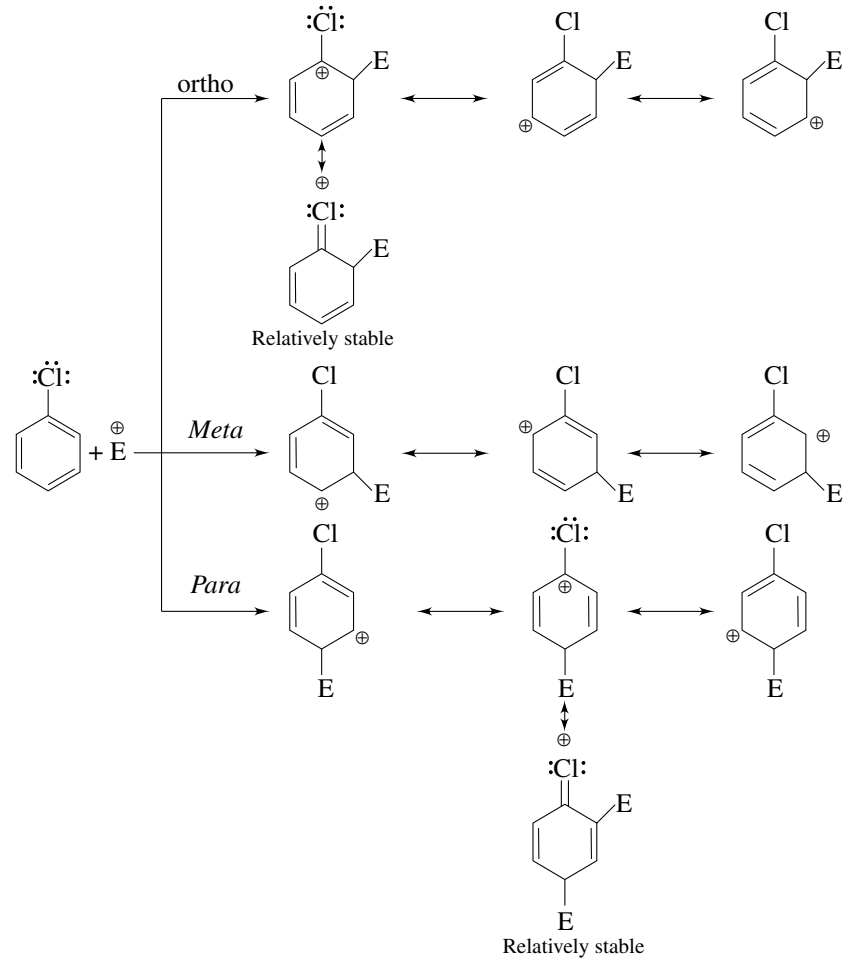


(b) When group is –M/–I group: Structures of the carbocation intermediates formed from the reaction of an electrophile with a substrate, having an –M group, at the ortho, meta and para position



Case-III: Halo Substituents : Deactivating Ortho-Para Directors

Structures of the carbocation intermediates formed from the reaction of an electrophile with a halogenated benzene at the ortho, meta and para position



EFFECT OF SUBSTITUTENTS ON REACTIVITY:

In presence of different substituents on benzene ring, rate of reaction increased or decreased is known as substitution effect.

$$\text{Reactivity of ArsE} \propto \text{Activating power} \propto \frac{1}{\text{Deactivating power}}$$

Classification of Substituents

ORTHO-PARA DIRECTIORS	META DIRECTORS
Strongly activating $-NR_2$, $-NHR$, $-NH_2$, $-OH$, $-O^-$ Moderately activating $-NHCOR$, $-OCOR$, $-OR$ Weakly activiating $-CH_3$, $-C_2H_5$, $-C_6H_5$ Weakly deactivating $-F$, $-Cl$, $-Br$, $-I$	Moderately Deativating $-C\equiv N$, $-SO_3H$, $-CO_2H$, $-CO_2R$, $-CHO$, $-COR$ Strongly deactivating $-NO_2$, $-NR_3^+$, $-CF_3$, $-CCl_3$

Summary of Substituent Effects on orientation

We can summarize the effect that groups have on orientation and reacvtivity in the following way.

Full or partial (+) charge on directly attached atoms	At least one nonbonding pair on directly attached atom		Alkyl or aryl
	Halogen	$-\ddot{N}H_2$, $-\ddot{O}H$, etc.	
← meta directing		ortho-para directing →	
← deactivating		activating →	

Aromatic Electrophilic Substitution Reactions of Polysubstituted Benzene

What happens when two or more substituent groups are attached to the benzene ring ? Where is the electrophile likely to attack? Some qualitative rules have been formulated to answer this question.

(i) The most activating group will control orientation.

(ii) No substitution occurs between two meta substituents because of crowding.

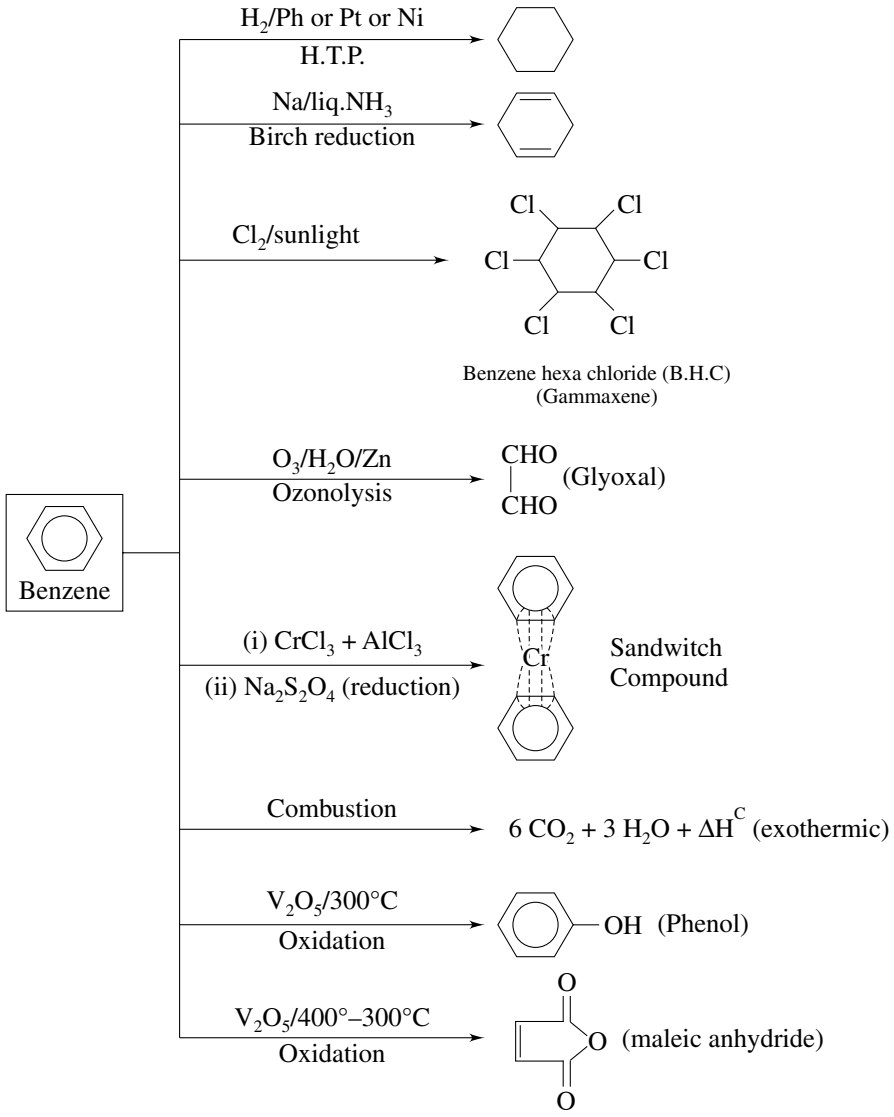
(iii) When both groups are meta directors, it is difficult to introduce third group.

Summary of main electrophilic substitutions on benzene

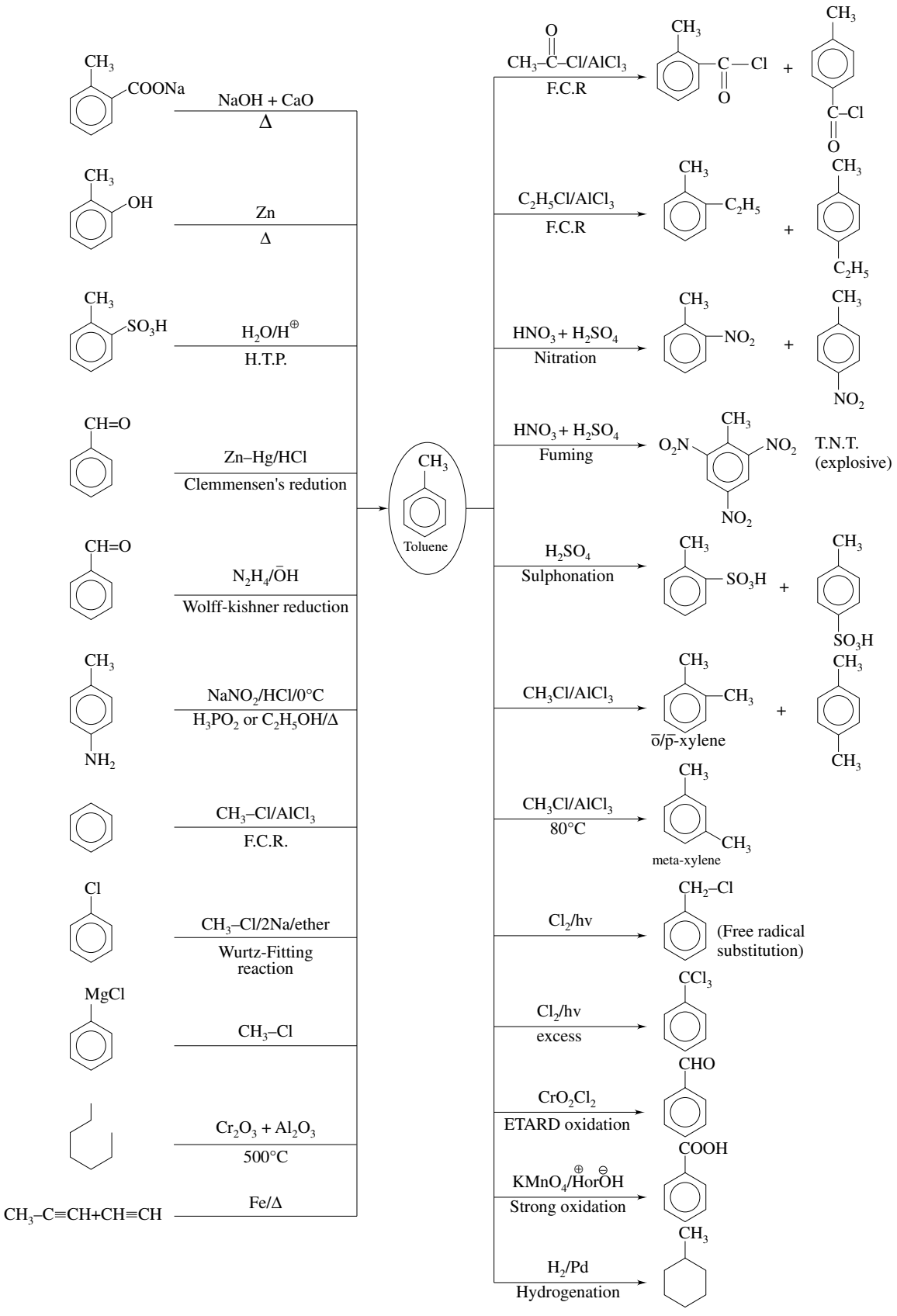
Reaction	Reagents	Electrophile	Products
Bromination	Br_2 and Lewis acid, e.g., $AlCl_3$, $FeBr_3$, Fe Powder, I_2	$Br-\overset{\oplus}{Br}-\overset{\ominus}{AlCl_3}$ $Br-\overset{\oplus}{Br}-Fe$	C_6H_5-Br
Nitration	$HNO_3 + H_2SO_4$	$-\overset{\oplus}{N}(=O)-\overset{\ominus}{O}$	$C_6H_5-NO_2$
Sulphonation	Concentrated H_2SO_4 or $H_2SO_4 + SO_3$(oleum)	$\overset{\oplus}{SO_3H}$ or SO_3	$C_6H_5-SO_3H$
Friedel–Crafts alkylation	R—X + Lewis acid usually $AlCl_3$	$R^{\oplus}$	C_6H_5-R
Friedel–Crafts acylation	RCOCl + $AlCl_3$	$R-C\equiv\overset{\oplus}{O}$	$C_6H_5-\overset{O}{\overset{\|}{C}}-R$

Gatterman–Koch	CO, HCl, $AlCl_3$, Cu_2Cl_2	$H-C\equiv\overset{\oplus}{O}$ ↕ $H-\overset{\oplus}{C}=O$	C_6H_5—CHO
Gatterman aldehyde	HCN, HCl/$AlCl_3$, H^+	$H-C\equiv\overset{\oplus}{N}H$ ↕ $H-\overset{\oplus}{C}=NH$	C_6H_5—CHO
Chloromethylation	CH_2O, HCl $ZnCl_2$	$\overset{\oplus}{C}H_2OH$	C_6H_5—CH_2OH
Mercuration	$Hg(OAc)_2/\Delta$	$\overset{\oplus}{Hg}(OAc)$	C_6H_5—HgOAc
Thallunation	$Tl(OCOCF_3)_3/\Delta$	$\overset{\oplus}{Tl}(OCOCF_3)_2$	C_6H_5—$Tl(OCOCF_3)_2$

Some other Reactions of benzene

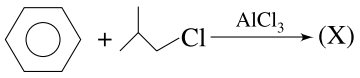


METHODS OF PREPARATION AND CHEMICAL PROPERIES OF TOLUENE:

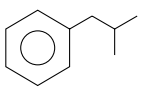


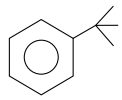
SOLVED EXAMPLE

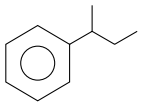
1. In the reaction

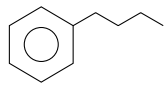


The major product (X) is

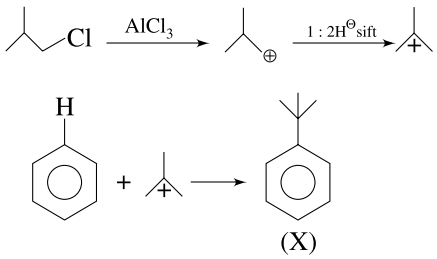
(1) 

(2) 

(3) 

(4) 

Sol. **[2]**



Friedel–Craft Reaction

2. Is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotized and then heated with potassium iodide. The reaction mixture so formed contains:

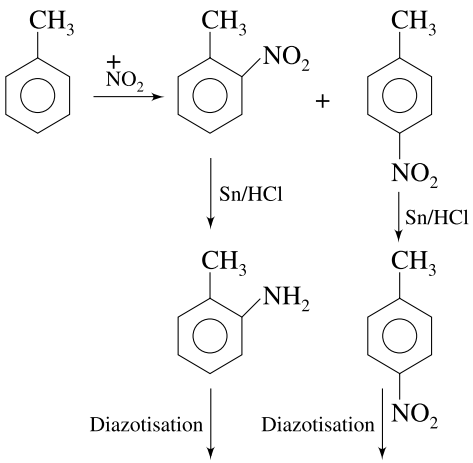
(1) Mixture of *o*– and *p*–iodotoluenes

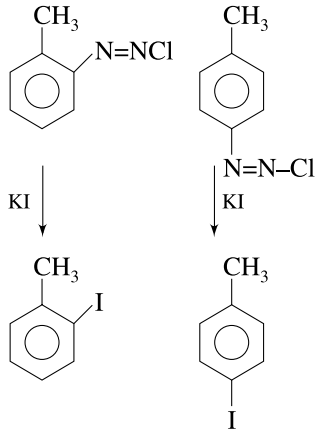
(2) Mixture of *o*– and *p*–diiodobenzenes

(3) Mixture of *o*– and *p*–iodoanilintes

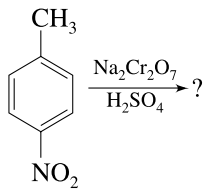
(4) Mixture of *o*– and *m*–iodotoluenes

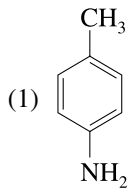
Sol. **[1]**

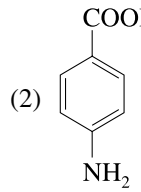


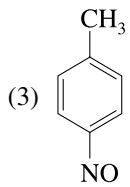


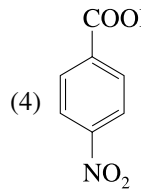
3. What is the product of the following reaction?



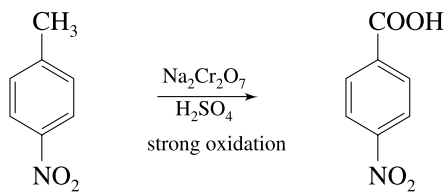
(1) 

(2) 

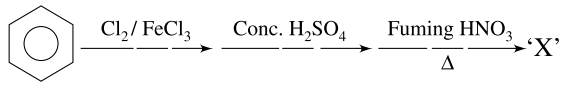
(3) 

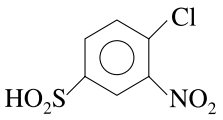
(4) 

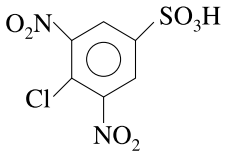
Sol. **[4]**

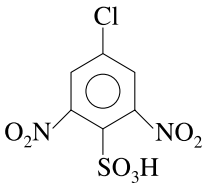


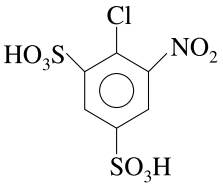
4. The intermediate product 'X' of following synthesis is identified as:



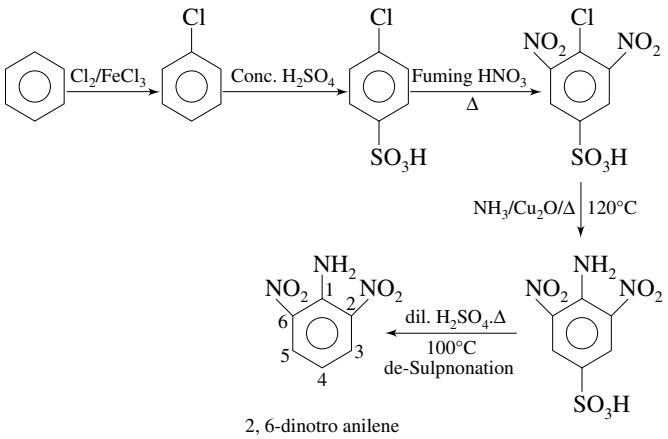
(1) 

(2) 

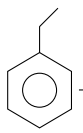
(3) 

(4) 

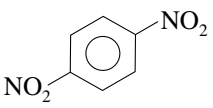
Sol. **[2]**

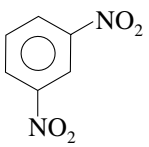


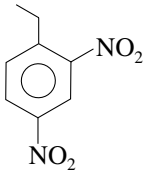
2, 6-dinotro anilene

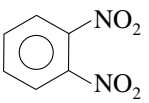
5. 

Product (C) of this reaction is:

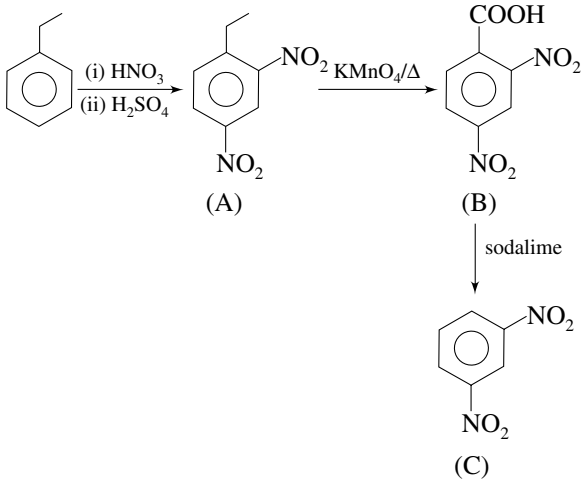
(1) 

(2) 

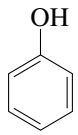
(3) 

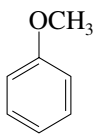
(4) 

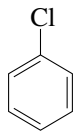
Sol. **[2]**

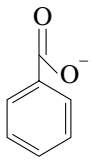


6. Each of the following compounds gives a Friedel–Crafts alkylation, except:

(1) 

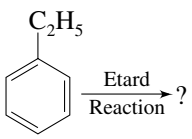
(2) 

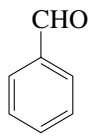
(3) 

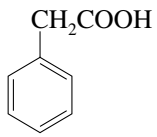
(4) 

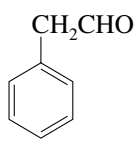
Sol. **[4]**

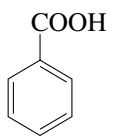
Due to presence of de-activating group Friedel–Craft reaction does not take place because σ complex is unstable

7. 

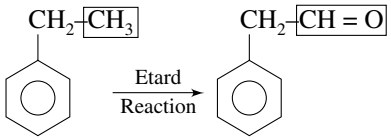
(1) 

(2) 

(3) 

(4) 

Sol. **[3]**

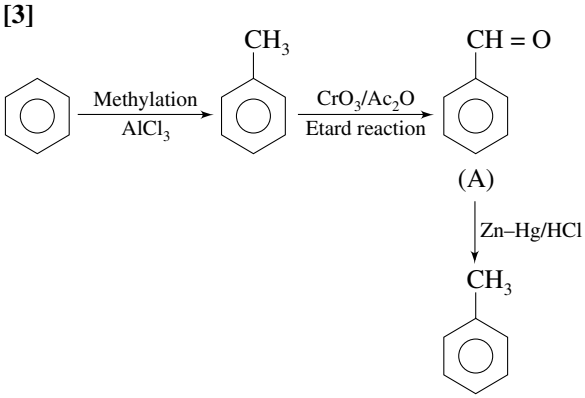


8. Benzene undergoes methylation in presence of $AlCl_3$ followed by oxidation with CrO_3 in the presence of $(CH_3CO)_2O$. It gives a product 'A' which on treatment with Zn-Hg/HCl produces:

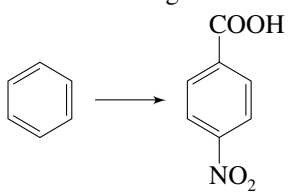
(1) C_6H_5COOH (2) C_6H_6

(3) $C_6H_5–CH_3$ (4) $C_6H_5–CH=O$

Sol. **[3]**



9. Provide the appropriate sequence of reagents that can bring about the following:



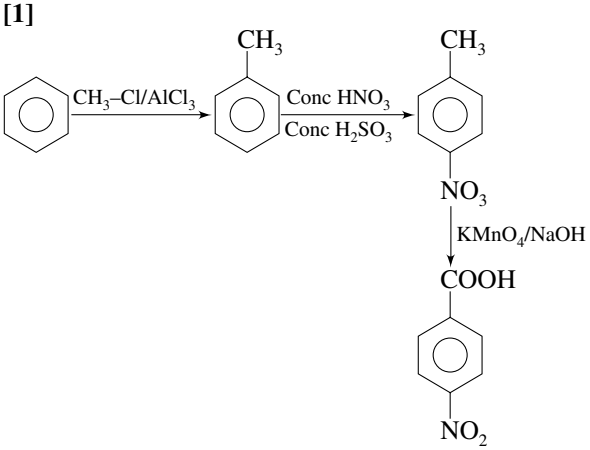
(1) $CH_3Cl/AlCl_3$ then conc. HNO_3/conc. H_2SO_4 then $KMnO_4$/NaOH

(2) Conc. HNO_3/Conc. H_2SO_4 then $CH_3Cl/AlCl_3$ then $KMnO_4$/NaOH

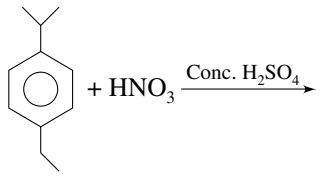
(3) $CH_3Cl/AlCl_3$ then $KMnO_4$/NaOH then conc. HNO_3/Conc. H_2SO_4

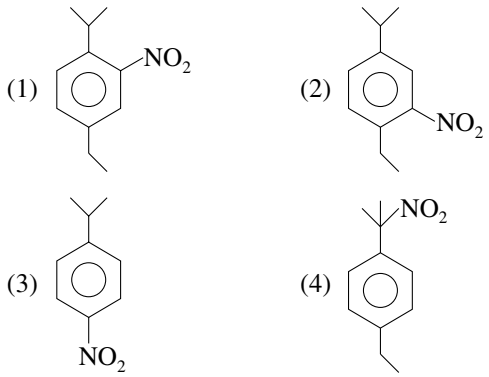
(4) Conc. H_2SO_4/conc. HNO_3 then $CH_3COCl/AlCl_3$ then $KMnO_4$/NaOH

Sol. **[1]**

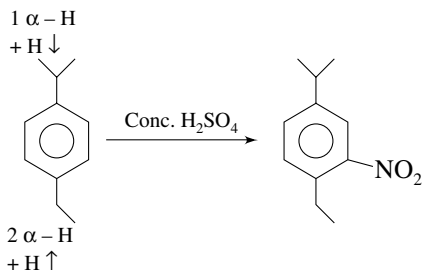


10. The major product formed in the reaction





Sol. **[2]**



11. The reactivites of $C_6H_5CH_3$ (I), $C_6H_5CH_2Cl$ (II), $C_6H_5CHCl_2$ (III), $C_6H_5CCl_3$ (IV) toward nitration are in the order

(1) I > II > III > IV (2) II > I > III > IV

(3) IV > III > II > I (4) III > I > II > IV

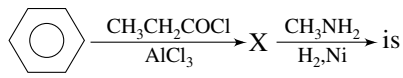
Sol. [1]

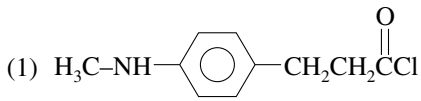
Nitration ≡ Ar–SE $\propto$ activating power

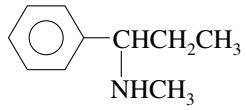
$$\propto \frac{1}{\text{De-activating power}}$$

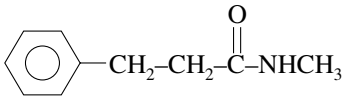
+ H (CH_3 > $–CH_2–Cl$ > $–CHCl_2$ > $–CCl_3$)

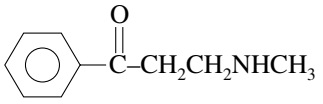
12. The final product obtained in the reaction



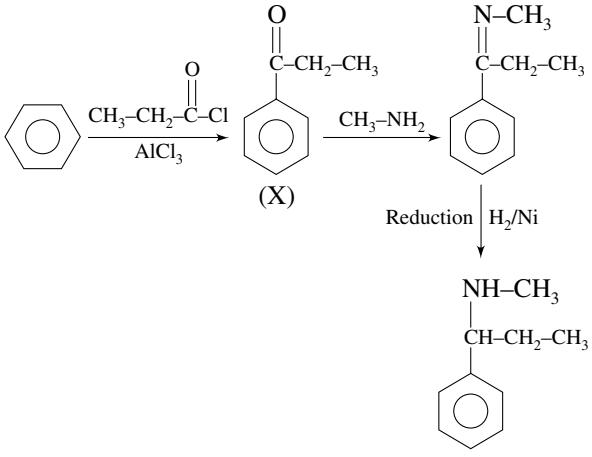
(1) 

(2) 

(3) 

(4) 

Sol. **[2]**



13. m-Nitrobenzoic acid can be obtained by

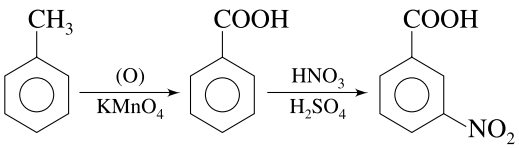
(1) toluene $\xrightarrow[KMnO_4]{[O]}$ A $\xrightarrow[H_2SO_4]{HNO_3}$

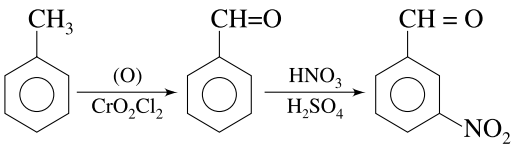
(2) toluene $\xrightarrow[CrO_2Cl_2]{[O]}$ A $\xrightarrow[H_2SO_4]{HNO_3}$

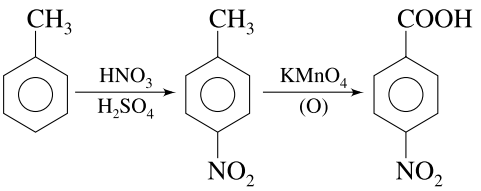
(3) toluene $\xrightarrow[HNO_3 + H_2SO_4]{\text{nitration}}$ A $\xrightarrow[KMnO_4]{[O]}$

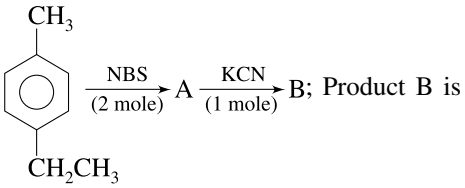
(4) All these methods

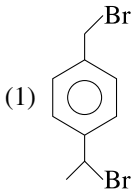
Sol. **[1]**

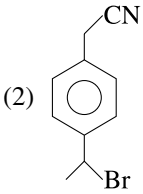
(1) 

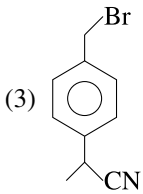
(2) 

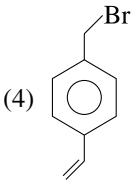
(3) 

14.  ; Product B is

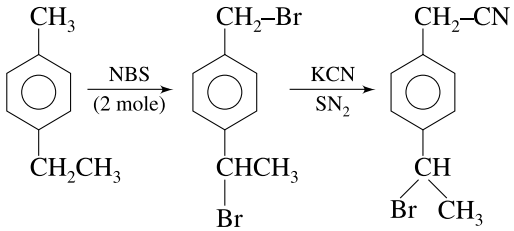
(1) 

(2) 

(3) 

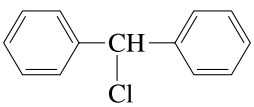
(4) 

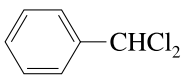
Sol. **[2]**

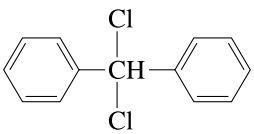


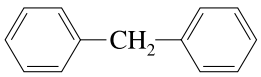
1° halide predominantly gives SN_2 reaction

15. Which of the following structures correspond to the product expected, when excess of C_6H_6 reacts with CH_2Cl_2 in presence of anhydrous $AlCl_3$?

(1) 

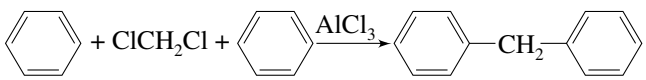
(2) 

(3) 

(4) 

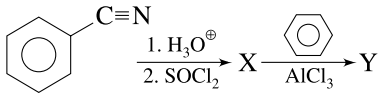
Sol. **[4]**

The reaction takes place as follows:

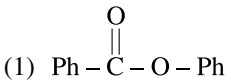


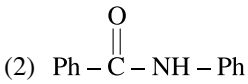
Diphenyhmethane

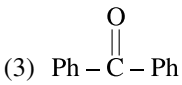
EXERCISE 1

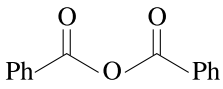
1. 

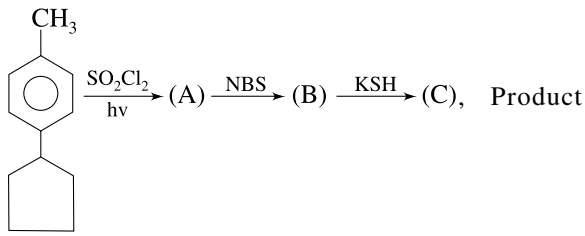
The structure of compound:

(1) 

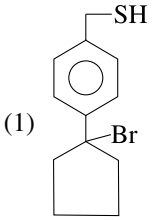
(2) 

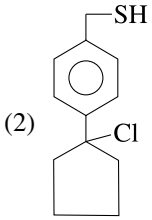
(3) 

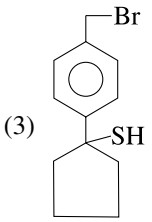
(4) 

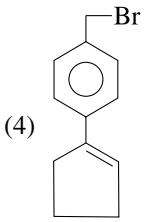
2. 

(B) is:

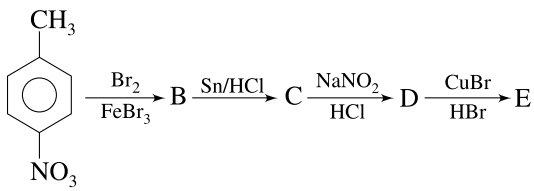
(1) 

(2) 

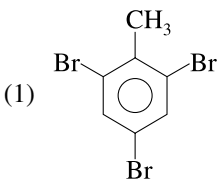
(3) 

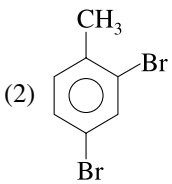
(4) 

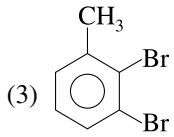
3. In a set of reactions, *p*–nitrotoluene yielded a product E

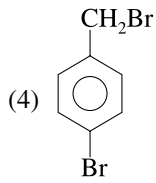


The product E would be:

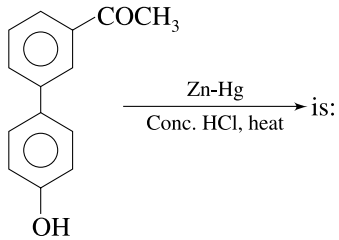
(1) 

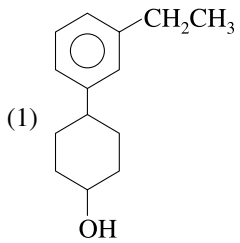
(2) 

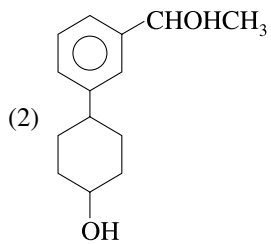
(3) 

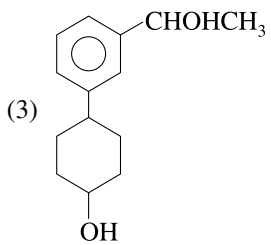
(4) 

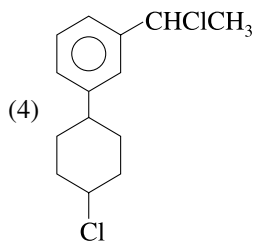
4. The major product formed in the reaction



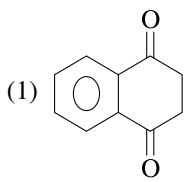
(1) 

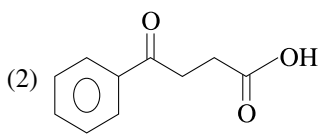
(2) 

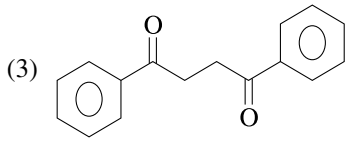
(3) 

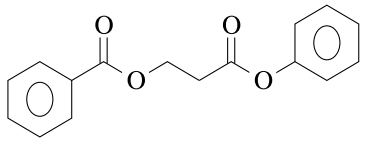
(4) 

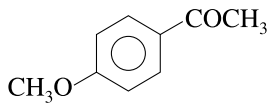
5. Benzene is allowed to react with succinic anhydride in the presence of anhydrous $AlCl_3$ and subsequently treated with dilute HCl. The product formed is:

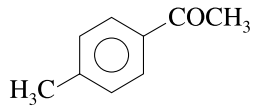
(1) 

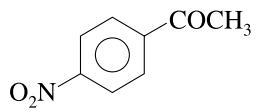
(2) 

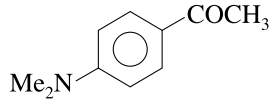
(3) 

(4) 

6. (I) 

(II) 

(III) 

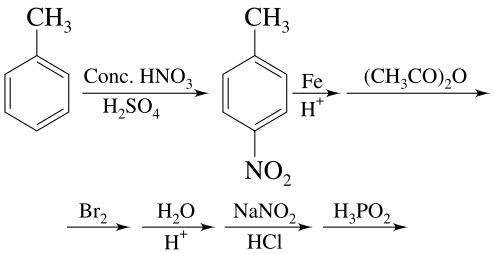
(IV) 

Friedel–Craft acylation reaction can be used to obtain the compounds

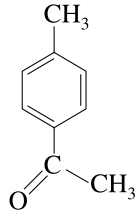
(1) II, III, and IV (2) I, III and IV

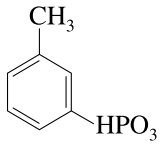
(3) I and II (4) II and III

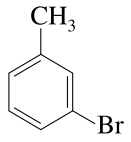
7. Consider the following reaction sequence:

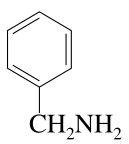


The final product of this reaction sequence is:

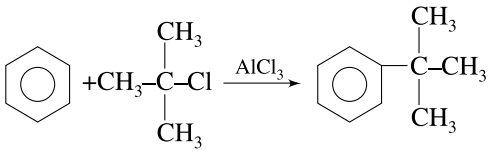
(1) 

(2) 

(3) 

(4) 

8. In the given reaction, the intermediate formed and name of the reaction is:



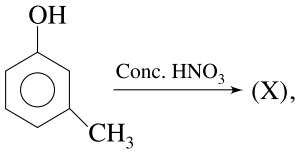
(1) Free Radical, Friedel–Craft alkyaltion

(2) Carbocation, Friedel–Craft alkyaltion

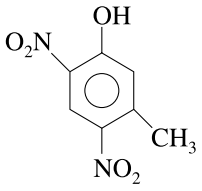
(3) Carbocation, Friedel–Craft acylation

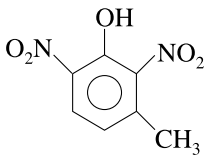
(4) Carbanion, Friedel–Craft alkylation

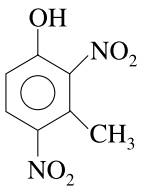
9. In the reaction for dinitration,

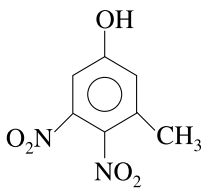


The major dinitrated product (X) is:

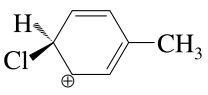
(1) 

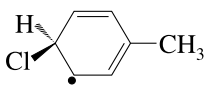
(2) 

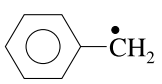
(3) 

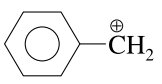
(4) 

10. Which represents an intermediate formed in the reaction of toluene and chlorine at elevated temperature in sunlight?

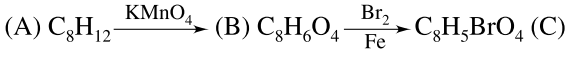
(1) 

(2) 

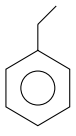
(3) 

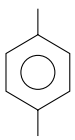
(4) 

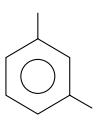
11. Deduce structure of (A) is:

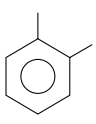


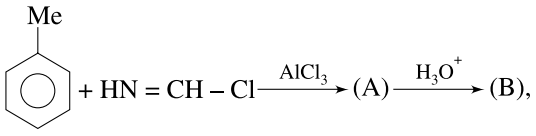
(One-product only)

(1) 

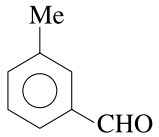
(2) 

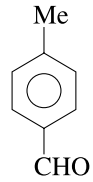
(3) 

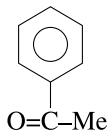
(4) 

12. 

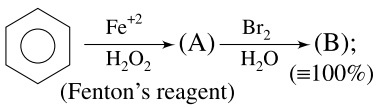
Product (B) of this reaction is:

(1) 

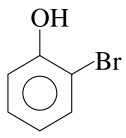
(2) 

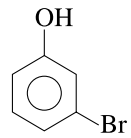
(3) 

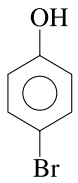
(4) No-reaction

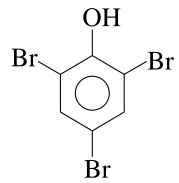
13. 

Major product (B) of this reaction is:

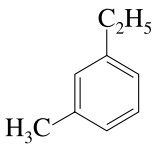
(1) 

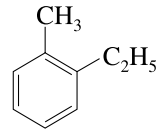
(2) 

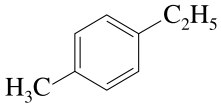
(3) 

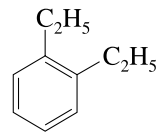
(4) 

14. Which of the following produces isophthalic acid upon oxidation?

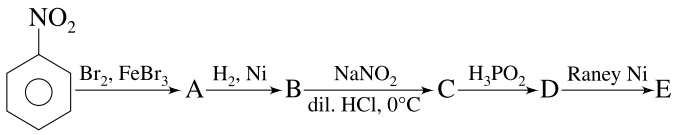
(1) 

(2) 

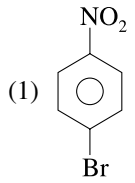
(3) 

(4) 

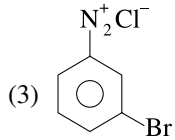
15. Consider the following sequence of reaction:

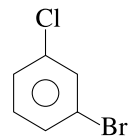


The end product (E) is:

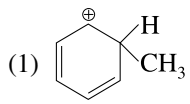
(1) 

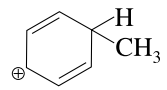
(2) 

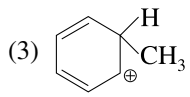
(3) 

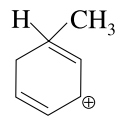
(4) 

16. In the alkylation of benzene, unstable σ-complex can be:

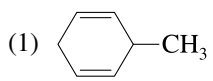
(1) 

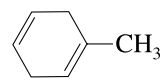
(2) 

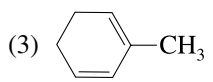
(3) 

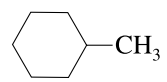
(4) 

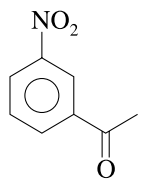
17. The Birch reduction of toluene gives

(1) 

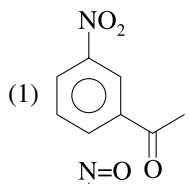
(2) 

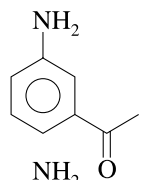
(3) 

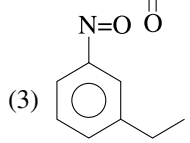
(4) 

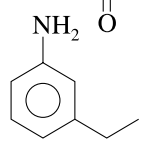
18. 

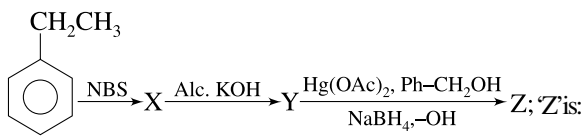
Zn–Hg/HCl → Product:

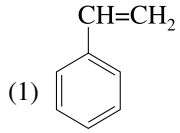
(1) 

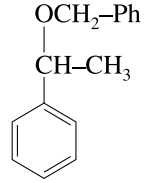
(2) 

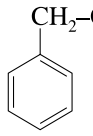
(3) 

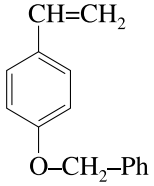
(4) 

19. 

(1) 

(2) 

(3) 

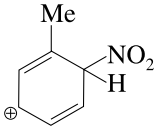
(4) 

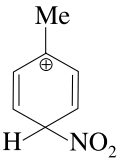
20. When an aromatic compound undergoes ozonolysis followed by treatment with H_2O/Zn, it produces glyoxal, monomethylglyoxal and dimethylglyoxal. It could be

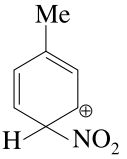
(1) benzene (2) toluene
(3) *o*-xylene (4) *m*-xylene

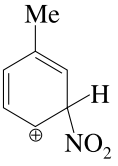
EXERCISE 2

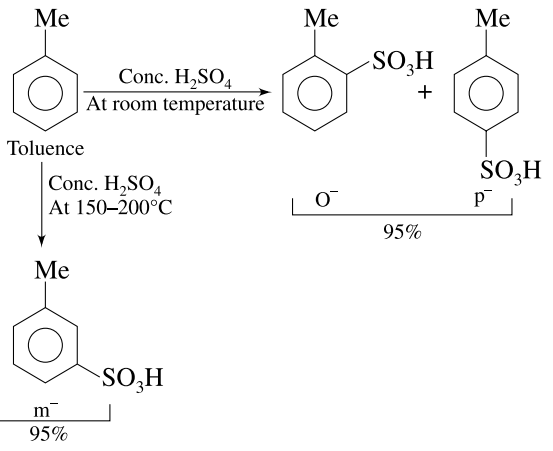
1 Which of the following is the most stable arenium or benzenium ion?

(1) 

(2) 

(3) 

(4) 

2. 

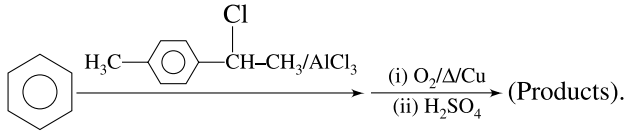
Which of the following statements is wrong about the reaction?

(1) At lower temperature, the reaction is kinetically controlled and *o*/*p* directive effects of the (Me) group operate.

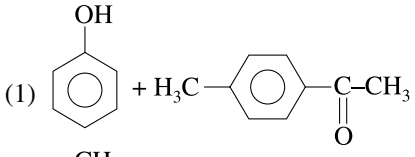
(2) At a higher temperature, the reaction is thermodynamically controlled, and longer reaction times are employed for equilibrium to be reached. The most stable form of m-toluene sulphonic acid is obtained.

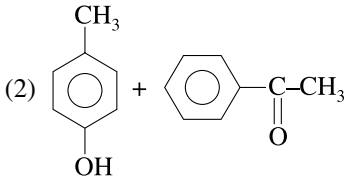
(3) (Me–) group is activated by +I effect, and o^-, p^- directing.

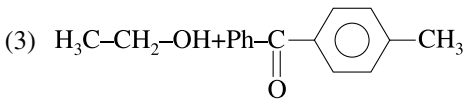
(4) (Me–) group is deactivating by hyperconjugation and is m directing

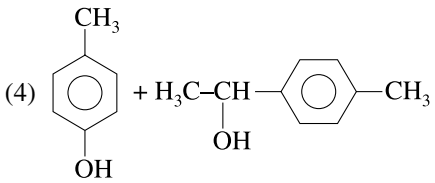
3. 

The final product is:

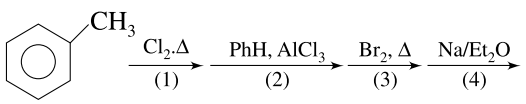
(1) 

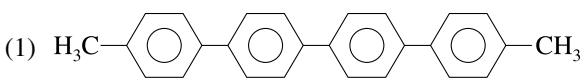
(2) 

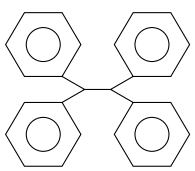
(3) 

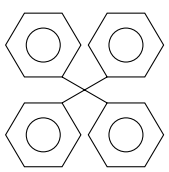
(4) 

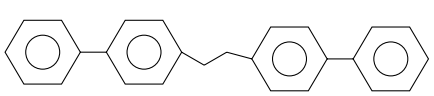
4. The end product of following sequence of reactions is:



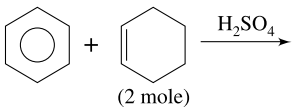
(1) 

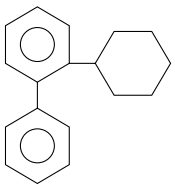
(2) 

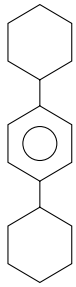
(3) 

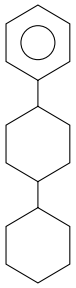
(4) 

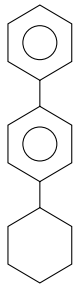
5. Major product obtained in given reaction is:

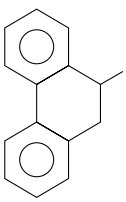


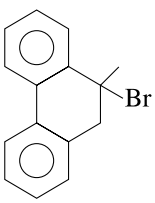
(1) 

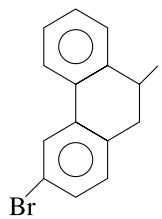
(2) 

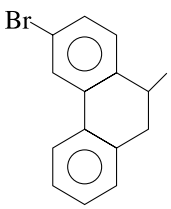
(3) 

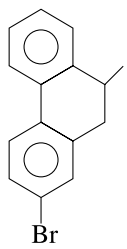
(4) 

6.  $\xrightarrow{Br_2/AlCl_3}$?, The most appropriate product is:

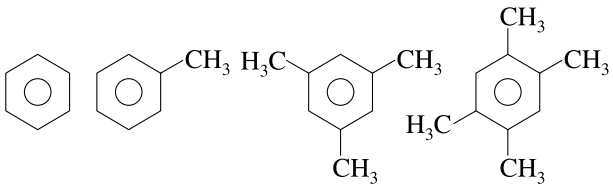
(1) 

(2) 

(3) 

(4) 

7. Arrange the following in order of decreasing boiling point.



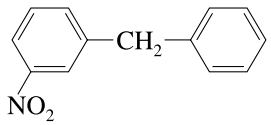
I II III IV

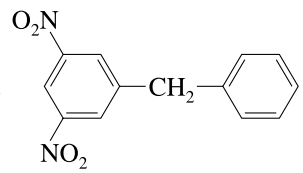
(1) I > II > III > IV (2) IV > III > II > I

(3) I > III > IV > II (4) II > III > I > IV

8. Which of the following statements is correct?

(1) Monobromination of *p*-toluenesulphonic acid followed by treatment with acid and superheated steam gives *m*-bromotoluene.

(2) The mononitration of 

gives the product 

(3) The reactivity towards ring nitration of 2, 4-dinitrotoluene is greater than that of *m*-dinitrobenzene.

(4) The reactivity towards ring nitration of 2, 4-dinitrophenol is smaller than that of 2, 4-dinitrochlorobenzene.

9. Which of the following statements is not correct?

(1) In electrophilic aromatic substitution reaction, the formation of intermediate arenium cation is the rate-determining step.

(2) The C–H bond in benzene is slightly stronger than the C–D bond in deuterated benzene (C_6D_6).

(3) The overall rate of an electrophilic substitution reaction, except sulphonation in benzene and deuterated benzene, are identical.

(4) The sulphonation reaction involving benzene is a reversible reaction.

10. Which of the following statements is correct?

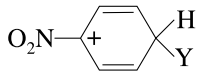
(1) The oxidation of naphthalene with $KMnO_4$ in acid gives phthalic acid.

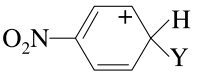
(2) The oxidation of naphthalene with O_2/V_2O_5 gives 1, 4-naphthaquinone.

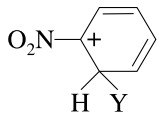
(3) Treatment of *p*-chlorotoluene with NaOH (aq.) at 340°C exclusively gives *p*-hydroxyoluene.

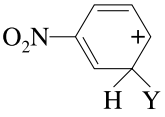
(4) Chlorine in *p*-chlorotoluene is replaced by OH when taken in NaOH (aq.) at 340°C. No such replacement occurs for 2,6-dimethylchlorobenzene.

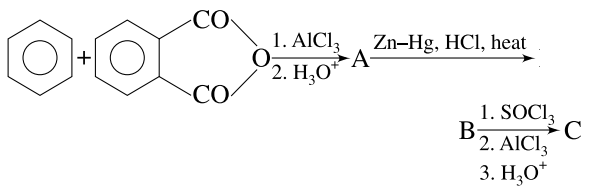
11. Which of the following carbocation is expected to be most stable?

(1) 

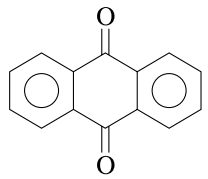
(2) 

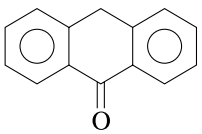
(3) 

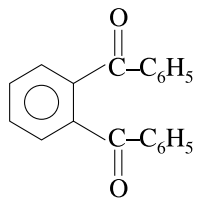
(4) 

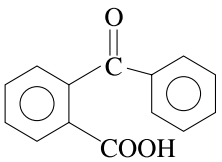
12. 

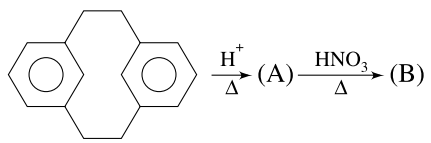
The end product (C) is:

(1) 

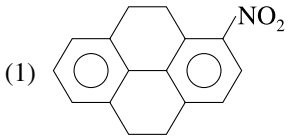
(2) 

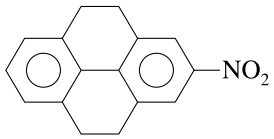
(3) 

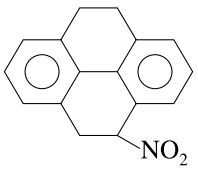
(4) 

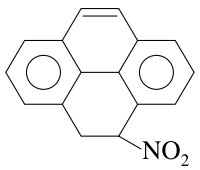
13. 

Product (B) in the above reactions is:

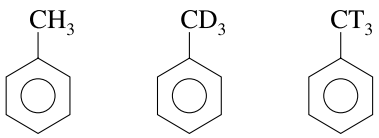
(1) 

(2) 

(3) 

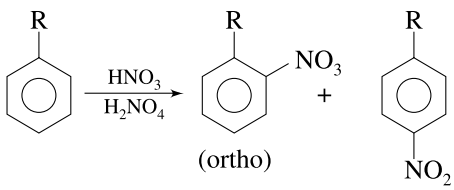
(4) 

14. Arrange the following in decreasing order of reactivity towards EAS (electrophilic aromatic substitution)



(1) a > b > c (2) c > b > a

(3) a > c > b (4) c > a > b

15. 

In the above reaction *o*/*p* ratio will be highest when:

(1) R = $-CH_3$ (2) R = $-CH_2-CH_3$

(3) R = $-CHMe_2$ (4) R = $-CMe_3$

EXERCISE 3

One and More Than One Option Correct Type Question

1. C_6H_{14} (n–hexane) $\xrightarrow{Al_2O_3/\Delta}$ (A) $\xrightarrow{(CO + HCl)/AlCl_3}$ (B)

Select the correct statement among following:

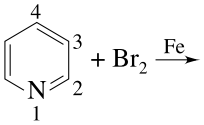
(1) Compound 'B' form silver mirror on reaction with $[Ag(NH_3)_2]OH$

(2) Compound 'B' can also be obtained by the reaction of toluene with chromyl chloride

(3) Compound 'A' can also be synthesised by reaction of benzene diazonium chloride with H_3PO_2

(4) Compound 'B' gives grey colour with aq. $HgCl_2$ solution

2. Consider the following reaction,



The correct statement(s) is/are

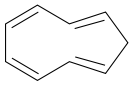
(1) Major bromination occur at C–2

(2) Major bromination occur at C–3

(3) Bromination at C–3 and C–4 are equally probable

(4) Bromination occur at a rate slower than that at benzene

3. What makes the following compound aromatic?



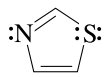
(1) Add one electron to π-bond to give $C_9H_{10}^-$

(2) Add two electrons to π-bond to give $C_9H_{10}^{2-}$

(3) Remove an ion, H^+, from sp^3 carbon

(4) Remove an ion, H^+ from sp^2 carbon

4. What is/are regarding sulphathiazole?



Sulphathiazole

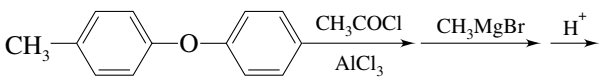
(1) It is an aromatic

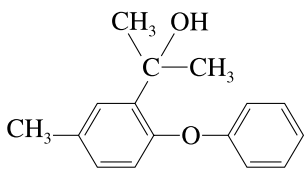
(2) It has six delocalised pi-electrons

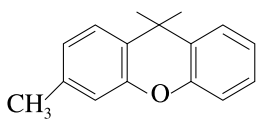
(3) Extent of delocalisation is equivalent to benzene

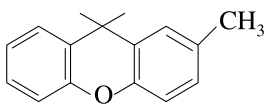
(4) It absorb Br_2 when reacted with Br_2-CCl_4

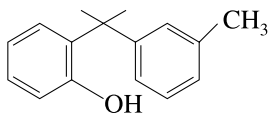
5. Predict major product of the reaction below.



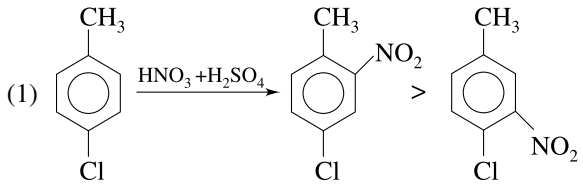
(1) 

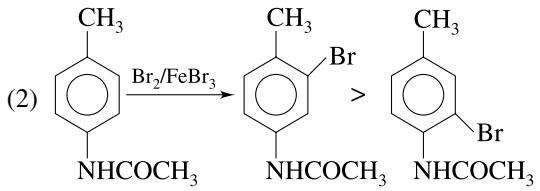
(2) 

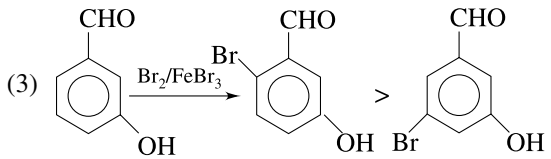
(3) 

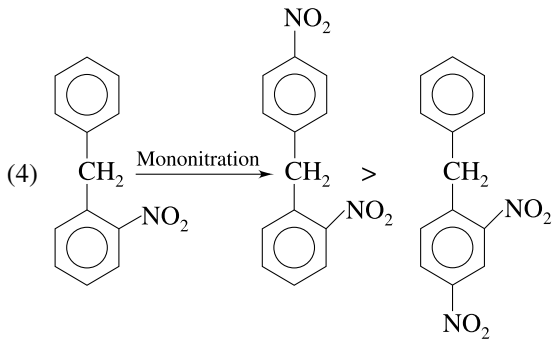
(4) 

6. Select the reaction in which the correct orientations have been mentioned in the major products.

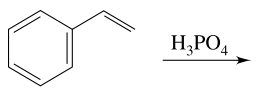
(1) 

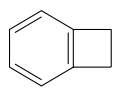
(2) 

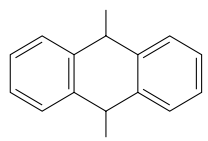
(3) 

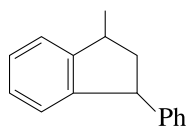
(4) 

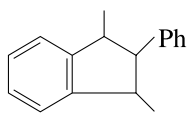
7. What is/are the principal products of the following reaction?



(1) 

(2) 

(3) 

(4) 

Assertion and Reason Type Question

(1) If both (A) and (R) are correct and (R) is the correct explanation for (A)

(2) If both (A) and (R) are correct and (R) is not the correct explanation

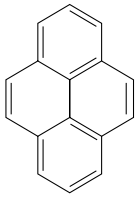
(3) If (A) is correct and (R) is incorrect

(4) If (A) is incorrect and (R) is correct

8. Assertion: Sulphonation of benzene is reversible in nature.

Reason: Deuterated benzene reacts slower than benzene in sulphonation with hot conc. H_2SO_4.

9. Assertion: Pyrene, although aromatic, decolourise brown colour of bromine water.


Pyrene

Reason: It has one pi-bond extra which is not the part of aromatic system.

10. Assertion: Both toluene and iso-propyl benzene give the same product on oxidation with $KMnO_4$.

Reason: $KMnO_4$ oxidises side aliphatic chain of arenes to –COOH group.

11. Assertion: Furan is an aromatic system, has resonance energy comparable to that of benzene.

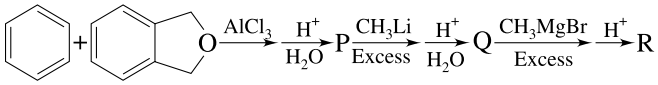
Reason: Furan decolourises the brown colour of bromine water solution.


(Furan)

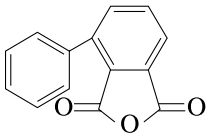
Comprehension Type Question

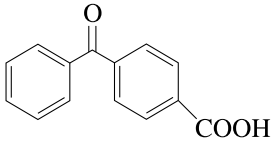
Comprehension (Q. 12-14)

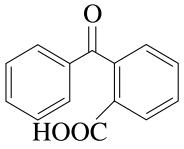
Consider the following road-map reaction,

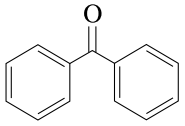


12. The most likely structure of P is

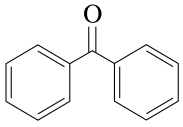
(1) 

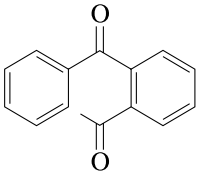
(2) 

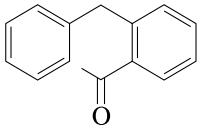
(3) 

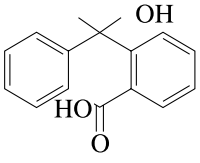
(4) 

13. What is Q?

(1) 

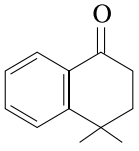
(2) 

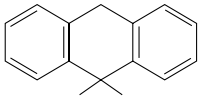
(3) 

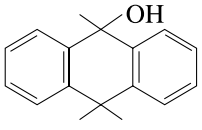
(4) 

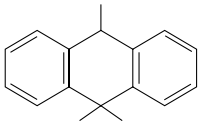
Sol. **[2]**

14. What is R?

(1) 

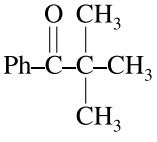
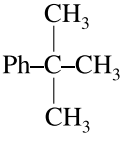
(2) 

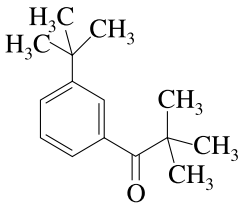
(3) 

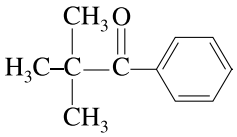
(4) 

Column Matching Type Question

15. Consider the compounds on left column and match with reactions form right column by

Column-I	***Column-II***
(A) 	(P) $C_6H_6 + (CH_3)_3CCl \xrightarrow{AlCl_3}$
(B) 	(Q) $C_6H_6+(CH_3)_2 C=CH_2 \xrightarrow{H_3PO_4}$

(C) 

(D) 

(R) $C_6H_6 + (CH_3)_3\ CCOCl \xrightarrow{AlCl_3}$

(S) $CH_6H_6 + (CH_3)_3\ COH \xrightarrow{HF}$

(T) $CH_6H_6 + \{(CH_3)_3CCO\}_2O \xrightarrow{AlCl_3}$

Code

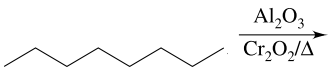
	A	B	C	D
(1)	P, Q	Q	R, T	R, S
(2)	S	R, S	Q	P, Q
(3)	S	R	P, T	Q
(4)	R, T	P, Q, R, S, T	R, T	R, T

16. Match the reactions from Column-I with expected product(s) from Column-I

Column-I

(A) $CH_6H_6 + CH_3Cl \xrightarrow{AlCl_3}$

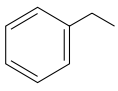
(B) $CH_6H_6 + CH_3CH_2\ Cl \xrightarrow{AlCl_3}$

(C) 

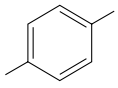
(D) $C_6H_6 + CH_3COCl \xrightarrow{Al_2O_3} \xrightarrow[NaOH/\Delta]{N_2H_4}$

Column-II

(P) 

(Q) 

(R) 

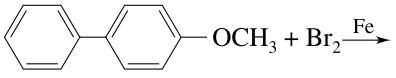
(S) 

Code

	A	B	C	D
(1)	P, R, S	Q	Q, R, S	Q
(2)	S	R, S	Q	P, Q
(3)	S	R, S	P, Q	Q, S
(4)	R, S	S	Q, R	P

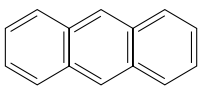
Single Digit Integer Type Question

17. If the following compound is treated with Br_2–Fe, how many mono bromination products are formed in principle?



18. How many isomers of C_8H_{10} when reacts with hot alkaline $KMnO_4$ give only aromatic dicarboxylic acid.

19. How many monobromo derivatives exist for anthracene?



Anthracene

20. How many isomers of C_7H_8O exists that has a phenyl ring?

EXERCISE 4

1. Phenyl magnesium bromide reacts with methanol to give **[JEE Main-2006]**

(1) a mixture of benzene and Mg(OMe)Br

(2) a mixture of toluene and Mg(OH)Br

(3) a mixture of phenol and Mg(Me)Br

(4) a mixture of anisole and Mg(OH)Br

2. The reaction of toluene with Cl_2 in presence of $FeCl_3$ gives predominantly **[JEE Main-2007]**

(1) benzoyl chloride (2) benzyl chloride

(3) *o*-and p-chlorotoluene (4) *m*-chlorotoluene

3. Presence of a nitro group in a benzene ring **[JEE Main-2007]**

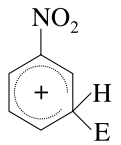
(1) activates the ring towards electrophilic substitution

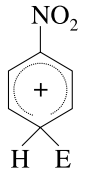
(2) renders the ring basic

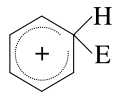
(3) deactivates the ring towards nucleophilic substitution

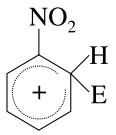
(4) deactivates the ritng towards electrophilic substitution

4. The electrophile E^+ attacks the benzene ring to generate the intermediate σ-complex. Of the following which σ-complex is of lowest energy? **[JEE Main-2008]**

(1) 

(2) 

(3) 

(4) 

5. Toluene is nitrated and the resulting product is reduced with Sn and hydrochloric acid. The product so obtained is diazotised and the heated with cuprous bromide. The reaction mixture so formed contains **[JEE Main-2008]**

(1) mixture of *o*- and *m*-bromotoluenes

(2) mixture of *o*- and *p*-bromotoluenes

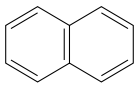
(3) mixture of *o*- and *p*-dibromobenzenes

(4) mixture of *o*- and *p*-bromoanilines

6. The nonaromatic compound along the following is **[JEE Main-2011]**

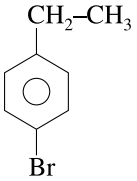
(1) 

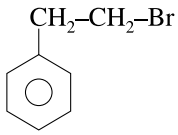
(2) 

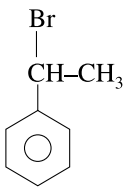
(3) 

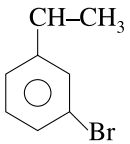
(4) 

7. The product of the reaction between ethyl benzene and N-bromo succinamide is: **[JEE Main Online-2012]**

(1) 

(2) 

(3) 

(4) 

8. Which of the following would not give 2-phenylbutane as the major product in a Friedel–Crafts alkylation reaction? **[JEE Main Online-2013]**

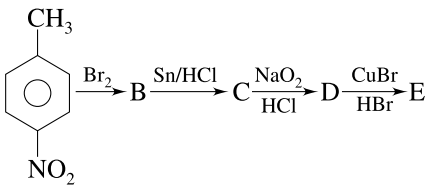
(1) 1-butene + HF

(2) 2-butanol + H_2SO_4

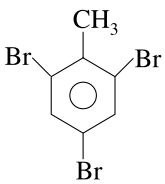
(3) butanoylchloride + $AlCl_3$ then Zn, HCl

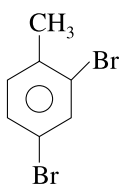
(4) Butyl chloride + $AlCl_3$

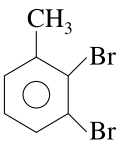
9. In a set of reactions p-nitrotoluene yielded a product E **[JEE Main Online-2014]**

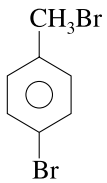


The product E would be:

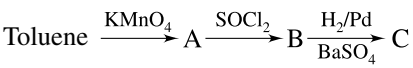
(1) 

(2) 

(3) 

(4) 

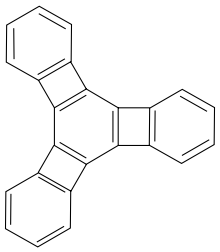
10. In the following sequence of reaction



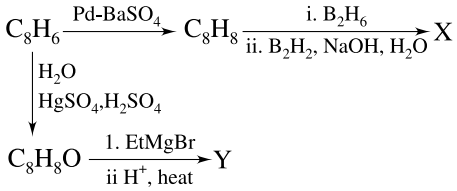
The product C is **[JEE Main-2015]**

(1) C_6H_5COOH (2) $C_6H_5CH_3$
(3) $C_6H_5CH_2OH$ (4) C_6H_5CHO

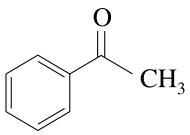
11. The compound below has four phenyl rings, but very less stable due to an opposing factor of stability. Therefore, this compound absorbs bromine in dark. How many bromine molecules, when added to this molecule, would make it stable and prevent further bromine addition? **[IIT-JEE 2005]**

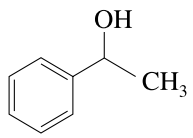


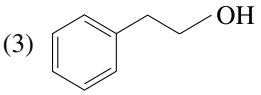
Comprehension (12 and 13)

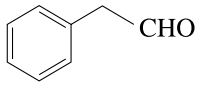


12. Compound X is **[JEE Adv.-2015]**

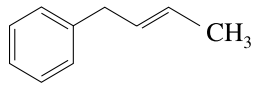
(1) 

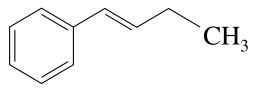
(2) 

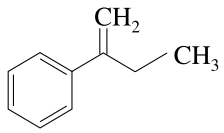
(3) 

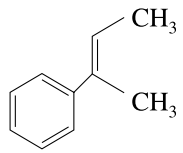
(4) 

13. The major compound Y is **[JEE Adv.-2015]**

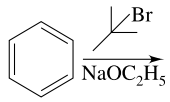
(1) 

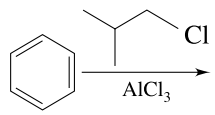
(2) 

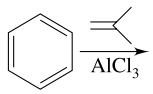
(3) 

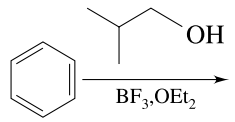
(4) 

14. Among the following reactions(s) which gives (give) tert-butyl benzene as the major product? **[JEE Adv.-2016]**

(1) 

(2) 

(3) 

(4) 

ANSWER KEY

EXERCISE # 1

1. (3)	2. (2)	3. (2)	4. (1)	5. (1)
6. (3)	7. (3)	8. (2)	9. (1)	10. (3)
11. (2)	12. (2)	13. (4)	14. (1)	15. (2)
16. (4)	17. (2)	18. (4)	19. (2)	20. (3)

EXERCISE # 2

1. (2)	2. (4)	3. (2)	4. (2)	5. (2)
6. (2)	7. (2)	8. (3)	9. (2)	10. (4)
11. (4)	12. (2)	13. (2)	14. (1)	15. (1)

EXERCISE # 3

1. (1,2,3,4)	2. (2,4)	3. (3)	4. (1,2,4)	5. (3)
6. (1,3,4)	7. (2,3)	8. (2)	9. (1)	10. (1)
11. (4)	12. (3)	13. (2)	14. (3)	15. (4)
16. (1)	17. (5)	18. (3)	19. (3)	20. (5)

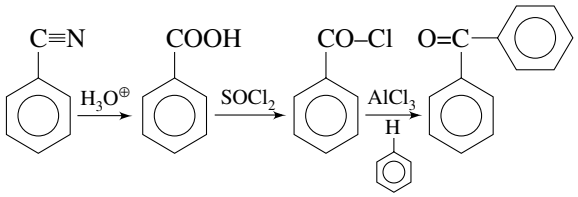
EXERCISE # 4

1. (1)	2. (3)	3. (4)	4. (3)	5. (2)
6. (2)	7. (3)	8. (3)	9. (2)	10. (4)
11. (3)	12. (3)	13. (4)	14. (2,3,4)	

HINT AND SOLUTION

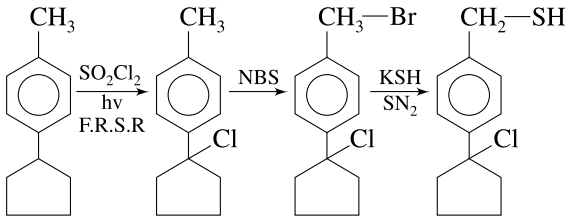
EXERCISE # 1

1. [3]

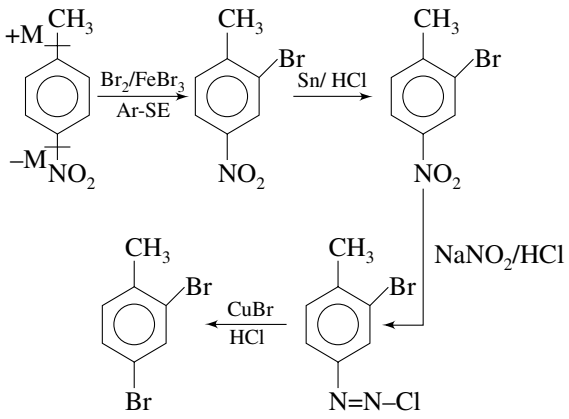


Friedel–Cracft acetylation

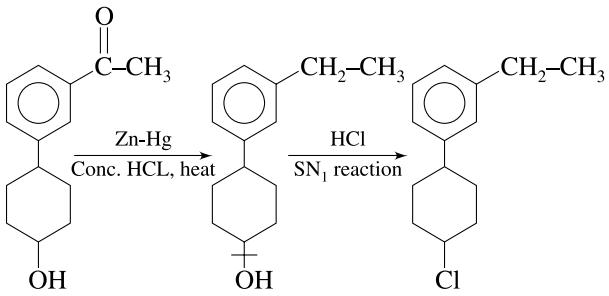
2. [2]



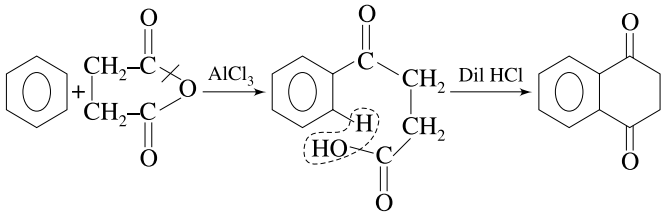
3. [2]



4. [1]



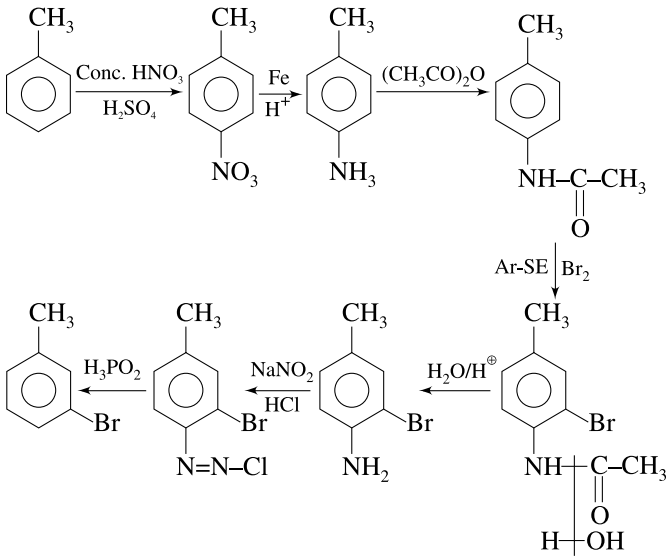
5. [1]



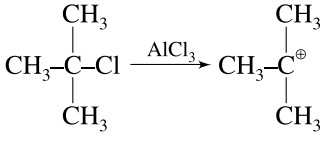
6. [3]

- De-activating group (–M) containing benzene ring do not give Friedel–Craft acylation due to instability of σ complex.
- $–NH_2$, its derivative containing benzene ring also does not give Friedel–Craft acylation because they form salt by acid base reaction with Lewis acid ($AlCl_3$)

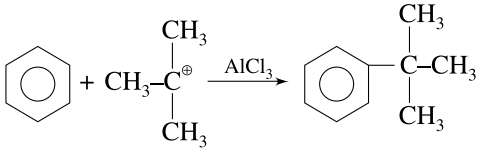
7. [3]



8. [2]



carbocation

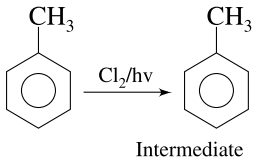


Friedel–Craft alkylation

9. [1]

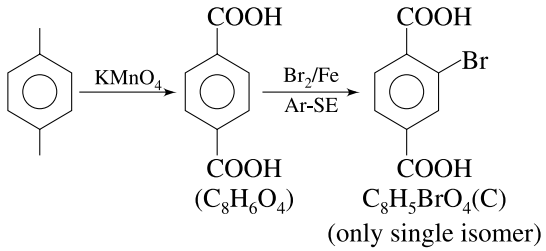
The most activating group will control orientation at least stericly hindred ortho and para position.

10. [3]

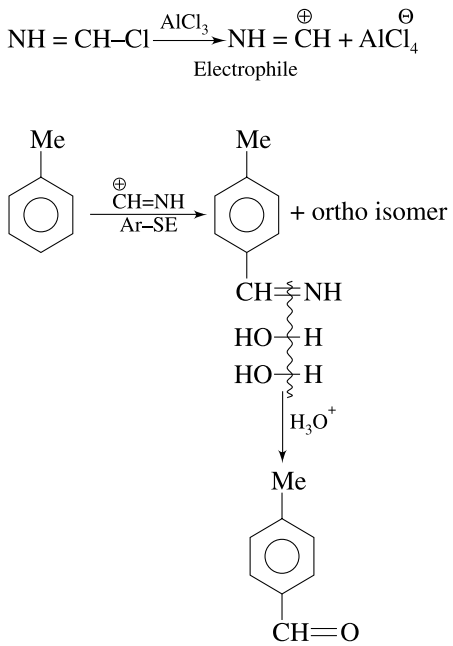


Free radical substitution reaction

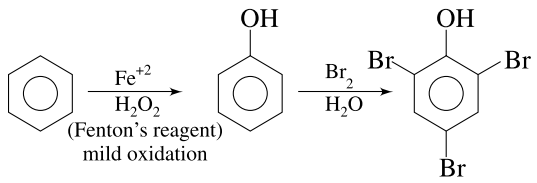
11. [2]



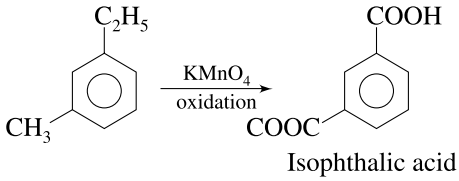
12. [2]



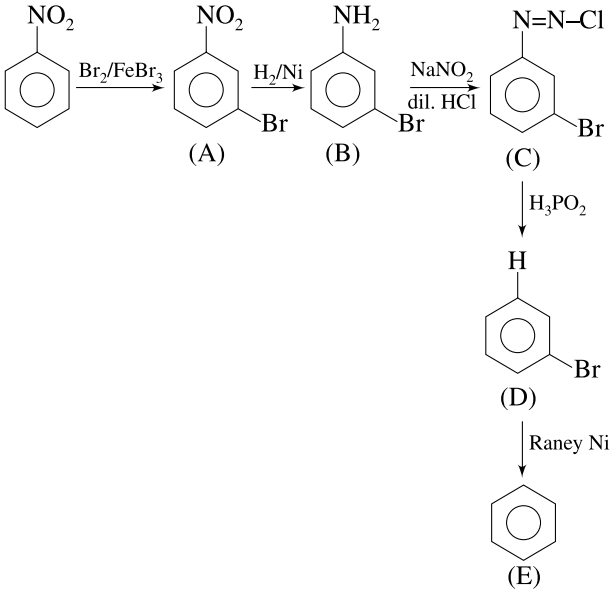
13. [4]



14. [1]



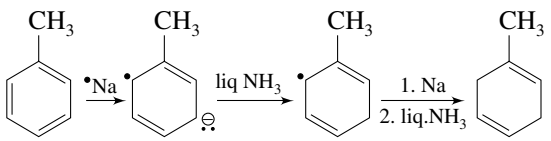
15. [2]



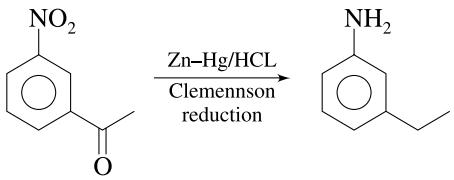
16. [4]

Resonance do not take place at mea position so that +ve charge is not occurred at meta position thus σ complex unstable at meta position.

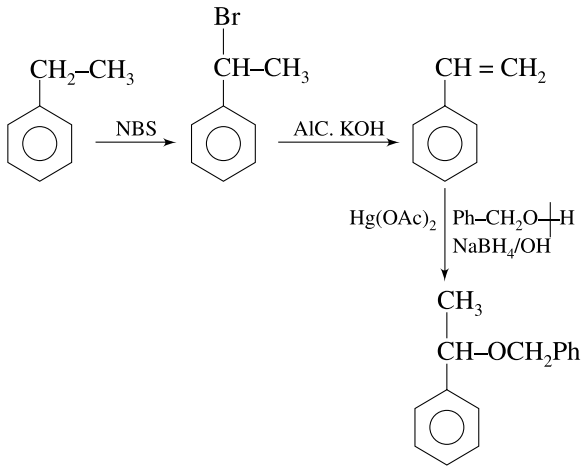
17. [2]



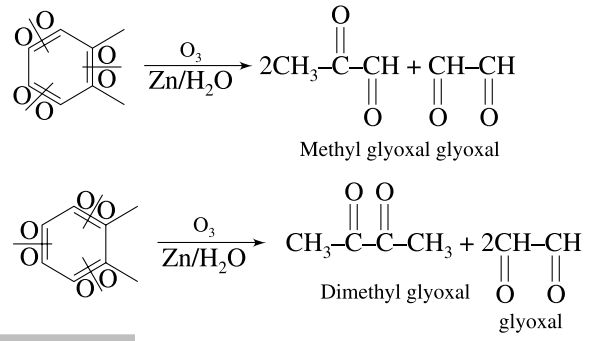
18. [4]



19. [2]

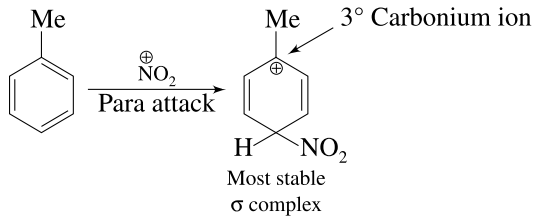


20. [3]



EXERCISE # 2

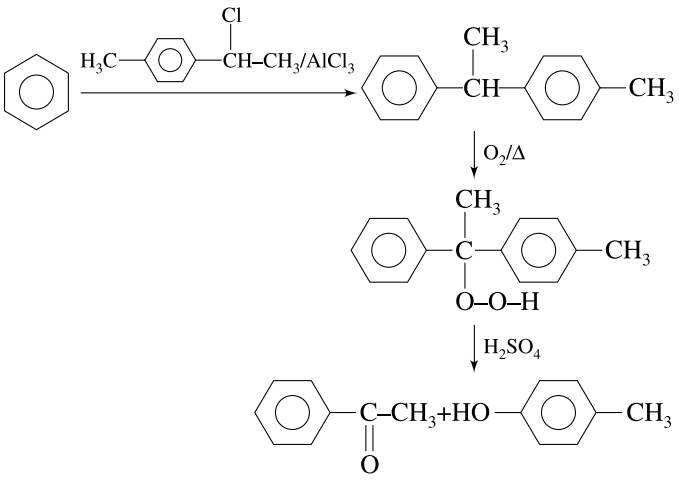
1. [2]



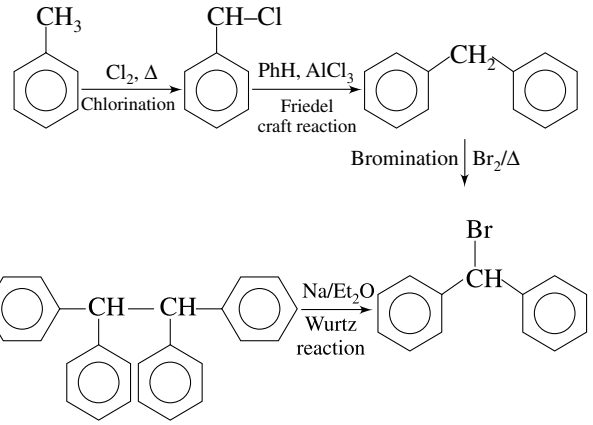
2. [4]

Due to hyperconjugation, Methyl group is activating and o/p director.

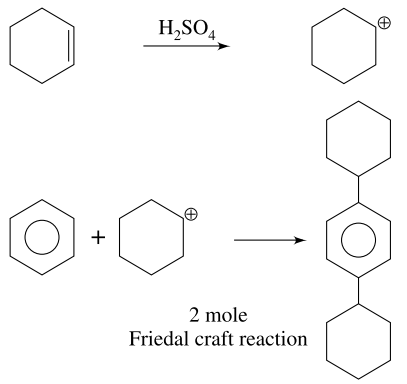
3. [2]



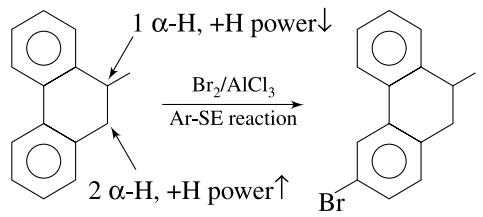
4. [2]



5. [2]



6. [2]

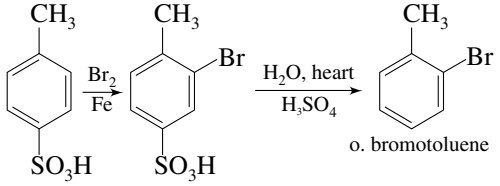


7. [2]

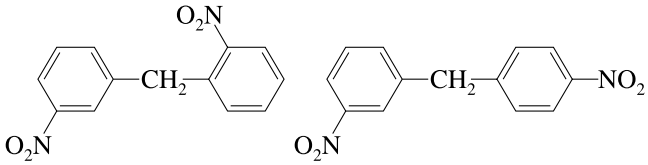
Boiling point α molecular weight

8. [3]

(1) The product is o-bromotoluene



(2) Substitution is faster in the ring that is not deactivated by $-NO_2$. Thus, the compounds obtained will be



(3) In 2,4-dinitrotoluene, there are two deactivating (NO_2) groups and one activating (CH_3) group while in m-dinitrobenzene, there are only two deactivating groups.

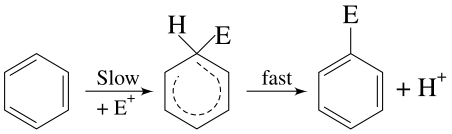
(4) 2,4-dinitrophenol contains a strongly activating group (–OH) while 2, 4 dinitrochlorobenzene contains weak deactivating group (–CL)

9. [2]

(1) The formation of intermediate arenium cation is slow while the elimination of H^+ from this cation is fast. The former involves the removal of aromaticity while the latter restores aromaticity

(2) The C–D bonds are stronger than C–H bonds. In fact, the bond with the heavier isotope is slightly stronger than that with the lighter isotope

(3) In electrophilic substitution reaction, the rate-determining step is the formation of arenium cation



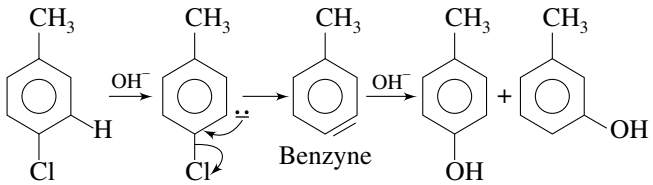
In this step, E^+ bonds to the aromatic ring without cleavage of a C–H bond. The latter is broken in the second step, which is fast as it restores the stable aromatic system. Since C–H or C–D bond is not broken in the rate-determining step, the overall rates of reaction are identical.

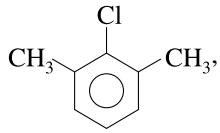
10. [4]

(1) The product is 1,4-naphthaquinone.

(2) The product is phthalic acid.

(3) Two products namely *p*-hydroxytoluene and *m*-hydroxytoluene are obtained. This reaction proceeds through the formation of benzyne and is known as elimination-addition reaction

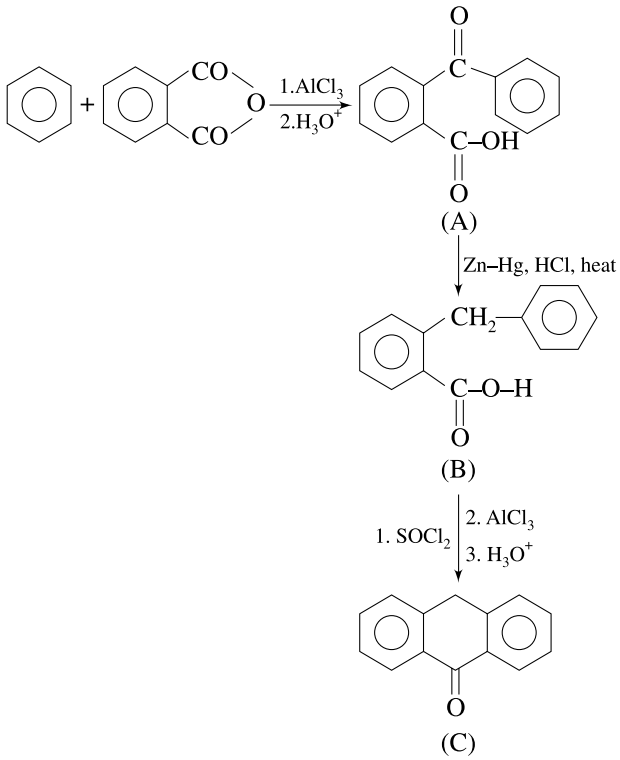


(4)  , there is no *Roth*-H, thus benzyne cannot form.

11. [4]

$–NO_2$ group is benzene deactivator, it is meta directing.

12. [2]



13. [2]

Intramolecular electrophilic aromatic substitution then nitration with respect to phenyl ring.

14. [1]

$–CH_3 > –CD_3 > –CT_3$

Order of hyperconjugation on the basis of bond energy

15. [1]

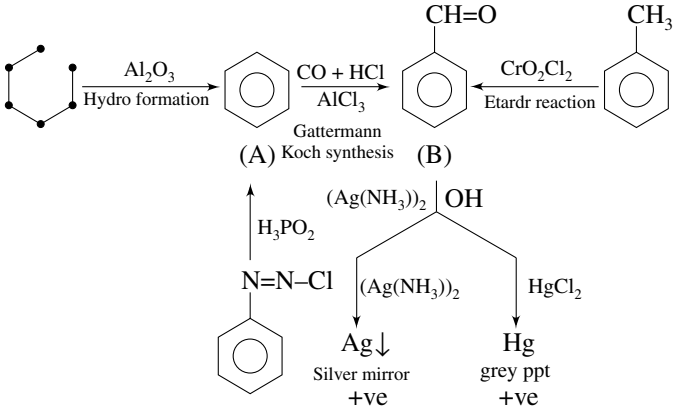
The steric demand of $H^{\ominus}$ is, however, extremely small, and when attack on C_6H_5Y is by any other electrophile, $E^{\oplus}$, which will necessarily be larger, there will be increasing interaction between E and Y in the transition state for attack at the position o- to Y (57 b, R = E) as attacking electrophile and substituent increase in size; there can be no such interaction in the transition state for p- attack (57 a, R = E). This will be reflected in an increasing ΔG^+ for o-attack, a consequently slower reaction, and the

relative proportion of o-product will thus fall as the size of E and / or Y increase. This is illustrated by the falling f_{o-}/f_{p-} ration which are observed for the nitration of alkylbenzenes (Y – $CH_3 \rightarrow CMe_3$) under comparable condition;

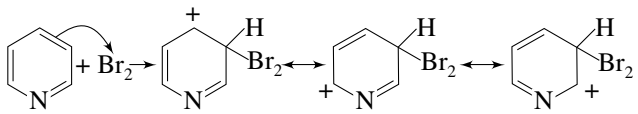
	Y	%o⁻	%p⁻
Increase in size of Y ↓	CH_3	58	37
	CH_2Me	45	49
	$CHMe_2$	30	62
	CMe_3	16	73

EXERCISE # 3

1. [1, 2, 3, 4]

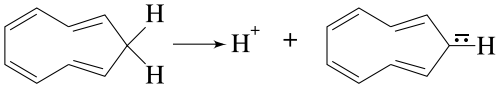


2. [2,4]



No such stabilisation of intermediate carbocation occurs by attack of Br^+ at C–2 or C–4 carbon. Electron withdrawing–I effect of nitrogen destabilises carbocation to some extent. Hence, pyridine is less reactive than benzene towards electrophilic substitution reaction.

3. [3]

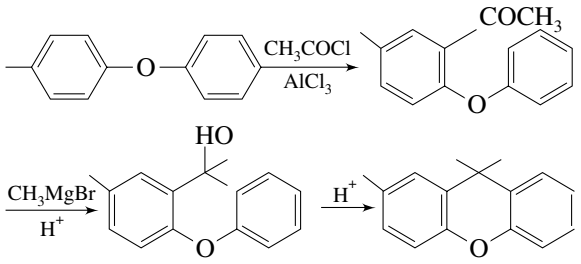


10 π -electrons
(aromatic)

4. [1, 2, 4]

It is aromatic, has six delocalised pi electrons but not as aromatic as benzene because 3p orbitals of S do not overlaps effectively with 2p orbitals of carbon. Hence, it does show reactions of alkenes to some extent.

5. [3]



6. [1, 3, 4]

When two group attach with benzene ring, then major product at the *o*/*p*-position of strong activating group

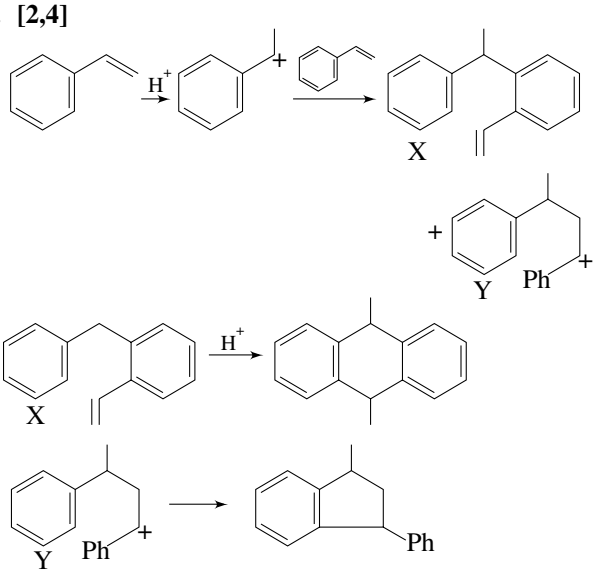
(1) + H (–CH_3) > +M (– Cl)

(2) + H (–CH_3) < + M (–NH–CO–CH_3)

(3) + M (–OH) > – M (–CH=O)

(4) Ring which is not de-active by –NO_2 group, will gives major product.

7. [2,4]

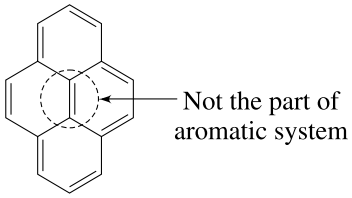


8. [2]

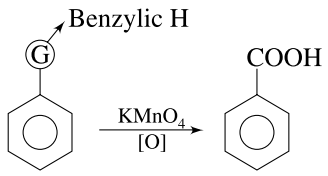
Both are correct, however, the correct explanation is small difference in the potential energies of two transition states in sulphonation reaction.

9. [1]

One of the resonance structure shown below indicates clearly that the central pi-bond is not involved in aromaticity, show the general reactions of a typical alkene.



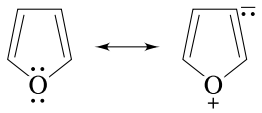
10. [1]



G → must have benzylic H

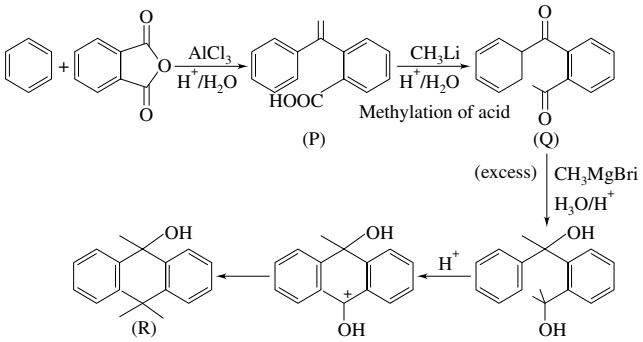
Both toluene and iso propyl have benzylic H

11. [4]



Due to abve resonance, furan acquire 6p electrons and show aromaticity but to a very small extent due to development of positive charge on electronegative oxygen atom. Hence, resonance stabilization of furan is much less than benzene. Due to this reason, furan show, to some extent, reactions of alkene.

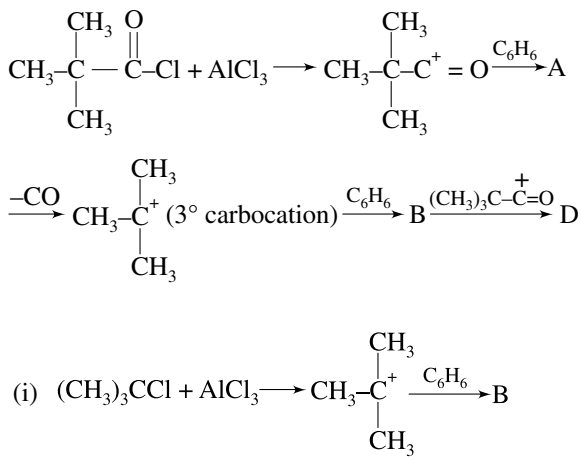
12. [3]



13. [2]

14. [3]

15. [4]



(i) $(CH_3)_3CCl + AlCl_3 \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C^+}}}} \xrightarrow{C_6H_6} B$

(ii) $CH_3-\overset{CH_3}{\underset{}{\overset{|}{C}}}=CH_2 \xrightarrow{H^+} CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C^+}}}} \xrightarrow{C_6H_6} B$

(iii) $(CH_3)_3COH \xrightarrow{H^+} CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C^+}}}} \xrightarrow{C_6H_6} B$

(iv) $\{(CH_3)_3CCO\}_2O \xrightarrow{AlCl} CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-C^+=O \xrightarrow{C_6H_6} A$

$CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C^+}}}} + CO \xrightarrow{C_6H_6} A$

16. [1]

(i) Friedel–Craft methylation and dimethylation gives P, R and S,

(ii) Friedel–Craft alkylation, i.e. ethyl group is added to benzene, thus, Q is the product

(iii) Aromatisation of octane gives all P, R and S.

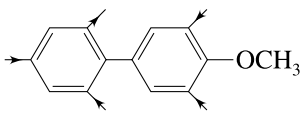
(iv) Friedel–Craft acylation produces benzophenone which on reduction produces 1-phenylethane.

(A) → P, R, S; (B) → Q; (C) → Q, R,S ;

(D) → (Q)

17. [5]

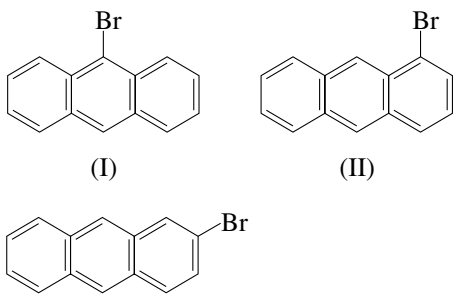
$-OCH_3$ is *ortho* and *para* directing



18. [3]

Ortho, meta and para xylene gives dicarboxylic acid on treatment with $KMnO_4$.

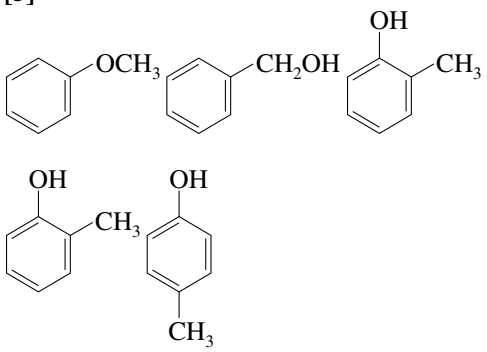
19. [3]



(I) (II)

(III)

20. [5]



EXERCISE # 4

1. [1]

$$Ph–MgBr \xrightarrow{Me–OH} Ph–H + Mg(OMe)Br$$

2. [3]

Toluene undergoes electrophilic substitution reaction in ortho and para positions, since the methyl group attached to benzene, being ring activator, is ortho and para directing group.

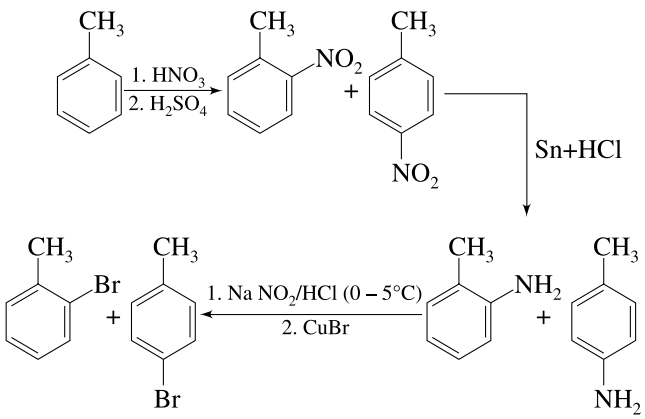
3. [4]

Nitro group is an electron-withdrawing group, thereby it deactivates the ring towards electrophilic substitution of benzene ring.

4. [3]

The nitro group is electron withdrawal group. This decreases the tendency of electrophilic substitution reaction. The intermediate σ-complex of nitrobenzene has larger energy as compared to that of benzene.

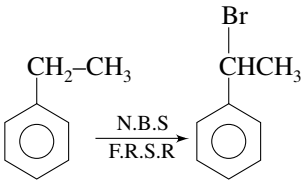
5. [2]



6. [1]

An aromatic compound has (4n + 2) π-electrons, where *n* is an integer. Cyclopentadiene has only 4π electrons and thus will be nonaromatic.

7. [3]



Substitution takes place at benzylic Carbon.

8. [3]

In (1), (2), (4) electrophile is alkyl carbocation which are stabilised by re-arrangement, so that 2-phenylbutane would not obtain as the major product.

(1) $CH_3–CH_2–CH=CH_2 \xrightarrow{HF} CH_3–CH_2–\underset{}{CH}–CH_3$

(2) $CH_3–CH_2–\underset{OH}{CH}–CH_3 \xrightarrow{H_2SO_4} CH_3–CH_2–CH–CH_3$

In (3) electrophile is acyl carbocation, which cannot be re-arranged.

(4) $CH_3–CH_2–CH_2–CH_2–Cl \xrightarrow{H_2SO_4} CH_3–CH_2–CH_2–\overset{+}{C}H_2$

$\downarrow$ 1 : 2 $H^{\ominus}$ shift

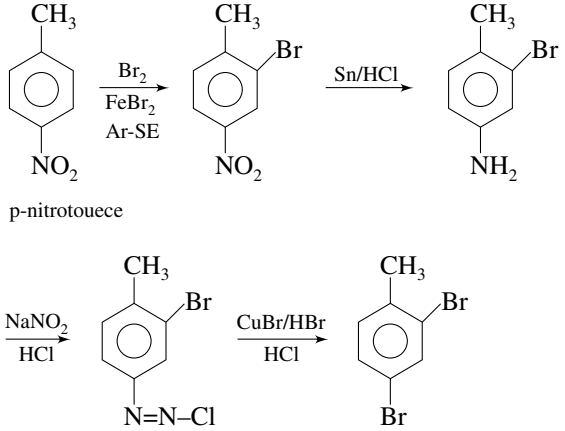
$CH_3–CH_2–\overset{+}{C}H–CH_3$

$CH_3–CH_2–\overset{+}{C}H–CH_3$ + benzene → $CH_3–\underset{}{CH}(CH_3)–CH_2CH_3$

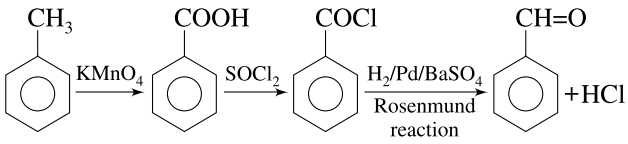
2-phenyl butane

(3) $CH_3–CH_2–CH_2–\underset{\underset{O}{\|}}{C}–Cl \xrightarrow{AlCl_3} CH_3–CH_2–CH_2–\overset{\oplus}{C}=O$

9. [2]



10. [4]

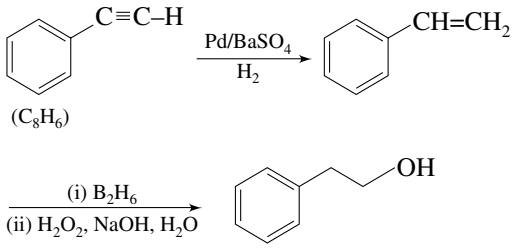


(C)
Benzaldehyde

11. [3]

It has three anti-aromatic (cyclobutadiene) rings which makes it unstable, if 3 molecules of Br_2 are added to central benzene, anti-aromaticity would be removed completely.

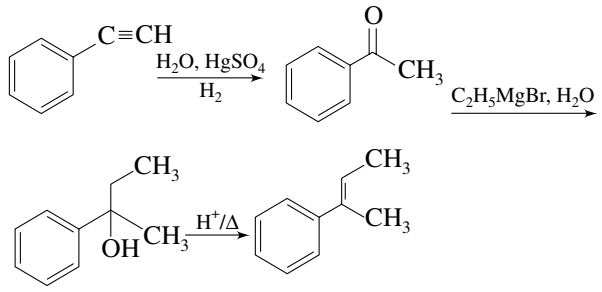
12. [3]



(2-phenyl ethanol)

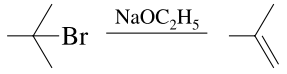
Hydroboration oxidation brings about anti-Markownikoff's hydration of alkene.

13. [4]



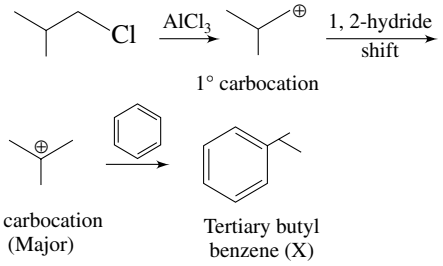
De-hydration takes places by syatzeff rule

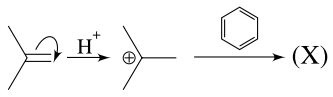
14. [2,3,4]

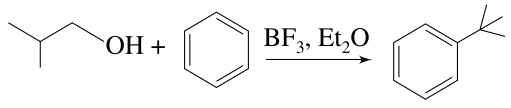
(1) 

C_2HO– (a strong nucleophile causes) El reaction to form isobutene as the major product.

(2)



(3) 

(4) 

CHAPTER 8

Purification and Characterisation of Organic Compounds

PURIFICATION OF ORGANIC COMPOUNDS

Purification means removal of undesirable impurities associated with a particular organic compound, i.e., to obtain the organic compound in pure state.

The methods commonly used for the separation and purification of organic compounds are:

(I) Crystallisation:
  (i) Simple crystallisation
  (ii) Fractional crystallisation
(II) Sublimation:
(III) Distillation:
  (i) Simple distillation
  (ii) Fractional distillation
  (iii) Vacuum distillation
  (iv) Steam distillation
(IV) Solvent extraction
(V) Chromatography

Methods Employed for Purification of Solids:

The methods employed depend on the physical state of the compound.

1. CRYSTALLISATION: This method is based on the differences in the solubility of the organic compound and its impurities in a solvent.

It is of two types.

(i) Simple Crystallisation: The complete operation of simple crystallisation involves the following steps:

(a) Preparation of the solution: Organic substance is powered and is dissolved in a suitable solvent by heating. The amount of solvent should be just sufficient to dissolve the whole of the solid on heating.

(b) Selection of a suitable solvent: The choice of solvent is very important in the crystallisation process. The main conditions of the solvent are:

(i) The organic substance should dissolve in the solvent upon heating and it should get separated on cooling.

(ii) The solvent should not dissolve the impurities.

(iii) The solvent should not react chemically with the substance.

Example: suppose we want to purify sugar containing an impurity of common salt. This can be done by treating the mixture with ethanol around 350 K. The sugar will dissolve whereas common salt remains insoluble.

(c) Filtration of the hot solution: The hot saturated solution is filtered preferably through a fluted filter paper placed in a glass funnel. The use of the fluted filter paper makes the filtration rapid. The jacket of the hot water funnel is heated from outside and this keeps the solution hot in the glass funnel. This will prevent the formation of crystals during filtration.

(d) Crystallisation: The hot filtrate is allowed to cool slowly and undisturbed in a beaker or in a crystallising dish. After some time the crystals of the pure compound are formed.

(e) Separation of the crystals: The crystals formed are separated from the mother liquor by filtration. The filtration is normally done by use of Buckner funnel and a suction pump. This enables the filtration under reduced pressure and is therefore, quite fast.

(f) Drying of crystals: The crystals are dried by pressing between the folds of filter paper and then placed in a steam of air oven for some time. The crystals are finally dried over sulphuric acid or calcium chloride in a desiccator.

Example: (i) Sugar mixed with common salt can be purified with ethanol.

(ii) Phthalic acid mixed with naphthalene can be purified with hot-water.

(ii) Fractional Crystallisation: The method is used for the separation of a mixture of two compounds which are soluble in the same solvent but their solubilities are different. The hot saturated solution of the mixture is allowed to cool when the less soluble component crystallizes out earlier than separated from time to time. These fractions are now separately put to crystallisation. A series of repeated crystallisations separate the two compounds in pure form.

2. SUBLIMATION: Certain organic solids directly change from solid to vapour state on heating. This process is called sublimation. The vapours on cooling change back to the solid form

$$\text{Solid} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \text{Vapours}$$

The sublimation process is used for the separation of those solids which sublime on heating from non-volatile solids. The process is generally used for the purification of camphor, naphthalene, anthracene, benzoic acid, etc. containing non-volatile impurities.

Methods Employed for purification of Liquids:

3. DISTILLATIOIN: Distillation is a process which involves two steps:

(i) Vaporisation: Liquid is converted into vapours.

(ii) Condensation: Vapours are condensed again into liquid.

(a) Simple distillation: This method is used for the purification of liquids which boil without decomposition and contain non-volatile impurities. The simple distillation involves its boiling point so that it is converted into vapours. On cooling the vapours, pure liquid is obtained.

The distillate contains pure liquid while the impurities are left behind in the distillation flask.

Examples (1) Ether and ethyl alcohol

(2) Benzene and aniline

(3) Chloroform and aniline

(4) Ether and toluene

(b) Fractional Distillation: This process is used to separate a mixture of two or more miscible liquids which have boiling points close to each other. The fractionating column is a long tube provided with obstructions to the passage of the vapours moving upwards and liquid moving downwards.

Since in this process, the distillate is collected in fractions under different tempratares, it is known as Fractional distillation.

This method may be used to separate a mixture of

(1) Acetone (b.p. 330 K) and methyl alcohol (b.p. 338 K)

(2) Benzene and toluene

(c) Distillation Under Reduced Pressure (Vacuum Distillation): Certain liquids tend to decompose at a temperature below their boiling points. Such liquids cannot be purified by ordinary distillation. Therefore, vacuum distillation is used for liquids which decompose at a temperature below their normal boiling points.

- Cane juice can also be concentrated by this method.
- This technique can be used to separate glycerol from spent lye in soap industry.

(d) Steam Distillation: The process of steam distillation is used for the separation and purification of liquid which is appreciably volatile in steam, from non-volatile components of a mixture. Thus, the process of steam distillations is used to purify the substances which

(i) are volatile in steam but are not miscible with water;
(ii) possess sufficiently higher vapour pressure at the boiling point temperature of water (100°C);
(iii) contain non-volatile impurities.

Examples

(i) The process of steam distillation can be applied for the separation of a mixture of *o*-nitrophenol and *p*-nitrophenol.
(ii) The method can also be used for the purification of impure sample of aniline, Chlorotoluenes, Nitrobenzene.
(iii) It is also employed in the isolation of essential oils from flowers.

(4) SOLVENT EXTRACTION: The process of separation of an organic compound from its aqueous solution by shaking with a suitable organic solvent is termed solvent extraction. The solvent should be immiscible with water and the organic compound,to be separated should be highly soluble in it.

(5) CHROMATOGRAPHY: This method is based on the differences in the rates at which the compounds of a mixture are adsorbed on a suitable adsorbent. There are many forms of chromatography such as column chromatography, paper chromatography, thin layer chromatography (TLC), gas chromatography, etc. The simplest method is column chromatography.

QUALTATIVE ANALYSIS

Detection of Carbon and Hydrogen

When the mixture is heated with copper oxide the carbon present in the compound is oxidised to carbon dioxide which turns lime water milky. The hydrogen present in the organic compound is oxidised to water which turns anhydrous copper sulphate in the bulb to blue.

Liebig's test

$C + 2CuO \xrightarrow{\Delta} CO_2 + 2Cu$

$2H + CuO \xrightarrow{\Delta} Cu + H_2O$

$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + H_2O$

$CuSO_4 + 5H_2O \longrightarrow CuSO_4 \cdot 5H_2O$

(white) (Blue)

This method is known as **copper oxide test**.

Detection of Nitrogen, Sulphur, Halogens

Lassaigne's test

These elements are tested in an organic compound by **Lassaigne's test.** The organic compound (containing N, S, and/or halogens) is fused with sodium metal as to convert these elements into ionisable inorganic substances, i.e., nitrogen into sodium cyanide, sulphur into sodium sulphide and halogens into sodium halides.

Test for Nitrogen: The nitrogen in the compound reacts with sodium metal to form sodium cyanide.

$Na + C + N \xrightarrow{\Delta} NaCN$

$FeSO_4 + 2NaCN \longrightarrow Fe(CN)_2 + Na_2SO_4$

$Fe(CN)_2 + 4NaCN \longrightarrow Na_4[Fe(CN)_6]$ sodium ferrocyanide

$3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow Fe_4[Fe(CN)_6]_3 + 12NaCl$ Ferric ferrocyanide (Prussian blue colour)

Special test for Nitrogen:

- **Sodalime test:** A pinch of an organic compound is heated strongly with soda lime (NaOH + CaO) in a test tube. If ammonia gas evolves, it indicated nitrogen.

$$\underset{\text{acetamide}}{CH_3CONH_2} + NaOH \xrightarrow[\Delta]{CaO} CH_3COONa + NH_3$$

- **Limitation:** This method has a limitation. A large number of organic compounds such as nitro and diazo compounds do not liberate ammonia on heating with sodalime.

Test for Sulphur:

The sulphur in the compound reacts with sodium metal to form sodium sulphide.

$$2Na + S \longrightarrow Na_2S$$

The Lassaigne's extract is divided into two parts and following test are performed.

(a) Sodium nitroprusside test: The one portion of the extract, a few drops of sodium nitroprosside are added. The appearance of violet colouration indicates sulphur.

$$\underset{\text{Sodium nitroprusside}}{Na_2S + Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{violet colouration}}{Na_4[Fe(CN)_5NO{\cdot}S]}$$

(b) Lead acetate test: The other part of the Lassaigne's extract is acidified with acetic acid and then lead acetate solution is added. Formation of black precipitate confirms the presence of sulphur.

$$Na_2S + \underset{\text{lead acetate}}{Pb(CH_3COO)_2} \longrightarrow \underset{\text{black}}{PbS} + 2CH_3COONa$$

Test for Nitrogen and Sulphur Present Together:

$$Na + C + N + S \longrightarrow NaCNS$$

$$Fe^{3+} + 3CNS^- \longrightarrow \underset{\text{Blood red colour}}{Fe(CNS)_3}$$

Test for Halogens:

Sodium will combine with the halogen (from the organic compound) to form sodium halide

$$Na + X \xrightarrow{\text{Fusion}} NaX(X = Cl, Br, I)$$

(i) A white precipitate soluble in ammonium hydroxide solution indicates the presence of chlorine in the organic compound

$$NaCl + AgNO_3 \longrightarrow \underset{\text{white ppt.}}{AgCl} + NaNO_3$$

(ii) A dull yellow precipitate partially soluble in ammonium hydroxide solution indicates the presence of bromine in the organic compound.

$$NaBr + AgNO_3 \longrightarrow \underset{\text{dull yellow ppt.}}{AgCl} + NaNO_3$$

(iii) A bright yellow precipitate, completely insoluble in ammonium hydroxide solution, indicates the presence of iodine in the organic compound.

$$NaI + AgNO_3 \longrightarrow \underset{\text{bright yellow ppt.}}{AgI} + NaNO_3$$

Special test for bromine and iodine (Layer test):

$$2NaBr + Cl_2 \longrightarrow \underset{\text{(turns } CS_2 \text{ layer orange)}}{2NaCl + Br_2}$$

$$2NaI + Cl_2 \longrightarrow \underset{\text{(turns } CS_2 \text{ layer violet)}}{2NaCl + I_2}$$

Test for phosphorus:

The compound is heated with an oxidising agent (sodium peroxide). The phosphorus present in the compounds is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + 12(NH_4)_2\,MoO_4 + 21HNO_3 \longrightarrow \underset{\text{Ammonium phosphomolybdate}}{(NH_4)_3PO_4 \cdot 12MoO_3} + 21NH_4NO_3 + 12H_2O$$

$$\underset{\text{Ammonium molybdate}}{}$$

QUANTITATIVE ANALYSIS

1. **Estimation of Carbon and Hydrogen:** By Liebig combustion method.

$$\boxed{\%\text{ of C} = \frac{12}{44} \times \frac{\text{Mass of } CO_2}{\text{Mass of organic compound}} \times 100}$$

$$\boxed{\%\text{ of H} = \frac{2}{18} \times \frac{\text{Mass of } H_2O \text{ formed}}{\text{Mass of organic compound}} \times 100}$$

2. **Estimation of Nitrogen:**

There are two methods for the estimation of nitrogen.

(i) Duma's method

$$\therefore\ \%\text{ of N} = \frac{28}{22400} \times \frac{\text{Volume of } N_2 \text{ at N.T.P}}{\text{Mass of organic compound}} \times 100$$

(ii) **Kjeldahl's method:** This method cannot be used for

(i) organic compounds containing nitrogen in the ring such as pyridine, quinoline, etc.

(ii) Organic compounds containing nitrogen ($-NO_2$) and diazo ($-N = N-$) groups.

$$\%\text{ of N} = \frac{1.4 \times N \times V}{W}$$

N = Normality of acid.

V = volume of acid used for neutralization of NH_3.

W = Weight of organic substance.

3. **Estimation of Halogens:** By Carius method.

$$\boxed{\%\text{ of X} = \frac{\text{Atomic mass of halogen} \times \text{Mass of silver halide}}{(108 + \text{At. mass of halogen}) \times \text{Mass of organic substance}} \times 100}$$

(i) $\%\text{ of Cl} = \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl}}{\text{Mass of organic substance}} \times 100$

(ii) $\%\text{ of Br} = \frac{80}{188} \times \frac{\text{Mass of AgBr}}{\text{Mass of organic substance}} \times 100$

(iii) $\%\text{ of I} = \frac{127}{235} \times \frac{\text{Mass of AgI}}{\text{Mass of organic substance}} \times 100$

4. Estimation of Sulphur: By Carius method.

$$\% \text{ of S} = \frac{32}{233} \times \frac{\text{Mass of } BaSO_4}{\text{Mass of organic compound}} \times 100$$

5. Estimation of Phosphorus: By Carius method.

$$\% \text{ of P} = \frac{62}{222} \times \frac{\text{Mass of Magnesium pyrophosphate}}{\text{Mass of organic compound}} \times 100$$

SOLVED EXAMPLE

1. In sodium fusion test of organic compounds, the nitrogen of an organic compound is converted to

(1) Sodamide (2) Sodium cyanide

(3) Sodium nitrite (4) Sodium nitrate

Sol. **[2]**

$$Na + C + N \xrightarrow{\text{fusion}} NaCN$$

2. The quantitative determination of halogen in an organic compound is known as:

(1) Duma's method (2) Carius method

(3) Kjeldahl's method (4) Liebig method

Sol. **[2]**

The quantitative determination of halogen in an organic compound is called as Carius method.

3. In a Dumas experiment, 0.5 g of an organic compound on heating with copper oxide liberated 112 mL of N_2 at STP. The percentage of nitrogen (by weight) in the compound is:

(1) 70 (2) 35

(3) 14 (4) 28

Sol. **[4]**

$$\% \text{ N} = \frac{28}{24000} \frac{\text{vol. of } N_2(\text{ml})}{\text{wt. of organic subs.}} \times 100$$

$$= \frac{28}{22400} \times \frac{122}{0.5} \times 100 = 28\%$$

4. An organic compound gave C = 92.31% and H = 7.69% If molecular weight of the compound is 78, its molecular formula is

(1) C_6H_6 (2) C_7H_7

(3) C_6H_{18} (4) C_8H_{20}

Sol. **[1]**

Element	Percentage	Atomic Mass	Relative number of atoms	Simplest ratio of atoms
Carbon	92.31	12	$\frac{92.31}{12} = 7.69$	$\frac{7.69}{7.69} = 1$
Hydrogen	7.69	1	$\frac{7.69}{1} = 7.69$	$\frac{7.69}{7.69} = 1$

Empirical formula = CH

Molecular formula = $(CH)_n$

$(12 + 1) \times n = 78$

$n = \frac{78}{13} = 6$

Thus, the molecular formula = C_6H_6

5. Aniline has high boiling point, high vapour pressure at 100°C and is insoluble in water. Aniline is therefore, separated by:

(1) Steam distillation

(2) Simple distillation

(3) Distillation at low pressure

(4) Sublimation

Sol. **[1]**

Aniline separated by steam distillation.

6. The most suitable method for separation of 1:1 mixture of *ortho*- and *para* nitrophenols is:

(1) Distillation (2) Crystallisation

(3) Sublimation (4) Chromatography

Sol. **[1]**

Due to intramolecular H-bond in *o*- nitrophenol its volatile nature increases so that separated by distillation.

7. 0.099 g of an organic compound when heated with fuming nitric in the presence of silver nitrate in a Carius tube gave 0.287 g silver chloride. The percentage of chlorine in the compound is about:

(1) 28.64 (2) 71.72

(3) 35.45 (4) 64.23

Sol. **[2]**

$$\% = \text{Cl} = \frac{35.5}{143.5} \times \frac{\text{wt. of AgCl}}{\text{wt. of organic compound}} \times 100$$

$$= \frac{35.5}{143.5} \times \frac{.287}{.099} \times 100$$

$$= 71.72\%$$

8. In Lassaigne's test the organic compound is fused with sodium metal to:

(1) Ignite the compound
(2) Oxidise the compound
(3) Convert the elements in ionic form
(4) Reduce the compound

Sol. **[3]**

$Na + C + N \longrightarrow NaCN$
(covalent) (Ionic)

9. The Lassaigne's extract is boiled with conc. HNO_3 while testing for the halogens. By doing so it:
(1) decomposes Na_2S and NaCN, if formed
(2) helps in the precipitation of AgCl
(3) increases the solubility product of AgCl
(4) increases the concentration of NO_3 ions

Sol. **[1]**

Before the test of halogen, Lassaigne's extract is boiled with conc. HNO_3 to remove Na_2S and NaCN in form of H_2S and HCN.

10. In the Kjeldahl's method for estimation of nitrogen present in a soil sample, ammonia evolved from 0.75 g of compound neutralised 10 mL of 1 M H_2SO_4. The percentage of nitrogen in the soil is:
(1) 37.33 (2) 45.33
(3) 35.33 (4) 43.33

Sol. **[1]**

$\% N = \frac{1.4\ NV}{W}$

10 mL 1M $H_2SO_4 \equiv$ evolved NH_3

$\because V = 10$ mL

N = n factor × M

$= 2 \times 1 = 2N$

$\%N = \frac{1.4 \times 2 \times 10}{0.75} = 37.33\%$

EXERCISE 1

1. A compound which does not give a positive test in the Lassaigne's test for 'N' is
(1) Glycine (2) Phenyl hydrazine
(3) Urea (4) Azobenzene

2. 0.395 g of an organic compound by Carius method for the estimation of sulphur gave 0.582 g of $BaSO_4$. The percentage of sulphur in the compound is
(1) 20.24 (2) 35
(3) 40 (4) 45

3. Liebig method is used for the estimation of
(1) Nitrogen (2) Sulphur
(3) Carbon and hydrogen (4) Halogens

4. The latest technique for the purification of organic compounds is
(1) Fractional distillation (2) Chromatography
(3) Vacuum distillation (4) Crystallization

5. p-nitrophenol and o-nitrophenol are separated by
(1) Crystallisation
(2) Fractional crystallisation
(3) Distillation
(4) Steam distillation

6. In the estimation of sulphur organic compound on treating with conc. HNO_3 is converted to
(1) SO_2 (2) H_2S
(3) H_2SO_4 (4) SO_3

7. How will you separate a solution (miscible) of benzene + $CHCl_3$?
(1) Sublimation (2) Filtration
(3) Distillation (4) Crystallisation

8. In Lassaigne's test for the detection of nitrogen in an organic compound, the appearance of the Prussian blue colour is due to the formation of:
(1) $NaFe^{III}[Fe^{II}(CN)_6]$ (2) $NaFe^{II}[Fe^{III}(CN)_6]$
(3) $Fe_4[Fe(CN)_6]_3$ (4) $Na_4[Fe(CN)_6]$

9. Fractional crystallisation is carried out to separate such mixtures:
(1) Organic solids mixed with inorganic solids
(2) Organic solids highly soluble in water
(3) Organic solids having small difference in their solubility in suitable solvent
(4) Organic solids having great difference in their solubility in suitable solvent

10. $AgNO_3$ solution does not give white ppt. with CCl_4 but with sodium extract of CCl_4, $AgNO_3$ gives white precipitate because:
(1) CCl_4 is covalent compound
(2) CCl_4 is partially ionised
(3) Sodium extract of CCl_4 contains Cl^- ions and Na^+ ion
(4) Sodium extract of CCl_4 contains ClO_3^- ions

11. If the sodium extract of an organic compound develops a blood red colour on treatment with $FeCl_3$ solution, which of the following ions must be present in the sodium extract that responds to this colour test?
(1) CN^- (2) CNO^-
(3) CNS^- (4) S^{2-}

12. In Kjeldahl's method of estimation of nitrogen, K_2SO_4 acts as:

(1) an oxidising agent (2) catalytic agent
(3) hydrolysing agent (4) boiling point elevator

13. To detect iodine in presence of bromine, the sodium extract is treated with $NaNO_2$ + glacial acetic acid + CCl_4. Iodine is detected by the appearance of
(1) yellow colour of CCl_4 layer
(2) purple colour of CCl_4
(3) brown colour in the organic layer of CCl_4
(4) deep blue colour in CCl_4

14. Lassaigne's test for the detection of nitrogen will fail in the case of
(1) NH_2CONH_2 (2) $NH_2CONHNH_2.HCl$
(3) $NH_2NH_2.HCl$ (4) $C_6H_5NHNH_2.2HCl$

15. In Kjeldahl's method, nitrogen present is estimated as
(1) N_2 (2) NH_3
(3) NO_2 (4) None of these

EXERCISE 2

1. In Lassaigne's test for nitrogen, the blue colour is due to the formation of
(1) Ferric ferrocyanide
(2) Potassium ferrocyanide
(3) Sodium ferrocyanide
(4) Sodium cyanide

2. 73 g of an amide obtained from a carboxylic acid, RCOOH, liberated 17 g of ammonia upon heating with alkali. The acid is
(1) Formic acid (2) Acetic acid
(3) propionic acid (4) benzoic acid

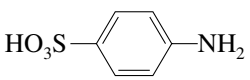
3. Anhydrous formic acid cannot be obtained from its aqueous solution by simple fractional distillation because
(1) Pure HCOOH is unstable
(2) HCOOH forms hydrogen bonds with water
(3) Boiling point of HCOOH is very close to that of water
(4) Constant boiling azeotropic mixture is formed with water

4. In Kjeldahl method function of $CuSO_4$ is
(1) B.P. elevator
(2) Catalyst
(3) Freezing point depressor
(4) None of these

5. If an organic compound contains both nitrogen and sulphur, its fusion with sodium converts these elements into:
(1) Na_2S and NaCN (2) NaSCN
(3) Na_2SO_3 and NaCN (4) Na_2S and NaCNO

6. Which of the following statement s is correct ?
(1) Two solid organic substances are said to be different if their mixed melting point is depressed below the melting points of both of these
(2) Ethanol and water cannot be separated from each other completely by simple distillation as they form azeotrpic mixture.
(3) Impure glycerine can be purified by vaccume distillation
(4) All of these

7. Silica gel is used for keeping away the moisture because it
(1) Absorbs H_2O (2) Adsorbs H_2O
(3) Reacts with H_2O (4) None of these

8. Which of the following will not give test for nitrogen in Lassaigne's test?
(1) $C_6H_5NHNH_2$
(2) H_2NCONH_2
(3) $NH_2–NH_2$
(4) 

9. Turpentine oil can be purified by
(1) Vacuum distillation (2) Fractional distillation
(3) Steam distillation (4) Simple distillation

10. Which of the following compound will give blood red colour while doing the Lassaigne's test for N?
(1) $(NH_2)_2C=O$ (2) $H_2N(C_6H_4)SO_3H$
(3) $C_6H_5SO_3H$ (4) $CHCl_3$

EXERCISE 3

Numerical Section

1. 0.50 g of an organic compound was Kjeldahlised and the NH_3 evolved was absorbed in a certain volume of 1N H_2SO_4. The residual acid required 60 cm^3 of N/2 NaOH. Find the volume of 1N H_2SO_4 taken if the percentage 6.
(1) 25 (2) 50
(3) 75 (4) 100

2. 0.25 g of an organic compound gave 31.1 mL, of N_2 by Duma's method. Calculate the % of N in this compound.

(1) 10.20% (2) 12.44%
(3) 15.55% (4) 20.66%

3. An organic compound has carbon and hydrogen percentages in the ratio 6 : 1 and carbon and oxygen percentage in the ratio 3 : 4. The compound has the empirical formula
(1) CH_2O (2) CH_4O
(3) C_2H_6O (4) CHO_2

4. 0.2 g of an organic compound containing C, H and O, on combustion gave 0.147g CO_2 and 0.12 g water. The percentage of oxygen in organic compound is
(1) 73.29% (2) 78.45%
(3) 83.23% (4) 89.50%

5. 2.79 g of an organic compound when heated in Carius tube with conc. HNO_3 and H_3PO_4 formed converted into $MgNH_4.PO_4$ ppt. The ppt. on heating gave 1.332 g of $Mg_2P_2O_7$. The percentage of P in the compound is
(1) 23.33 (2) 13.33
(3) 33.33 (4) 26.66

6. In Duma's method of estimation of nitrogen 0.35 g of an organic compound gave 55 mL of nitrogen collected at 300 K temperature and 715 mm pressure. The percentage composition of nitrogen in the compound would be (Aqueous tension at 300 K = 15 mm)
(1) 14.45 (2) 15.45
(3) 16.45 (4) 17.45

7. 0.2475 g of an organic compound gave on combustion 0.4950 g of carbon dioxide and 0.2025 g of water. The percentage of carbon and hydrogen are
(1) 54.54, 9.09 (2) 52.54, 8.09
(3) 120, 5.8 (4) None of these

Assertion and Reason Type Question

(1) If both (A) and (R) are correct and (R) is the correct explanation for (A)
(2) If both (A) and (R) are correct and (R) is not the correct explanation
(3) If (A) is correct and (R) is incorrect
(4) If (A) is incorrect and (R) is correct

8. **Assertion:** A mixture of plant pigments can be separated by chromatography.
Reason: Chromatography is used for the separation of coloured substance into individual components.

9. **Assertion:** Duma's method is more applicable to nitrogen containing organic compounds than Kjeldahl's method.
Reason: Kjeldahl's method does not give satisfactory results for compounds in which N is linked to nitrogen.

Column Matching Type Question

10.

Column-I	*Column-II*
(A) Kjeldahl's method	(p) Empirical formula of Acetone as well as glucose.
(B) Nitrogen of organic compound compound is converted is into free N_2 gas (q)	(q) Nitrogen of organic compound is converted into ammonium sulphate
(C) $Na_4[Fe(CN)_5NOS]$	(r) Compound formed in Lassaigne's test for N it sulphur is also present.
(D) $Fe(CNS)_3$	(s) Purple colouration to the Lassaigne's test for S.
(E) Methanal	(t) Duma's method.

(1) A → q; B → t; C → s; D → r; E → p
(2) A → t; B → q; C → s; D → r; E → p
(3) A → q; B → t; C → r; D → p; E → s
(4) A → s; B → r; C → q; D → t; E → p

EXERCISE 4

1. The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is **[JEE Mains-2004]**
(1) $Fe_4[Fe_4(CN)_6]_3$ (2) $Na_3[Fe(CN)_6]$
(3) $Fe(CN)_3$ (4) $Na_4[Fe(CN)_5NOS]$

2. The ammonia evolved from the treatment of 0.30 g of an organic compound for the estimation of nitrogen was passed in 100 mL of 0.1 M sulphuric acid. The excess of acid required 20 mL of 0.5 M sodium hydroxide solution for complete neutralisation. The organic compound is **[JEE Mains-2004]**
(1) acetamide (2) benzamide
(3) urea (4) thiourea

3. 29.5 mg of an organic compound containing nitrogen was digested accordingto Kjeldahl's method and the evolved ammonia was absorbed in 20 mL of 0.1 M HCl solution. The excess of the acid required 15 mL of

0.1 M NaOH solution for complete neutralization. The percentage of nitrogen in the compound is **[JEE Mains-2010]**

(1) 29.5 (2) 59.0

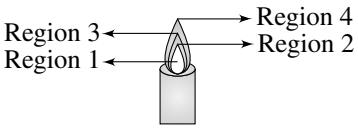
(3) 47.4 (4) 23.7

4. In Carius method of estimation of halogens, 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is: (atomic mass Ag = 108; Br = 80) **[JEE Mains-2015]**

(1) 24 (2) 36

(3) 48 (4) 60

5. The hottest region of Bunsen flame shown in the figure given below is **[JEE Mains-2016]**



(1) region 2 (2) region 3

(3) region 4 (4) region 1

6. The distillation technique most suited for separating glycerol from spent lye in the soap industry is **[JEE Mains-2016]**

(1) fractional distillation

(2) steam distillation

(3) distillation under reduced pressure

(4) simple distillation

ANSWER KEY

EXERCISE # 1

1. (4)	2. (1)	3. (3)	4. (2)	5. (4)
6. (3)	7. (3)	8. (3)	9. (3)	10. (3)
11. (3)	12. (4)	13. (2)	14. (3)	15. (2)

EXERCISE # 2

1. (1)	2. (2)	3. (3)	4. (2)	5. (2)
6. (4)	7. (2)	8. (3)	9. (3)	10. (2)

EXERCISE # 3

1. (2)	2. (3)	3. (1)	4. (1)	5. (2)
6. (3)	7. (1)	8. (2)	9. (2)	10. (1)

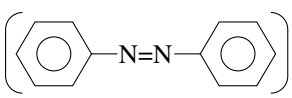
EXERCISE # 4

1. (1)	2. (3)	3. (4)	4. (1)	5. (1)
6. (3)				

HINT AND SOLUTION

EXERCISE # 1

1. [4]



Does not give positive test in Lassaigne's test for N.

2. [1]

$$\%S = \frac{32}{233} \times \frac{\text{wt of } BaSO_4}{\text{wt of org. Sub.}} \times 100$$

$$\frac{32}{233} \times \frac{.582}{.395} \times 100 = 20.24\%$$

3. [3]

Liebig's method is used for the estimation of carbon and hydrogen.

4. [2]

The latest technique for the purification of organic compounds is chromatography

5. [4]

p-nitrophenol and o-nitrophenol are separated by steam distillation (refer Key concept)

6. [3]

$$S + HNO_3 \text{ (fuming)} \xrightarrow{\text{Heat}} H_2SO_4$$

7. [3]

Separation a solution (miscible) of benzene + $CHCl_3$ by distillation

8. [3]

$Na + C + N \longrightarrow NaCN$

$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$

$6NaCN + Fe(OH)_2 \longrightarrow Na_4[Fe(CN)_6] + 2NaOH$

$3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow Fe_4[Fe(CN)_6]_3 + 12NaCl$

Sodium ferrocyanide (ferric ferrocyanide) — Prussian blue or green

9. [3]

Fractional crystallisation is carried out to separate mixtures of organic solids having small difference in their solubilities in suitable solvent. (refer Key concept)

10. [3]

Sodium extract of CCl_4 contains Cl^- ions and Na^+ ion.

11. [3]

$Na + C + N + S \longrightarrow NaCNS$

$3CN\overset{\ominus}{S} + Fe^{3+} \longrightarrow [Fe(CNS)]_3$
Blood red color

12. [4]
On adding K_2SO_4 boiling point increased so it is boiling point clevator.

13. [2]
$2NaI + Cl_2 \longrightarrow 2NaCl + I_2$
(turns CS_2 layer violet)

14. [3]
$NH_2–NH_2$ (Inorganic compound give –ve Lassaigne's test).

15. [2]
Organic compound + H_2SO_4(conc.) $\longrightarrow (NH_4)_2SO_4$
$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + Na_2SO_4 + 2H_2O$
NH_3 is estimated volumetrically by titrating against standard solution of acid.

EXERCISE # 2

1. [1]
In Lassaigne's test substance is heated strongly with sodium metal then water extract is boiled with alkaline $FeSO_4$ solution and after cooling $FeCl_3$ solution and excess of HCl is added in it. If Prussian blue or green ppt. is obtained, then nitrogen is confirmed:
$Na + C + N \longrightarrow NaCN$
$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$
$6NaCN + Fe(OH)_2 \longrightarrow Na_4[Fe(CN)_6] + 2NaOH$
$3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow Fe_4[Fe(CN)_6]_3 + 12NaCl$
Sodium ferrocyanide (ferric ferrocyanide) — Prussian blue ferric ferrocyanide

2. [2]

$$R–\underset{\underset{O}{\|}}{C}–OH \longrightarrow R–\underset{\underset{O}{\|}}{C}–NH_2 \xrightarrow{NaOH} NH_3$$

Equivalent of Acid ≡ Equivalent of amide = Equivalent of NH_3

$$\frac{73}{\text{mol.wt.}} = \frac{17}{17}$$

Mol. wt. of amide = 73
$C_n H_{2n+1}NO$
$12n + 2n + 1 + 14 + 16 = 73$

$$n = \frac{42}{14} = 3$$

acid also must have 3C, i.e., propionic acid

3. [3]
Anhydrous formic acid cannot be obtained from its aqueous solution by simple fractional distillation because boiling point of HCOOH is very close to that of water.

4. [2]
$CuSO_4$ acts catalyst.

5. [2]
$Na + C + S + N \longrightarrow NaSCN$

6. [4]
Theory base

7. [2]
Silica gel is used for keeping away the moisture because it Adsorbs H_2O.

8. [3]
Inorganic Substance ($NH_2–NH_2$) fails for the estimation of N by Lassaigne's List.

9. [3]
Turpentine oil can be purified by Steam distillation

10. [2]
Compound containing both N and S, will give blood red colour.
$Na + C + N + S \longrightarrow NaCNS$
$Fe^{3+} + 3CNS^- \longrightarrow Fe(CNS)_3$
Blood red colour

EXERCISE # 3

1. [2]
Let the vol. of 1N H_2SO_4 taken = V mL.
Now 60 mL of N/2 NaOH = 30 mL of 1N NaOH = 30 mL of 1N H_2SO_4
Thus, vol. of acid unused = 30 mL of 1N H_2SO_4
$\therefore$ Vol. of 1N H_2SO_4 used = (V – 30) mL
Now % of N is given by the relation, % of

$$N = \frac{1.4 \times N_1 \times V}{W}$$

$$\text{or } 56 = \frac{1.4 \times 1 \times (V - 30)}{0.50} \text{ or } V = 50 \text{ mL.}$$

2. [3]
% N (By Duma's method)

$$= \frac{28 \times \text{Volume of } N_2 \text{ at NTP} \times 100}{22400 \times \text{weight of compound}}$$

$$= \frac{28 \times 31.1 \times 100}{22400 \times 0.25} = 15.55\%$$

3. [1]
$\therefore$ C : H : O = 6 : 1 : 8, % C : H : O

$$= \frac{6}{15} \times 100 : \frac{1}{15} \times 100 : \frac{8}{15} \times 100$$

$$= 40 : 6.67 : 53.3$$

$$= \frac{40}{12} : \frac{6.67}{1} : \frac{53.3}{16}$$

$$= 3.33 : 6.67 : 3.33$$

$$= 1 : 2 : 1 \quad \text{i.e. } CH_2O$$

4. [1]

$$\% \text{ C} = \frac{12}{44} \times \frac{\text{wt of } CO_2}{\text{wt of org. sub}} \times 100$$

$$= \frac{12}{44} \times \frac{147}{0.2} \times 100 = 20\%$$

$$\%\text{H} = \frac{2}{18} \times \frac{\text{wt of } H_2O}{\text{wt of org. sub}} \times 100$$

$$= \frac{2}{18} \times \frac{.12}{.2} \times 100 = 6.66\%$$

$$\% \text{ oxygen} = 100 - (20 + 6.66)$$

$$= 73.3\%$$

5. [2]

$$\%\text{ of P} = \frac{62}{222} \times \frac{\text{wt. of magnesium pyrophosphate}}{\text{wt. of organic compound}} \times 100$$

$$= \frac{62}{222} \times \frac{1.332}{2.79} \times 100$$

$$= 13.33\%$$

6. [3]

Gas equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{700 \times 55}{300} = \frac{760 \times V_2}{273}$$

Aqueous tension at 300 K = 15 mm

$$V_2 = \frac{700 \times 273 \times 55}{760 \times 300}$$

= 46 mL at N.T.P.

$$\therefore \%\text{ of N} = \frac{28}{22400} \times \frac{\text{Volume of } N_2 \text{ at N.P.T}}{\text{Mass of organic compound}} \times 100$$

$$\% \text{ N} = \frac{28.}{22400} \times \frac{46}{.35} \times 100 = 16.45\%$$

7. [1]

Wt. of organic compound = 0.2475 g

Wt. of CO_2 produced = 0.4950 g

Wt. of H_2O produced = 0.2025 g

Percentage of carbon

$$= \frac{12}{44} \times \frac{\text{Wt. of } CO_2}{\text{Wt. of compound}} \times 100$$

$$= \frac{12}{44} \times \frac{0.4950}{0.2475} \times 100 = 54.54$$

Percentage of hydrogen

$$= \frac{2}{18} \times \frac{\text{Wt. of } H_2O}{\text{Wt. of compound}} \times 100$$

$$= \frac{2}{18} \times \frac{0.2025}{0.2475} \times 100 = 9.09$$

8. [2]

9. [2]

Theory based

10. [1]

Theory based

EXERCISE # 4

1. [1]

Lassaigne's test involves the reactions

$Na + C + N \longrightarrow NaCN$

$Fe^{2+} + 6CN^- \longrightarrow [Fe(CN)_6]^{4-}$

$Fe^{3+} + [Fe(CN)_6]^{4-} \longrightarrow Fe_4[Fe(CN)_6]_3$

2. [3]

Amount of H^+ used for the neutralization of NH_3

N = 2(0.1 mol L^{-1}) (0.1 L) – (0.5 mol L^{-1}) (0.02 L) = 0.01 mol

Amount of N = Amount of NH_3 = Amount of H^+ used = 0.01 mol

Mass of N = (0.01 mol)(14 g mol^{-1}) = 0.14 g

Mass per cent of N in the compound = $\left(\frac{0.14}{0.2\text{g}}\right)$ (100) = 46.67%

Mass per cent of N in the given compounds are as follows

Acetamide (CH_3CCONH_2) $\frac{14}{59} \times 100 = 23.73$

Benzamide ($C_6H_5CONH_2$) it is less than 23.73

Urea (NH_2CONH_2) $\frac{28}{60} \times 100 = 46.67$

The compound is urea.

3. [4]

Volume of 0.1 M HCl taken = 20 mL

Volume of 0.1 M NaOH used for neutralisation = 15 mL

Volume of 0.1 M HCl unused = 20 – 15 = 5 mL

$$\% \text{ N} = \frac{1.4 \times \text{N} \times \text{V(mL)}}{\text{W(g)}} = 27$$

Since n-factor of HCl = 1

So, 0.1 M ≡ 0.1 N

$$\% \text{ N} = \frac{1.4 \times 0.1 \times 5}{29.5 \times 10^{-3}} = \frac{1.4 \times 1 \times 5}{29.5\ 10^{-2}} = 23.7$$

4. [1]

$$\%\text{ of Br} = \frac{80}{188} \times \frac{\text{Mass of AgBr}}{\text{Mass of organic substance}} \times 100$$

$$= \frac{80}{188} \times \frac{141}{250} \times 100$$

$$= 24\%$$

5. [1]

Region 1 (Pre-heating zone)

Region 2 (Primary combustion zone, hottest zone)

Region 3 (Internal zone)

Region 4 (Secondary reaction zone)

6. [3]

Glycerol with high boiling point (290°C) can be separated from spent lye by distillation under reduced pressure. This process is used to purify liquids having very high boiling points. By this process, liquid is made to boil at lower temperature than its boiling point by lowering the pressure on its surface.

CHAPTER 9

Environmental Chemistry

COMPONENTS OF ENVIRONMENT

1. **Atmosphere:** It is a protective blanket of gases which is surrounding the earth.
   (i) Composition: The constituents which make up the atmosphere are gases, water vapours and aerosols.
   The major gases in the air are nitrogen and oxygen. Pure dry air, on an average, constitutes 78% nitrogen and 21% oxygen by volume. Remaining 1% accounts for other gases.
   Major components: N_2, O_2, water vapours
   Minor components: Ar, CO_2
   Tracer components: He, Ne, Kr, Xe, CH_4, H_2, CO, N_2O, NO, NO_2, SO_2, NH_3, O_3 HCHO, etc.
   (ii) Structure or Regions of the atmosphere: The atmosphere is divided into four major regions depending on the height as shown below:

Region	Height range (km)	Temperature range (°C)	Main constituents
Troposphere	0–11	15 to −56	O_2, N_2, H_2O, CO_2
Stratosphere	11–50	−56 to −2	O_3
Mesosphere	50–90	−2 to −92	O_2^+, NO^+
Thermosphere	90–500	−92 to 1200	O_2^+, O^+, NO^+, N^+

2. **Hydrosphere:** The total water present on the earth in solid, liquid and gaseous phases constitutes the hydrosphere, Water covers 71% of the total surface of the earth. Earth is sometimes called a water planet.
3. **Lithosphere:** It is the solid component of the earth consisting of soil, rocks, mountains, etc. It is the region which interacts with hydrosphere, atmosphere and biosphere. The earth comprises of three layers, viz., **crust, mantle and outer** and **inner core**.
4. **Biosphere:** It refers to that part of the earth in which all life forms exist. Biosphere represents an interface between the non-living and the living organisms.

TYPE OF POLLUTANTS

The agents causing pollution are termed as pollutants.

Classification

(A) On the basis of their occurrence

(i) Primary pollutants These are present in the same form in which they are produced, e.g., carbon monoxide, DDT.

(ii) Secondary pollutants These are formed by reaction between the primary pollutants in the presence of sunlight e.g., PAN, Ozone, HNO_3 H_2SO_4, etc.

Nitrogen oxides and hydrocarbons react photochemically to produce peroxyacetyl nitrates (PAN) and ozone.

The secondary pollutants may be more toxic than the primary once. The phenomenon is called **synergism**.

(B) On the basis of their degradation

(i) Biodegradable Pollutants Pollutants which are decomposed or degraded by biological or microbial action are called biodegradable pollutants e.g. domestic sewage.

(ii) Non-biodegradable Pollutants Pollutants which are not decomposed or degraded by living organisms or micro-organisms are called non-biodegradable pollutants, e.g., DDT, glass, plastics, aluminium cans, phenolic compounds, pesticides, radioactive substance, heavy metals like mercury, lead, cadmium etc.

(C) On the basis of their existence in nature

(i) Quantitative pollutants These are naturally present in nature and are also added by man. These become pollutants only when their concentration reaches beyond a threshold value in the environment, e.g., CO_2.

(ii) Qualitative pollutants These are not present in the nature but are added in nature only due to human activities, e.g., insecticides, fungicides, herbicides, etc.

Kinds of Polution

On the basis of environmental study pollution is of following types.

(1) Air pollution
(2) Water pollution
(3) Soil pollution
(4) Noise pollution
(5) Radioactive pollution

(1) AIR POLUTION

- Air pollution is mainly caused by industries and automobiles.
- Automobiles are the greatest polluters of the atmosphere and are responsible for 75% of noise pollution and about 60–80% of air pollution of big cities.
- Combustion of fossil fuels (coal, oil, gas, etc.) releases CO, CO_2, nitrogen oxides, fluorides, hydrocarbons, etc., into atmosphere usually in the form of smoke causing air pollution.
- Particulate matters released by mills, factories and mines also cause air pollution.
- Some of the natural air pollutants are pollen grains, spores, volcanoes, etc.

Major Air Pollutants:

(1) Carbon monoxide (CO)

- Carbon monoxide is formed by incomplete combustion of fuels in various industries, automobiles, etc.
- CO accounts for about 50% of total air pollution.
- CO combines with haemoglobin producing **carboxyhaemoglobin** and therefore decreases oxygen carrying capacity leading to hypoxia, headache, decreased vision, muscular weakness, nausea, exhaustion, etc.
- When 50% of haemoglobin has been transformed into carboxyhaemoglobin, then death occurs due to CO-poisoning leading to anoxia (oxygen starvation).

(2) Carbon dioxide (CO_2)

- Carbon dioxide is a **greenhouse gas.**
- It is produced due to combustion of fuels, volcanic eruptions and during the process of respiration.
- Its average concentration in the atmosphere is 300 ppm (0.03%).
- It is normally not an atmospheric pollutants, but under very high concentration it may act as a pollutant.
- It causes **Global warming**.

(3) Sulphur dioxide (SO_2)

- Sulphur dioxide is produced during combustion of fossil fuels (mainly coal) and smelting of sulphur containing ores.
- It causes acid rain (gaseous SO_2 oxidises to SO_3, which on combination with water forms H_2SO_4).
- Acid rain is 60–70% due to SO_2 and SO_3, and 30–40% due to NO_2 and NO_3.

- Due to acid rain leaves of trees develop chlorotic and necrotic spots.
- SO_2 corrodes stones, metals, leather, paper and fabrics. There is fading of colour and deterioration of lustre of fabrics, stones and painted surfaces.
- In plants and animals, SO_2 destroys all membrane systems.
- In human beings SO_2 increase the chances of occurrence of asthma.

(4) Hydrocarbons

- Hydrocarbons are produced naturally (e.g., natural discharge of marsh gas, CH_4) and by burning of petroleum.
- Benzene (C_6H_6) is a major constituent of petrol and automobile exhaust.
- Hydrocarbons are carcinogenic, cause irritation of eyes and mucous membrane.
- Benzene is a known **leukaemia-**causing carcinogen.
- Ethylene (C_2H_4) causes premature senescence and abscission in many plants especially in orchids and cotton.
- Methane (marsh gas) has the potential of destroy ozone.

(5) Nitrogen oxides

- There are three oxides of nitrogen which act as air pollutants: nitric oxide (NO), nitrogen dioxide (NO_2) and nitrogen trioxide.
- NO is less toxic but NO_2 is a poisonous gas.
- Nitrogen oxides are responsible for forming photochemical smog.
- They also cause acid rain due to formation of HNO_3.
- They produce lesions, necrosis, defoliation, dieback and death of many plants.
- Like SO_2, they corrode metals and deteriorate paints, textiles as well as various articles.
- They cause eye irritation, dilation of arteries, and injury of lungs, liver and kidneys.

(6) Fluorides

- Fluorides are emitted during refinement of aluminium and rock phosphates.
- Fluorides cause necrosis and chlorosis of leaf tips and leaf margins.
- In human, fluorides cause mottling of teeth, weak bones, boat-shaped posture, knocking knees etc.
- Disease caused by fluoride is known as **fluorosis.**

(7) Particulate matter

- Particulate matter is the non-gaseous matter in the atmosphere.
- It consists of soot, dust, mist, fibres, fly ash, fur, spores pollen grains, etc.
- It is of two types: settleable (larger than 10 μm) and suspended (less than 10 μm).
- SPM (suspended particulate matter) is classified into 3 categories-
  (a) Aerosols (less than 1 μm)
  (b) Dust (solid particles with more than 1 μm diameter)
  (c) Mist (liquid particles with more than 1 μm diameter)
- Particulate matter is added in the atmosphere by burning of fuels.
- Particulate matter causes about 10–15% of air pollution

(8) Aerosols

- Aerosols are chemicals released in the air with force in the form of mist or vapour by jet planes.
- Aerosols contain **CFC (chlorofluoro-carbons)** which destroys ozone layer in the stratosphere, thereby allowing U.V. radiations that cause skin cancer and increase mutation rates, to reach the earth.
- Ozone acts as preventive shield against the U.V. rays.
- Freons are several CFMS (chlorofluoromethanes) released into troposphere where they dissociate and release free chlorine that causes depletion of ozone.
- Freon or CFC is also used in refrigerator, air conditioners and in making plastic foams.

Effect of air pollutants: Air pollutants are involved in causing four major environmental effects:

(i) Smog, (ii) Acid rain, (iii) Global warming, and (iv) Ozone layer depletion.

(i) SMOG

- The term smog was coined by Des Voeux.
- Smog is produced by the combination of smoke and fog.
- It causes silvering/glazing and necrosis in plants, allergies and asthma/bronchitis in human.
- Smog is of two types:

(a) Classical smog:

- Classical smog is also called London smog or sulphurous acid smog.
- It occurs at low temperature.
- This smog is produced from gases like SO_2, H_2S, smoke, dust and particles particulates at high humidity.
- It produces irritation in eyes, nose and throat.

(b) Photochemical smog:

- Photochemical smog is also called Los Angeles smog.
- It occurs at high temperature.
- This type of smog is formed by combination of particulates (smoke, dust, fog) with oxides of nitrogen and hydrocarbons in presence of sunlight to produce ozone (O_3) and PAN (peroxy acetyl nitrate).
- It is highly harmful to human beings, animals and plants.

(ii) ACID RAIN

- Both SO_2 and NO_2 are converted to acids (H_2SO_4 and HNO_3, respectively), when the gases combine with water vapour in the presence of O_2 in the atmosphere. These acids return to the earth as acid rain.

$$NO + O_3 \longrightarrow NO_2 + O_2$$
$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$
$$NO_2 + NO_3 \longrightarrow N_2O_5$$
$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$
$$2SO_2 + O_2 \longrightarrow 2SO_3$$
$$SO_2 + H_2O \longrightarrow H_2SO_4$$

- Pure rain has a pH of about 5.6 while the acid rain has pH below 5.6.
- Ph of drinking water lies between 5.5 and 9.5.
- Acid rain is actually a mixture of H_2SO_4 and HNO_3 (usually 60–70% H_2SO_4 and 30–40% HNO_3)

(iii) GREEN HOUSE EFFECT AND GLOBAL WARMING:

- Gases like CO_2, CH_4, CFCs, NO_2 are strong absorbers of long-wave or infra-red radiation emitted by the surface of the earth, and warm the earth's atmosphere. This is called the **Greenhouse effect** because it is like the glass panel of a greenhouse that allows sunlight to pass through and then traps the resulting heat inside the structure.
- CO_2 is the principal greenhouse gas responsible for warming of the earth.

(iv) OZONE LAYER DEPLETION:

- The ozone layer present in the stratosphere acts as an ultraviolet absorbent thus protecting the earth form its harmful effect.
- The ozone layer depletion is caused by chlorine atoms. These chlorine atoms come from the breakdown of CFCs. These atoms combine with ozone and remove the oxygen atoms one by one.

$$CF_2Cl_2 \xrightarrow{h\nu} CF_2Cl + Cl$$
$$CFCl_3 \xrightarrow{h\nu} CFCl_2 + Cl$$
$$Cl + O_3 \longrightarrow ClO + O_2$$
$$ClO + O \longrightarrow Cl + O_2$$

Net reaction $O_3 + O \xrightarrow{Cl} 2O_2$

- One atom of chlorine can destroy upto 100,000 molecules of ozone.

(2) WATER POLLUTION:

- Water pollution is caused by the addition of some substances or factors (i.e., heat).
- It degrades the quality of water so that it either becomes health hazard or unfit for use.

Kind of water pollution:

(a) Physical pollution: It involves the changes in the physical properties of water, e.g., colour, taste, odour, temperature, turbidity, etc.

(b) Chemical pollution: It is caused due to change in the chemical properties of water. They mainly include the pH, dissolved O_2, inorganic or organic chemicals, heavy metals, etc.

Inorganic chemicals include fluorides, chlorides, phosphates and nitrates. Organic chemicals include phenols, dyes, pesticides and chlorocompouds.

(c) Biological pollution: It is caused due to the presence of living organisms in water such as algae, fungi, bacteria, viruses, protozoans, insects, etc.

Sources of water pollution and effects of water pollutants: The principal sources of water pollution and effects of water pollutants are as follows.

Domestic wastes and sewage:

- Sewage containing human faeces, urine, kitchen and cloth washings, organic waste, industrial waste, etc. is usually poured into water bodies, which cause water pollution.
- Decomposers/microorganisms causing decomposition of sewage take up most of the oxygen present dissolved in water. So in this water BOD (Biological oxygen demand or Biochemical oxygen demand) increased very much.
- BOD of clean water is less than 5 ppm.
- A weak organic waste will have BOD below 1500 mg/L, medium organic waste between 1500–4000 mg/L while in strong waste above 4000 mg/L.
- The degree of pollution is directly proportional to BOD.

Industrial effluents (or industrial discharges): Industries usually discharge waste water into ponds, lakes and rivers. Industrial waste water contains heavy metals (mercury, lead, copper, arsenic and cadmium), inorganic pollutants (acids, alkalies and bleaching liquors), organic pollutants (phenol, naphtha, proteins, aromatic compound, cellulose fibres, etc.) industrial effluents are the most hazardous pollutants on land and water.

(A) Mercury (Hg):

- Mercury is released during combustion of coal, smelting of metallic ores, paper and paint industries.
- Mercury is highly persistent. In water it gets changed into water soluble dimethyl form $[(CH_3)_2]Hg$ and enters the food chain (undergoes biomagnification).
- It kills fish and poisons the remaining fauna. Human beings feeding on such poisoned animals develop a crippling deformity called minamata disease which is characterized by impairment of various senses, diarrhoes, haemolysis, meningitis and death.

(B) Lead (Pb):

- The sources of lead pollution are smelters, battery industry, paint, chemical and pesticide industry, automobiles exhausts, etc.
- Lead is pollutant of air, soil and water.
- It is used as anti-knock reagent in petrol and released by automobile exhausts.
- Lead is persistant pollutant and may show biological amplification or biomagnification.
- It is a mutagenic and causes anaemia, headache, vomiting, colic, loss of muscle power, bluish lines around the gumes, loss of appetite and damage of liver, kidney and brain.

(C) Cadminum (Cd):

- Cadmium is added to the environment by metal industries, welding and electroplating, pesticides, and phosphate industries.
- Cd shows biological amplification and accumulates inside kidneys, liver, pancreas and spleen.
- It causes hypertension, anaemia, diarrhoea and damages liver and kidneys.

(3) SOIL POLUTION:

- Unfavourable alteration of soil by addition or removal of substances and factors which decrease soil productivity, quality of plant products and ground water is called soil pollution.
- Soil pollutants include pesticides, fertilizers, industrial wastes, salts, radio-nuclides, tin, iron, lead, copper, mercury, aluminium, plastics, paper, glass, broken bottles, discarded food, etc.
- Soil pollution is of two main types.

(1) Negative soil pollution:

- Negative soil pollution includes overuse of soil and erosion.
- Soil erosion is caused by water and wind.
- Water erosion of soil is found near the hills where high speed flooding removes top soil.
- Soil erosion also occurs by high speed winds which bring sand particles from dry desert.

(2) Positive soil pollution:

- Positive soil pollution is caused by addition of undesirable substance (e.g., pesticides, fertilizers, industrial waste, air pollutant washed down from atmosphere through rain)
- Dichloro diphenyl trichloroethane (DDT), benzene hexachloride (BHC) or gamaxine, aldrin, dieldrin, endrin, heptachlor, etc., are chlorinated hydrocarbons used as pesticides.

(4) NOISE POLLUTION:

- Various kinds of undesirable loud sounds, which disturb our environment are called noise pollutants.
- Noise pollution is produced by loud sounds of various machines, loudly played radio, automobiles, thundering of jet planes, loud speakers, etc.
- Green plants are being planted along the road sides to check the noise pollution. This is called as **Green muffler**.
- Noise may damage ear drum and eye sight.

(5) RADIOACTIVE POLLUTION:

- Radioactive pollution is a special type of physical pollution of air, water and soil with radioactive materials.
- Nuclear explosion results into production of radioactive substances as Sr^{90}, U^{235}. I^{131}, and cause pollution of air, water and soil.

BHOPAL GAS TRAGEDY

The tragedy in Bhopal occurred on 2nd December 1984, when a poisonous gas **methyl isocynate (MIC)** leaked in the atmosphere from a fertilizer plant of Union Carbide company. MIC was used to manufacture an insecticide marked in the name of SAVIN. The gas caused death of about 2500 persons. December 2 is recalled as National Pollution Prevention Day.

SOLVED EXAMPLE

1. Which of the following is a primary pollutant?

(1) PAN (2) CO

(3) Aldehydes (4) H_2SO_4

Sol. **[2]**

CO is a primary pollutant.

2. Choose the biodegradable pollutant out of the following.

(1) DDT

(2) Cow dung

(3) Alkyl benzene sulphonate

(4) Mercury

Sol. **[2]**

Cow dung is a biodegradable pollutant.

3. Identify the incorrect statement from the following.

(1) Oxides of nitrogen in the atmosphere can cause the depletion of ozone layer

(2) Ozone absorbs infrared radiation

(3) Depletion of ozone layer is because of its chemical reactions with chlorofluoroalkanes

(4) Ozone absorbs the intense ultraviolet radiation of the sunlight

Sol. **[2]**

Ozone absorbs the intense ultraviolet radiation of the sunlight not infrared radiation.

4. Phosphate pollution is caused by

(1) Sewage and agricultural fertilizers

(2) Agricultural fertilizers only
(3) Phosphate rocks and sewage
(4) Weathering of phosphate rocks only

Sol. **[1]**
Phosphate pollution is caused by sewage and agricultural fertilizers.

5. Lead is considered as:
(1) Water pollutant (2) Soil pollutant
(3) Air pollutant (4) Radioactive pollutant

Sol. **[3]**
Lead is an air pollutant.

EXERCISE 1

1. Which of the following chemical, harmful to ozone, it released by chlorofluorocarbon?
(1) Sulphur dioxide (2) Chlorine
(3) Fluorine (4) Nitrogen dioxide

2. Pick up the correct statement:
(1) Classical smog is good for health but not photochemical smog
(2) During formation of smog ozone level in atmosphere decreases
(3) Classical smog has an oxidizing character while photochemical smog is reducing in character
(4) Photochemical smog occurs in day time whereas the classical smog occurs in early morning

3. Which one of the following dissolves more rapidly in haemoglobin than oxygen?
(1) Ozone (2) SO_2
(3) N_2O (4) CO

4. The type of pollution caused by spraying of DDT
(1) Air, water, and soil (2) Air and water
(3) Air (4) Air and soil

5. Water pollution is caused by
(1) Aeroplanes (2) Fly ash
(3) Auto exhaust (4) Pesticides

6. The greenhouse effect is caused by
(1) CO (2) NO_2
(3) NO (4) CO_2

7. The substance having the largest concentration in acid rain?
(1) H_2CO_3 (2) HNO_3
(3) HCl (4) H_2SO_4

8. Which of the following is not a consequence of greenhouse effect?
(1) Climatic conditions will be changed
(2) Plants in warmer climates with adequate rainfall would grow faster
(3) The incidence of infectious diseases is likely to increase
(4) Malaria will be controlled as the mosquitoes will not survive

9. Presence of which fuel gas in exhaust fumes shows incomplete combustion of fuel?
(1) Sulphur dioxide
(2) Carbon monoxide and water vapour
(3) Carbon monoxide
(4) Nitrogen dioxide

10. Formation of ozone in the upper atmosphere from oxygen takes place by the action of
(1) Nitrogen oxides (2) Ultraviolet rays
(3) Cosmic rays (4) Free radicals

11. The chemical entities present in thermosphere of the atmosphere are
(1) O^{+2}, O^+, NO^+ (2) O_3
(3) N_2, O_2, CO_2, H_2O (4) O3, O_2^+, O_2

12. What is not correct about greenhouse effect?
(1) It results in global warming.
(2) CO_2 is one of the main chemical species responsible for it.
(3) It results in lowering of levels of ocean over the years.
(4) CH_4, O_3, CFC also contribute to greenhouse effect.

13. Which of the following belongs to secondary air pollutant?
(1) CO (2) Hydrocarbon
(3) Peroxyacetyl Nitrate (4) None of these

14. Which of the following is not considered to be a pollutant?
(1) NO_2 (2) CO_2
(3) O_3 (4) SO_3

15. Environmental pollution affects:
(1) biotic components
(2) human beings only
(3) plants only
(4) biotic and abiotic components of environment

EXERCISE 2

1. Persistent pesticides such as DDT pass into food chain and increase in amount per unit weight of organism due to their accumulation in fat. This phenomenon is called
(1) biomagnification (2) biodegradation
(3) biosynthesis (4) decomposition

2. Negative soil pollutant is
(1) converting fertile land into barren land by dumping ash, sludge, and garbage
(2) reduction in soil productivity due to addition of pesticides and industrial wastes
(3) reduction in soil productivity due to erosion and over use
(4) None of the above

3. Which of the following is the coldest region of atmosphere?
(1) Thermosphere (2) Troposphere
(3) Mesosphere (4) Stratosphere

4. The biggest particulate matter is
(1) HNO_3 droplets (2) Fly ash
(3) H_2SO_4 droplets (4) Soot

5. Which causes death of fish in water bodies polluted by sewage?
(1) Decreases in DO
(2) Pathogens
(3) Clogging of gills by silt
(4) Foul smell

6. Ozone is an important constituent of stratosphere because it
(1) destroys bacteria which are harmful to human life
(2) prevents the formation of smog over large cities
(3) absorbs ultraviolet radiation which is harmful to human life
(4) removes poisonous gases of the atmosphere by reacting with them

7. Which of the following statements about polar stratosphere clouds (PSCs) is not correct?
(1) PSCs do not react with chlorine nitrate and HCl
(2) Type I clouds are formed at about –77°C and contain solid $HNO_3.3H_2O$
(3) Type II clouds are formed at about – 85°C and contain some ice
(4) A tight whirlpool of wind called polar vortex is formed which surrounds Antarctica

8. Fluorosis, the bone disease, is caused by the presence of:
(1) pesticides in water
(2) fluorides in water
(3) carbon monoxide in air
(4) sulphur dioxide in air

9. The point of temperature inversion between troposphere and ionosphere is called
(1) stratopause (2) mesopause
(3) ionopause (4) tropopause

10. Identify the wrong statement in the following.
(1) Chlorofluorocarbons are responsible for ozone layer depletion.
(2) Greenhouse effect is responsible for global warming.
(3) Ozone layer does not permit infrared radiation from the sun to reach the earth.
(4) Acid rain is mostly because of oxides of nitrogen and sulphur.

11. Ozone layer of stratosphere required protection from indiscriminate use of
(1) balloons (2) pesticides
(3) aerosols and high flying jets
(4) atomic explosions

12. Particulate air pollutants are finely divided solids and liquids. Which of the following is not a particulate?
(1) Dust and mists
(2) Smoke and fumes
(3) Photochemical smog and soot
(4) None of the above

13. Which of the following statement about photochemical smog is not correct?
(1) Carbon monoxide does not play any role in photochemical smog formation
(2) Photochemical smog is an oxidizing agent in character
(3) Photochemical smog is formed through photochemical reactions involving solar energy
(4) Photochemical smog does not cause irritation in eyes and throat

14. Ozone in the stratosphere is depleted by:
(1) CF_2Cl_2 (2) C_9F_{16}
(3) $C_6H_6Cl_6$ (4) C_6F_6

15. Which forms the part of hazy fumes of photochemical smog?
(1) SO_2 (2) Aldehydes
(3) PAN formation (4) Nitrogen dioxide

EXERCISE 3

One and More Than One Option Correct Type Question

1. Which is correct statement for classical smog?
(1) It occurs in cool humid climate
(2) It is a mixture of smoke, fog and sulphur dioxide
(3) It is called reducing smog
(4) It is called oxidising smog

2. Which of the following statements is True (T) and which one is False (F)? Mark them and select the answer from the codes given below.
(I) Ozone is not responsible for greenhouse effect.
(II) Ozone can oxidize SO_2 present in the atmosphere to SO_3.
(III) Ozone hole is thinning of ozone layer present in stratosphere.
(IV) Ozone is produced in the upper stratosphere by the action of UV-rays on oxygen.

Code

	I	II	III	IV
(1)	F	T	T	T
(2)	T	F	T	F
(3)	F	F	T	T
(4)	T	T	F	F

3. Select the correct statement(s) about stratosphere.
(1) Temperature increase slowly from 220 to 270 K.
(2) Supersonic aircrafts fly in the lower region of the stratosphere.
(3) Both (a) and (b) are correct.
(4) None of the two are correct.

4. The gases which are responsible for photochemical smog are:
(1) oxides of nitrogen (2) hydrocarbons
(3) carbon monoxide (4) inert gases

5. If the greenhouse effect or global warming remains unchecked, it alters:
(1) sea levels (2) ozone layer
(3) rainfall (4) temperature

6. The following reactions occur in the stratosphere:
(1) $O_2 + UV \rightarrow O + O$
(2) $O_2 + O \rightarrow O_3$
(3) $Cl + O_3 \rightarrow ClO + O_2$
(4) $SO_3 + H_2O \rightarrow H_2SO_4$

Assertion and Reason Type Question

(1) If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I
(2) If both Statement-I and Statement-II are correct and Statement-II is not the correct explanation for Statement-I
(3) If Statement-I is correct and Statement-II is incorrect
(4) If Statement-I is incorrect and Statement-II is correct

7. Assertion: Photochemical smog is produced by nitrogen oxides
Reason: Vehicular pollution is a major source of nitrogen oxides:

8. Assertion: Rain water is slightly acidic.
Reason: Water dissolves atmospheric CO_2 forming H_2CO_3.
$H_2O + CO_2 \rightleftharpoons H_2CO_3$

9. Assertion: IF BOD level of water in a reservoir is less than 5 ppm, it is highly polluted.
Reason: High biological oxygen demand means low activity of bacteria in water

10. Assertion: PAN is main constituent of photochemical smog.
Reason: It is formed by the action of oxides of nitrogen and hydrocarbons in presence of sunlight.

11. Assertion: CO is a toxic air pollutant.
Reason: CO binds with haemoglobin of blood and reduces oxygen transport efficiency of blood.

12. Assertion: For greenhouse effect, presence of green plants is essential.
Reason: Greenhouse effect is responsible for global warming.

13. Assertion: Photochemical smog is produced by oxides of nitrogen.
Reason: Automobiles are a major source of oxides of nitrogen.

Column Matching Type Question

14. Match List-I with List-II and select the correct answer using the codes given below the lists:

List-I (Pollutant)	List-II (Source)
(A) Microorganisms	(1) Chemical fertilizers
(B) Plant nutrients	(2) Abandoned coal mines
(C) Sediments	(3) Domestic sewage
(D) Mineral acids	(4) Erosion of soil by strip mining
	(5) Detergents

	A	B	C	D
(1)	1	3	2	4
(2)	2	5	3	1
(3)	3	1	4	2
(4)	4	2	1	5

15.

Column-I	Column-II
(A) CO	(p) Greenhouse effect
(B) CO_2	(q) Most abundant hydrocarbon pollutant
(C) SO_2	(r) Chlorosis
(D) CH_4	(s) Decreases oxygen carrying ability of blood

	A	B	C	D
(1)	s	p	r	p, q
(2)	p	s	r	p, r
(3)	r	s	r	q, p
(4)	p, s	q	s	r

16.

Column-I	Column-II
(A) Classical smog	(p) Oxides of nitrogen
(B) Volcanic eruptions	(q) Oxides of sulphur
(C) Acid rain	(r) Oxidising nature
(D) Photochemical smog	(s) Reducing nature

	A	B	C	D
(1)	s	q	p, q	p, r
(2)	s	q, r	p, q	p
(3)	q	s	p, q	p, r,
(4)	s	q	p	r

17. Match the different regions of the atmosphere in Column-I with their temperature range in Column-II and select answer from the codes given below.

Column-I	Column-II
(A) Stratosphere	(p) 180–1500 K
(2) Mesosphere	(q) 220–270 K
(3) Thermosphere (ionosphere)	(r) 270–180 K
(4) Troposphere	(s) 290–220 K

Code

	A	B	C	D
(1)	q	r	p	s
(2)	p	q	s	r
(3)	r	p	s	q
(4)	s	p	q	r

18. Match the terms in Column-I with the compounds in Column-II and select answer from the answer codes given below

Column-I	Column-II
(A) Acid rain	(p) $CHCl_2 - CHF_2$
(B) Photochemical smog	(q) CO
(C) Combination with haemoglobin	(r) CO_2
(D) Depletion of ozone layer	(s) SO_2
(E) Global warming	(t) Unsaturated hydrocarbon

Code

	A	B	C	D	E
(1)	p	q	r	s	t
(2)	s	p	r	q	t
(3)	p	r	s	t	q
(4)	s	t	q	p	r

19. Match the Column-I with Column-II:

Column-I	Column-II
(A) Greenhouse effect	(p) Primary pollutant
(B) Smoke	(q) Particulate
(C) Nitric oxide	(r) Global warming
(D) PAN	(s) Photochemical oxidant

Code

	A	B	C	D
(1)	q	p	s	r
(2)	r	q	p	s
(3)	q	r	p	s
(4)	r	q	s	p

20. Match the Column-I with Column-II:

Column-I	Column-II
(A) Fluorosis	(p) Non-biodegradable
(B) Noise	(q) Bone disease
(C) Plastic	(r) Physical pollutant
(D) Ozone depletion	(s) Chlorofluorocarbons

Code

	A	B	C	D
(1)	r	p	q	s
(2)	p	q	r	s
(3)	q	r	p	s
(4)	p	r	q	s

EXERCISE 4

1. When rain is accompanied by a thunderstorm, the collected rain water will have a pH value **[JEE Main-2003]**

(1) Slightly lower than that of rain water without thunderstorm

(2) Slightly higher than that when the thunderstorm is not there

(3) uninfluenced by the occurrence of thunderstorm

(4) Which depends on the amount of dust in air

2. The smog is essentially caused by the presence of **[JEE Main-2004]**

(1) O_2 and O_3

(2) O_2 and N_2

(3) oxides of sulphur and nitrogen

(4) O_3 and N_2

3. Identify the wrong statements in the following. **[JEE Main-2008]**

(1) Chlorofluorocarbons are responsible for ozone layer depletion.

(2) Greenhouse effect is responsible for global warming.

(3) Ozone layer does not permit infrared radiations from the sun to reach the earth.

(4) Acid rain mostly occurs because of oxides of nitrogen and sulphur.

4. Identify the incorrect statement from the following. **[JEE Main-2011]**

(1) Oxides of nitrogen in the atmosphere can cause the depletion of ozone layer.

(2) Ozone absorbs the intense ultraviolet radiations of the sun.

(3) Depletion of ozone layer is because of its chemical reactions with chlorofluoroalkanes.

(4) Ozone absorbs infrared radiations.

5. What is DDT among the following? **[JEE Main-2012]**

(1) Greenhouse gas

(2) A fertiliser

(3) Biodegradable pollutant

(4) Non-biodegradable pollutant

6. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was **[JEE Main-2013]**

(1) methyl isocyanate (2) methylamine

(3) ammonia (4) phosgene

7. Smoke is an example of: **[JEE Main Online-2013]**

(1) solid dispersed in solid

(2) solid dispersed in gas

(3) gas dispersed in solid

(4) gas dispersed in liquid

8. Which of the following compounds is not expected to show Lassaigne's test for nitrogen? **[JEE Main Online-2013]**

(1) Propanenitrile

(2) Hydroxylamine hydrochloride

(3) Nitromethane

(4) Ethanamine

9. Global warming is due to increase of: **[JEE Main Online-2014]**

(1) methane and nitrous oxide in atmosphere

(2) methane and CO in atmosphere

(3) methane and CO_2 in atmosphere

(4) methane and CO_3 in atmosphere

10. Photochemical smog consists of excessive amount of X, in addition to aldehydes, ketones, peroxy acetyl nitrite (RCO_3NO_2) and so forth. (X) is **[JEE Main online-2015]**

(1) CH_4 (2) CO

(3) CO_2 (4) O_3

11. Addition of phosphate fertilizers to water-bodies causes **[JEE Main Online-2015]**

(1) enhanced growth of algae

(2) increase in amount of dissolved oxygen in water

(3) deposition of calcium phosphate

(4) increase in fish population

12. **Statement I:** Nitrogen and oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen. **[JEE Main-2015]**

Statement II: The reaction between nitrogen and oxygen requires high temperature.

(1) If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I

(2) If both Statement-I and Statement-II are correct and Statement-II is not the correct explanation for Statement-I

(3) If Statement-I is correct and Statement-II is incorrect

(4) If Statement-I is incorrect and Statement-II is correct

ANSWER KEY

EXERCISE # 1

1. (2)	2. (4)	3. (4)	4. (1)	5. (4)
6. (4)	7. (4)	8. (4)	9. (3)	10. (2)
11. (1)	12. (3)	13. (3)	14. (2)	15. (4)

EXERCISE # 2

1. (1)	2. (3)	3. (3)	4. (2)	5. (1)
6. (3)	7. (1)	8. (2)	9. (4)	10. (3)
11. (3)	12. (4)	13. (4)	14. (2)	15. (4)

EXERCISE # 3

1. (1,2,3)	2. (1)	3. (3)	4. (1,2,3)	
5. (1,3,4)	6. (1,2,3)	7. (2)	8. (1)	9. (4)
10. (1)	11. (1)	12. (3)	13. (2)	14. (3)
15. (1)				

EXERCISE # 4

1. (1)	2. (1)	3. (3)	4. (4)	5. (4)
6. (1)	7. (2)	8. (2)	9. (3)	10. (4)
11. (1)	12. (1)			

HINT AND SOLUTION

EXERCISE # 3

1. [1, 2, 3]

Classical smog occurs in humid climate. It is a mixture of smoke, fog and SO_2 which is reducing in nature. It is not the oxidising smog.

2. [1]

(I) There are several gases that are even stronger IR absorbers than CO_2. These are CH_4, O_3, N_2 and CFC.

Thus, these gases are responsible for greenhouse effect.

Thus, given statement is false.

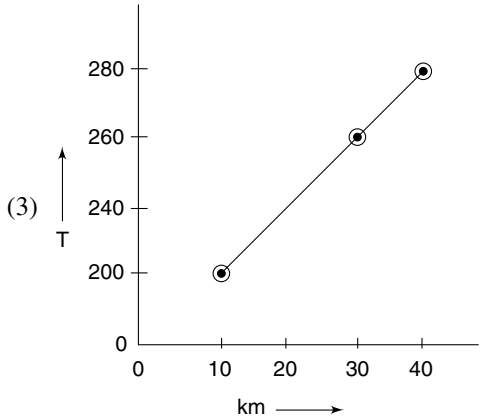
(II) $SO_2 + O_3 \longrightarrow SO_3 + O_2$ (True)

(III) (True)

(IV) $O_2 \xrightarrow[(l < 2420\text{Å})]{(h\nu)} 2[O]$

$O_2 + O \longrightarrow O_3$ [True]

3. [3]



(1) Temperature in the layer of air from 10 to 40 km increases slowly from 220 K to 270 K-correct.

(2) Supersonic aircrafts fly in lower region-correct.

8. [1]

Rain water has dissolved CO_2 in the form of weak acid.

$H_2O + CO_2 \rightleftharpoons H_2CO_3$

$H_2CO_3 \rightleftharpoons H+ + HCO_3^-$

It is feebly ionized hence is slightly acidic pH = 7 (but < 7) Thus, Statement-I and Statement-II are correct and statement-II is the correct explanation of Statement-I

9. [4]

If BOD < 5 ppm, it means water is pure. High BOD means low activity of bacteria in water.

Thus, Statement-I is incorrect and Statement-II is correct.

10. [1]

This type of smog is formed by combination of particulates (smoke, dust, fog) with oxides of nitrogen and hydrocarbons in presence of sunlight to produce ozone (O_3) and PAN (peroxy acetyl nitrate).

11. [1]

CO combines with haemoglobin, produces **carboxyhaemoglobin** (200 times more affinity than oxygen for haemoglobin). Due to formation of carboxylhaemoglobin (HbCO), the quantity of oxygen available to the body cells gets reduced.

18. [4]

(A) Acid rain is due to SO_2.

(A) $\rightarrow$ (s)

(B) Photochemical smog is due to unsaturated hydrocarbons.

CH_2=CH CHO. (along with PAN)

Thus, (B) $\rightarrow$ (t)

(C) $HbO_2 + CO \rightarrow HbCO + O_2$

(C) $\rightarrow$ (q)

(D) CFC is responsible for depletion of ozone layer.

Thus, (D) $\rightarrow$ (p)

(E) Global warming is due to CO_2.

(E) $\rightarrow$ (r)

EXERCISE #4

1. [1]

During thunderstorm, there is the formation of NO which changes to NO_2 and ultimately to HNO_3 (acid rain)

$N_2 + O_2 \longrightarrow NO \xrightarrow{O_2} NO_2$

$4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$ [pH < 7]

2. [1]

Smog is formed by the action of sunlight on unsaturated hydrocarbons and nitrogen oxides.

Smog mainly contains higher concentration of Peroxy acetyl nitrate (PAN) formed by the reaction of NO_2, O_3 and unsaturated hydrocarbons.

$NO_2 \xrightarrow{h\nu} NO + O$

$O + O_2 \rightleftharpoons O_3$

$NO + O_3 \longrightarrow NO_2 + O_2$

$NO + O_3 + \text{unsaturated hydrocarbons} \longrightarrow PAN$

3. [3]

Ozone layer permits the infrared radiations to pass through but doesn't permit the higher range of ultraviolet radiations to pass through.

4. [4]

(1) $NO + O_3 \longrightarrow NO_2 + O_2$

$O_3 + h\nu \longrightarrow O_2 + O$

$NO_2 + O \longrightarrow NO + O_2$

Net reaction $2O_3 + h\nu \longrightarrow 3O_2$

Thus, ozone layer is depleted by oxides of nitrogen.

(1) is the correct statement.

(2) Ozone layer is a protective layer and absorbs harmful UV rays from the sun.

Thus, (2) is also the correct statement.

(3) $Cl + O_3 \longrightarrow \dot{Cl}O + O_2$

$O_3 + h\nu \longrightarrow \dot{O} + O_2$

$ClO + \dot{O} \longrightarrow \dot{Cl} + O_2$

Net reaction

$2O_3 + h\nu \longrightarrow 3O_2$

Thus, ozone layer is also depleted by reaction with freons.

(3) is also the correct statement.

(4) it is an incorrect statement as ozone layer is permeable for infrared rays.

5. [4]

DDT is a non-biodegradable pollutant. It is the first chlorinated organic insecticide.

6. [1]

Methyl isocyanate, CH_3–N=C=O (MIC) gas was leaked from the storage tank of the Union carbide plant in Bhopal gas tragedy.

7. [2]

8. [2]

9. [3]

10. [4]

In polluted cities, there is smog that causes irritation. Gases in smog are mainly PAN, RCHO, RCOR and O_3.

11. [1]

Addition of phosphate fertilisers enhance algae growth, thus O_2 concentration in water is decreased.

12. [1]

Nitrogen is an inert gas because of the presence of strong bond. That's why although there is 78% N_2 in the atmosphere but nitrogen oxide in not formed under ordinary conditions.

But when temperature is high enough i.e., $\approx$ 2000 K, it reacts with oxygen to form nitrogen oxide.

$N_2 + O_2 \xrightarrow{\approx 2000K} 2NO$

Thus,

If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I