

ORGANIC CHEMISTRY

BY- Er. ADITYA KATYAL

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ALKYL & ARYL HALIDES

NOMENCLATURE OF ALKYL & ARYL HALIDES

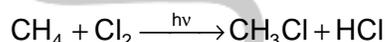
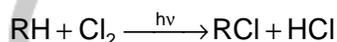
In the common system, aliphatic halogen derivatives are named as alkyl halides. The words n—, sec—, tert—, iso—, neo— & amyl are usually used in writing the common names. In IUPAC nomenclature they are named as halo alkanes.

Example:

Formula	Common name	IUPAC name
CH ₃ Cl	Methyl chloride	Chloro methane
CH ₃ CH ₂ CH ₂ Cl	n – propyl chloride	1 – chloro propane
$ \begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{CHCl} \\ \diagup \\ \text{H}_3\text{C} \end{array} $	Isopropyl chloride	2 – chloro propane

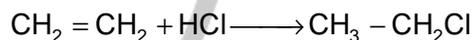
PREPARATION

(1) From Alkanes: Alkanes react with halogens in the presence of light to give alkyl halides.

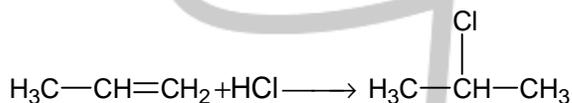


Alkyl halides formed further react with halogen to give di, tri and tetra halogen compounds.

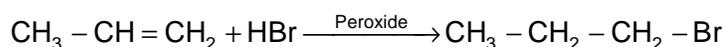
(2) From alkenes: Alkenes add halogen acids to give halides. For example

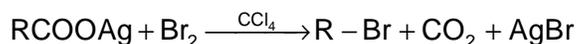


Markonikoff's rule: In the addition reactions of unsymmetrical alkenes the –ve part attaches to the carbon atom having lesser number of H-atoms. E.g.



In case of HBr if peroxide is added antimarkonikoff's addition takes place which is also called Kharash effect or peroxide effect e.g.

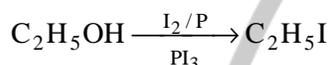
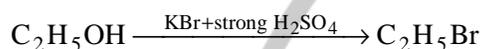
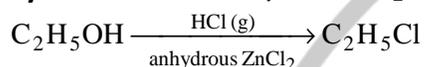


(3) From silver salt of carboxylic acids:

This reaction is called Borodine Hunsdiecker reaction.

(4) Finkelstein reaction: Alkyl chlorides and bromides reacts with NaI in acetone to give alkyl iodides.

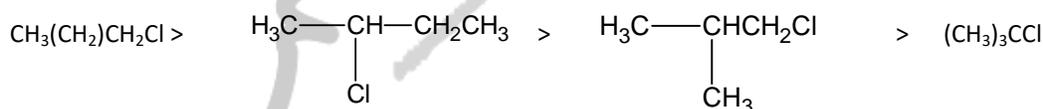
This reactions is possible because NaI is soluble in acetone but NaCl and NaBr are insoluble in acetone.

(5) By the action of HCl, P and Br₂ and P and I₂, PCl₅, SOCl₂ on alcohols.**PHYSICAL PROPERTIES****Halo Alkanes****1. Boiling Points**

The boiling points of haloalkanes are in the order $\text{RCl} < \text{RBr} < \text{RI}$. It is because with increase in size and mass of halogen atom the magnitude of Vander Waal's forces of attraction increases.

Among isomeric alkyl halides, the boiling point decreases with increase in branching in alkyl group.

e.g the decreasing order of boiling point among the isomers of butane is



For same halogen, the boiling point increases with increase in molecular mass.

e.g. CH_3Cl has lower boiling point than $\text{CH}_3\text{CH}_2\text{Cl}$

The boiling points of various halogen compounds increase with increase in number of halogen atoms.

For e.g. boiling point of CCl_4 is more than boiling point of CHCl_3 which is further more than CH_2Cl_2

Halo Arenes**1. Boiling point**

The boiling points of mono halogen derivatives of benzene follows the order:

Iodo > Bromo > Chloro

Mechanism

Nucleophilic substitution reactions in halides containing C – X bond may take place through either of the two different mechanism – SN^1 & SN^2 .

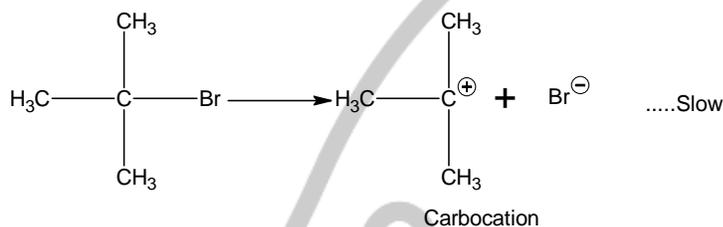
 SN^1 mechanism (Unimolecular Nucleophilic Substitution)

In this type the rate of reaction is dependent only on the concentration of alkyl halide i.e.

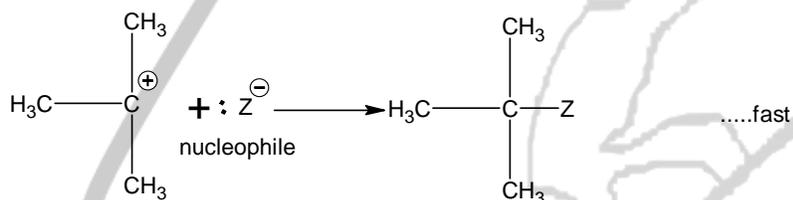
$$\text{Rate} = k[\text{RX}]$$

Step1:

In this step the alkyl halide slowly dissociates into halide ion & carbocation.

**Step 2:**

In the 2nd step carbocation at once combines with the nucleophile to form the final substituted product.

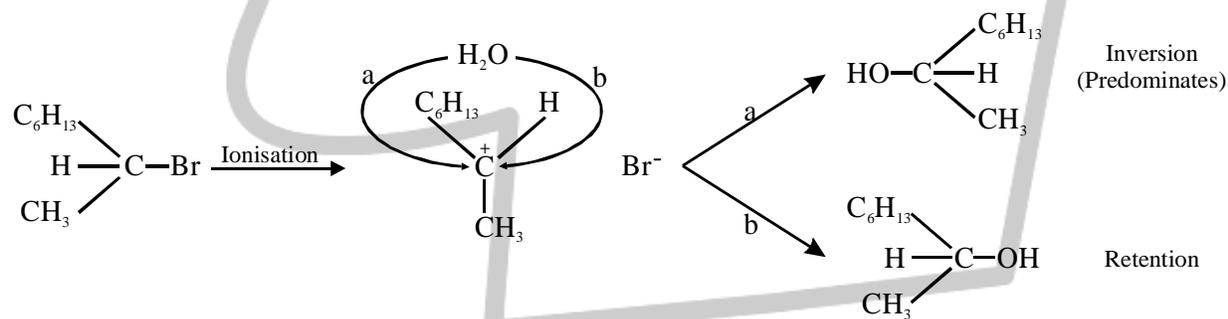


The order of reactivity of various alkyl halides through SN^1 mechanism is

$$3^\circ > 2^\circ > 1^\circ$$

Allylic & benzylic halides show greatest reactivity through SN^1 mechanism due to stability of allylic & benzylic carbocations.

Stereochemistry of $\text{S}_{\text{N}}1$ reactions: In $\text{S}_{\text{N}}1$ reactions, carbonium ions are the intermediates and these are planar chemical species. The attack of the nucleophile on this carbonium ion can take place with equal ease from either face of this flat ion. Thus, if the alkyl halide is optically active but it would be a racemic mixture.



Bromooctane ionizes to produce the planar 2-octyl carbonium ion. Now if the attack were purely random, then we would expect equal amounts of the two isomers *i.e.*, we would get a racemic modification. **But the product is not completely racemised because the inverted product exceeds its enantiomer.**

NOTES OF PERIODIC PROPERTIES

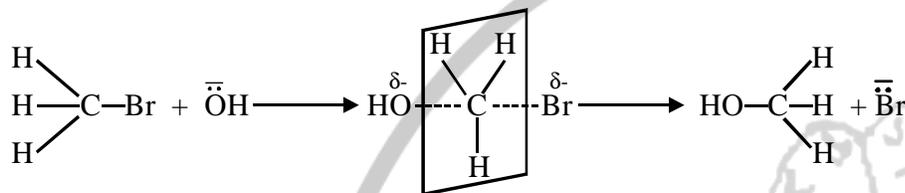
The most plausible answer to this question lies in the fact that the attack of the nucleophile occurs before the departing ion has completely left the neighbourhood of the carbonium ion.

S_N² Mechanism (Bimolecular Nucleophilic Substitution)

In this type the rate of reaction is dependent on the concentration of alkyl halide as well as nucleophile i.e.

$$\text{Rate} = k[\text{RX}][\text{OH}^-]$$

Primary alkyl halides react by S_N² mechanism via formation of transition state.



The order of reactivity of various alkyl halides through S_N² mechanism is

$$1^\circ > 2^\circ > 3^\circ$$

Stereochemistry of S_N² reactions: In S_N² reactions, attack of the nucleophile (e.g., OH⁻) takes place from the back *i.e.*, from the side remote from the leaving group (e.g., Br⁻) and hence such reactions are always attended by inversion of configuration

Factors affecting SN1 & SN2 Mechanism

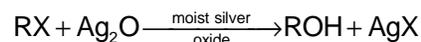
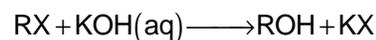
The reaction mechanism, SN1 or SN2, followed by nucleophilic substitution depends upon a number of factors. These factors are

- 1. Nature of alkyl halides:** Primary alkyl halides react through SN2 & tertiary alkyl halides through SN1 mechanism.
- 2. Nature of Nucleophile:** Strong nucleophile favour SN2 mechanism whereas weak nucleophile favours SN1 mechanism.
- 3. Concentration of Nucleophile:** High concentration of nucleophile favours SN2 while low concentration favours SN1 mechanism.
- 4. Nature of Solvent:** Polar solvents favour SN1 mechanism.

Some nucleophilic reactions are as follows:

1. Replacement by hydroxyl group (formation of alcohols)

Haloalkanes on treatment with aqueous solution of KOH or moist silver oxide give alcohol.



2. Replacement by Alkoxy (Williamson's synthesis)

Haloalkanes on treatment with alcoholic sodium or potassium hydroxide form ethers. This reaction is known as Williamson's synthesis .



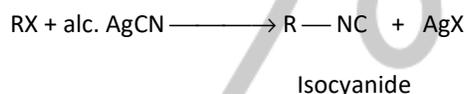
3. Replacement by cyano group

Haloalkanes on treatment with alcoholic KCN give alkyl nitriles or alkyl cyanides as major product.



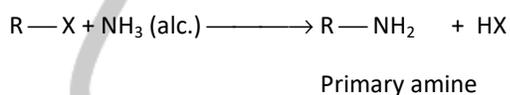
4. Replacement with Isocyanide Group

On reaction with alcoholic silver cyanide solution, haloalkanes give alkyl carbylamines or alkyl isocyanides as the major product along with or small amount of alkyl cyanide.



5. Replacement by Amino Group

On heating haloalkanes with alcoholic ammonia solution in a sealed tube, halogen is replaced by $-NH_2$ group to form primary amine.

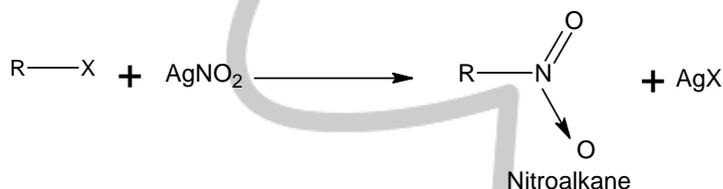


In case haloalkanes is in excess, the other 2 hydrogen atoms of amino group are also replaced by alkyl groups leading to the formation of secondary & tertiary amines.



6. Replacement by Nitro group

On treating ethanolic solution of haloalkanes with silver nitrite ($Ag-O-N=O$), nitro alkane is formed.

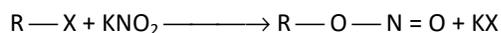


It is because the bond between $Ag-O$ being covalent, the lone pair on nitrogen act as attacking site for nucleophilic substitution.

7. Replacement by Nitrite group

On treatment of haloalkanes with potassium nitrite alkyl nitrite is formed.

NOTES OF PERIODIC PROPERTIES



Alkyl nitrite

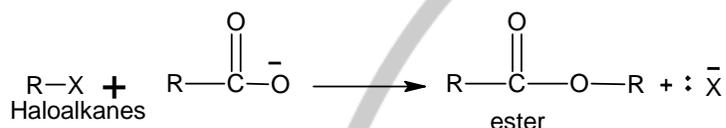
10. Replacement by Alkynyl Group

On treating halo alkanes with sodium alkynide $\text{RC}\equiv\text{C}^-\text{Na}^+$, higher alkynes are formed.



11. Replacement by Carboxylate Group

Haloalkanes on treatment with silver salt of carboxylic acids in ethanol give esters.



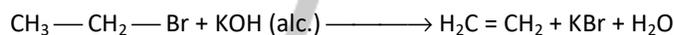
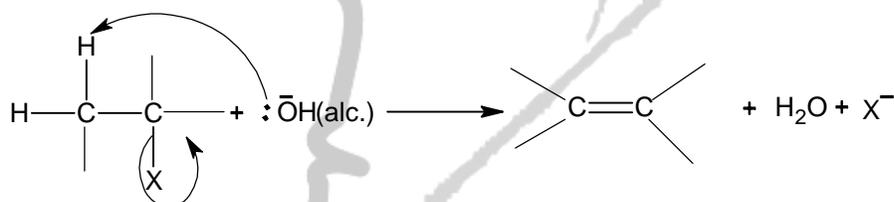
12. Replacement by Hydride Ion

Alkyl halides on reaction with lithium aluminium hydride in the presence of dry ether as solvent yield corresponding hydrocarbon.



Dehydrohalogenation Reactions or β - elimination Reactions

When halo alkanes are heated with alcoholic KOH, they undergo dehydrohalogenation to form alkenes. These reactions are called β - elimination because the hydrogen atom present at β - position of halo alkanes is removed.



Ethene

The reactivity of haloalkanes towards elimination reaction follows the order

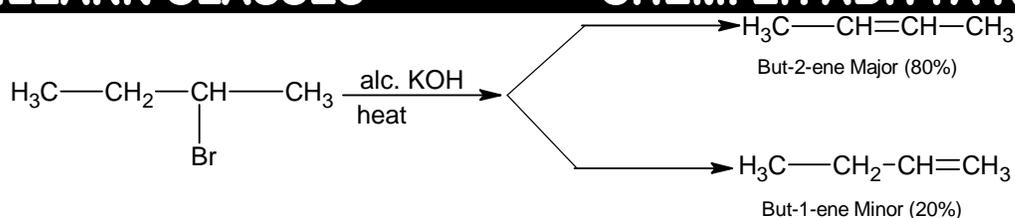
Tertiary > secondary > Primary

This is because tertiary alkyl halides on dehydrohalogenation form most substituted alkenes which are more stable & are formed at faster rate.

Among various halides with same alkyl group the order of reactivity is



In case the haloalkanes can eliminate hydrogen halide in 2 - different ways, the preferred alkene is the one which is maximum alkylated (most substituted).

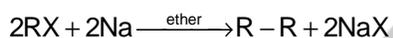


for e.g.

Reactions with Metals

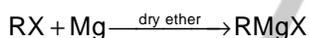
1. Reaction with sodium (Wurtz reaction)

Haloalkanes react with sodium in the presence of ether to form alkanes.



2. Reaction with Magnesium

Haloalkanes react with magnesium in the presence of dry ether to form alkyl magnesium halide (Grignard reagents)



Grignard reagents are organometallic compounds, i.e. compounds having metal carbon bond. Grignard reagents are highly reactive. They react with proton donors (acids) to give hydrocarbons.

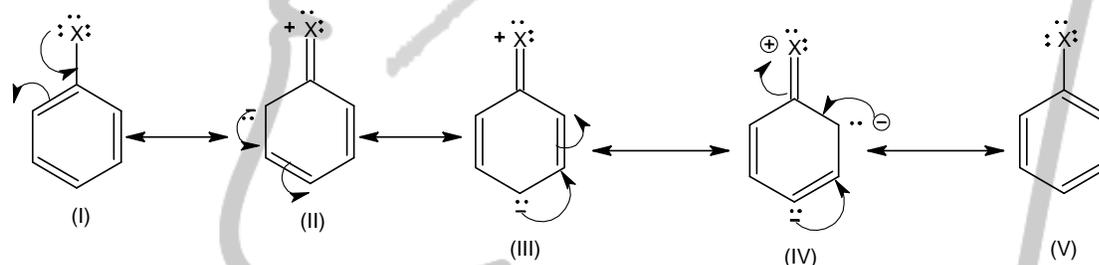


Difference in Reactivity of C – X bond in Alkyl halides & Aryl halides

Aryl halides are much less reactive towards nucleophilic substitution reaction than haloalkanes. The less reactivity of aryl halides can be explained as follows:

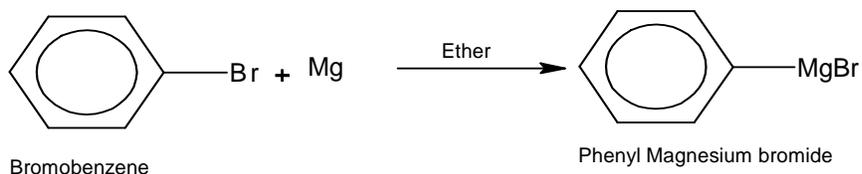
1. Withdrawal of Electrons by benzene & stabilization by resonance

In aryl halide, the electron pair of halogen atom is in conjugation with π electrons of benzene ring. Thus halobenzene is a resonance hybrid of following structures:



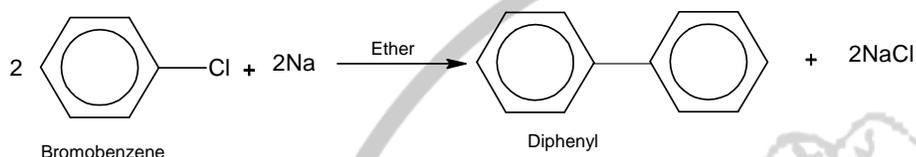
The contributing structures II, III & IV indicate that C—X bond has partial double bond characters.

As a result the C—X bond in halobenzene is shorter & hence stronger as compared to that in alkyl halides. Thus cleavage of C—X bond in halobenzene becomes difficult which makes it less reactive towards nucleophilic substitution.

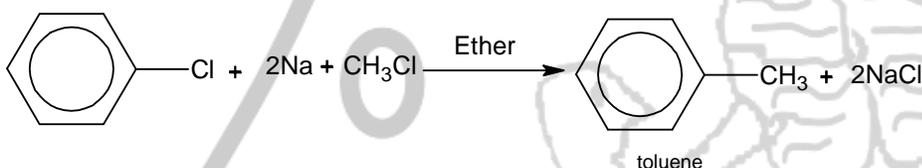


2. Reaction with Sodium

Aryl halides react with sodium in the presence of ether. During reaction two phenyl rings unite. The reaction is called Fittig reaction.



However aryl halides when treated with halo alkane & sodium in dry ether undergo Wurtz fitting reaction.



RING SUBSTITUTION REACTIONS

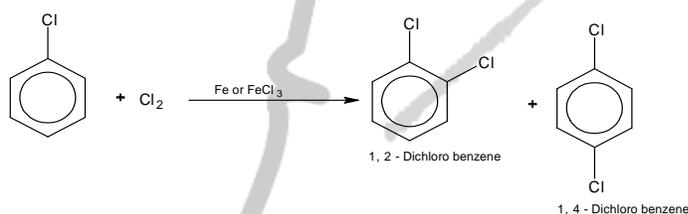
An aryl halide undergoes electrophilic substitution reactions in benzene ring. The presence of halogen atom in the ring directs the incoming substituent to the ortho & para position.

Aryl halides are less reactive than benzene towards electrophilic substitution reactions.

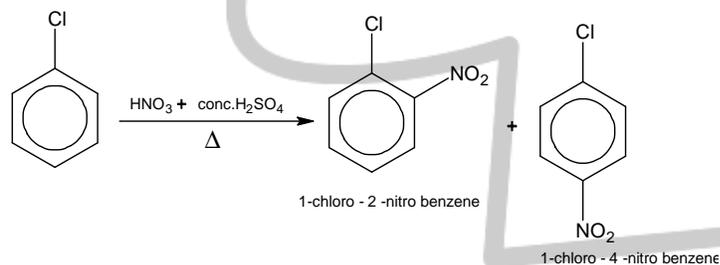
Some ring substitution reactions of aryl halides are given below:

1. Halogenation

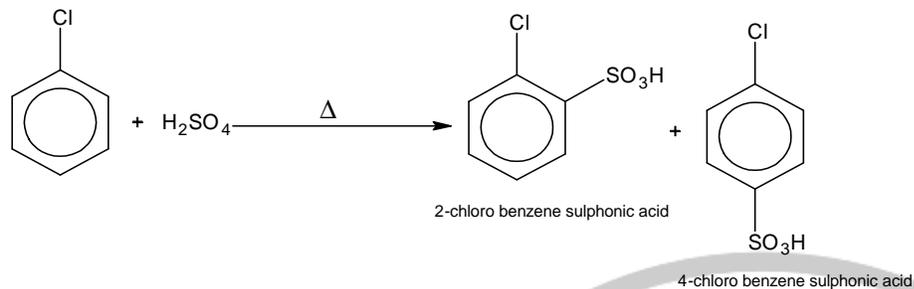
Halogenation takes place in the presence of iron or FeCl₃ or anhydrous AlCl₃ as a catalyst.



2. Nitration

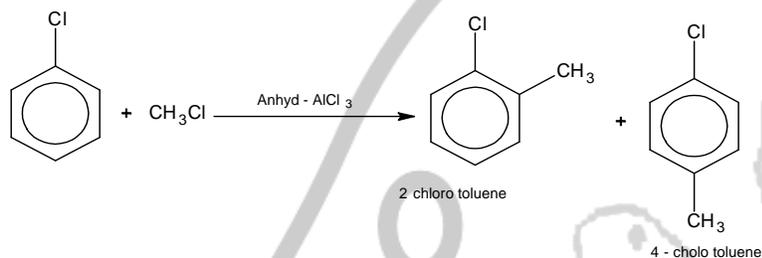


3. Sulphonation

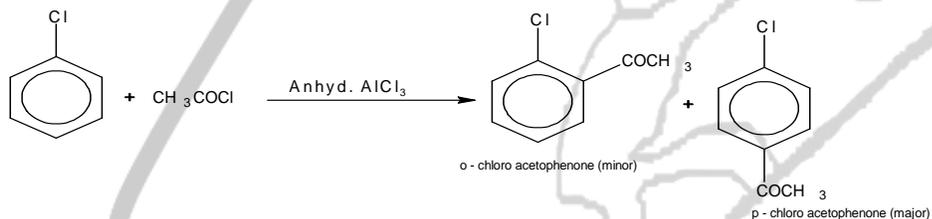


4. Friedel Craft's Alkylation

With alkyl halide in presence of anhydrous AlCl_3 , alkylation takes place for e.g.



5. Friedel Craft's Acylation



(SUBJECTIVE ASSIGNMENT)**CONCEPTUALS**

1. The bond length of C–Cl bond is larger in haloalkanes than that in haloarenes.

Ans. In haloalkane halogen is attached to sp^3 hybridized carbon whereas in haloarenes it is attached to sp^2 carbon.

In sp^2 , the % of s-character is more so it is more closer to nucleus as compared to sp^3 .

2. Although alkyl halides are polar in nature but are not soluble in water.

Ans. Because the energy required to break is more than energy released when new attraction is set up between haloalkane and water. So it is not soluble.

3. *tert*-butyl bromide has lower boiling point than n-butyl bromide.

Ans. The *tert*-butyl bromide is a branched compound which will occupy less surface area so it has low boiling point as compared to n-butyl bromide.

4. haloalkanes react with KCN to form alkyl cyanide as main product while with AgCN alkyl isocyanide is the main product.

Ans. KCN is ionic and provides CN^- ions in solution. So alkyl will attack through carbon because of C-C strong bond.

But AgCN is a covalent compound in which only nitrogen is free to donate pair so it forms isocyanide.

5. Sulphuric acid is not used in the reaction of alcohol with KI.

Ans. In the presence of H_2SO_4 , KI produces HI. Since H_2SO_4 is an oxidising agent it oxidises HI to form I_2

So Rx between alcohol and HI is not possible.

6. Thionyl chloride is the preferred reagent for converting ethanol to chloroethane.

Ans. Because the byproduct formed in this reaction are in gaseous state which can be removed easily [$SO_2(g)$ & $HCl(g)$]

7. Haloalkanes undergo nucleophilic substitution reaction easily but haloarenes do not undergo nucleophilic substitution under ordinary conditions.

Ans. (i) Due to resonance in haloarenes the (C-X) bond acquires partial double bond character which is difficult to break resonance structure

(ii) In haloarenes, the phenyl cation is unstable.

(iii) Because of the repulsion by (-)ve charge in benzene ring nucleophile is not able to approach the benzene ring.

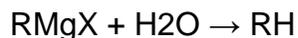
8. 2, 4-dinitro chlorobenzene is much more reactive than chlorobenzene towards hydrolysis reaction with NaOH.

Ans. The NO_2 group at ortho and para position withdraws electron density from benzene ring and this attachment of nucleophile takes place easily.

NOTES OF PERIODIC PROPERTIES

9. **Grignard reagent should be prepared under anhydrous conditions.**

Ans. Because even traces of moisture will react with Grignard reagent to form alkanes.



10. **the dipole moment of chlorobenzene is lower than that of cyclohexylchloride.**

Ans. In chloro benzene the Cl atom is linked to sp^2 hybridised carbon atom. In cyclohexyl chloride the Cl is linked to sp^3 carbon atom. sp^2 hybridized has more s-character than sp^3 hybridised. So density of e^- 's of C-Cl bond is more in Chlorobenzene and hence its bond length is shorter.

11. **neopentyl bromide undergoes nucleophilic substitution reactions very slowly**

Ans. Due to large steric hindrance in neopentyl chloride, and also the carbon attached to halogen is 1° (primary). So nucleophilic subs. is difficult.

12. **vinyl chloride is unreactive in nucleophilic substitution reaction.**

Ans. The carbocation formed in Vinyl chloride is unstable so it does not show this Rxn.

13. **An optically inactive product is obtained after the hydrolysis of optically active 2-bromobutane.**

Ans. The hydrolysis occurs by $\text{SN}1$ pathway. The carbocation is formed first which gives a mixture of (+) butan-2-ol in second step.

14. **The treatment of alkyl chloride with aqueous KOH leads to the formation of alcohol but in the presence of alcoholic KOH, alkene is the major product.**

Ans. In aqueous solution, KOH is almost completely involved to give OH^- ion which being a better nucleophile gives a substitution reaction on alkyl halides to form alcohol. But an alcoholic solution of KOH containing alkoxide (RO^-) ions which being a much stronger base than OH^- ion preferentially snatches a H^+ ion from an alkyl chloride to form alkenes.

15 **Haloalkanes undergo nucleophilic substitution whereas haloarenes undergo electrophilic substitution. Explain.**

Ans. In haloarenes $-ve$ charge gets localised on arenes using resonance, therefore they undergo electrophilic substitution.

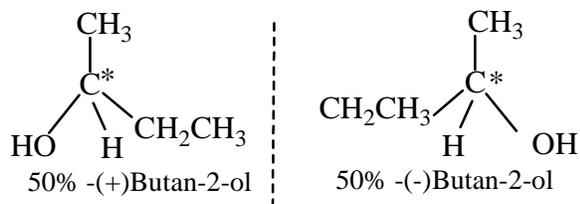
Haloalkanes have electrophilic carbon centre due to polarity of $\text{C} \rightarrow \text{X}$ bond.

16 **What is the function of anhyd. ZnCl_2 in the reaction of alcohols with conc. HCl (or Lucas reagent)?**

The function of anhydrous zinc chloride is to help in the cleavage of C – O bond. Being a Lewis acid anhydrous ZnCl_2 co-ordinates to the O-atoms of R – OH and thus weakens the C – O bond which then breaks to give carbocation. Moreover anhyd. ZnCl_2 acts as a dehydrating agent and helps the reaction to go in the forward direction.

17 **Why is (\pm)-butan-2-ol is optically inactive?**

ans. The (\pm)-Butan-2-ol is optically inactive because it exists in two enantiomeric forms which are non-superimposable mirror images of each other. Both the isomers are present in equal amounts therefore, it does not rotate the plane of polarized light and is optically inactive.



18. Although chlorine is an electron withdrawing group, yet it is ortho-,para- directing in electrophilic aromatic substitution reactions. Why?

19. p-dichlorobenzene has higher melting point than those of o- and m-isomers.

Ans. *P*-Dichlorobenzene has higher melting point than those of *o*- and *m*-isomers because it is more symmetrical and packing is better in solid form.

Hence, it has stronger intermolecular force of attraction than *o*- and *m*-isomers.

FOR PRACTICE

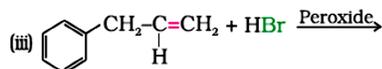
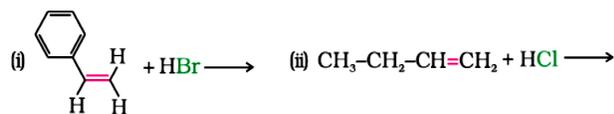
19. Account for the following :

- (i) Sulphuric acid is not used during the reaction of alcohols with KI.
- (ii) *p*-methoxybenzyl bromide reacts faster than *p*-nitrobenzyl bromide with ethanol to form an ether product.
- (iii) Organic halogen compounds used as solvents in industry are chlorides rather than bromides and iodides.
- (iv) Wurtz reaction fails in case of tert-alkyl halides.
- (v) Alkyl halides are insoluble in water though they contain a polar C -X bond.

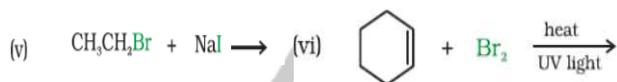
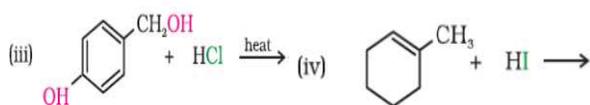
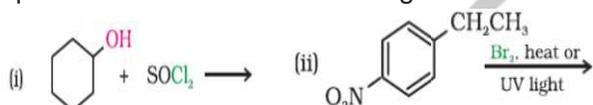
20. Benzyl chloride is more reactive than chlorobenzene towards nucleophilic substitution. Explain.

REACTION COMPLETION

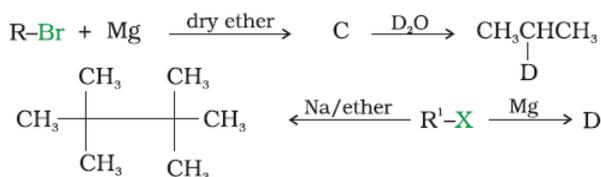
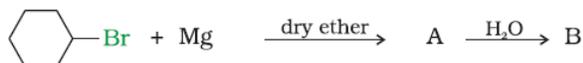
1. Write the products of the following reactions:



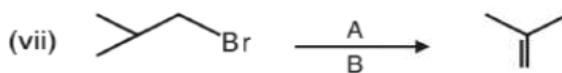
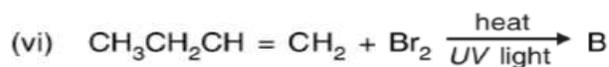
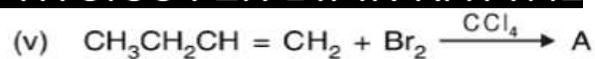
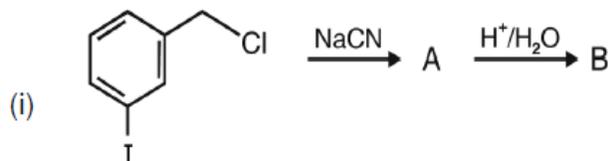
2. Draw the structures of major monohalo products in each of the following reactions:



3. Identify A, B, C, D, E, R and R₁ in the following:



4. Identify the products formed in the following sequence :



6. What happens when

(i) n-butyl chloride is treated with alcoholic KOH,

(ii) bromobenzene is treated with Mg in the presence of dry ether,

(iii) chlorobenzene is subjected to hydrolysis,

(iv) ethyl chloride is treated with aqueous KOH,

(v) methyl bromide is treated with sodium in the presence of dry ether,

(vi) methyl chloride is treated with KCN?

**INCREASING/
DECREASING ORDER**

1. Arrange each set of compounds in order of increasing boiling points.

(i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.

(ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

2. In the following pairs of halogen compounds, which would undergo SN₂ reaction faster?

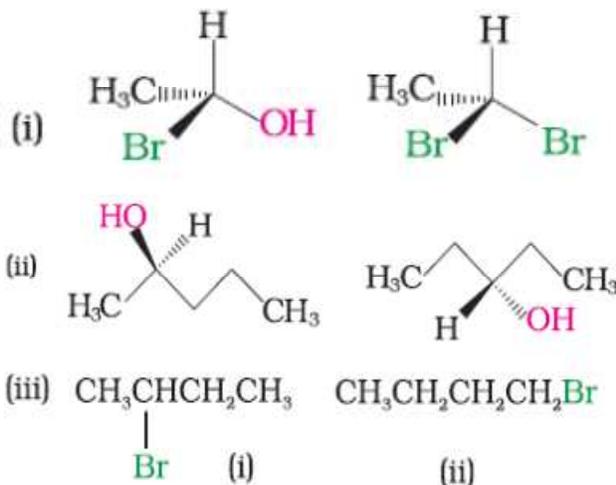


3. Predict the order of reactivity of the following compounds in SN₁ and SN₂ reactions:

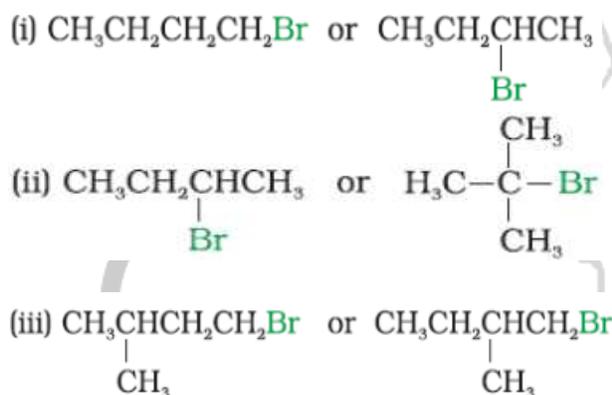
(i) The four isomeric bromobutanes

(ii) C₆H₅CH₂Br, C₆H₅CH(C₆H₅)Br, C₆H₅CH(CH₃)Br, C₆H₅C(CH₃)(C₆H₅)Br

4. Identify chiral and achiral molecules in each of the following pair of compounds.



5. Which alkyl halide from the following pairs would you expect to react more rapidly by an SN2 mechanism? Explain your answer.



9. In the following pairs, which halogen compound undergoes faster (i) SN1 and (ii) SN2 reaction?

- a) $(\text{CH}_3)_3\text{CCl}$ and $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$
 b) $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ and $\text{C}_6\text{H}_5\text{C}(\text{Cl})\text{C}_6\text{H}_5$
 c) $\text{CH}_2 = \text{CH}-\text{Cl}$ and $\text{CH}_2 = \text{CH}-\text{CH}_2\text{Cl}$
 d) $\text{C}_6\text{H}_6\text{C}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Br}$ and $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$.

9. Arrange the following in the increasing order of properly indicated :

(i) bromomethane, chloromethane, dichloromethane. (Increasing order of boiling points).

(ii) 1-chloropropane, isopropyl chloride, 1-chlorobutane (Increasing order of boiling point)

(iii) dichloromethane, chloroform, carbon tetrachloride. (Increasing order of dipole moment.

(iv) CH_3F , CH_3Cl , CH_3Br , CH_3I (Increasing reactivity towards nucleophilic substitution and increasing order of dipole moment)

(v) o,m,p-dichlorobenzenes (Increasing order of melting points).

10. Arrange the compounds of each set in order of reactivity towards SN2 displacement:

(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2-methylbutane

(iii) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane.

PREDICTION

1. Identify all the possible monochloro structural isomers expected to be formed on free radical monochlorination of $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$. Write structures of different dihalogen derivatives of propane.

2. Among the isomeric alkanes of molecular formula C_5H_{12} , identify the one that on photochemical chlorination yields

- (i) A single monochloride.
 (ii) Three isomeric monochlorides.
 (iii) Four isomeric monochlorides.

3. A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound $\text{C}_5\text{H}_9\text{Cl}$ in bright sunlight. Identify the hydrocarbon.

4. Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:

- (i) 1-Bromo-1-methylcyclohexane
 (ii) 2-Chloro-2-methylbutane
 (iii) 2,2,3-Trimethyl-3-bromopentane..

7. Primary alkyl halide (A) $\text{C}_4\text{H}_9\text{Br}$ reacted with alc.KOH to give 'B'. 'B' when reacted with HBr to give 'C', which is an isomer of 'A'. When 'A' reacted with Na metal, it gave a compound 'D'

C_8H_{18} that was different from the compound, when n-butyl bromide was reacted with Na. Give the structural formulas of 'A' to 'D' and write the chemical equations of reactions involved.

8. An alkyl halide X having molecular formula $C_6H_{13}Cl$ on treatment with potassium tert-butoxide gives two isomeric alkenes Y and Z but alkene y is symmetrical. Both alkenes on hydrogenation give 2, 3-dimethylbutane. Identify X, Y and Z.

9. A hydrocarbon .A. (C_4H_8) is added with HBr in accordance with Markonikov.s rule to give compound .B. which on hydrolysis with aqueous alkali forms tertiary alcohol .C. ($C_4H_{10}O$). Identify A, B and C.

10. An organic compound (A) having molecular formula C_3H_7Cl on reaction with alcoholic solution of KCN gives compound B. The compound B on hydrolysis with dilute HCl gives compound C. C on reduction with H_2/Ni gives 1-aminobutane. Identify A, B and C

D.P. – 1

1. Write structural formula of the following

- (i) Benzyl chloride
- (ii) 4 – chloropent – 2 – ene
- (iii) 1 – bromo – 2, 2 – dimethyl propane
- (iv) 3 – chloro – 2, 4 – dimethyl pentane

2. Explain why chloroform ($CHCl_3$) is not soluble in water although it is polar.

3. Melting and boiling points of alkyl halides are higher than their corresponding alkanes. Why?

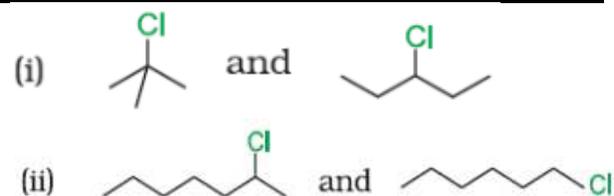
4. Arrange the following in increasing order of density



5. Arrange each set of compounds in order of increasing boiling point.

- (i) Methyl bromide, methylene bromide, bromoform.
- (ii) n – butyl chloride, iso – butyl chloride, tert – butyl chloride.

6. In the following pairs of halogen compounds, which compound undergoes faster SN_1 reaction?



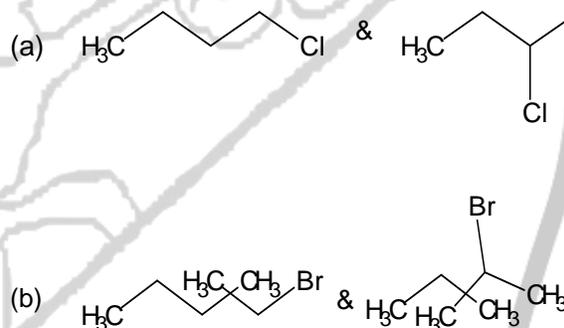
7. Out of ethyl bromide and ethyl chloride which one has higher boiling point and why?

8. Arrange the following compounds in decreasing order of SN_1 reactions.

- (i) $CH_3CH_2CH_2Cl, CH_2=CHCHClCH_3, CH_3CH_2CHClCH_3$
- (ii) $BrC_2H_5, CH_3CH(Br)CH_3, (CH_3)_3CBr$

9. Of the two bromo derivatives $C_6H_5CH(CH_3)Br$ and $(C_6H_5)_2CHBr$, which one is more reactive in SN_1 substitution reaction and why?

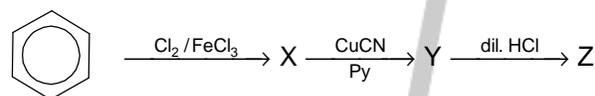
10. Which is faster in following pairs of halogen compound in SN_2 reactions?



D.P. – 2

1. Vinyl chloride does not give S_N reaction but allyl chloride gives. Explain.

2. Find X, Y & Z in the following sequence of reaction:



3. Tert-butyl bromide reacts with aq. NaOH by SN_1 mechanism while n-butylbromide reacts with SN_2 mechanism. Why ?

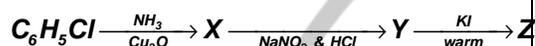
4. Why alkyl halides are generally not prepared in laboratory by free radical halogenations of alkanes ?

5. Hydrolysis of 2-bromo-3-methylbutane (2°) gives only α -methyl-2-butanol (3°). Explain.

7. How may the two substances in each of the following pairs be distinguished from each other?

- Chlorobenzene and hexyl chloride.
- $\text{CH}_2 = \text{CH} - \text{CH}_2\text{Br}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$
- p-Bromobenzyl chloride and chlorobenzyl bromide

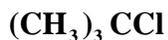
8. Identify X, Y & Z in the following reactions



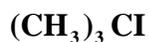
9. Write the structure of the major organic product in each of the following reactions:

- $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{NaI} \rightarrow$
- $(\text{CH}_3)_3\text{CBr} + \text{KOH} \rightarrow$
- $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_3 + \text{NaOH} \rightarrow$
- $\text{CH}_3\text{CH}_2\text{Br} + \text{KCN} \rightarrow$
- $\text{C}_6\text{H}_5\text{ONa} + \text{C}_2\text{H}_5\text{Cl} \rightarrow$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{SOCl}_2 \rightarrow$
- $\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 + \text{HBr} \rightarrow$
- $\text{CH}_3\text{CH} = \text{C}(\text{CH}_3)_2 + \text{HBr} \rightarrow$

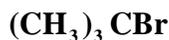
10. Arrange the following compound according to decreasing order reactivity towards S_N^1 reaction



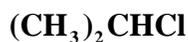
(I)



(III)



(II)



(IV)

D.P. - 3

1. Identify and indicate the presence of centre of chirality, if any, in the following molecules. How many stereoisomers are possible for those containing chiral centre :

- 1, 2-dichloropropane

(ii) 3-bromopent-1-ene

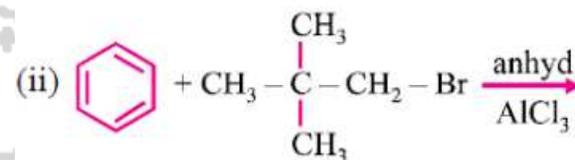
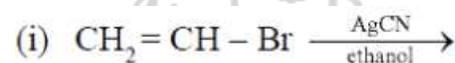
2. Write the main products when :

- n-butyl chloride is treated with alcoholic KOH
- 2, 4, 6-trinitrochlorobenzene is subjected to hydrolysis.
- Methyl chloride is treated with AgCN .

3. The end product "Z" in the following reaction, ethylamine $\xrightarrow{\text{HNO}_2} \text{X} \xrightarrow{\text{PCl}_5} \text{Y} \xrightarrow{\text{NH}_3} \text{Z}$ is

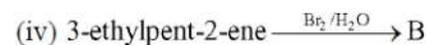
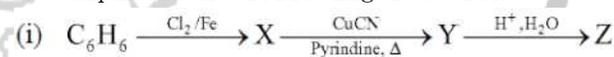
4. Why alkyl halides are generally not prepared in laboratory by free radical halogenations of alkanes ?

5. Write major product of the following reactions :



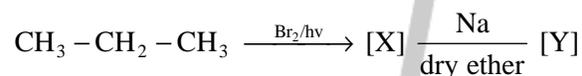
D.P. - 4

1. Complete the following reactions :



3. Predict the order of reactivity of following compounds in dehydrohalogenation $\text{CH}_3\text{CH}(\text{Br})\text{CH}_3$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$, $(\text{CH}_3)_2\text{CH} - \text{CH}_2\text{Br}$, $(\text{CH}_3)_3\text{C} - \text{CH}_2\text{Br}$

Product [Y] in the following reaction will be



COMPETITION SECTION

OBJECTIVE QUESTIONS (HALOALKANES & HALOARENES)

- $(C_2H_5)CHBr$ is
 - pri-pentyl bromide
 - sec-pentyl bromide
 - ter-pentyl bromide
 - iso-pentyl bromide
- Alkyl halides are
 - Mono halogen derivatives
 - dihaloalkanes
 - monohaloalkanes
 - mono, di and trihaloalkanes
- C_4H_9X is a
 - pri-alkyl halide
 - ter-alkyl halide
 - see-alkyl halide
 - pri or see or ter-alkyl halide
- $$\begin{array}{c} CH_3 - CH - X - CH_3 \\ | \\ C_2H_5 \end{array}$$
 - 2-halo, 3-ethyl butane
 - 2-halo, 3-ethyl pentane
 - 2-halo, 3-methyl butane
 - 2-halo, 3-methyl pentane
- $(CH_3)_2CH.CH_2Br$ is named as
 - 1-bromo, 2-methyl propane
 - 1-bromo, 2-methyl butane
 - pri-butyl bromide
 - 1-butyl bromide
- $(CH_3)_3C.Br$ is called
 - 2-bromo, 2-methyl propane
 - 2-bromo, 2-methyl butane
 - iso-butyl bromide
 - 1-bromo, 2-methyl propane
- 2-bromo, 2-methyl propane has the structural formula as

a) $(CH_3)_3Br$	b) $(CH_3)_3CH_2Br$
c) $(CH_3)_3C.Br$	d) $(CH_3)_3CHBr$
- About alkanes some statements are given below
 - Chlorination and bromination take place slowly in dark.
 - Iodination is carried out in the presence of HNO_3
 - Halogenation can be carried out by the action of HX .
 - They are obtained by the reduction of RI by HI .
- Among the above, the true statements are
 - only A and B
 - A, B and D
 - only B and C
 - A, C and D
- In iodination of alkanes, iodic acid is used to
 - catalyse the reaction.
 - remove HI by reduction and to prevent reverse reaction.
 - oxidise HI to prevent reverse reaction
 - to liberate free I_2 necessary for iodination
- Halogenation of alkanes with halogen gives
 - only alkyl halides
 - alkyl halides and geminal dihalides only
 - alkyl halides and vicinal dihalides only
 - mixture of all possible halogen derivatives of alkanes.
- In the reaction, $C_3H_6 + HBr + A$; A is
 - n-propyl bromide
 - sec. butyl bromide
 - iso-propyl bromide
 - dibromopropane
- Butene-1 when treated with HBr gives
 - sec. butyl bromide
 - n-butyl bromide
 - 1-bromo butane
 - 2-butyl bromide
- In the reaction, 2-Methyl propene + $HI + B$; B is

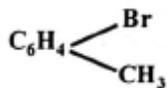
a) ter-butyl iodide	b) 2-iodobutane
c) iso-butyl iodide	d) 1-butyl iodide
- In the reaction $A + HBr$ ter-butyl bromide; A is
 - 2-methyl prop-1-ene
 - 2-methyl propane
 - 2-methyl propene
 - but-1-ene
- Propene undergoes addition of HBr in the presence of benzoyl peroxide to give
 - 1-bromo butane
 - 1-bromo propane
 - 2-bromo butane
 - 2-bromo propane
- In addition of HBr to but-2-ene, which of the following is true ?
 - The Markownikoff's Rule is obeyed.
 - Abnormal addition will take place in the, presence of peroxide.
 - Normal and abnormal addition will give the isomers.
 - In any case the product is same.
- Peroxide effect is observed in addition, to propene, of

a) HBr and HCr	b) HBr and HI
c) Only HBr	d) Only HI
- In the reaction $ROH \xrightarrow{RI} RI + A$ A is

a) H_3PO_2	b) H_3PO_3
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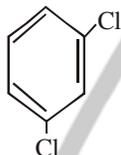
- c) H_3PO_4 d) HPO_3
19. In the reaction,
 $\text{A} + \text{PCl}_5 \rightarrow (\text{CH}_3)_2\text{CHCl} + \text{POCl}_3 + \text{HCl}$; A is
 a) 2-hydroxy propane
 b) sec. propyl alcohol
 c) iso-propanol
 d) 2-propyl alcohol
20. Thionyl chloride reacts with monohydric alcohols to give
 a) alkyl halides b) haloalkanes
 c) chloroalkanes d) all these.
21. In the addition of halogen acids to alkenes, the alkene being same, the order of reactivity is
 a) $\text{HCl} > \text{HBr} > \text{HI}$ b) $\text{HI} > \text{HCl} > \text{HBr}$
 c) $\text{HBr} > \text{HCl} > \text{HI}$ d) $\text{HI} > \text{HBr} > \text{HCl}$
22. In the substitution of X in RX, by OH^- ion, the alkyl radical being same the order of reactivity is
 a) $\text{RI} > \text{RCI} > \text{RBr}$ b) $\text{RI} > \text{RBr} > \text{RCI}$
 c) $\text{RCI} > \text{RBr} > \text{RI}$ d) $\text{RBr} > \text{RCI} > \text{RI}$
23. In the substitution of Br by OH^- ion, the most reactive is
 a) $\text{CH}_3\text{CH}_2\text{Br}$ b) CH_3Br
 c) $(\text{CH}_3)_3\text{C.Br}$ d) $(\text{CH}_3)_2\text{CHBr}$
24. An alkyl halide can be converted to an alcohol by the action of
 a) $\text{Ag}_2\text{O} + \text{H}_2\text{O}$ b) aq. KOH
 c) aq. KCN d) boiling water
25. Acetonitrile is obtained by the action of aq. KCN on
 a) acetic acid b) ethyl bromide
 c) acetone d) methyl bromide
26. Some statements are given below about iodoethane.
 (A) It reacts with aq. potassium cyanide to give acetonitrile.
 (B) It gives ethanol on treatment with moist Ag_2O .
 (C) It reacts with Na in ether to give propane.
 (D) With sodium methoxide it gives dimethyl ether.
 Among the above, the incorrect statements are
 a) A, B and C only b) A, C and D only
 c) C and D only d) all these.
27. Silver propionate when heated with iodomethane gives.
 a) ethyl propionate b) methyl propionate
 c) ethyl acetate d) methyl acetate.
28. A solution of iodoethane in ether, when treated with metallic sodium, mainly gives
 a) iso-butane b) propane
 c) n-butane d) sodium propoxide
29. Reaction of ethyl halide with alkali alkoxide is called.
 a) Wurtz reaction
 b) Williamson's synthesis
 c) Elimination reaction
 d) Carbylamine reaction
30. In the preparation of Grignard's reagent the use of iodine is
 a) to lower down the temperature.
 b) to prevent reverse reaction.
 c) to remove impurities.
 d) as a catalyst.
31. 2-iodopropane when boiled with aq. KOH gives
 a) propene b) prop-1-ene
 c) prop-2-ene d) propane
32. Some statements are given below
 (A) Wurtz reaction can be used to ascend the alkane series
 (B) An alcohol reacts with thionyl chloride with the evolution of SO_2
 (C) In the reaction of an alcohol with phosphorus pentachloride one of the products is PCl_3
 (D) Dehydrohalogenation of alkyl halide is possible by the action of aq. KOH.
 Among the above, the true statements are
 a) Only B, C and D b) Only A, B and C
 c) Only A and B d) Only B and D
33. In the heterolytic fission of carbon-halogen bond in 2-methyl-2-bromopropane the carbocation obtained is
 a) sec-butyl b) sec-propyl
 c) pri-propyl d) ter-butyl
34. The reagent, which is useful for the synthesis of a large number of organic compounds is obtained by the action of alkyl halide with
 a) Mg b) Zn
 c) Pb d) Li
35. Which one of the following is true about $\text{S}_\text{N}2$ reaction? (alkaline hydrolysis of alkyl halide)
 a) The rate of reaction is equal to $[\text{RX}][\text{OH}^-]$
 b) The formation of C-X bond and fission of C-OH bond are simultaneous.
 c) C-X bond undergoes heterolytic fission.
 d) The first step is slower than the second step.
36. The reaction with chances of both, retention as well as inversion of configuration is
 a) $\text{S}_\text{N}1$ b) $\text{S}_\text{N}2$
 c) both d) none
37. In reaction which of the following is true?
 a) is always negative.

- b) The order of reactivity of alkyl halide is; $\text{pri} > \text{sec} > \text{ter}$
 c) It is a second order reaction.
 d) It is favoured by polar solvents.
38. Among the following, which one is true for nucleophilic reactions ?
 a) Their rates are always affected by concentration of alkali.
 b) They all pass through only one transition state.
 c) They involve the homolytic fission of carbon-halogen bond.
 d) Their kinetics depend on the alkyl halide taken.



39. _____ can definitely be called
 a) o-bromotoluene b) m-bromotoluene
 c) p-bromotoluene d) bromotoluene
40. In chlorobenzene and benzyl chloride, the Cl-atom is linked to C-atom whose hybridisation is respectively
 a) sp^2 , sp b) sp^2 , sp^3
 c) sp , sp^3 d) sp^3 , sp^2

41. The IUPAC name of is



- a) m-dichlorobenzene
 b) 2,4-dichlorobenzene
 c) 1,3-dichlorobenzene
 d) p-dichlorobenzene
42. The C-X bond in haloarenes is less reactive than that in haloalkanes due to
 a) more electronegativity of C-atom bearing X-atom in haloarenes
 b) acquiring partial double bond character for C-X bond in haloarenes.
 c) both these d) none of these.
43. The halogen atom attached to C-atom in the benzene ring is
 a) o-directing with activation
 b) p-directing with activation
 c) o, p-directing with deactivation
 d) m-directing with deactivation

44. Which of the following when obtained from chlorobenzene, represents a nucleophilic substitution reaction?
 a) phenol b) o-Nitrochlorobenzene
 c) phenyl cyanide d) Both a) and c)

45. An electrophilic substitution reaction involves the replacement of Cl-atom from chlorobenzene by

- a) NH_2 b) OCH_3
 c) CN d) none of these.

46. An example of an electrophilic substitution reaction is that when chlorobenzene reacts with

- a) $\text{Cl}_2/\text{FeCl}_3$
 b) conc, HNO_3 + conc, H_2SO_4
 c) $\text{CH}_3\text{COCl}/\text{Anhyd. AlCl}_3$
 d) any of these.

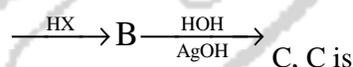
47. Friedal- Craft is acetylation of benzene ring involves the use of

- a) CH_3Cl b) CH_3COCl
 c) CH_3COOH d) either b) or c)

49. Aromatic ketones can be obtained from chlorobenzene by

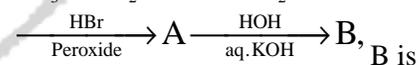
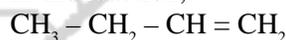
- a) Friedal-crafts acetylation
 b) nitration
 c) Friedal-crafts alkylation
 d) none of these

50. In the reaction, $\text{R}-\text{H}=\text{CH}_2$



- a) n-propyl alcohol b) isopropyl alcohol
 c) primary alcohol d) secondary alcohol

51. In the reaction,



- a) butan-1-ol b) butan-2-ol
 c) butan-1, 2-diol d) butan-2,3-diol

52. $\text{R}-\text{CH}=\text{CH}_2 \xrightarrow{\text{HCl}} \text{A} \xrightarrow[\text{alc. KOH}]{\text{alc. KOH}} \text{B}$ In

this reaction A and B are respectively

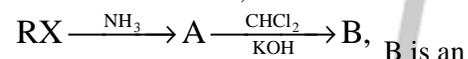
- a) alkyl halide and alkene
 b) alkene and alkyl halide
 c) 1-chloropropane and propyl alcohol
 d) iso-propyl chloride and propene

53. In the reaction, $\text{RX} \xrightarrow{\text{KCN}} \text{B} \xrightarrow[\text{HCl}]{\text{HOH}} \text{C}$,

C is a/an

- a) alcohol b) aldehyde
 c) acetic acid d) fatty acid

54. In the reaction,

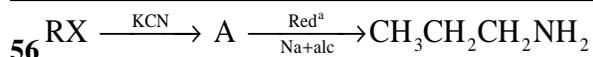


- a) alkyl nitrile b) alkyl isocyanide
 c) alkyl nitrite d) amide

55. 1-chloropropane $\xrightarrow{\text{alc. KOH}} \text{B} \xrightarrow{\text{HX}} \text{C}$

In this reaction C is

- a) 1-chloropropene b) alkyl halide
 c) 2-chloropropane d) sec. alkyl halide

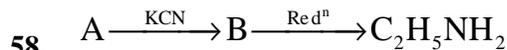


In this reaction R is

- a) ethyl halide b) methyl chloride
c) ethyl group d) propyl group

57. Grignard's reagent is prepared by heating magnesium metal with

- a) methyl amine b) ethyl amine
c) ethyl iodide d) methyl alcohol



Compound A in the reaction is,

- a) C_2H_5I b) C_2H_5OH
c) CH_3OH d) CH_3I

59. Ethyl bromide reacts with $AgCN$ to form-

- a) ethyl cyanide b) ethyl isocyanide
c) ethyl isocyanate d) ethyl cyanate

60. Which one of the following cannot be used for replacing OR group by Cl atom?

- a) S_2Cl_2 b) PCl_3
c) PCl_5 d) $SOCl_2$

61. Ethyl bromide reacts with sodium alkoxide to form

- a) n-butane b) an alcohol
c) an ether d) an alkane

62. The reaction of Cl_2 or Br_2 with the silver salt of a fatty acid, to give alkyl halide, is called

- a) Wurtz reaction
b) haloform reaction
c) Hunsdiecker reaction
d) dehalogenation.

63. Haloforms are trihalogen derivatives of

- a) ethane b) propane
c) methane d) alkane

64. The starting substance for preparing iodomethane is

- a) C_2H_5OH b) CH_3COCH_3
c) CH_3CHO d) CH_3OH

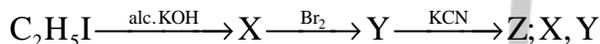
65. Which one of the following is used as a refrigerant?

- a) CCl_2F_2 b) $CH_2Cl.CO.CH_3$
c) CCl_4 d) CF_4

66. n-propyl bromide on treatment with ethanolic caustic potash produces

- a) propane b) propene
c) prop-2-ene d) propyne

67. In the reaction,

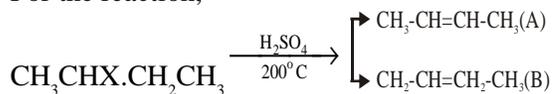


and Z are respectively

- a) $C_2H_4, C_2H_5Br, C_2H_5CN$
b) $C_2H_5OH, C_2H_5Br, C_2H_5CN$
c) $C_2H_4, CH_2Br-CH_2Br, CH_2CN.CH_2CN$



68. For the reaction,



which one of the following is true about the products?

- a) A predominates
b) B predominates.
c) A and B are in equal proportions
d) The ratio of A and B depends on X.

69. Which one of the following is the product of the reaction of but-1-yne with excess of HBr ?

- a) 2, 2-dibromobutane
b) 1, 2-dibromobutane
c) 1, 2-dibromobutene
d) 1, 1, 2, 2-tetrabromobutane

70. Reaction of ethyl chloride with sodium in ether leads to the formation of

- a) propane b) pentane
c) iso-butane d) n-butane

72. An organic compound "A" on treatment with KCN followed by hydrolysis gives propionic acid. Then A is

- a) CH_3Cl b) $CH_3CH_2CH_2Cl$
c) CH_3CH_2Cl d) $CH_3CHCl.CH_3$

73. Which one of the following cannot give alkyl halide when treated with alcohol ?

- a) PCl_5 b) $HCl + ZnCl_2$
c) $NaCl$ d) $HCl + ZnCl_2$

74. The group which can be easily replaced by a halogen atom is

- a) hydroxyl b) aldehydic
c) ketonic d) nitro.

75. The reaction, $C_2H_5Cl + KOH(aq) \rightarrow C_2H_5OH + KCl$ is the example of a/an

- a) electrophilic addition
b) electrophilic substitution
c) nucleophilic addition
d) nucleophilic substitution.

76. Which one of the following methods cannot yield alkyl halide ?

- a) $C_2H_5OH + HCl$
b) $CH_3COOAg + Br_2$
c) $CH_2 = CH_2$
d) $CH_3CH_2OH + HX$

77. Propene can be obtained by the action of ethanolic potassium hydroxide on

- a) propyl bromide b) propanol
c) propane d) propyne

78. Reaction of Mg pieces with ethyl iodide in ether gives

- a) alkyl. magnesium iodide

- b) ethyl magnesium halide
c) ethyl magnesium iodide
d) alkyl magnesium halide
79. Alcohols give alkyl halides on treatment with
a) PCl_5 b) PCl_3
c) SOCl_2 d) all these
80. Alkyl halides on treatment with aqueous KOH give
a) olefins b) alkanes
c) alcohols d) acids
81. Sodium methoxide reacts with ethyl iodide to give
a) ethyl alcohol b) methoxy ethane,
c) diethyl ether d) ethylene
82. 1-chloro, 2-methylpropane with alc.KOH gives
a) propane b) but-1-ene
c) propyne d) isobutene
83. Which one of the following gives alkyl cyanide on treatment with an alkyl halide?
a) KCN b) AgCN
c) none of these d) both of these.
84. Alkyl isonitrile can be obtained from alkyl halide by the reaction with .
a) KCN b) AgCN
c) NaCN d) none of these.
85. Amongst the following the substance used as an antiseptic is
a) chloroform b) iodoform
c) acetone d) methanol
86. A silver salt of a fatty acid on heating with an alkyl halide gives an
a) ether b) alcohol
c) aldehyde d) ester
87. Which of the following is ethylene bromide?
a) $\text{CH}_3\text{CH}_2\text{Br}$ b) $\text{CH}_2\text{Br}\cdot\text{CH}_2\text{Br}$
c) $\text{CH}_3\cdot\text{CHBr}_2$ d) $\text{Br}_2\text{CHCHBr}_2$
88. In which one of the following reactions the alkyl halide undergoes nucleophilic substitution?
a) $\text{RX} + \text{H}_2\text{RH} + \text{HX}$
b) $\text{RX} + \text{KCN} \rightarrow \text{RCN} + \text{KX}$
c) $2\text{RX} + 2\text{NaR} \rightarrow \text{R-R} + 2\text{NaX}$
d) $\text{RX} + \text{Mg} \rightarrow \text{RMgX}$
89. Heterolysis of C-Cl bond in 2-methyl-2-chloro propane gives
a) t-butyl carbonium ion and chlorine free radical
b) t-butyl carbanion and chloride free radical.
c) t-butyl carbocation and chloride ion.
d) iso-butyl carbocation and chloride ion.
90. About SN^2 reaction some statements are given below.
(A) The rate of reaction is independent of the concentration of the nucleophile.
(B) The nucleophile attacks the carbon on the side opposite to that of leaving group.
(C) The reaction proceeds with bond formation and bond breaking, taking place simultaneously.
Among the above the true statements are
a) A and B b) A and C
c) B and C d) all
91. Alc. KOH is used for
a) dehydrogenation b) dehydrohalogenation
c) dehalogenation d) dehydration
92. Anti-Markownikoffs addition of HBr is not observed in
a) propene b) but-1-ene
c) but-2-ene d) pent-2-ene
93. In addition of HX to but-2-ene, the number of possible product(s) is / are
a) 1 b) 2
c) 3 d) unpredictable
94. Which one of the following is an example of elimination reaction ?
a) methane methyl chloride
b) alcohol alkene
c) alkene alkyl halide
d) ethylene ethanol
95. Three electron pairs are present, on central carbon atom, in
a) carbocation b) carbanion
c) free radical d) none of these
96. Which one of the following types of reactions takes place when a compound contains a double bond? .
a) substitution b) photolysis
c) addition d) none of these
97. Heterolytic fission of C-Cl bond gives a species in which the carbon atom is
a) sp^2 hybridised b) sp hybridised
c) sp^3 hybridised d) sp^2 hybridised
98. Which one of the following undergoes hydrolysis by SN^1 mechanism ?
a) n-butyl bromide b) n-propyl bromide
c) iso-butyl bromide d) ter-butyl bromide
99. The alkene which does not show Kharasch peroxide effect is
a) but-1-ene b) propene
c) but-2-ene d) 2-methyl propene
100. The peroxide effect is
a) Abnormal addition of HBr on symmetrical alkene
b) Effect of molecular weight of alkene on its properties.
c) Normal addition of HI on symmetrical alkene.

- d) Abnormal addition of HBr on unsymmetrical alkene.
101. In which one of the following, anti-Markownikoff's addition of HBr is possible?
- - $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$
 - $\text{C}_2\text{H}_5-\text{CH}=\text{CH}_2-\text{CH}_3$
 - all these
102. If A, B, C denote methyl iodide, methyl bromide and methyl chloride respectively, then the order of polarity of these molecules is
- $A > B > C$
 - $B > A > C$
 - $C > B > A$
 - $C > A > B$
103. The mixture of ethyl iodide and 1-iodopropane when treated with sodium metal, the possible product(s) is/are
- $\text{C}_4\text{H}_{10}, \text{C}_6\text{H}_{14}, \text{C}_5\text{H}_{12}$
 - $\text{C}_5\text{H}_{12}, \text{C}_6\text{H}_{14}$
 - $\text{C}_4\text{H}_{10}, \text{C}_6\text{H}_{14}$
 - C_5H_{12}
104. An organic compound A reacts with PCl_5 to give B. B reacts with sodium metal to give n-butane. A and B are respectively
- $\text{C}_2\text{H}_5\text{OH}, \text{C}_2\text{H}_5\text{ONa}$
 - $\text{C}_2\text{H}_5\text{Cl}, \text{C}_2\text{H}_5\text{OH}$
 - $\text{C}_2\text{H}_5\text{Cl}, \text{C}_2\text{H}_5\text{ONa}$
 - $\text{C}_2\text{H}_5\text{OH}, \text{C}_2\text{H}_5\text{Cl}$
105. An alkyl halide may be converted into an alcohol by
- addition
 - hydration
 - hydrolysis
 - dehydration
106. Which one of the following statements is true about ethyl bromide
- It reacts with AgCN to give ethyl cyanide
 - It reacts with alcoholic KOH to form ethanol
 - On treatment with Na it forms diethyl ether.
 - None
107. Both, ethane and methane can be separately prepared in a single step from
- CH_3Br
 - $\text{C}_2\text{H}_5\text{Br}$
 - CH_3CHO
 - $\text{C}_2\text{H}_5\text{OH}$
108. The no. of sp^2 and sp^3 -hybridised C-atoms in 2-phenylpropane are respectively
- 6,3
 - 6,2
 - 3,6
 - 2,6
109. The reactivity of halogen atom is maximum in
- isopropyl chloride
 - n-propyl bromide
 - n-propyl chloride
 - isopropyl bromide
110. C-X bond is strongest in
- CH_3Cl
 - CH_3Br

c) CH_3F d) CH_3I

Assertion and Reason Type-I

Choose the correct option out of the choices given below each question.

- (i) Both A and R are true and R is the correct explanation of A.
 (ii) A is true but R is false.
 (iii) A is false but R is true.
 (iv) Both A and R are false.

1. Assertion : Phosphorus chlorides (tri and penta) are preferred over thionyl chloride for the preparation of alkyl chlorides from alcohols.

Reason : Phosphorus chlorides give pure alkyl halides.

2. Assertion : The boiling points of alkyl halides decrease in the order : RI > RBr > RCl > RF

Reason : The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass.

3. Assertion : KCN reacts with methyl chloride to give methyl isocyanide

Reason : CN⁻ is an ambident nucleophile.

4. Assertion : *tert*-Butyl bromide undergoes Wurtz reaction to give 2, 2, 3, 3-tetramethylbutane.

Reason : In Wurtz reaction, alkyl halides react with sodium in dry ether to give hydrocarbon containing double the number of carbon atoms present in the halide.

5. Assertion : Presence of a nitro group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution.

Reason : Nitro group, being an electron withdrawing group decreases the electron density over the benzene ring.

6. Assertion : In monohaloarenes, further electrophilic substitution occurs at ortho and para positions.

Reason : Halogen atom is a ring deactivator.

7. Assertion : Aryl iodides can be prepared by reaction of arenes with iodine in the presence of an oxidising agent.

Reason : Oxidising agent oxidises I₂ into HI.

8. Assertion : It is difficult to replace chlorine by -



OH in chlorobenzene in comparison to that in chloroethane.

Reason : Chlorine-carbon (C—Cl) bond in chlorobenzene has a partial double bond character due to resonance.

9. Assertion : Hydrolysis of (–)-2-bromooctane proceeds with inversion of configuration.

Reason : This reaction proceeds through the formation of a carbocation.

10. Assertion : Nitration of chlorobenzene leads to the formation of *m*-nitrochlorobenzene

Reason : —NO₂ group is a *m*-directing group.

1. (ii) 2. (v) 3. (iv) 4. (i) 5. (i) 10. (v)
 11. (iii) 12. (i) 13. (iii) 14. (iv)

Assertion and Reason Type-II

1. If both Assertion & Reason are True and Reason is the correct explanation of Assertion.

2. If both Assertion & Reason are True but Reason is not the correct explanation of Assertion.

3. If Assertion is True but Reason is False.

4. If both Assertion & Reason are False.

1. Assertion : Addition of HBr on 2-butene gives two isomeric products.

Reason : Addition of HBr on 2-butene follows Markovnikov's rule.

2. Assertion : Benzyl bromide when kept in acetone water it produces benzyl alcohol.

Reason : The reaction follows S_N2 mechanisms.

3. Assertion : Alkyl benzene is not prepared by Friedel Crafts alkylation of benzene.

Reason : Alkyl halides are less reactive than aryl halides.

4. Assertion : Chloral is more reactive than acetaldehyde.

Reason : Chloro group increases the magnitude of positive charge on carbonyl carbon atom.

5. Assertion : Benzene yields only one product on monochlorination.

Reason : All the hydrogen atoms in benzene molecule are equivalent.

6. Assertion : In S_N¹ reaction if the alkyl halide is optically active then the product is a racemic mixture.

Reason : All tertiary halides gives racemic mixture.

7. **Assertion:** Chlorobenzene does not react with NaOH whereas ethyl chloride reacts.

Reason : The partial double bond between C and Cl causes less reactivity towards nucleophilic substitution.

8. **Assertion:** Alkyl halides are not soluble in water.

Reason : Alkyl halide does not form H-bonds with water although alkyl halide is polar in nature.

9. **Assertion:** Chloritone gives legal test.

Reason : Chloritone contains a keto group.

10. **Assertion:** Aryl halides are more reactive than alkyl halide towards NSR.

Reason : Intermediate carbocation obtained from Aryl halide is more stable .

11. **Assertion:** CHCl_3 is filled in dark coloured bottles upto top level of the bottle.

Reason : CHCl_3 gives phosgene when it comes in contact with air.

12. **Assertion:** CHI_3 gives yellow ppt with AgNO_3 while CHCl_3 does not gives any ppt.

Reason : CHCl_3 is colourless liquid while CHI_3 is yellowish solid.

13. **Assertion:** Ethyl chloride is more reactive than vinyl chloride towards nucleophilic substitution reactions.

Reason : Vinyl group is electron donating.

14. **Assertion:** Nucleophilic substitution reaction on an optically active halide gives a mixture of enantiomers.

Reason : Reaction should be in accordance with mechanism.

15. **Assertion:** $\text{CH}_3\text{CH}_2\text{Br} + \text{AgCN} \longrightarrow$

Reason : $-\text{CN}$ is an ambident nucleophile, therefore, reaction gives both cyanide and isocyanide.

Multiple Choice Questions
TYPE-2

- 01) Which of the following is a primary halide ?
 a) Isopropyl iodide
 b) *sec* - Butyl iodide
 c) *tert* - Butyl bromide
 *d) Neohexyl chloride.
- 02) Pick up the correct statement about alkyl halides
 a) They are associated with each other by H - bonds.
 b) They dissolve easily in organic solvents
 *c) They dissolve easily in organic solvents
 d) They do not contain any polar bond in their molecular
- 03) Which of the following will not form yellow ppt. on heating with alkaline solution of iodine ?
 a) $\text{CH}_3\text{CH}_2\text{OH}$ b) CH_3COCH_3
 *c) CH_3OH d) $(\text{CH}_3)_2\text{CHOH}$
- 04) Alkyl halides can be obtained by all methods except
 a) $\text{CH}_3\text{CH}_2\text{OH} + \text{HCl} / \text{ZnCl}_2 \longrightarrow$
 b) $\text{CH}_3 - \text{CH}_2 - \text{CH}_3 + \text{Cl}_2 \xrightarrow{\text{U.V. light}}$
 *c) $\text{C}_2\text{H}_5\text{OH} + \text{NaCl} \longrightarrow$
 d) $\text{CH}_3\text{COOAg} + \text{Br}_2 / \text{CCl}_4 \longrightarrow$
- 05) How many isomers are possible for $\text{C}_4\text{H}_9\text{Cl}$?
 a) 1 *b) 4
 c) 8 d) 10
- 06) For the preparation of chloroethane,
 *a) HCl gas is passed through ethanol in the presence of anhydrous ZnCl_2
 b) ethanol is treated with sodium chloride in the presence of dimethylamine
 c) ethyl sulphide is treated with hydrogen chloride
 d) Any of the above method can be employed.

ANSWERS

Q:	1	2	3	4	5	6
A :	4	2	4	1	1	3
Q:	7	8	9	10	11	12
A :	1	1	4	4	1	2
Q:	13	14	15			
A :	3	1	1			

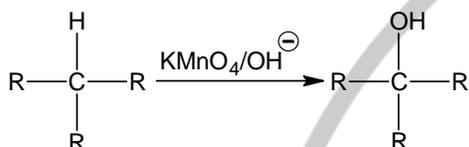
- 07) Which of the following compound is optically active ?
 a) 1 - butanol
 b) Isopropyl alcohol
 c) Acetaldehyde
 *d) 2 - butanol
- 08) For the preparation of n - propyl bromide from n - propyl alcohol which of the following reagent is most preferred ?
 *a) P_4/Br_2 b) HBr
 c) Br_2 d) NaBr.
- 09) Chlorination of methane proceeds by
 a) Electrophilic substitution
 b) Nucleophilic substitution
 *c) Free radical mechanism
 d) None of these
- 10) When silver propanoate is treated with iodine in CCl_4 , the main product formed is
 a) Iodoethane
 b) Propyl propanoate
 *c) Ethyl propanoate
 d) 1 - Iodopropane.
- 11) In order to prepare 1 - chloropropane which of the following reactants can be employed ?
 a) Propene and HCl in the presence of peroxide
 b) Propene and Cl_2 followed by treatment with aq KOH
 *c) Propanol - 1 and $SOCl_2$ / pyridine
 d) Any of the above can be used
- 12) Which of the following alkane forms halides in good yield ?
 a) Butane b) Propane
 c) Isobutane *d) Neopentane.
- 13) Thionyl chloride is preferred in the preparation of chlorine compounds from alcohols because
 a) The reaction goes to completion
 *b) They by products being gases, escapes hence there is no problem of separation of the product
 c) The reagent is cheap
 d) None of these
- 14) Only two isomeric monochloro derivatives are possible from
 a) n - Pentane
 b) 2, 4 - Dimethylpentane
 c) Benzene
 *d) 2 - Methylpropane.
- 15) Best conditions for SN^1 reaction is
 a) weak nucleophile and less polar solvent
 *b) weak nucleophile and more polar solvent
 c) strong nucleophile and more polar solvent
 d) strong nucleophile and less polar solvent
- 16) Neopentyl chloride on reaction with ethanolic KOH is likely to give
 a) Neopentyl alcohol b)
 Pentylene
 *c) 2 - Methyl - 2- butene
 d) undergo no reaction
- 17) In the reaction, $CH_3C \equiv \bar{C} \bar{N}^+ + (CH_3)_2CHCl$ the product formed is
 a) 4 - Methyl - 2 - pentyne only
 b) Propyne
 c) Propyne and propylene
 *d) Mixture of propene, propyne and 4 - methyl - 2 - pentyne.
- 18) During hydrolysis of 3^0 butyl bromide if concentration of aq KOH is doubled, rate of reaction is
 a) doubled
 *b) does not change
 d) may change
 d) may not change
- 19) An optically active halide when allowed to react with CN^- gives a racemic mixture, the halide is most likely
 a) primary b) sec - halide
 *c) tert - halide d) none of these
- 20) How many asymmetric carbon atom(s) is/are present in lactic acid.
 a) 2 b) 3
 d) 0 *d) 1.

ALCOHOLS, PHENOLS & ETHERS

PREPARATION OF ALCOHOLS

1. From Alkanes

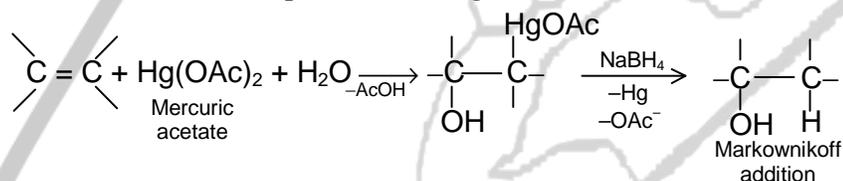
Alkanes having tertiary carbon on oxidation with cold alkaline KMnO_4 give tertiary alcohol.



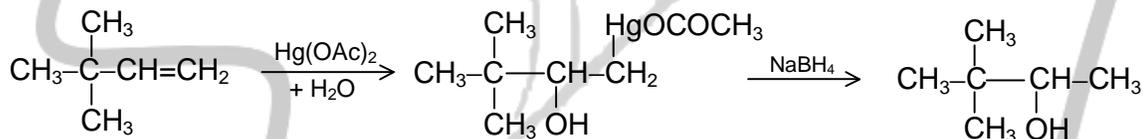
2. From Alkenes

Oxymercuration–Demercuration

Alkenes can be converted into alcohols by oxymercuration–demercuration reaction. In this reaction, addition of water takes place according to Markownikoff's rule.

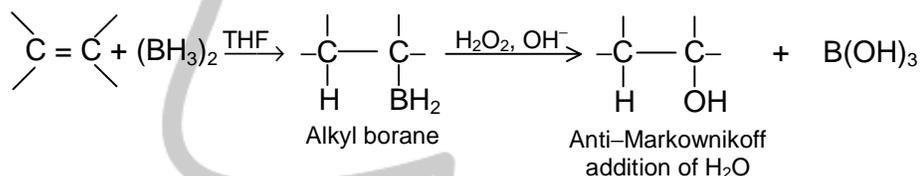


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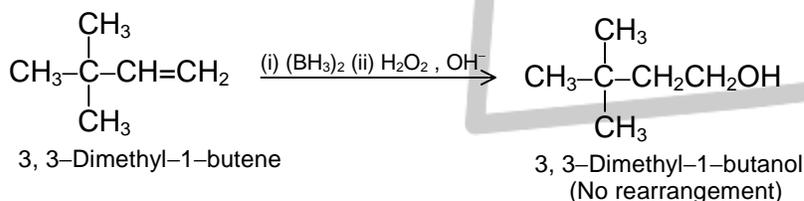


HYDROBORATION–OXIDATION

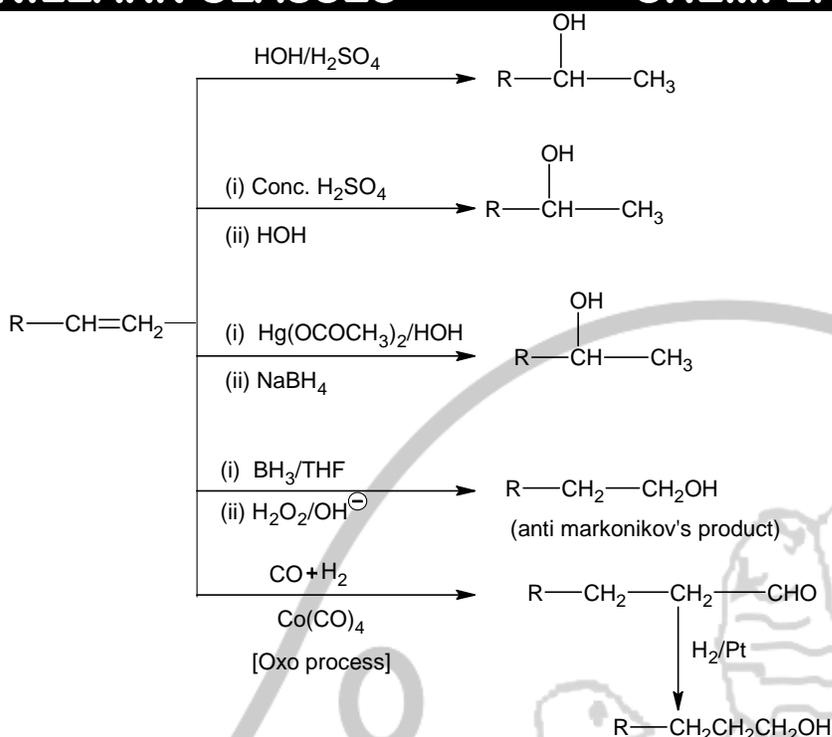
Alkenes react with diborane to form trialkyl boranes, which upon treatment with alkaline H_2O_2 give alcohols via anti-Markownikoff's addition of water.



For example,



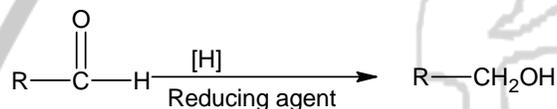
Alkenes can be converted into alcohol by the following reactions:



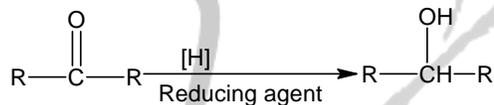
3. Reduction of aldehydes and ketones

(a) Reduction by reducing agents

(i) Aldehyde gives primary alcohol



(ii) Ketone gives secondary alcohol



Reducing agents

(i) LiAlH_4

(ii) NaBH_4

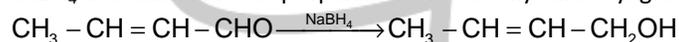
(iii) $\text{Na/C}_2\text{H}_5\text{OH}$

(iv) Metal (Zn, Fe or Sn)/Acid (HCl, dil H_2SO_4 or CH_3COOH)

(v) (a) Aluminium isopropoxide/isopropylalcohol (b) H_2O

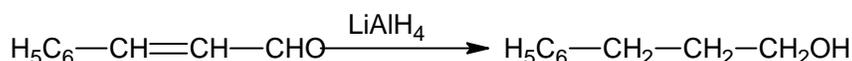
(vi) H_2/Ni

- NaBH_4 and aluminium isopropoxide reduces only carbonyl group and has no effect on any other group.



- Reduction with aluminium isopropoxide is known as Meerwein – Ponndorf Verley (MPV) reduction.

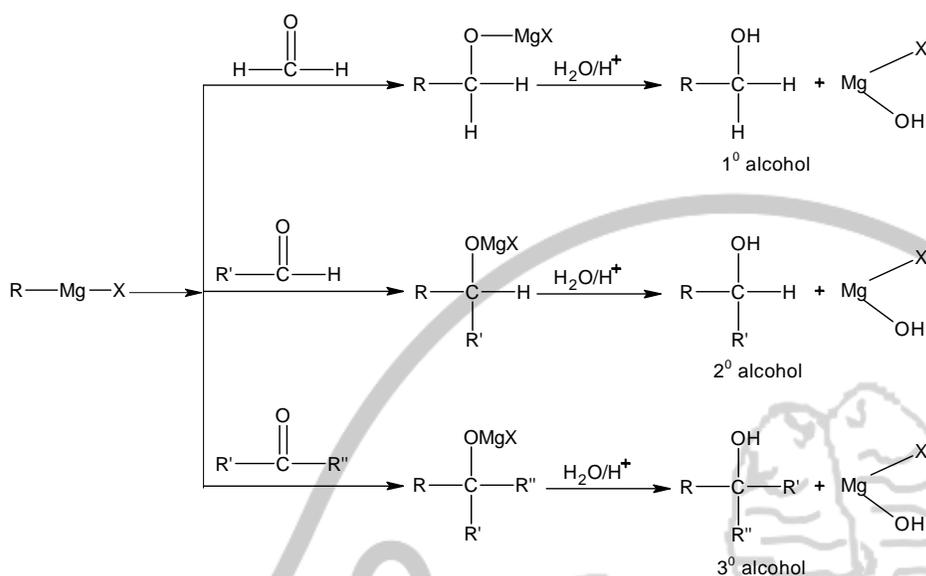
- LiAlH_4 has no effect on double and triple bonds but if compound is β -aryl, α, β -unsaturated carbonyl compound then double bond also undergoes reduction.



NOTES OF ALCOHOLS & ETHERS

(b) Reduction by Grignard reagents

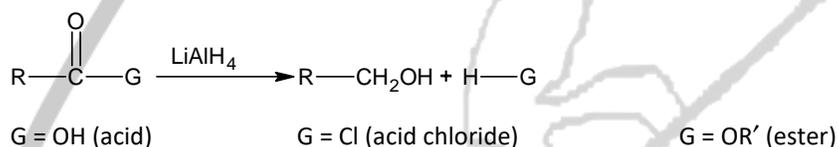
Addition followed by hydrolysis



- Methanol can not be prepared by this method.

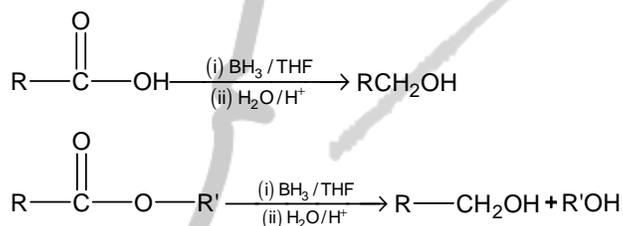
5. Reduction of carboxylic acid, Acid chlorides and esters:

(a) Reduction by LiAlH_4



(b) Reduction by BH_3

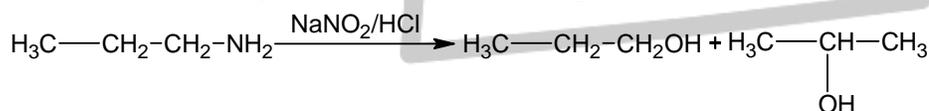
Carboxylic acids and esters are reduced in to primary alcohol by BH_3 .



6. From aliphatic primary amines

It react with nitrous acid to give alcohol.

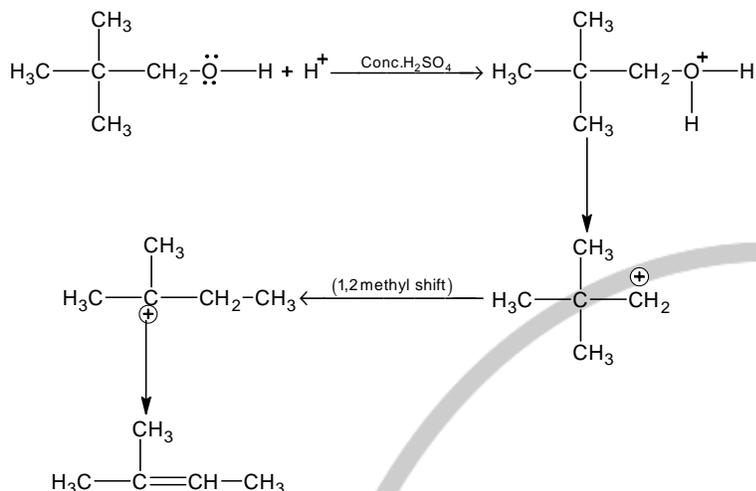
- Nature of alcohol depends on the nature of carbon having $-\text{NH}_2$ group.
- Reaction proceeds through carbocation hence rearranged alcohol is obtained.



PHYSICAL PROPERTIES

NOTES OF ALCOHOLS & ETHERS

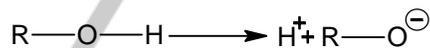
E₁ mechanism: follow saytzeff's rule.



(B) Reactions due to breaking of oxygen hydrogen bond.

(Reactions due to acidic character of alcohols)

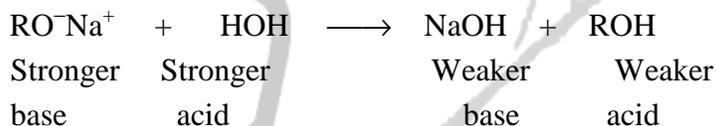
- (a) Alcohols are acidic in nature because hydrogen is present on electro negative oxygen atom.
 (b) Alcohol is weaker acid



acidity \propto stability of acid anions.

Acidity of $1^\circ > 2^\circ > 3^\circ$

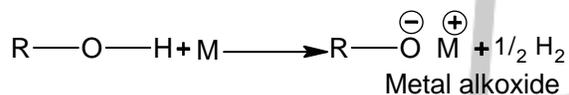
Alcohols give following reactions due to breaking of oxygen – hydrogen bond.



The order of acidity for some compounds is

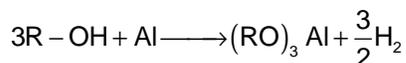


(i) Reaction with metal

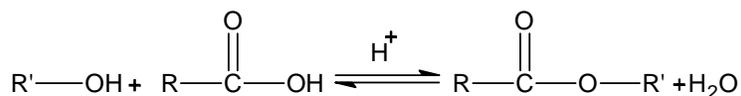


M = 1st group metal.

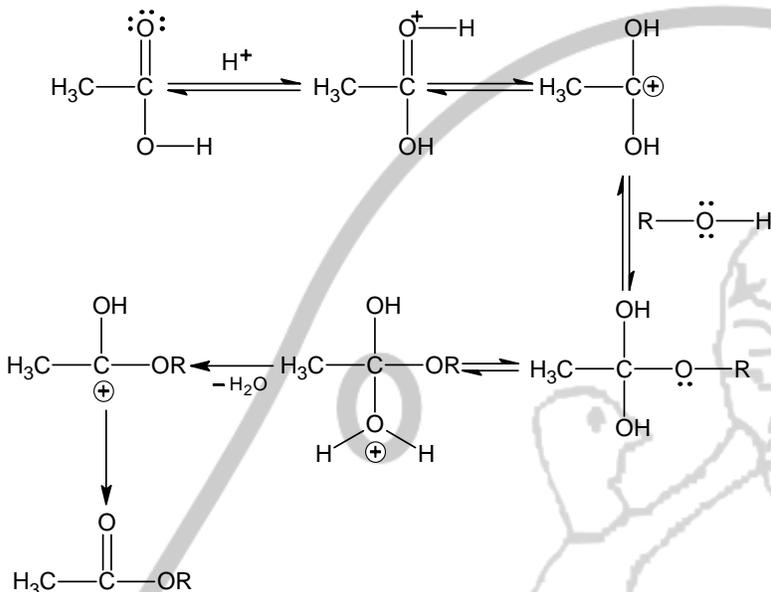
M = Al, Mg, Zn



Aluminium alkoxide

(ii) Esterification (With carboxylic acid)

It is reversible acid catalysed reaction. It follows S_N1 mechanism.



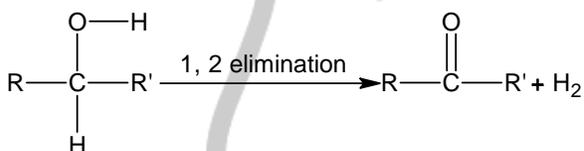
Increasing the size of alkyl group on alcohol part decreases the nucleophilic character because steric hindrance increases.

$$\left[\text{Reactivity} \propto \frac{1}{\text{Steric hindrance in RCOOH/ROH}} \right]$$

Order of reactivity of alcohols $CH_3OH > 1^\circ \text{ alc} > 2^\circ \text{ alc} > 3^\circ \text{ alc}$

Oxidation of alcohol

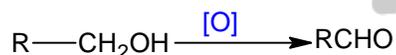
Oxidation of alcohol is dehydrogenation reaction which is 1, 2 – elimination reaction.



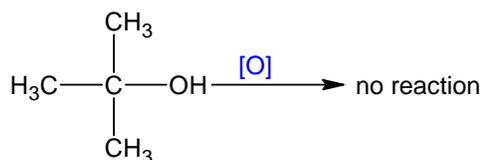
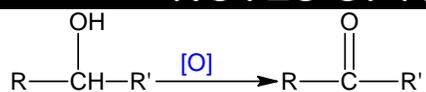
So oxidation of alcohol \propto numbers of α - hydrogen atom.

(a) With mild oxidising agents:

- | | |
|--|---------------------------------------|
| (i) X_2 | (ii) Fenton reagent $[FeSO_4/H_2O_2]$ |
| (iii) Jones reagent / $CH_3COCH_3 [CrO_3/dil. BaSO_4]$ | (iv) $K_2Cr_2O_7/H^+$ cold |



NOTES OF ALCOHOLS & ETHERS

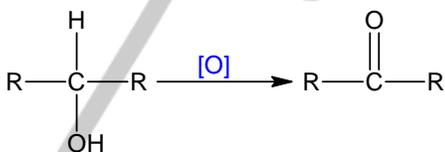
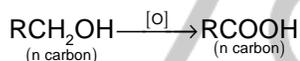
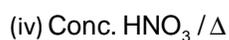
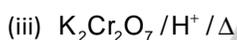


Note:

PCC (Pyridinium chloro chromate) is a selective reagent which converts 1° alc to aldehyde.

(b) With strong oxidising agent

Oxidising agents are

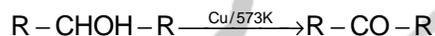


(C) Dehydrogenation with Cu/573K or Ag/573K

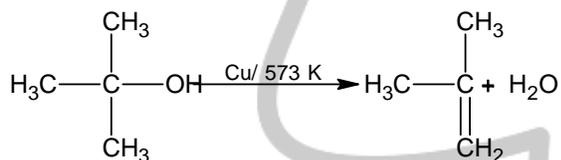
(a) 1° alcohol \longrightarrow aldehyde



(b) 2° alcohol \longrightarrow ketone



(c) 3° alc \longrightarrow undergo dehydration to form alkene.



Reduction



Distinguishing 1°, 2°, 3° alcohol

Test	1° alc	2° alc	3° alc
------	--------	--------	--------

(I) Lucas test $[ZnCl_2 + HCl]$	No reaction at room temperature	White turbidity after 5 – 10 min. $RCH(OH)R + HCl$ $\downarrow ZnCl_2$ $R-\underset{\substack{ \\ Cl}}{CH}-R + H_2O$	White turbidity instantaneously $R_3C-OH + HCl$ $\downarrow ZnCl_2$ R_3C-Cl
(II) Victor Meyer test $(P/I_2, AgNO_2, HNO_2, NaOH)$	Red colour	Blue colour	Colourless
	RCH_2OH $\downarrow P/I_2$ RCH_2I $\downarrow AgNO_2$ RCH_2NO_2 $\downarrow HONO$ $R-\underset{\substack{ \\ NOH}}{C}-NO_2$ Nitrolic acid $\downarrow NaOH$ $R-\underset{\substack{ \\ NO^-Na^+}}{C}-NO_2$ Sodium nitrostate (red)	$R-\underset{\substack{ \\ CHOH}}{CHOH}$ $\downarrow P/I_2$ $R-\underset{\substack{ \\ CHI}}{CHI}$ $\downarrow AgNO_2$ $R-\underset{\substack{ \\ CHNO_2}}{CHNO_2}$ $\downarrow HNO_2$ $R-\underset{\substack{ \\ N=O}}{C}-NO_2$ (Pseudo nitrole) $\downarrow NaOH$ Blue	R_3C-OH $\downarrow P/I_2$ R_3C-I $\downarrow AgNO_2$ R_3C-NO_2 $\downarrow HNO_2$ No reaction (colourless)

PHENOL

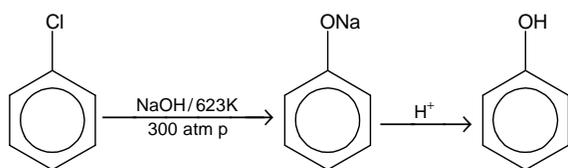
These are organic compounds a hydroxyl group attached directly to a benzene ring.

Preparation

(i) From chloro benzene (Dow's process)

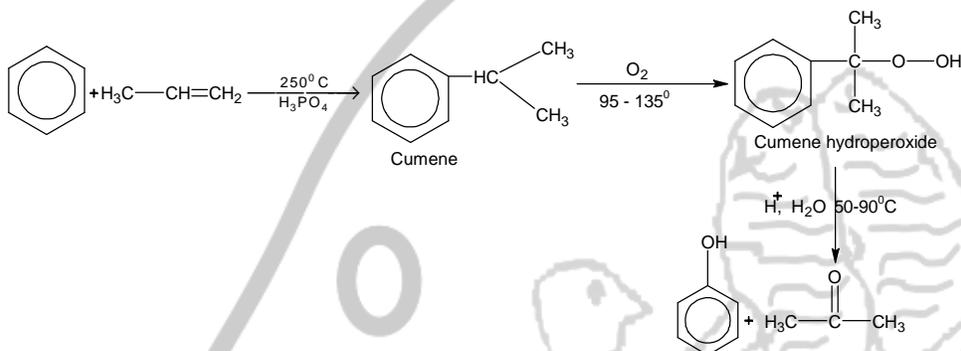
NOTES OF ALCOHOLS & ETHERS

Chlorobenzene is heated with NaOH at 673 K and under pressure of 300 atm to produce sodium phenoxide which on acidification yields phenol.



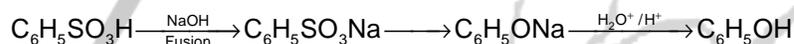
(ii) Cumene Process

Cumene obtained from propene & benzene cumene on air oxidation followed by acidification with H_2SO_4 gives phenol & acetone.



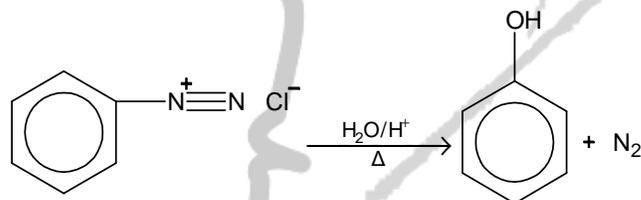
(iii) From benzene sulphonic acid

It is fused with NaOH gives sodium salt of phenol.



(iv) From benzene diazonium chloride

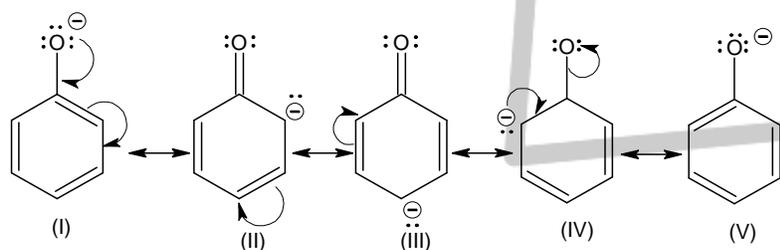
This gives Ar SN1 reaction with H_2O to form phenol.



Acidity of phenol

Phenol is weak acid. It reacts with aqueous NaOH to form sodium phenoxide, but does not react with sodium bicarbonate.

The acidity of phenol is due to the stability of the phenoxide ion, which is resonance stabilized as shown below:

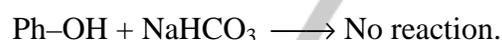


The C-atom in phenol is sp^2 -hybridised. So it is more electron withdrawing than the sp^3 -hybridised carbon atom of alcohols.

In substituted phenols, the presence of electron withdrawing groups at ortho and para positions such as nitro group, stabilizes the phenoxide ion resulting in an increase in acid strength. It is due to this reason that ortho and para nitro phenols are more acidic than phenol.

On the other hand, electron releasing groups such as alkyl group, do not favour the formation of phenoxide ion – resulting in decrease in acid strength.

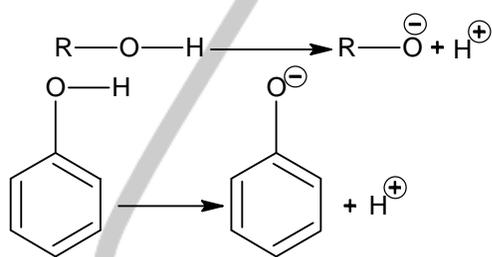
Phenol dissolves in NaOH, but it is insoluble in sodium bicarbonate solution as phenol is stronger acid than H_2O but weaker than carbonic acid.



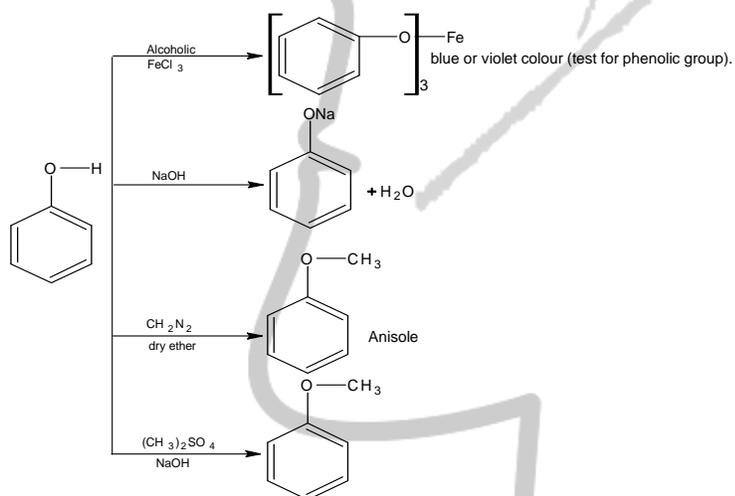
CHEMICAL REACTIONS

(A) Reaction due to breaking of O – H bond

Phenol is more reactive than alcohol for this reaction because phenoxide ion is more stable than the alkoxide ion.

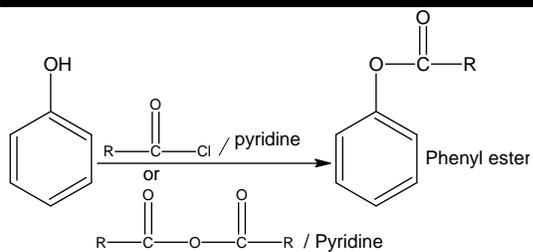


Reactions of phenol due to breaking of —O—H bond are given below:

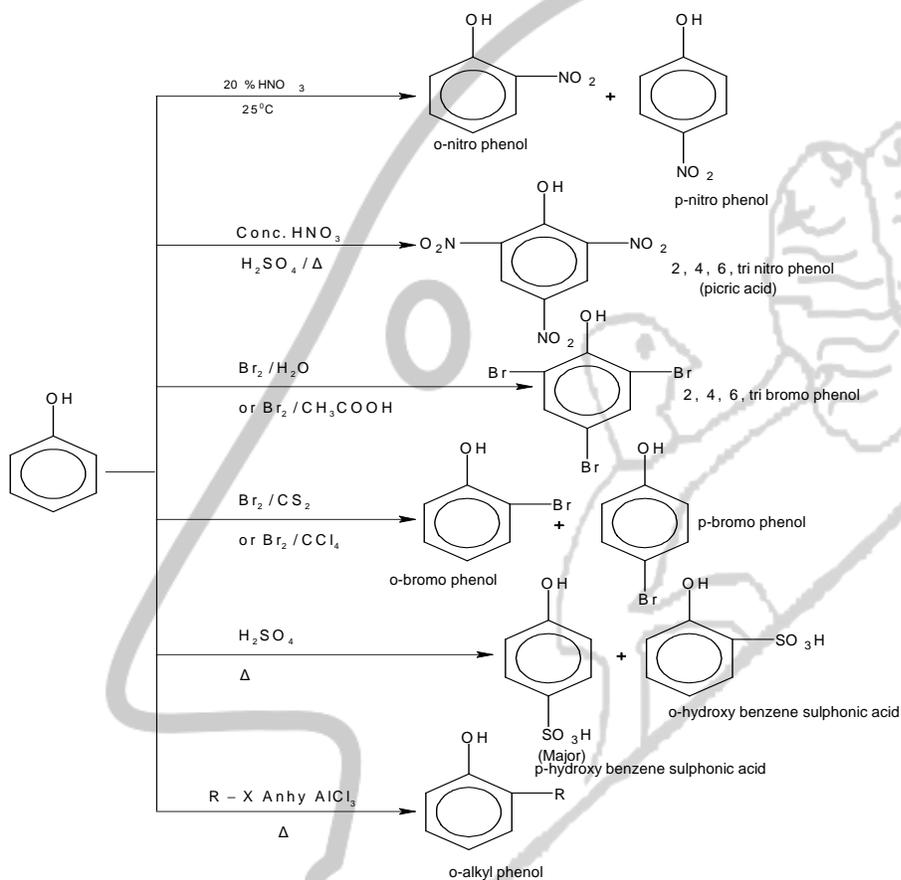


Acylation

NOTES OF ALCOHOLS & ETHERS

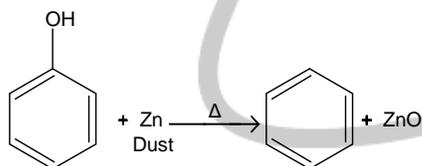


(C) **EAS in Phenol:** It is strong activating group.

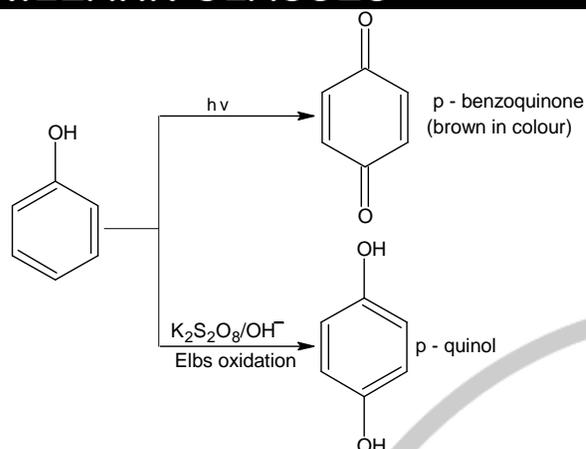


Miscellaneous reaction

(i) Reaction with Zn dust



(ii) Oxidation

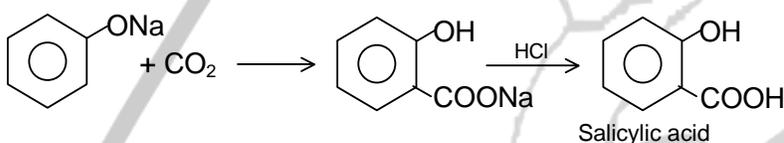


Mechanism of some important reactions

1. Reimer Tieman reaction



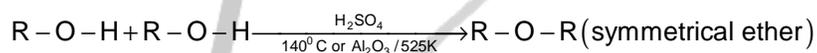
2. Kolbe's reaction



PREPARATION OF ETHERS

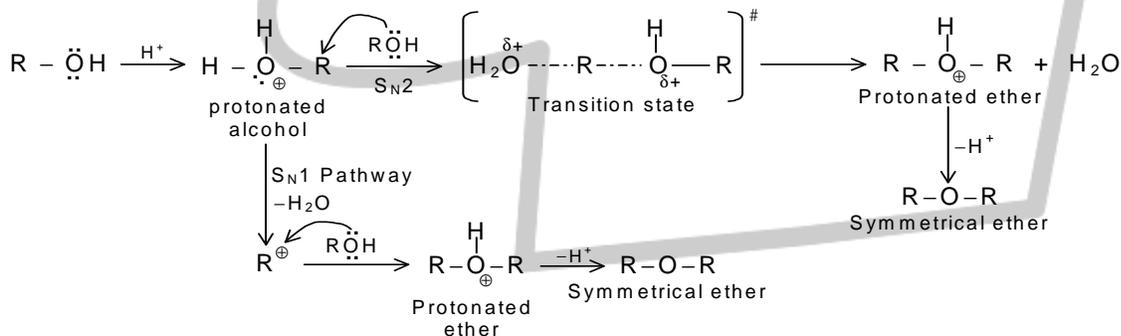
From 1° alcohol

(a) With H₂SO₄



Order of dehydration 1° > 2° > 3° alcohol

Dehydration of alcohols to ether is useful for the preparation of symmetrical ethers only. If we try to prepare unsymmetrical ether using a combination of two alcohols (ROH & R'OH), it leads to the formation of a mixture of three ethers (R-O-R, R-O-R' and R'-O-R').

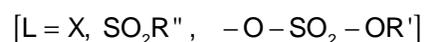
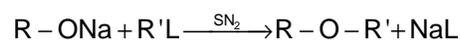


NOTES OF ALCOHOLS & ETHERS

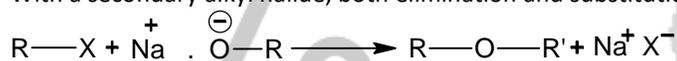
The reaction can proceed by S_N1 or S_N2 process. Primary alcohols react by S_N2 process and secondary & tertiary alcohols undergo reaction by S_N1 process.

Williamson's synthesis

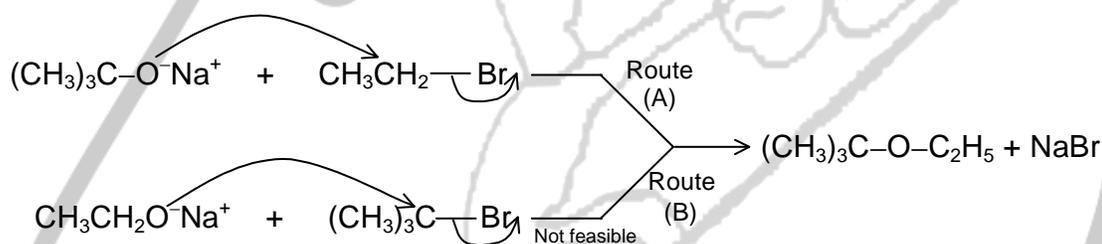
S_N2 reaction of a sodium alkoxide with alkyl halide, alkyl sulphonate or alkyl sulphate is known as Williamson synthesis of ethers.



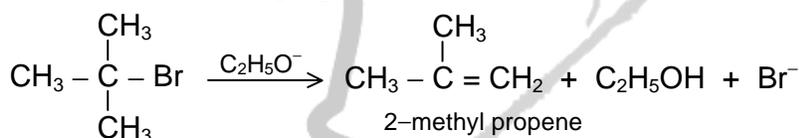
- In this reaction alkoxide may be alkoxide of primary, secondary as well as tertiary alcohol.
- Alkyl halide must be primary.
- In case of tertiary alkyl halide, elimination occurs giving alkenes
- With a secondary alkyl halide, both elimination and substitution products are obtained.



Suppose, we want to prepare ethyl *tert*-butyl ether. There are two possible routes to prepare it.



Route (A) is more suitable to prepare given ether as the alkyl halide involved in this route is a primary one while in route (B), the halide being a 3° , it will lead to elimination reaction forming an alkene, 2-methyl propene.

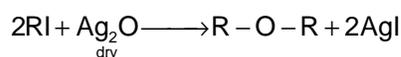


From Grignard reagent

Higher ethers can be prepared by treating α -halo ethers with suitable reagents.

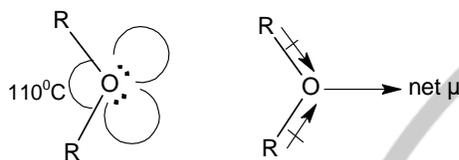


From Alkyl halide



PROPERTIES OF ETHERS**Dipole nature of ether**

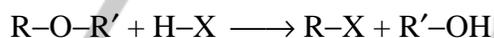
Ethers have a tetrahedral geometry i.e. oxygen is sp^3 hybridized. The C—O—C bond angle in ether is 110° . Because of the greater electronegativity of oxygen than carbon, the C—O bonds are slightly polar and are inclined to each other at an angle of 110° , resulting in a net dipole moment.



The bond angle is slightly greater than the tetrahedral angle due to repulsive interaction between the two bulky groups.

Chemical Reaction**1. Cleavage By Heating With Acids**

Ethers on reaction with acids (HX) in presence of heat undergoes cleavage to form an alkyl halide and an alcohol. Alcohol on further reaction with HX gives second molecule of alkyl halide.

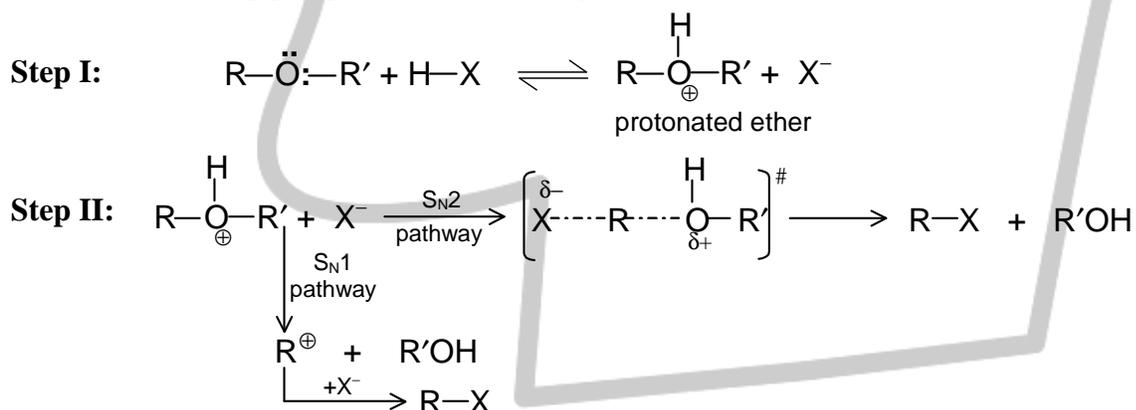


HI is more reactive towards ether than HBr and HBr is more reactive than HCl.

The cleavage of ethers takes place in vigorous conditions i.e. concentrated acids (HI and HBr) and at elevated temperatures.

Mechanism:

In the first step, ether is protonated by HX to give protonated ether. In the second step, halide ion acts as nucleophile and attacks protonated ether to undergo cleavage. This step is favoured because the leaving group (alcohol) is weakly basic.

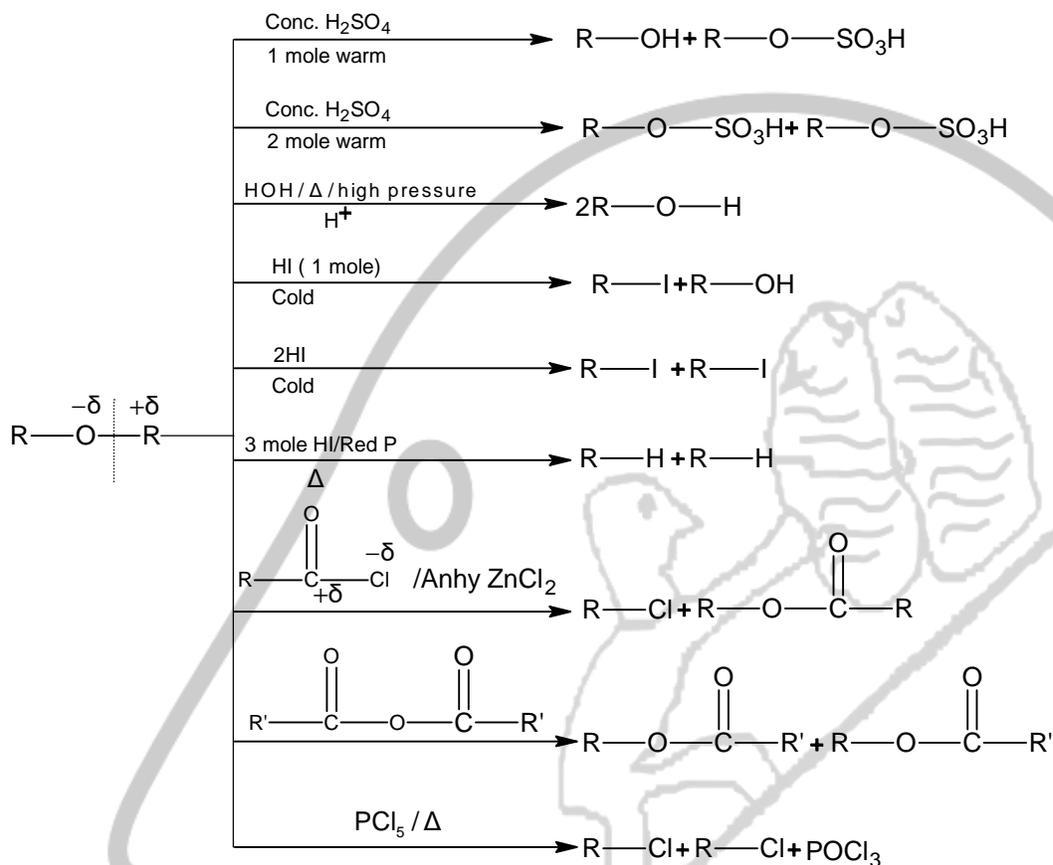


Reaction in second step can take the direction of S_N1 or S_N2 pathway, depending upon the conditions employed and the structure of ether. When both the alkyl groups are methyl or 1° , it

NOTES OF ALCOHOLS & ETHERS

will follow S_N2 reaction and when atleast one of the alkyl group is 3° , the reaction follows S_N1 pathway.

Nucleophilic substitution reactions



CH: Alcohols, Phenols & Ethers

(SUBJECTIVE ASSIGNMENT)

CONCEPTUALS

1. The C–O–C bond angle in dimethyl ether is 111.7°.

Ans. The bond angle is slightly greater than tetrahedral angle due to the repulsive interaction between the two bulky groups.

2. Alcohols have higher boiling points than ethers of comparable molecular masses.

Ans. It is due to the presence of strong inter molecular Hydrogen bonding in alcohols.

3. Phenols are more acidic than alcohols.

Ans. Due to high electronegativity of sp² hybridised carbon of phenol to which –OH is attached, electron density decreases on oxygen. This increases polarity of –OH bond and hence ionisation of phenol is easier as compared to alcohol

Also phenoxide is more stable than alkoxide ion so it favours the ionisation of phenol.

4. Nitrophenol is more acidic than o methoxyphenol.

Ans. Nitro group is electron withdrawing group which increases the acidic strength of phenol by stabilising the phenoxide ion.

Methoxy group is electron releasing group which decreases stability of phenoxide ion.

5. Phenol is more reactive towards electrophilic substitution reaction than benzene.

Ans. The –OH group is ortho, para directing and activates the benzene ring towards electrophilic substitution reaction.

6. Write the suitable reaction for the preparation of 1-methoxy-4-nitrobenzene

Ans. The major product is 2-methyl propene. Because sodium ethoxide is a nucleophile as well as base. So elimination reaction predominates over substitution.

To prepare t-butyl ethyl ether we use sodium alkoxide as tertiary.

7. o-nitrophenol is steam volatile but p-nitrophenol is not.

Ans. In O-nitro phenol intra molecular H-bond is formed while in p-nitro phenol intermol. H-bond is formed.

So O-nitro phenol is steam volatile.

8. phenol is less polar than ethanol.

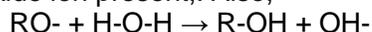
Ans. The (C-OH) in phenol possesses partial double bond character due to which its bond length is less so its dipole moment is small and hence it is less polar.

9. phenyl methyl ether reacts with HI to form phenol and iodomethane and not iodobenzene and methanol.

Ans. Phenoxide ion is more stable than methoxide ion due to delocalisation of –ve charge so phenol is formed.

10. methanol is less acidic than water.

Ans. Methoxide ion is less stable as compared to hydroxide ion because of electron releasing group methoxide ion present. Also,



This reaction shows that water is a better proton donor than alcohol.

11. Acidic dehydration of alcohol is only suitable to prepare primary ethers only? Why.

Ans. Because the dehydration of 2° and 3° alcohol will lead to elimination reaction due to which alkene is formed.

NOTES OF ALCOHOLS & ETHERS

As the 3° or 2° carbocation is more stable and due to hindrance in 2° or 3° carbocation substitution will not occur.

12. In esterification Rxn with acid chloride we use pyridine also? Why?

Ans. Pyridine is used to neutralise HCl which formed during the reaction. So it shifts the equilibrium to right hand side.

13. phenols do not give protonation reaction readily.

Ans. The lone pair on oxygen of O-H in phenol is being shared with benzene ring through resonance. Thus, lone pair is not fully present on oxygen and hence phenols do not undergo protonation reactions.

14. Explain why propanol has higher boiling point than that of the hydrocarbon, butane?

OR

Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

Ans. The molecules of Butane are held together by weak van der Waal's Forces of attraction while those of propanol are held together by stronger intermolecular hydrogen bonding.

15. Dehydration of alcohols to form an alkene is always carried out with conc. H_2SO_4 and not with conc. HCl or HNO_3 . Explain.

Ans. In acidic medium alcohols protonated then loses H_2O to form a carbo cation. If HCl Cl- strong nucleophile cause nucleophilic substitution, HNO_3 causes oxidation.

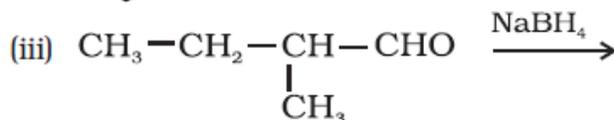
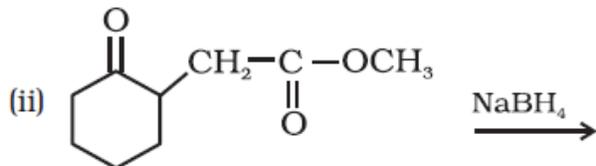
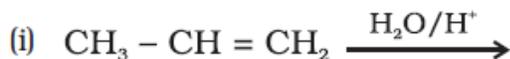
FOR PRACTICE

- alcohols can act as weak base as well as weak acids.
- Explain why nucleophilic substitution reactions are not very common in phenols.
- Out of benzene and phenol, which one is more easily nitrated and why?
- Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.
- Explain the fact that in aryl alkyl ethers (i) the alkoxy group activates the benzene ring towards electrophilic substitution and (ii) it directs the incoming substituents to ortho and para positions in benzene ring.
- Ortho and para nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.
- Propanol has higher boiling point than butane.
- ortho-Nitrophenol is more acidic than o-methoxyphenol.

REACTION COMPLETION

INCREASING/DECREASING ORDER

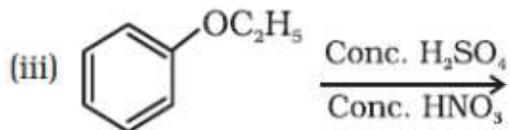
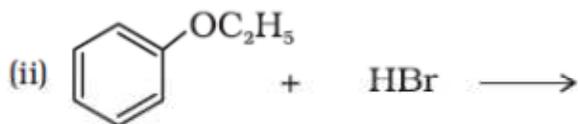
1. Write structures of the products of the following reactions:



2. Predict the major product of acid catalysed dehydration of

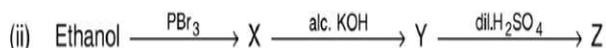
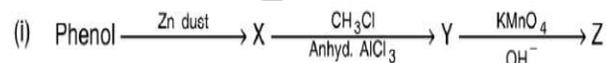
(i) 1-methylcyclohexanol and (ii) butan-1-ol

3. Predict the products of the following reactions:



4. Write the reactions of Williamson synthesis of 2-ethoxy-3-methylpentane starting from ethanol and 3-methylpentan-2-ol.

5. Identify X, Y and Z in the following sequence of reactions :



1. Arrange the following sets of compounds in order of their increasing boiling points:

(a) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol.

(b) Pentan-1-ol, n-butane, pentanal, ethoxyethane.

2. Arrange the following compounds in increasing order of their acid strength:

Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-methylphenol.

3. Arrange the following in the increasing order of property shown :

(i) methanol, ethanol, diethylether, ethyleneglycol. (Boiling points)

(ii) phenol, o-nitrophenol, m-nitrophenol, p-nitrophenol. (Acid strength)

(iii) dimethylether, ethanol, phenol. (Solubility in water)

(iv) butanol, 2-methylpropan-1-ol, 2-methylpropan-2-ol. (Acid strength)

PREDICTION

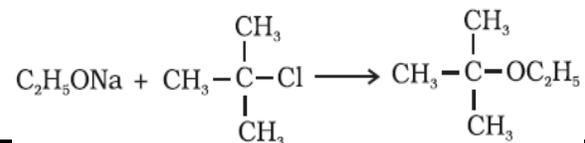
1. Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal ?



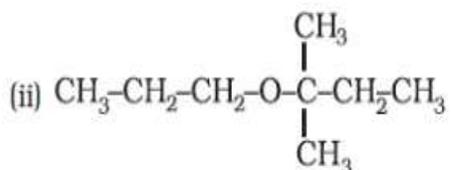
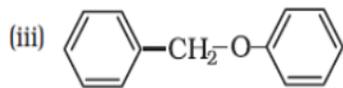
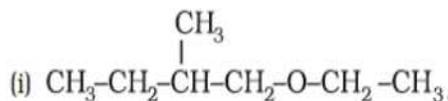
2. The following is not an appropriate reaction for the preparation of t-butyl ethyl ether.

(i) What would be the major product of this reaction ?

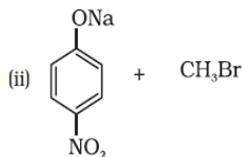
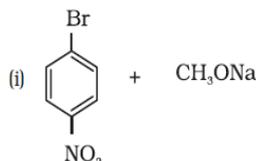
(ii) Write a suitable reaction for the preparation of butylethyl ether.



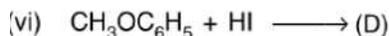
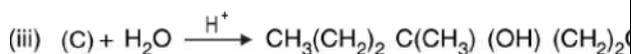
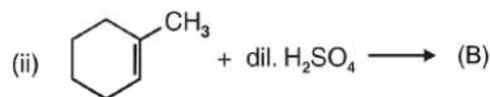
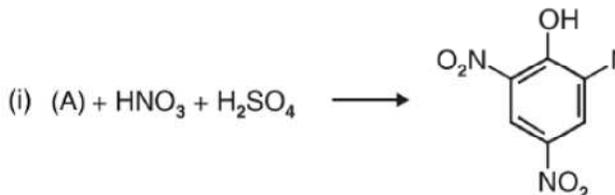
3. Give the major products that are formed by heating each of the following ethers with HI.



4. Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?



5. Identify the missing reactant or product A to D in the following equations:



6. Name the reagents used in the following reactions:

(i) Benzyl alcohol to benzoic acid.

(ii) Dehydration of propan-2-ol to propene.

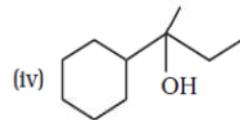
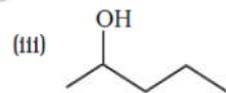
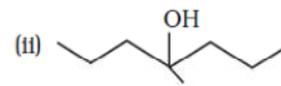
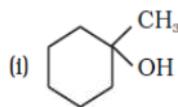
(iii) Butan-2-one to butan-2-ol.

7. Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

(i) 1-Propoxypropane (ii) Ethoxybenzene

(iii) 2-Methoxy-2-methylpropane (iv) 1-Methoxyethane

8. Show how would you synthesise the following alcohols from appropriate alkenes?



9. An alcohol A ($\text{C}_4\text{H}_{10}\text{O}$) on oxidation with acidified potassium dichromate gives carboxylic acid B ($\text{C}_4\text{H}_8\text{O}_2$). Compound A when dehydrated with conc. H_2SO_4 at 443 K gives compound C. Treatment of C with aqueous H_2SO_4 gives compound D ($\text{C}_4\text{H}_{10}\text{O}$) which is an isomer of A. Compound D is resistant to oxidation but compound A can be easily oxidised. Identify A, B, C and D and write their structures.

[Ans. : [A] : $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$

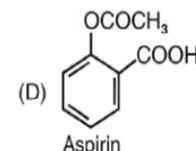
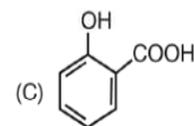
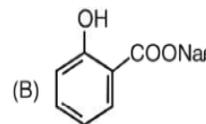
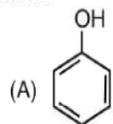
[B] : $\text{CH}_3\text{CH}(\text{CH}_3)\text{COOH}$

[C] : $(\text{CH}_3)_2\text{C}=\text{CH}_2$ [D] : $(\text{CH}_3)_3\text{C}-\text{OH}$

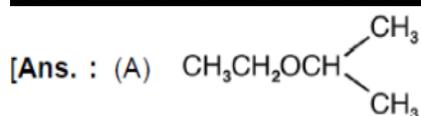
10. An organic compound A having molecular formula $\text{C}_6\text{H}_6\text{O}$ gives a characteristic colour with aqueous FeCl_3 . When A is treated with NaOH and CO_2 at 400 K under pressure, compound B is obtained. Compound B on acidification gives compound C which reacts with acetyl chloride to form D which is a popular pain killer. Deduce the structure of A, B, C and D.

What is the common name of Drug D?

[Ans. :

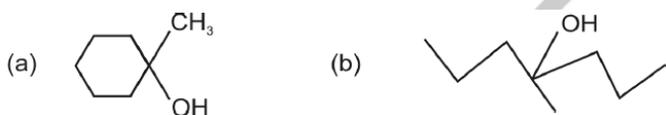


11. An ether A ($\text{C}_5\text{H}_{12}\text{O}$) when heated with excess of hot concentrated HI produced two alkyl halides which on hydrolysis from compounds B and C. Oxidation of B gives an acid D whereas oxidation of C gave a ketone E. Deduce the structures of A, B, C, D and E.



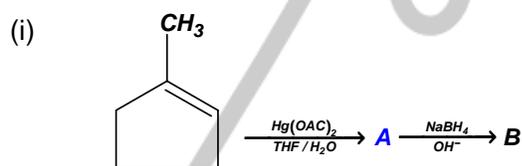
- (B) $\text{CH}_3\text{CH}_2\text{OH}$
- (C) $\text{CH}_3\text{CHOHCH}_3$
- (D) CH_3COOH
- (E) CH_3COCH_3

12. Synthesise the following alcohols from suitable alkenes.

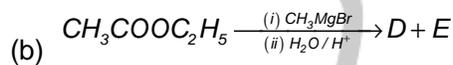
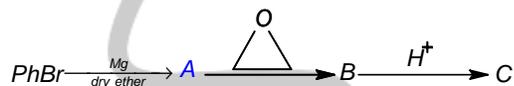


D.P-1

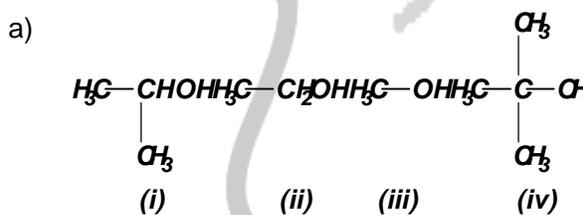
1. Find A and B.



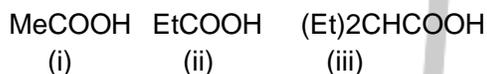
2. (a) Find A, B, C, D, E.



3. Arrange the following in increasing order of acidic strength.



(b) Arrange the following in increasing order of esterification:



4. Arrange the following alcohols in order of ease of dehydration.

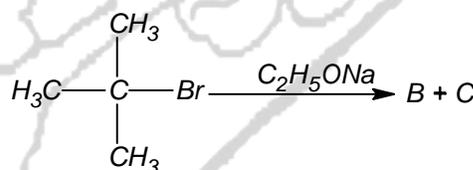
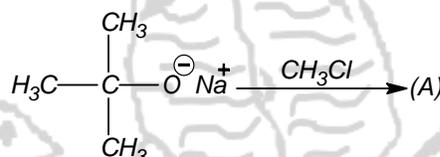


D.P-2

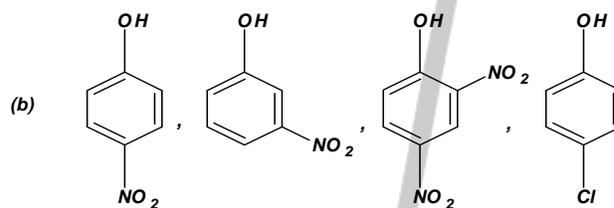
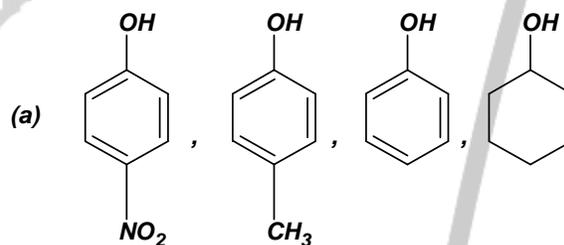
1. Give equations of the following reactions:

- (i) Oxidation of propan-1-ol with alkaline KMnO_4 solution.
- (ii) Bromine in CS_2 with phenol.
- (iii) Dilute HNO_3 with phenol.
- (iv) Treating phenol with chloroform in presence of aqueous NaOH .

2. Write the product



3. Arrange each group of compounds in order of decreasing acidity:



4. Name the reagents used in the following reactions:

- (i) Oxidation of a primary alcohol to carboxylic acid.

- (ii) Oxidation of a primary alcohol to aldehyde.
 (iii) Bromination of phenol to 2,4,6-tribromophenol.

5. Write the structures of the major products expected from the following reactions:

- (a) Mononitration of 3-methylphenol
 (b) Dinitration of 3-methylphenol
 (c) Mononitration of phenyl methanoate.

6. Write the equation of the reaction of hydrogen iodide with:

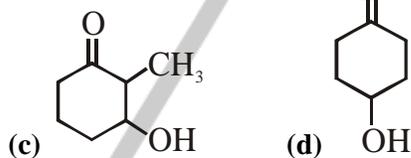
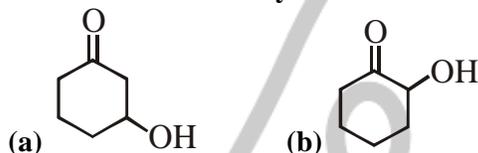
- (i) 1-propoxypropane (ii) methoxybenzene and
 (iii) benzyl ethyl ether.

7. A compound A (C_2H_6O) on oxidation by PCC gave B, which in treatment with aqueous alkali and subsequent heating furnished C. B on oxidation by $KMnO_4$, forms a monobasic carboxylic acid with molar mass $60g\ mol^{-1}$. Deduce the structure of A, B and C.

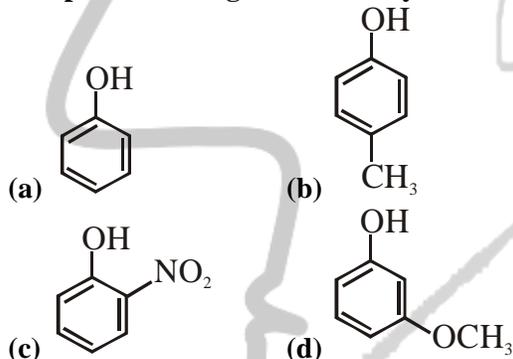
OBJECTIVE QUESTIONS (ALCOHOL, PHENOLS & ETHER)

- Which of the following alcohols is prepared by acid catalysed hydration of alkenes?
 - Butan - 1 - ol.
 - Propan - 1 - ol
 - ethanol
 - methanol
- Which of the following alcohols can be prepared by direct hydration of corresponding alkene in presence of 50% sulphuric acid?
 - Butan - 1 - ol
 - Butan - 2 - ol
 - 2 - Methylpropan - 1 - ol
 - 2-Methylpropan - 2 - ol
- Which of the following alcohols cannot be prepared by reduction of carbonyl compounds?
 - Pentan - 1 - ol
 - Pentan - 2 - ol
 - 2 - Methylpentan - 2 - ol
 - 3 - Methylpentan - 2 - ol
- Which of the following conversions explains the acidic nature of alcohols?
 - EthanolBromoethane
 - EthanolSodium ethoxide
 - EthanolChloroethane
 - EthanolChloroethane
- Which of the following compounds gives 3-ethylpentan-3-ol by the action of ethyl magnesium iodide followed by acid hydrolysis?
 - Propanone
 - Butanone
 - Pentan - 2 - one
 - Pentan - 3 - one
- Which of the following compound is obtained as major product on reaction of ethoxybenzene with nitrating mixture?
 - 2 - Nitro ethoxybenzene
 - 3 - Nitro ethoxybenzene
 - 4 - Nitro ethoxybenzene
 - Nitrobenzene
- Benzyl phenyl ether reacts with hydrogen bromide to give
 - benzyl bromide and phenol
 - benzyl alcohol and bromobenzene
 - benzyl bromide and bromobenzene
 - benzyl alcohol and phenol
- Ethers are considered as
 - monoalkyl derivatives of water

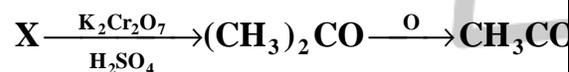
- (b) alkoxy derivatives of alkanes
 (c) alkyl derivatives of fatty acids
 (d) condensation products of acid and alcohol
9. Which of the following compounds is not isomeric with ethoxyethane?
 (a) 1 - Methoxypropane
 (b) 2 - Methoxypropane
 (c) 2 - Methylpropan - 2 - ol
 (d) 2 - Methylbutan - 2 - ol
10. Which one of the following compounds dissolves in hot dilute sulphuric acid but does not reacts with sodium metal?
 (a) ethyl bromide (b) acetic acid
 (c) ethyl alcohol (d) diethyl ether
11. Which of the following alcohol will have the fastest rate of dehydration?



12. The phenol having lowest acidity is



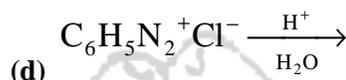
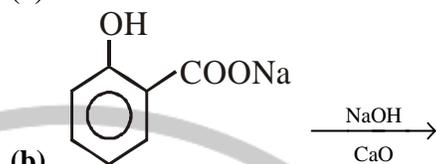
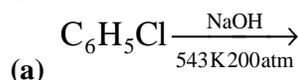
14. Which of the following is an excellent antiseptic?
 (a) Benzaldehyde (b) Benzyl alcohol
 (c) Phenol (d) Acetic acid
16. Which of the following gives anisole?
 (a) Phenyl and methyl chloride
 (b) Benzyl alcohol and sodium hydroxide
 (c) Aniline with nitrous acid
 (d) Sodium phenoxide and methyl chloride
17. In the reaction



the compound X is

- (a) Ethyl alcohol (b) Isopropyl alcohol

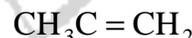
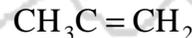
- (c) Tert-butyl alcohol (d) n-Propyl alcohol
18. Which of the following methods does not give phenol?



19. Which of the following groups increases the acidity of phenol?

- (a) -CN (b) -X (halogen)
 (c) -NO₂ (d) all

21. Vinyl carbinol is



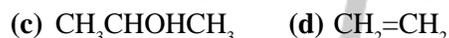
22. Intramolecular hydrogen bonding is found in

- (a) o-bromophenol (b) o-nitrophenol
 (c) m-nitrophenol (d) p-nitrophenol

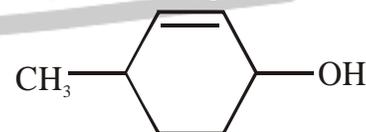
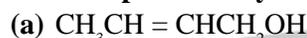
23. How many isomeric acyclic alcohols and ethers are possible for C₄H₈O?

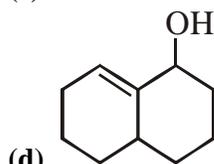
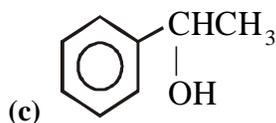
- (a) 3 (b) 4
 (c) 5 (d) 7

24. Unknown compound (X) on hydration by conc. H₂SO₄ gives (Y). The compound (Y) on oxidation gives acetone. The compound (X) is



25. An example of benzylic alcohol is





26. Which of the following isomers of butanol has a chiral structure?

- (a) $(\text{CH}_3)_3\text{CH}_2\text{OH}$
 (b) $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$
 (c) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$
 (d) $\text{CH}_3(\text{CH}_2)_3\text{OH}$

27. A compound X with molecular formula $\text{C}_3\text{H}_8\text{O}$ can be oxidised to a compound Y with the molecular formula $\text{C}_3\text{H}_6\text{O}_2$. X is most likely to be

- (a) Primary alcohol (b) sec. alcohol
 (c) aldehyde (d) ketone

28. Raney nickel is a/an

- (a) alloy of Al and Ni leached in sodium hydroxide solution
 (b) alloy of Al and Fe leached in caustic soda solution
 (c) alloy of Fe and Co leached in soda bicarbonate
 (d) all of these

29. Phenol is less acidic than

- (a) Ethanol (b) Methanol
 (c) o-Nitrophenol (d) p-Methyl phenol

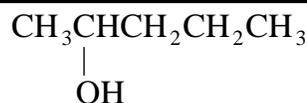
30. The increasing order of acidity among phenol:

p-methyl, m-nitrophenol and p-nitrophenol is

- (a) phenol, p-methyl phenol, p-nitrophenol, m-nitrophenol
 (b) p-methyl phenol, phenol, m-nitrophenol, p-nitrophenol
 (c) p-nitrophenol, m-nitrophenol, phenol, p-methyl phenol
 (d) m-nitrophenol, p-nitrophenol, phenol, p-methyl phenol

31. An alcohol having molecular formula $\text{C}_6\text{H}_{11}\text{OH}$ on dehydration gives an alkene, which on oxidation yield a mixture of ketone and acid. The alcohol is

- (a) $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$



- (b) $(\text{CH}_3)_2\text{CHCH}(\text{OH})\text{CH}_3$
 (c) $(\text{CH}_3)_3\text{CCH}_2\text{OH}$

32. The correct IUPAC name of the compound $\text{CH}_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2(\text{OH})\text{CH}_3$ is

- (a) 2-Ethylpentan-4-ol
 (b) 2-Hydroxy-4-methyl pentane
 (c) 4-Ethylpentan-2-ol
 (d) 4-Methylhexan-2-ol

33. Phenol can be industrially prepared from cumene. It is

- (a) Isopropyl benzene
 (b) o-Dimethylbenzene
 (c) Phenyl acetate
 (d) 2-Acetoxybenzoic acid

34. Consider the following alkyl halides

- 1) $(\text{CH}_3)_3\text{CBr}$ 2) CH_3Br
 3) $\text{C}_2\text{H}_5\text{Br}$ 4) $\text{CH}_3\text{CHBrCH}_3$

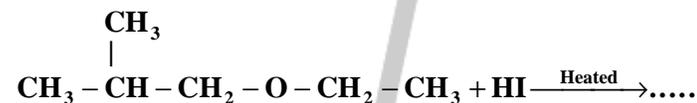
Arrange these alkyl halides in decreasing order of reactivity in Williamson's reaction.

- (a) $2 > 3 > 4 > 1$ (b) $4 > 3 > 2 > 1$
 (c) $1 > 4 > 3 > 2$ (d) $1 > 2 > 3 > 4$

35. Which one of the following compound is most acidic

- (a) $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{OH}$ (b)
- (c) (d)

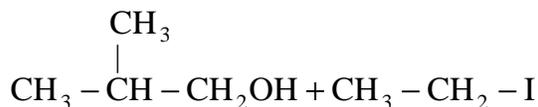
36. In the reaction



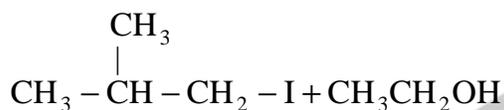
Which of the following compounds will be formed

- (a) $\text{CH}_3 - \overset{\text{CH}_3}{\underset{|}{\text{C}}} - \text{CH}_3 + \text{CH}_3\text{CH}_2\text{OH}$
 (b) $\text{CH}_3 - \overset{\text{CH}_3}{\underset{|}{\text{C}}} - \text{CH}_2\text{OH} + \text{CH}_3\text{CH}_3$

(c)



(d)



37. During dehydration of alcohols to alkenes by heating with conc. H_2SO_4 , the initial step is

- (a) formation of an ester
- (b) protonation of alcohol molecule
- (c) formation of carbocation
- (d) elimination of water

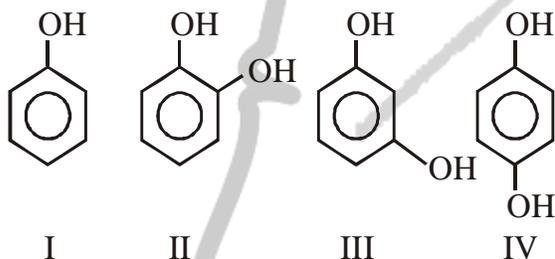
38. Which of the following alcohols cannot be prepared by the action of a suitable Grignard reagent as an aldehyde or a ketone followed by hydrolysis?

- (a) Ethyl alcohol
- (b) Isopropyl alcohol
- (c) n-Propyl alcohol
- (d) Methanol

39. The best reagent to convert pent-2-en-2-ol into pent-3-en-2-one is

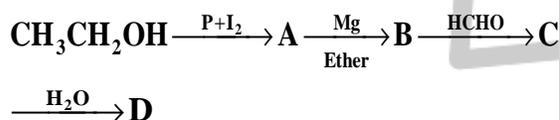
- (a) acidic permagnate
- (b) acidic dichromate
- (c) chromic anhydride in glacial acetic acid
- (d) pyridinium chloro chromate

40. Arrange the following compounds according to decreasing boiling points



- (a) (IV) > (III) > (II) > (I)
- (b) (III) > (IV) > (II) > (I)
- (c) (I) > (II) > (III) > (IV)
- (d) (III) > (II) > (I) > (IV)

41. In the following sequence of reactions



The compound 'D' is

- (a) n-butyl alcohol
- (b) n-propyl alcohol
- (c) propanal
- (d) butanal

42. Hydrolysis of 2-bromo-2-methylbutane by SN^1 mechanism gives mainly

- (a) 3-methylbutan-2-ol
- (b) 2-methylbutan-2-ol
- (c) 2,2-dimethylpropan-2-ol
- (d) 2-methylbutan-1-ol

43. In the following reaction, C is _____



- (a) $\text{H}_2\text{C}=\text{CH}$
- (b) $\text{CH}_3\text{CH}_2\text{OH}$
- (c) $\text{C}_2\text{H}_5-\text{OC}_2\text{H}_5$
- (d) $\text{C}_2\text{H}_5-\text{OSO}_3\text{H}$

44. The compound which is not isomeric with diethyl ether is

- (a) n-Propyl methyl ether
- (b) butan-1-ol
- (c) 2-Methylpropan-2-ol
- (d) Butanone

45. The most suitable reagent for the conversion of primary alcohol into aldehyde with the same number of carbon is

- (a) acidic $\text{K}_2\text{Cr}_2\text{O}_7$
- (b) acidified KMnO_4
- (c) Pyridinium chlorochromate
- (d) CrO_3

46. A compound 'X' undergoes reduction with LiAlH_4 to yield 'Y'. when vapours of 'Y' are passed over freshly reduced copper at 300°C , 'X' is formed. What is 'Y'?

- (a) CH_3COCH_3
- (b) CH_3CHO
- (c) $\text{CH}_3\text{CH}_2\text{OH}$
- (d) CH_3OCH_3

47. n-Propyl alcohol and isopropyl alcohol can be chemically distinguished by which reagent?

- (a) PCl_5
- (b) reduction
- (c) oxidation with potassium dichromate
- (d) ozonolysis

48. When $\text{CH}_2=\text{CH}-\text{COOH}$ is reduced with LiAlH_4 , the compound obtained will be

- (a) $\text{CH}_3-\text{CH}_2-\text{COOH}$
- (b) $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$
- (c) $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{OH}$
- (d) $\text{CH}_3-\text{CH}_2-\text{CHO}$

49. Which type of carbocation is formed as an intermediate during the dehydration 4,4-dimethylpentanol?

- (a) 1°
- (b) 2°

- (c) 3^0 (d) All the three
50. The relative acidic character of $\text{CH}_3\text{CH}_2\text{OH}$, $(\text{CH}_3)_2\text{CHOH}$ and $(\text{CH}_3)_3\text{COH}$ can be explained on the basis of
- (a) resonance (b) inductive effect
(c) hyperconjugation (d) hybridization

Answerkey

1 - c	2 - d	3 - c	4 - b	5 d
6 - c	7 - a	8 - b	9 - d	10 d
11 - c	12 - b	13 - d	14 - c	15 c
16 - d	17 - b	18 - c	19 - d	20 a
21 - a	22 - b	23 - d	24 - a	25 c
26 - c	27 - a	28 - a	29 - c	30 b
31 - c	32 - d	33 - a	34 - a	35 c

Assertion and Reason Type-I

- (i) Assertion and reason both are correct and reason is correct explanation of assertion.
(ii) Assertion and reason both are wrong statements.
(iii) Assertion is correct statement but reason is wrong statement.
(iv) Assertion is wrong statement but reason is correct statement.
(v) Both assertion and reason are correct statements but reason is not correct explanation of assertion.

1. Assertion : Addition reaction of water to but-1-ene in acidic medium yields butan-1-ol
Reason : Addition of water in acidic medium proceeds through the formation of primary carbocation.

2. Assertion : *p*-nitrophenol is more acidic than phenol.
Reason : Nitro group helps in the stabilisation of the phenoxide ion by dispersal of negative charge due to resonance.

3. Assertion : IUPAC name of the compound

$$\begin{array}{c} \text{CH}_3-\text{CH}-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$

is 2-Ethoxy-2-methylethane.

Reason : In IUPAC nomenclature, ether is regarded as hydrocarbon derivative in which a hydrogen atom is replaced by —OR or —OAr group [where R = alkyl group and Ar = aryl group]

4. Assertion : Bond angle in ethers is slightly less than the tetrahedral angle.

Reason : There is a repulsion between the two bulky (—R) groups.

5. Assertion : Boiling points of alcohols and ethers are high.

Reason : They can form intermolecular hydrogen-bonding.

6. Assertion : Like bromination of benzene, bromination of phenol is also carried out in the presence of Lewis acid.

Reason : Lewis acid polarises the bromine molecule.

7. Assertion : *o*-Nitrophenol is less soluble in water than the *m*- and *p*-isomers.

Reason : *m*- and *p*- Nitrophenols exist as associated molecules.

8. Assertion : Ethanol is a weaker acid than phenol.

Reason : Sodium ethoxide may be prepared by the reaction of ethanol with aqueous NaOH.

9. Assertion : Phenol forms 2, 4, 6 – tribromophenol on treatment with Br₂ in carbon disulphide at 273K.

Reason : Bromine polarises in carbon disulphide.

10. Assertion : Phenols give *o*- and *p*-nitrophenol on nitration with conc. HNO₃ and H₂SO₄ mixture.

Reason : —OH group in phenol is *o*-, *p*- directing.

Assertion and Reason Type-I

1. (ii) 2. (i) 3. (iv) 4. (iv) 5. (ii) 6. (iv) 7. (v) 8. (iii)
9. (ii) 10. (iv)

Assertion and Reason Type-II

- If both Assertion & Reason are True and Reason is the correct explanation of Assertion.
- If both Assertion & Reason are True but Reason is not the correct explanation of Assertion.
- If Assertion is True but Reason is False.
- If both Assertion & Reason are False.

1. Assertion : Among isomeric butyl alcohols, sec-butyl alcohol exhibits enantiomerism.

Reason : sec-Butyl alcohol has a chiral centre.

2. Assertion : 3° alcohols undergo dehydration more readily than 1° alcohols

Reason : 3° alcohols are less acidic than 1° alcohols.

3. Assertion : Phenol is stronger acid than alcohols.

Reason : Phenol is stabilized by resonance whereas alcohols are not.

4. Assertion : 1-Propanol and 2- propanol can be distinguished by iodoform test.

Reason : All secondary alcohols on reaction with NaOH and I₂ yield a yellow precipitate of iodoform.

5. Assertion : —OH group in phenols can not be substituted easily.

Reason : C – O bond in phenols has partial double bond character due to resonance.

6. Assertion : Ter-butyl alcohol is more soluble in water than n-butyl alcohol.

Reason : Solubility of an alkyl alcohol in water increases with increase in branching in an alkyl group.

7. Assertion : In Lucas test, 3° alcohols react immediately.

Reason : An equimolar mixture of anhydrous ZnCl₂ and conc. HCl is called Lucas reagent.

8. Assertion : Ethers behave as bases in presence of mineral acids.

Reason : Due to the presence of lone pairs of electrons on oxygen.

9. Assertion : Anisole on reaction with HI gives phenol and CH₃I.

Reason : Phenol–oxygen bond is stronger than methyl–oxygen bond in anisole and hence is not cleaved by HI.

10. Assertion : Phenol is less acidic than *p*-nitrophenol.

Reason : Phenolate ion is more stable than *p*-nitrophenolate ion.

11. Assertion : *p*-nitrophenol is a strong acid than *o*-nitrophenol.

Reason : Intramolecular H–bonding makes *o*-isomer weaker than *p*-isomer.

12. Assertion : The boiling point of ethanol is much higher than that of dimethyl ether.

Reason : In ethanol, the molecules are associated by the formation of intermolecular hydrogen bonding, whereas in diethyl ether it is absent.

13. Assertion : Phenetol on cleavage with HI yields phenol and ethyl iodide.

Reason : Phenetol is a mixed aromatic ether.

14. Assertion : The C–O–C bond angle in ethers is higher than H–O–H angle in water.

Reason : Oxygen is sp³-hybridized in both ethers and water.

15. Assertion : Anisole undergoes electrophilic substitution at ortho and para positions.

Reason : Anisole is less reactive than phenol towards electrophilic substitution reactions.

ANSWERS

Q:	1	2	3	4	5	6
A:	1	2	2	3	1	4
Q:	7	8	9	10	11	12
A:	2	1	1	3	1	1
Q:	13	14	15			
A:	2	2	3			

ALDEHYDE, KETONES & CARBOXYLIC ACIDS

INTRODUCTION

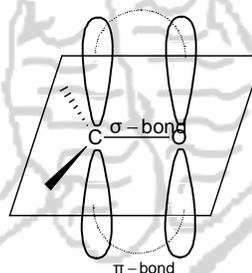
Both aldehydes & ketones contain carbonyl group as their functional group.

Structure of carbonyl group

Both aldehydes & ketones have carbonyl group as the functional group. The carbonyl carbon is sp^2 hybridised & it uses sp^2 hybrid orbitals to form 3σ bonds, one with oxygen atom & remaining 2 with two other atoms or groups (R or H). All these 3σ bonds lie in same plane at the angle of 120° .

The unhybridized p-orbital of carbonyl carbon form π -bond with oxygen atom by sidewise overlapping with half filled p-orbital of oxygen atom.

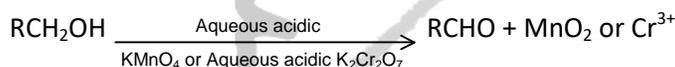
Since carbon & oxygen have different values of electronegativity, the bond between carbon & oxygen is polar. Infact electron density around the oxygen atom is increased which causes the development of partial positive charge (δ^+) on carbon & partial negative charge (δ^-) on oxygen.



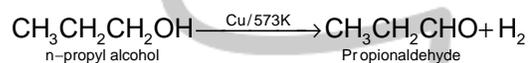
Orbital picture of carbonyl group

Thus the carbonyl carbon is an electrophilic & carbonyl oxygen is nucleophilic centre.

METHODS OF PREPARATION OF ALDEHYDES & KETONES

1. From Alcohols**(a) By Direct oxidation:****(b) By catalytic dehydrogenation**

When vapours of 1° or 2° alcohols are passed over copper gauze, they get dehydrogenated to form aldehydes or ketones.



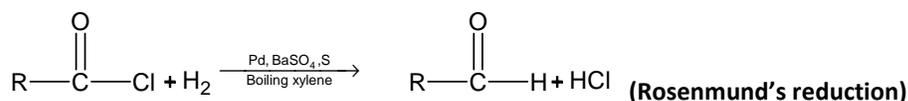
Dehydrogenation reaction is a better method of preparation because there is no risk of further oxidation of aldehyde.

(c) By using PCC

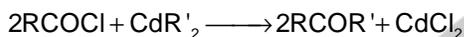
PCC stands for pyridinium chlorochromate. It is an equimolar mixture of CrO_3 , HCl and pyridine. It is used to oxidise 1° alcohol to aldehyde and 2° alcohol to ketones without affecting double or triple bond.

2. From Acid chlorides

Aldehydes are prepared from acid chlorides by reaction with H_2 in the presence of palladium catalyst supported on $BaSO_4$.



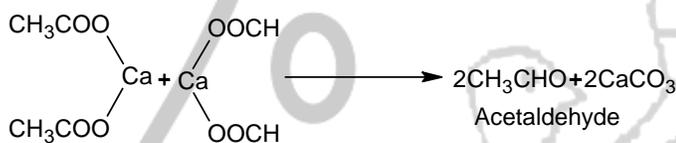
Ketones are obtained by reacting acid chlorides with dialkyl cadmium.



3. From fatty acids

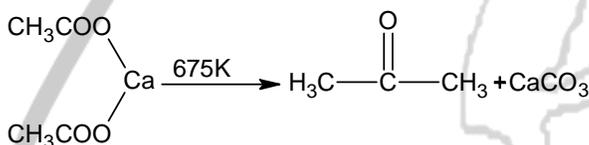
(a) By heating calcium salt of fatty acid

Aldehydes are obtained by heating calcium salt of fatty acids with calcium formate.

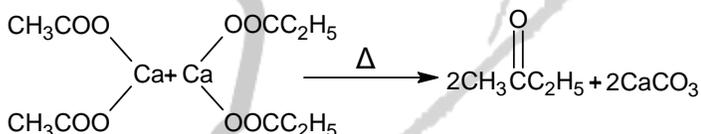


Calcium acetate Calcium formate

Ketones are formed by distilling calcium salt of fatty acids alone.



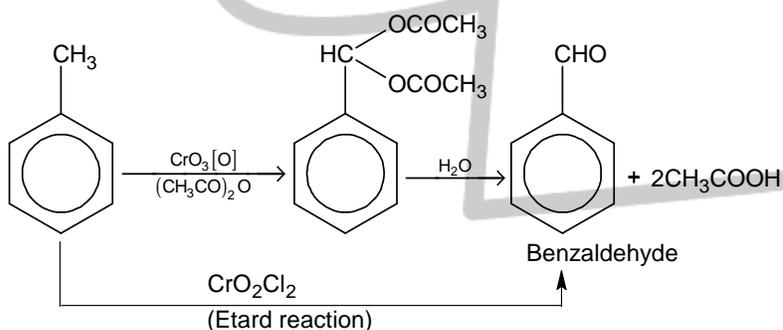
Similarly mixed ketones, can also be obtained by similar reactions:



PREPARATION OF AROMATIC ALDEHYDES & KETONES

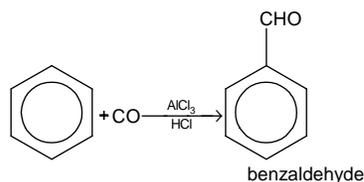
1. By oxidation of alkyl benzene

Aromatic aldehydes are obtained by oxidation of side chain in the aromatic ring.



3. By Gattermann Koch Reaction

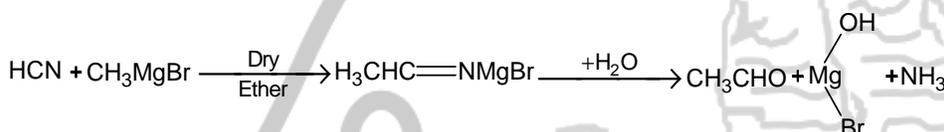
In this method aromatic aldehydes are prepared by formylation of aromatic ring with carbon monoxide.



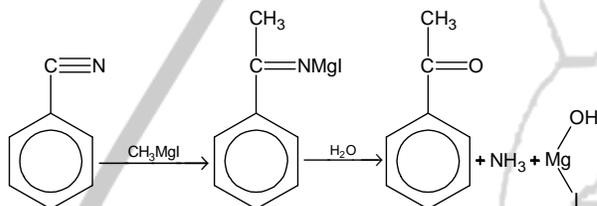
4. From Grignard's reaction

Both aliphatic & aromatic aldehyde can be obtained by this method.

HCN on treatment with Grignard's reagent & subsequently followed by hydrolysis yield an aldehyde.



Similarly



PHYSICAL PROPERTIES OF ALDEHYDES & KETONES

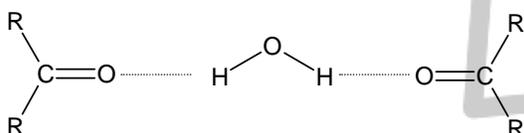
Boiling points

Aldehydes & ketones have relatively high boiling points as compared to hydrocarbons of comparable molecular masses due to polar carbonyl group, which bring stronger intermolecular dipole – dipole interactions between the opposite ends of C = O dipoles.

Ketones are relatively more polar than their corresponding isomeric aldehydes due to the presence of two electron repelling alkyl group around the carbonyl carbon.

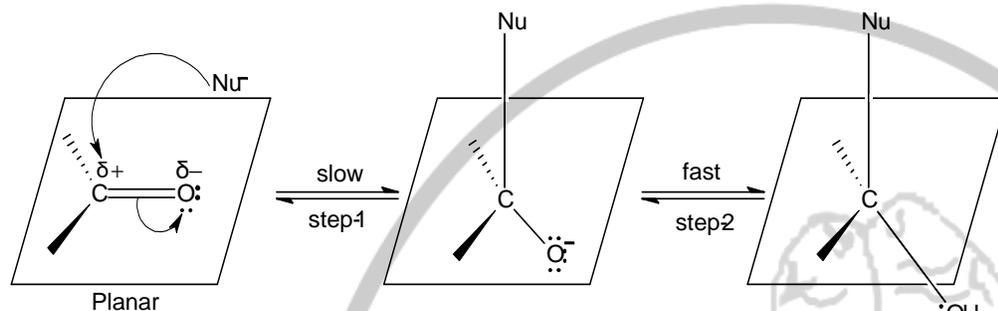
Solubility

The lower members of aldehydes & ketones (upto four carbon atoms) are soluble in water. It is due to their capability of forming hydrogen bonds with water molecules. The solubility of these compounds in water decreases with the increase in the size of alkyl group because of the increase in magnitude of non polar part in the molecule.



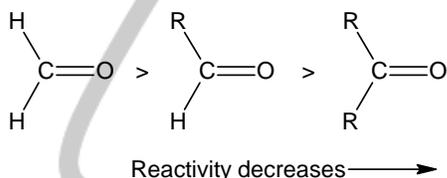
CHEMICAL PROPERTIES

Aldehydes & ketones are highly reactive compounds, they undergo nucleophilic addition reactions. Their reactivity is due to presence of a polar carbonyl group. The positively charged carbon atom of carbonyl group is readily attacked by nucleophilic species for initiation of the reaction. This leads to formation of intermediate anion which further undergoes the attack of H^+ ion or other positively charged species to form the final product. The reaction in general may be represented as:

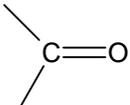

Relative reactivity of aldehydes & ketones

In general ketones are less reactive than aldehydes on a account of following facts:

- (i) Electron releasing effect of two alkyl groups, decreases the magnitude of positive charge on ketones.
- (ii) Steric effect caused by two alkyl groups also hinders the approach of the nucleophile to the carbonyl carbon.


TYPE OF CHEMICAL REACTIONS IN CARBONYL COMPOUNDS
1. Addition across C = O bond

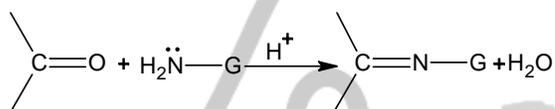
Sr. No.	Addition of	Substrate	Product
1.	Hydrogen cyanide		
2.	Sodium bisulphite (NaHSO_3)		
3.	Grignard reagent (RMgX) followed by hydrolysis	HCHO	$\text{H}_3\text{C}-\text{CH}_2-\text{OH}$ (1° alcohol)
		Aldehydes	2° alcohol

		(except formaldehyde)	
		Ketones	3° alcohol
4.	Alcohols (R—OH)		Hemiacetal which finally converts to acetal

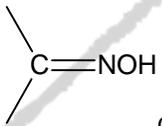
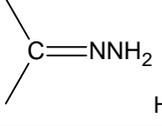
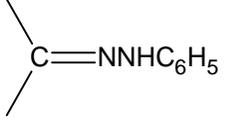
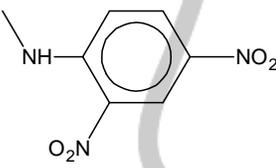
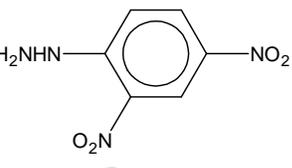
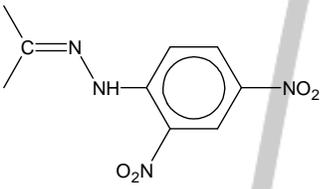
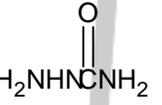
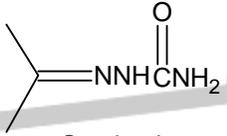
2. Replacement of carbonyl oxygen atom with other groups

(a) Reaction with ammonia derivatives

Aldehydes & ketones react with a number of NH_3 derivatives such as hydroxyl amine, hydrazine, semicarbazide etc, in weak acidic medium. In general, if we represent these derivatives by $\text{NH}_2\text{—G}$, then their reaction with aldehydes & ketones can be represented as follows:

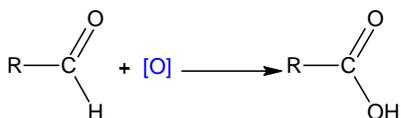


Ammonia derivatives & their products with carbonyl compounds

—G	Ammonia Derivative	Product obtained
—OH	NH_2OH Hydroxylamine	 Oxime
— NH_2	NH_2NH_2 Hydrazine	 Hydrazone
— NHC_6H_5	$\text{NH}_2\text{NHC}_6\text{H}_5$ Phenyl hydrazine	 Phenyl Hydrazone
	 2, 4 – dinitrophenyl hydrazine	 2, 4 – dinitrophenyl hydrazone
— NHCONH_2	 Semicarbazide	 Semicarbazone

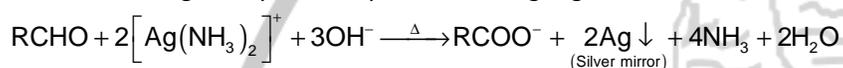
3. Oxidation

Aldehydes are easily oxidised to carboxylic acids containing the same number of carbon atoms, as in parent aldehyde.

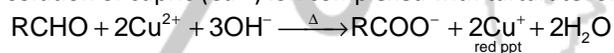


The reason for this easy oxidation is the presence of a hydrogen atom on the carbonyl carbon, which can be converted into —OH group without involving the cleavage of any other bond. Hence, aldehydes are oxidised not only by strong oxidizing agent but also by weak oxidizing agents. As a result, aldehydes act as strong reducing agents.

- Aldehydes reduce Tollen's reagent to Ag & appear in the form of silver mirror. This test is called silver mirror test. It is given by all aldehydes & reducing sugars.

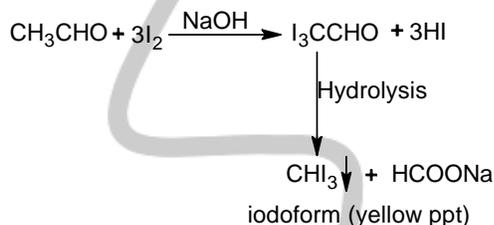


- Aldehydes (except benzaldehyde) reduce Fehling's solution (Cu^{+2} reduced to Cu^+) which is an alkaline solution of cupric (Cu^{2+}) ion complexed with tartarate ion.



- Aldehydes also reduce Benedict's solution (Cu^{2+} complexed with citrate ion) to Cu^+ .

Haloform Reaction



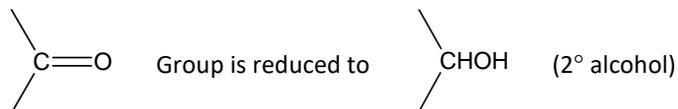
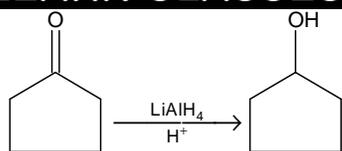
Due to the formation of **yellow ppt. of iodoform** in this reaction, it is known as iodoform test & used in for characterizing compound containing $\text{CH}_3\text{CO}-$ or a group like $\text{CH}_3\text{CH}_2\text{OH}$ which can be easily oxidised to $\text{CH}_3\text{CO}-$ group by halogens.

4. Reduction

Carbonyl compounds can be reduced to 1° or 2° alcohol, by LiAlH_4 , NaBH_4 or direct reduction with H_2/Ni .

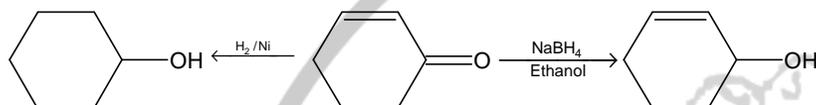


with LiAlH_4 —CHO group is reduced to — CH_2OH (1° alcohol) and $\text{C}=\text{C}$ bond is also reduced when it is in conjugation with carbonyl groups.

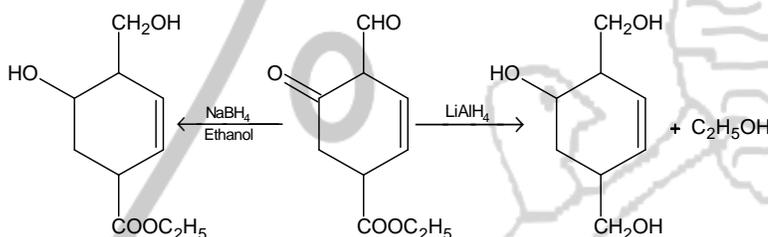


- LiAlH₄ also reduces ester & acid chloride to alcohols.

- (b) NaBH₄ has similar function. But this reagent does not affect (C = C) double bond.

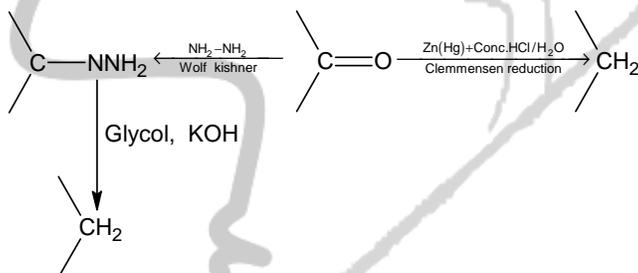


NaBH₄ does not reduce ester & acid chloride



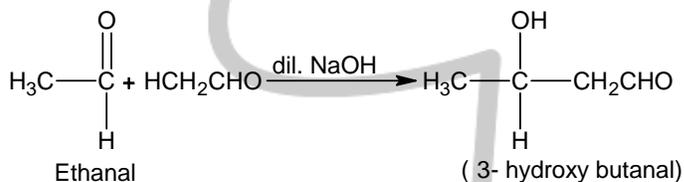
- (c) Amalgamated zinc, Zn(Hg) & conc. HCl (**Clemmensen reduction**) & hydrazine (NH₂-NH₂) followed by reaction with strong base like KOH in alkaline glycol

(Wolf Kishner reduction) reduces carbonyl group to alkyl group.

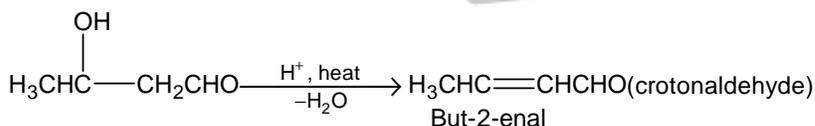


(A) Aldol Condensation

Two molecules of an aldehydes or a ketone having atleast one α - hydrogen atom, condense in presence of a dilute alkali to give a β - hydroxyaldehyde or β - hydroxy ketone.



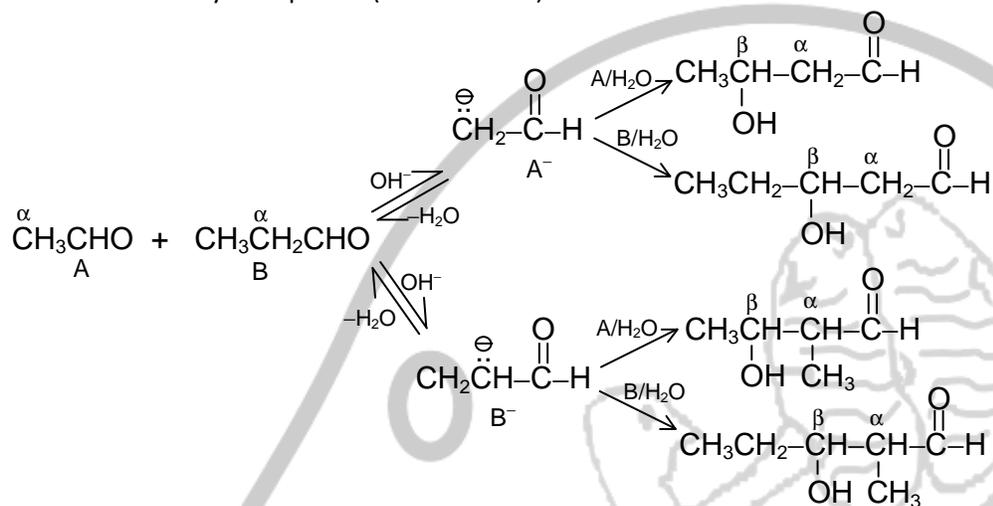
The products of aldol condensation when heated with dilute acids undergo dehydration to form α, β - unsaturated aldehydes or ketones.



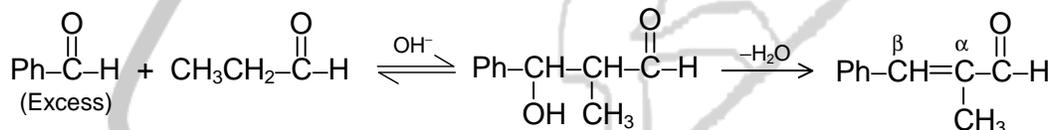
In general all aldehydes & ketones which contain α - hydrogen can undergo this reaction. Those which do not contain α - hydrogen like HCHO, C₆H₅CHO etc, do not undergo this reaction.

Crossed aldol condensation:

When two different carbonyl compounds (with α -H atoms) are used in an aldol condensation, four products are formed because each carbonyl compound can react with itself (self aldol) as well as with the other carbonyl compound (crossed aldol).

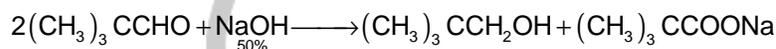


When one of the carbonyl compound does not have any α -hydrogen, it cannot form carbanion and number of possible products reduces to two.

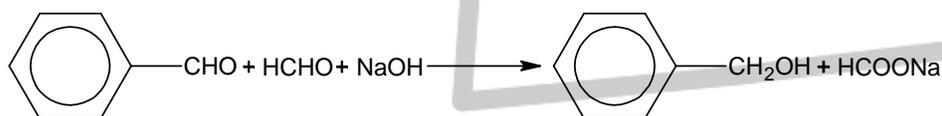


(B) Cannizzaro's reaction

Aldehydes that have no α -hydrogen atom (or acidic hydrogen) undergo cannizzaro reaction (CR) in which disproportionation reaction takes place one being reduced to alcohol & other being oxidised to salt of the corresponding carboxylic acid. The reaction takes place with 50% aqueous or ethanolic alkali solution.



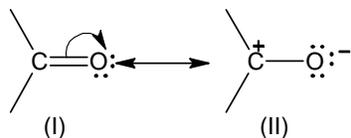
When an aldehyde (showing CR) is treated with HCHO & 50% base, then HCHO undergo oxidation (rather than any other aldehyde). This reaction is called crossed CR.



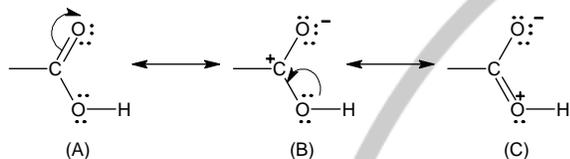
CR involving different aldehydes or same aldehydes is proton (H⁺), hydride (H⁻) transfer reaction.

Comparison of resonating structures of carboxylic group and carbonyl group

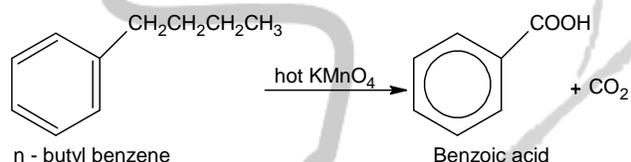
Carbonyl group has two resonance structures (I and II)



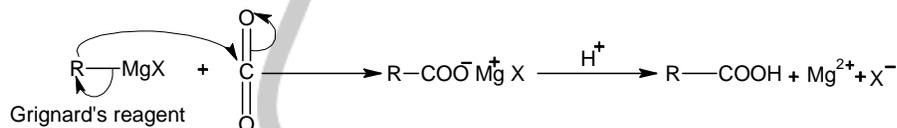
However, for a carboxyl group, three resonance structures (A, B and C) can be written.



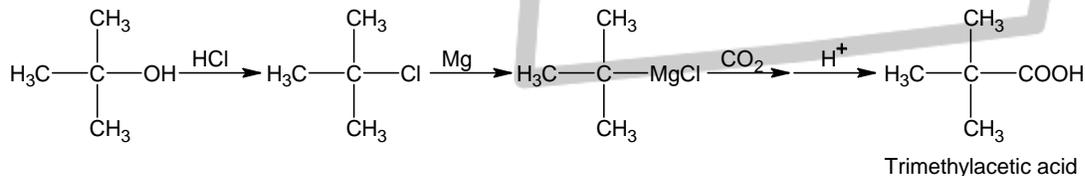
In both structures (A) and (C), the C – atom and the two O – atoms have eight electrons in their respective valence shells while in structure (B), C – atom has only six electrons. Therefore, structure (B) is less stable than structure (C), in other words the two important resonance structures of carboxyl group are structures (A) and (C). In both these structures, carboxyl carbon is electrically neutral. However in case of aldehydes and ketones, only one structure i.e. I is electrically neutral. As a result, the carboxyl carbon of the resonance hybrid is less positive and hence less electrophilic than the carbonyl carbon of aldehydes and ketones. However, it may be noted that like carbonyl group, carboxyl group is also polar due to resonance structures (B) and (C).

GENERAL METHODS OF PREPARATION**Oxidation of alkyl benzenes**

This reaction is used for two purposes (a) synthesis of carboxylic acids and (b) identification of alkyl benzenes.

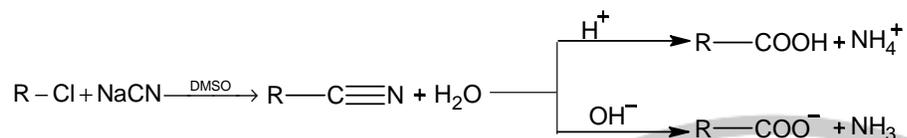
Carbonylation of Grignard reagents

The Grignard's reagent can be prepared from primary, secondary, tertiary or aromatic halides. The method is limited only by the presence of other reactive group in the molecule. The following synthesis illustrate the application of this method.



Hydrolysis of nitriles

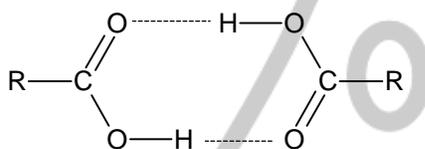
Aliphatic nitriles are prepared by treatment of alkyl halides with sodium cyanide in a solvent that will dissolve both reactants. In dimethyl sulfoxide (DMSO), reaction occurs rapidly and exothermically at room temperature. The resulting nitrile is then hydrolysed to the acid by boiling with aqueous alkali or acid.



PHYSICAL PROPERTIES

Boiling points

Due to intramolecular hydrogen bonding dimerization of acid takes place and boiling point of carboxylic acid is higher than expected.



CHEMICAL REACTIONS

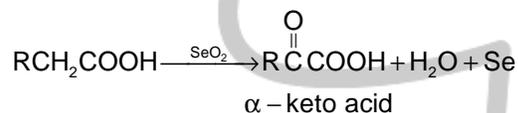
Carboxylic acids can also show various types of reactions.

- (i) Removal of H^+ (due to cleavage of $O-H$ bond) by reaction with a base (at 'a' above)
- (ii) $C-O$ bond breaks at b (by PCl_5 , PCl_3 , $SOCl_2$, NH_3/Δ)
- (iii) Nucleophilic attack at point (c) in carboxyl carbon (Ester formation)

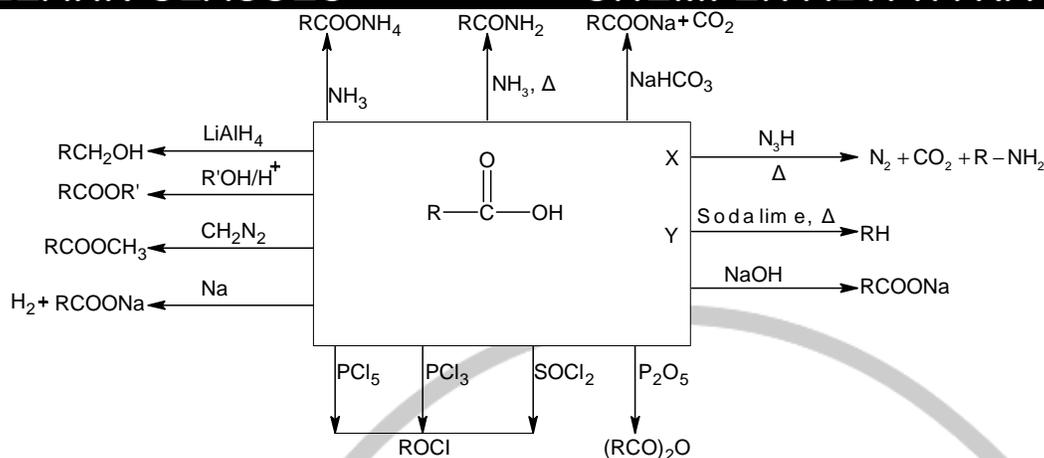
Reaction in which OH is replaced by $-NH_2$, Cl is S_N type



- (iv) Halogenation at α - C by P/Br_2 at point d (Hell - Volhard Zelinsky reaction)
- (v) Oxidation of α - methylene group by SeO_2

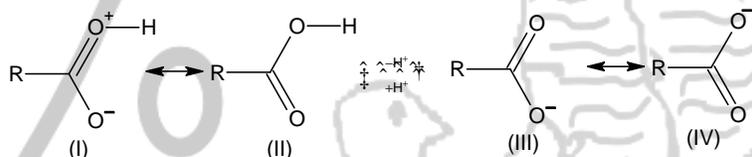


Some reactions are summarized below:



Acidity of Carboxylic Acids

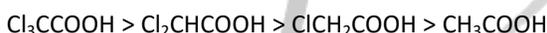
The acidity of a carboxylic acid is due to the resonance stabilization of its anion.



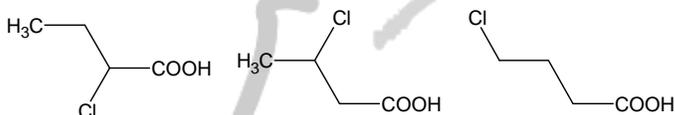
Because of the resonance, both the carbon oxygen bond in the carboxylate anion have identical bond length. In the carboxylic acid, these bond lengths are no longer identical.

The acidity of carboxylic acid depends very much on the substituent attached to $-COOH$ group. Since acidity is due to the resonance stabilization of anion, substituent causing stabilization of anion increases acidity whereas substituent causing destabilization of anion decrease acidity. For example, **electron withdrawing group disperses the negative charge of the anion and hence makes it more stable** causing increase in the acidity of the corresponding acid, on the other hand, electron-releasing group increases the negative charge on the anion and hence makes it less stable causing the decrease in the acidity. In the light of this, the following are the orders of a few substituted carboxylic acids.

(a) Increase in the number of Halogen atoms on α -position increases the acidity, eg.

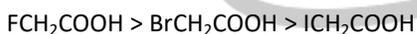


(b) Increase in the distance of Halogen from $COOH$ decreases the acidity e.g.



This is due to the fact that inductive effect decreases with increasing distance.

(c) Increase in the electronegativity of halogen increases the acidity.

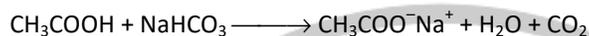
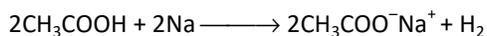


SALT FORMATION Carboxylic acids are weak acids and their carboxylate anions are strong conjugate bases and are slightly alkaline due to the hydrolysis of carboxylate anion compared to other species, the order of acidity and basicity of corresponding conjugate bases are as follows:

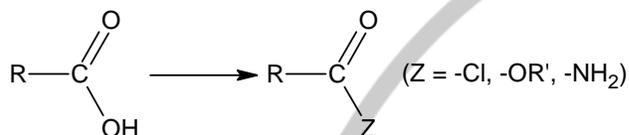
Acidity $RCOOH > HOH > ROH > HC \equiv CH > NH_3 > RH$

Basicity $\text{RCOO}^- < \text{HO}^- < \text{RO}^- < \text{HC}\equiv\text{C}^- < \text{NH}_2^- < \text{R}^-$

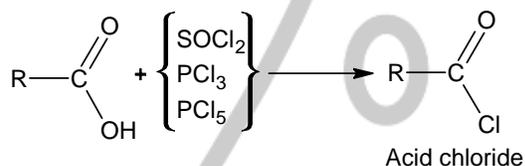
1. The carboxylic acids react with metals to liberate hydrogen and are soluble in both NaOH and NaHCO_3 solutions. For example.



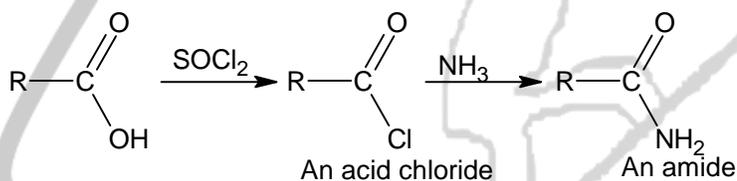
2. Conversion into functional derivatives



(a) Conversion into acid chlorides



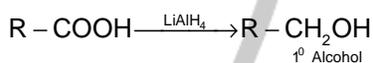
(b) Conversion into amides



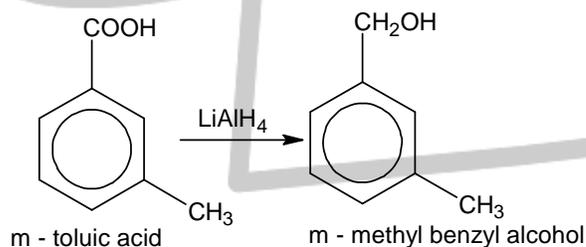
Example:



3. Reduction



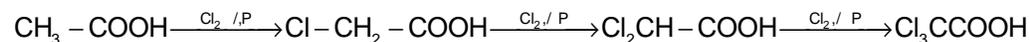
Examples:



4. Substitution in alkyl or aryl group

Halogenation of Aliphatic Acids (Hell-Volhard-Zelinsky Reaction)

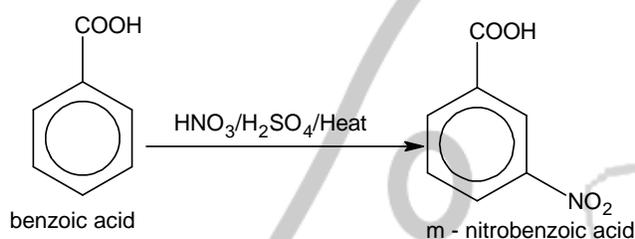
In the presence of phosphorus, aliphatic carboxylic acids react smoothly with chlorine or bromine to yield a compound in which α -hydrogen has been replaced by halogen.



(b) Ring substitution in aromatic acids:

—COOH deactivates and directs incoming electrophilic to meta position.

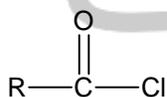
Example:



CARBOXYLIC ACID DERIVATIVES

There are four carboxylic acid derivatives. These are generally represented as $\text{R} - \overset{\text{O}}{\parallel}{\text{C}} - \text{Z}$,

(a) When Z is halogen (usually Cl), the derivatives are called as acid chlorides.



(b) When Z is —OR', the derivatives are called as esters.

(c) When Z is $-\text{O} - \overset{\text{O}}{\parallel}{\text{C}} - \text{R}'$, the derivatives are called **carboxylic anhydrides**.

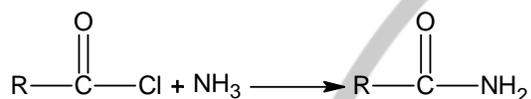
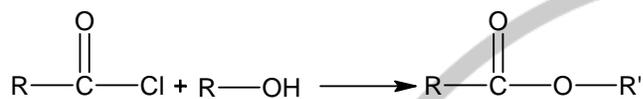
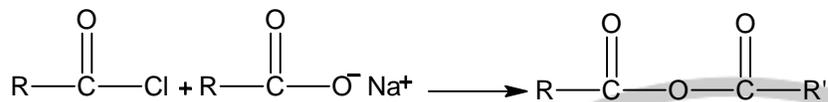
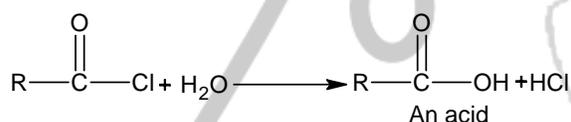
(d) Where Z is —NH₂, the derivatives are called amides. When Z is —NHR' or —NR₂' they are called **N - substituted amides**.

Synthesis of acid derivatives

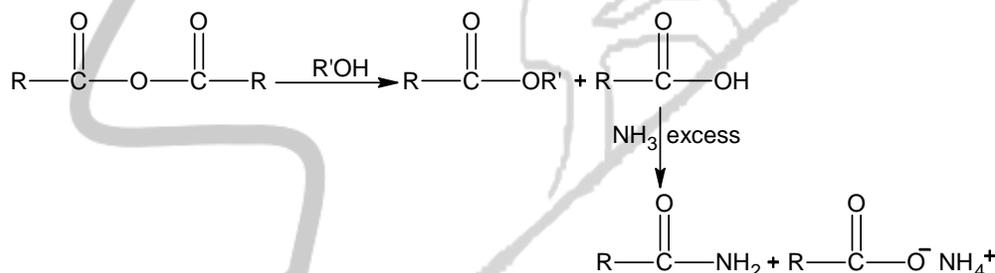
Carboxylic acid derivatives are exclusively prepared from carboxylic acids. The preparation methods of carboxylic acid derivatives are already discussed under the chemical reactions of carboxylic acids.

CHEMICAL REACTIONS OF ACID DERIVATIVES**(i) Acyl chloride**

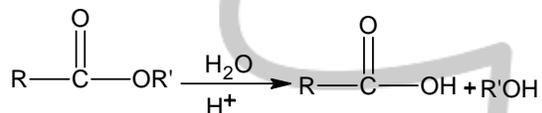
We have already seen that acyl chlorides are the most reactive of all acid derivatives. As a result, acyl chlorides are often selected as the starting material for the preparation any other acid derivative. Let us see how this is done.

**Conversion into acids: Hydrolysis.****(ii) Carboxylic acid anhydrides**

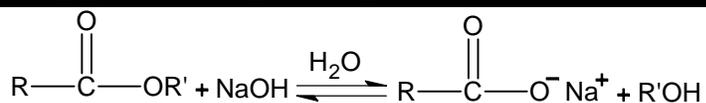
Carboxylic acid anhydrides can be used to prepare esters and amides.

**(iii) Esters****Ester hydrolysis**

Acid catalysed esterification is an essentially reversible reaction. If you follow the backward course of reactions of esterification it gives you the mechanism for ester hydrolysis.

**Base promoted hydrolysis of esters: Saponification**

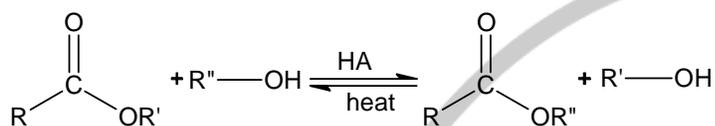
Esters undergo base promoted hydrolysis also. This reaction is known as **saponification**, because it is the way most of the soaps are manufactured. Refluxing an ester with aqueous NaOH produces an alcohol and the sodium salt of the acid.



This reaction is essentially irreversible because carboxylate ion is inert towards nucleophilic substitution.

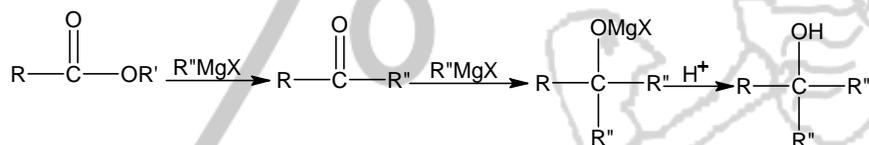
Transesterification

Esters can also be prepared by transesterification (an alcohol displacing another from an ester)



Reaction of esters with Grignard reagents

The reaction of carboxylic esters with Grignard's reagent is a good method for the preparation of 3° alcohols.



Initially ketones are formed. However, as we know, ketones themselves readily react with Grignard reagent to yield tertiary alcohols.

CH: Aldehydes, Ketones & Carboxylic Acids**(SUBJECTIVE ASSIGNMENT)****CONCEPTUALS**

1. Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not.

Ans. Preparation of cyanohydrin is a nucleophilic addition reaction. So if three methyl (electron releasing groups) are attached then it will decrease the charge on carbon atom of carbonyl group. As a result nucleophilic addition does not occur.

Q2. Benzaldehyde does not give Fehling's test?

Ans. Those aldehydes which do not have hydrogen atom will not form enolate ion. So it does not show Fehling's test.

Q3. The α -H atom in aldehydes and ketones is acidic?

Ans. It is due to strong electron withdrawing effect of carbonyl group and resonance stabilisation of conjugate base.

Q4. p-nitrobenzaldehyde is more reactive than benzaldehyde towards nucleophilic addition Rxn?

Ans. Because NO_2 group is an electron withdrawing group and it will make the carbon atom of carbonyl group more reactive as towards nucleophilic addition as compared to benzaldehyde.

Q5. Aldehydes are more reactive as compared to ketones towards nucleophilic addition?. Why.

Ans. In ketones the presence of two large substituents will hinder the attack of nucleophile as compared to aldehyde in which only one such substituent is present.

Q6. Benzoic acid is a stronger acid than ethanoic acid?

Ans. It is because of greater E.N. of sp^2 hybridised carbon to which carboxyl carbon is attached. This will make the $-\text{OH}$ bond polar.

Q7. Electrophilic substitution of benzoic acid takes place at a m-position?

Ans. The carboxylic group is an electron withdrawing group so it will decrease the reactivity of benzene ring for electrophilic attack. Hence the attack takes place only at m-position.

Q8. Carboxylic acid does not give characteristic reaction of carbonyl group?

Ans. Because of resonance stabilisation the positive charge of carbonyl carbon is not available so it will not show Rxn of carbonyl group.

Q9. There are two $-\text{NH}_2$ groups in semicarbazide. However only one $-\text{NH}_2$ group is involved in the formation of semicarbazone?

Ans. The lone pair present on one of the NH_2 groups is involved in resonance with the carbonyl group and hence it is not free.

10. During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

Ans. The formation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst is a reversible reaction.



To shift the equilibrium in the forward direction, the water or ester formed should be removed as fast as it is formed.

11. Sodium Bisulphite is used for the purification of aldehydes and ketones. Explain.

Ans. Aldehydes and Ketones form addition compounds with NaHSO₃ whereas impurities do not. On hydrolysis we get pure aldehydes and Ketones back.

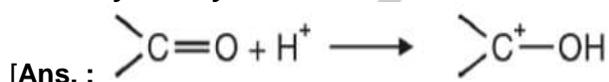
12. Why pH of reaction should be carefully controlled while preparing ammonia derivatives of carbonyl compound?

Ans. In strongly acidic medium ammonia derivatives being basic will react with acids and will not react with carbonyl compound. In basic medium, OH⁻ will attack carbonyl group. pH of a reaction should be carefully controlled.

13. During reaction of carbonyl compound with 2,4-DNP reagent, the pH of the reaction mixture has to be maintained between 3 and 4. Why?

[Ans. : H⁺ ions increase the electrophilicity of carbonyl carbon. When H⁺ ions are in excess, they protonate the NH₂ group of 2,4-DNP. After protonation -NH₃⁺ group does not act as nucleophile.]

14. During the reaction of a carbonyl compound with a weak nucleophile, H⁺ ions are added as catalyst. Why?



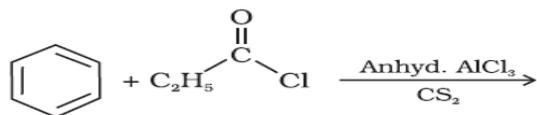
H⁺ ions get attached to oxygen atom and make carbonyl carbon more electrophilic in nature.]

FOR PRACTICE

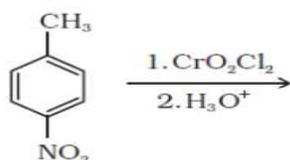
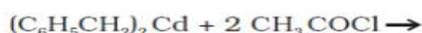
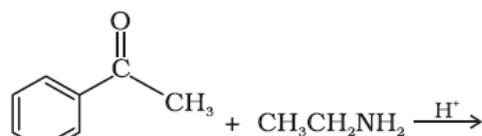
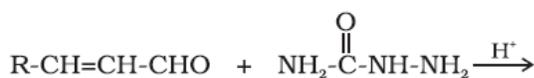
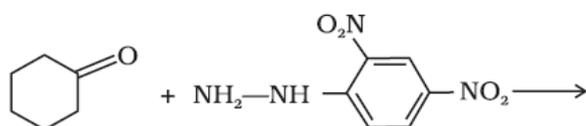
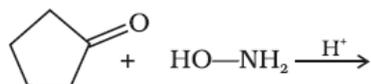
1. Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer.
2. Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?
3. Chloroacetic acid has higher *p*K_a value than acetic acid.
4. Electrophilic substitution in benzoic acid takes place at meta-position.
5. Carboxylic acid have higher boiling points than alcohols of comparable molecular masses.
6. Benzaldehyde does not give Fehling's test.
7. Acetic acid does not give sodium bisulphite addition product.
8. Aldehydes are more reactive towards nucleophilic reagents than ketones.
9. *tert*-butylbenzene cannot be oxidised with KMnO₄.
10. Benzoic acid is less soluble in water than acetic acid.
11. Formic acid is a stronger acid than acetic acid.
12. Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer

REACTION COMPLETION

1. Write the structures of products of the following reactions;



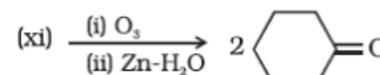
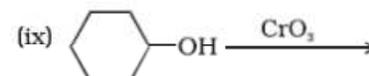
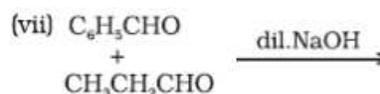
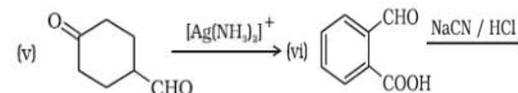
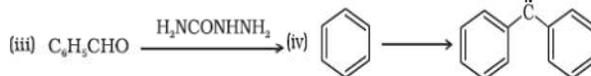
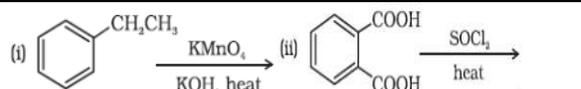
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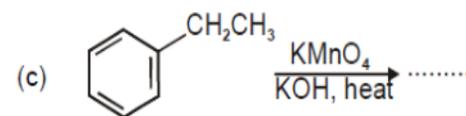
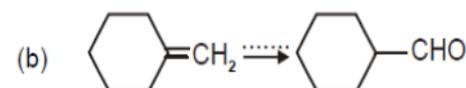
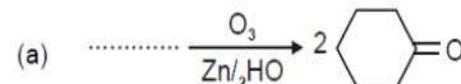
3. Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents.

- PhMgBr and then H_3O^+
- Tollens' reagent
- Semicarbazide and weak acid
- Excess ethanol and acid
- Zinc amalgam and dilute hydrochloric acid

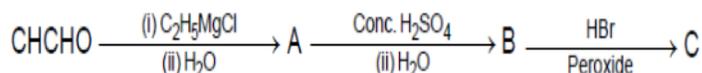
4. Complete each synthesis by giving missing starting material, reagent or products



5. Complete the following reaction statements by giving the missing starting material, reagent or product as required :



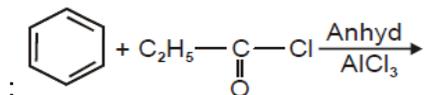
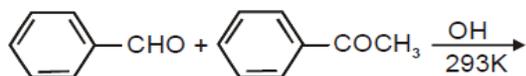
6. Identify A, B and C in the following sequence of reactions :



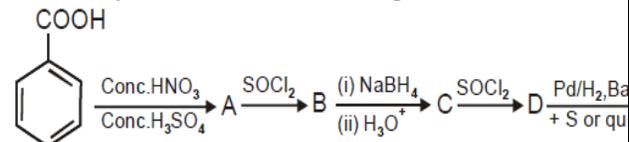
7. Predict the structures of products formed when benzaldehyde is treated with

- Conc. NaOH
- $\text{HNO}_3/\text{H}_2\text{SO}_4$ (at 273K–283K)

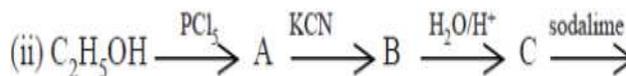
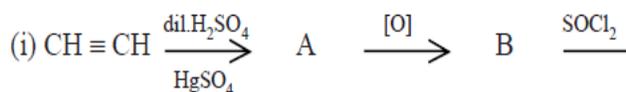
8. Predict the products of the following reactions



9. Identify A to E in the following reactions :



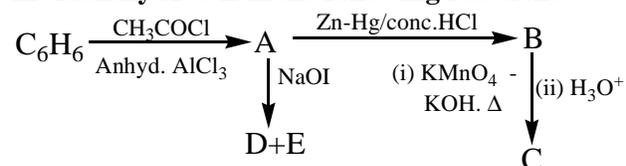
10. Complete the following equations by writing the missing A, B, C, D etc.



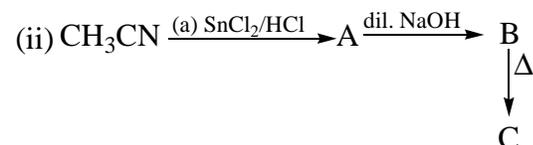
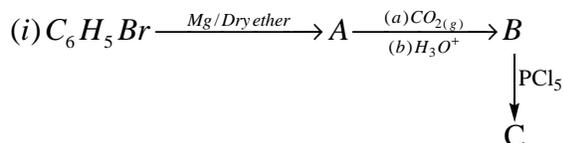
11. Draw the structure of the following derivatives :

- 2, 4-dinitrophenylhydrazone of $\text{C}_6\text{H}_5\text{CHO}$
- Cyclopropanone oxime
- Acetaldehydedimethylacetal
- Semicarbazone to cyclobutanone
- Ethylene ketal of hexan-3-one
- Methylhemiacetal of formaldehyde

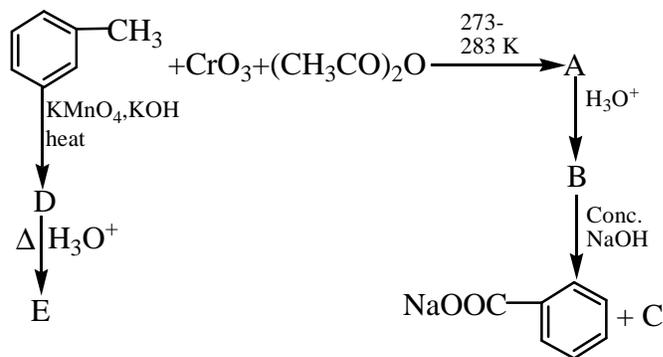
12. Identify A to E in the following reactions:



13. Write the structures of compounds A, B and C in each of the following reaction:

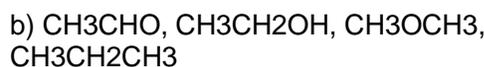
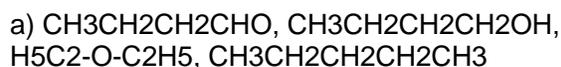


14. Identify A and E in the following series of reactions:

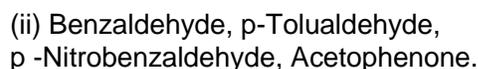


INCREASING/DECREASING ORDER

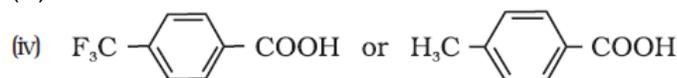
1. Arrange the following compounds in the increasing order of their boiling points:



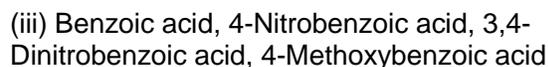
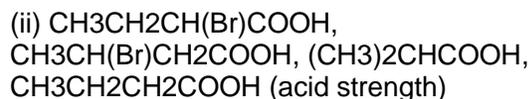
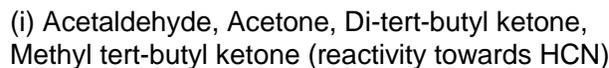
2. Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.



3. Which acid of each pair shown here would you expect to be stronger?



4. Arrange the following compounds in increasing order of their property as indicated:



(acid strength)

PREDICTION

1. Which of the following compounds would undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.

- | | |
|--------------------------|------------------------|
| (i) Methanal | (ii) 2-Methylpentanal |
| (iii) Benzaldehyde | (iv) Benzophenone |
| (v) Cyclohexanone | (vi) 1-Phenylpropanone |
| (vii) Phenylacetaldehyde | (viii) Butan-1-ol |
| (ix) 2,2-Dimethylbutanal | |

2. Write structural formulas and names of four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde acts as nucleophile and which as electrophile.

3. An organic compound (A) with molecular formula C_8H_8O forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollens' or Fehlings' reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (B) having molecular formula $C_7H_6O_2$. Identify the compounds (A) and (B) and explain the reactions involved.

4. An organic compound with the molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.

5. An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene.

6. Write equations for the reactions involved. An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogen sulphite and give positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound.

7. An organic compound A on treatment with acetic acid in the presence of sulphuric acid produces an ester B. A on mild oxidation gives C. C with 50% KOH followed by acidification with dil. HCl generates A and D. D with PCl_5 followed by reaction with ammonia gives E. E on dehydration produces hydrocyanic acid. Identify the compounds A, B, C, D and E.

[Therefore, (A) : Methyl alcohol

(B) : Methyl acetate

(C) : Formaldehyde]

8. A ketone A (C_4H_8O) which undergoes a haloform reaction gives compound B on reduction. B on heating with sulphuric acid gives a compound C which forms mono-ozonide D. D on hydrolysis with zinc dust gives only E. Identify A, B, C, D and E. Write the reactions involved.

9. An organic compound (A) (mol. formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid also produced B. On dehydration (C) gives but-2-ene. Write the equations for the reactions involved.

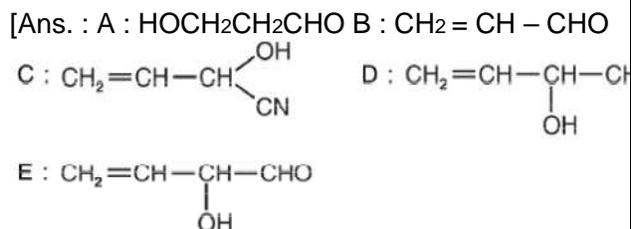
10. An organic compound A ($C_7H_6Cl_2$) on treatment with NaOH solution gives another compound B (C_7H_6O). B on oxidation gives an acid ($C_7H_6O_2$) which on treatment with a mixture of conc. HNO_3 and H_2SO_4 gives a compound D ($C_7H_5NO_4$). B on treatment with conc. NaOH gives a compound E (C_7H_8O) and C_6H_5COONa . Deduce the structures of A, B, C, D and E.

11. Compound A ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ yields two compounds B and C. The compound B on oxidation gave D which on treatment with aqueous alkali and subsequent heating furnished E. The latter on catalytic hydrogenation gave 'C'. The compound D on further oxidation gave CH_3COOH . Deduce the structures of A, B, C, D and E.

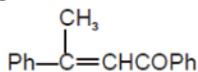
12. An organic compound (A) having molecular formula $C_5H_{10}O$ gives a positive 2,4-DNP test. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogen sulphite. On reaction with I_2 in alkaline medium, it forms a yellow precipitate of compound B and another compound C having molecular formula $C_4H_7O_2Na$. On oxidation with $KMnO_4$, [A] forms two acids D and E having molecular formula $C_3H_6O_2$ and $C_2H_4O_2$ respectively. Identify A, B, C, D and E.

Ans. A : $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3$ B : CHI_3
 C : $\text{CH}_3\text{CH}_2\text{CH}_2\text{COONa}$
 D : $\text{CH}_3\text{CH}_2\text{COOH}$ E : CH_3COOH

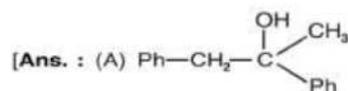
13. Formaldehyde and acetaldehyde on treatment with dil. NaOH form A which on heating changes to B. When B is treated with HCN, it forms C. Reduction of C with DIBAL- H yields D which on hydrolysis gives E. Identify A, B, C, D and E.



14. A tertiary alcohol 'A' on acid catalyzed dehydration gave product 'B'. Ozonolysis of 'B' gives compounds 'C' and 'D'. Compound 'C' on reaction with KOH gives benzyl alcohol and compound 'E'. Compound 'D' on reaction with KOH gives $\alpha\beta$ -unsaturated ketone having the following structure:



Identify A, B, C, D and E

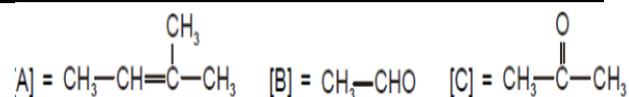


15. An aromatic compound X with molecular formula C_9H_{10} gives the following chemical tests :

- (i) forms 2,4-DNP derivative
- (ii) reduces Tollens' reagent
- (iii) undergoes Cannizzaro reaction
- (iv) On vigorous oxidation gives 1,2-benzenedicarboxylic acid.

Identify X and write its IUPAC name. Also write the reactions involved in the formation of above mentioned products.

16. An alkene 'A' (Mol. formula C_5H_{10}) on ozonolysis gives a mixture of two compounds 'B' and 'C'. Compound 'B' gives positive Fehling's test and also forms iodoform on treatment with I_2 and NaOH. Compound 'C' does not give Fehling's test but forms iodoform. Identify the compounds A, B, and C. Write the reaction for ozonolysis and formation of iodoform from B and C.



17. An aromatic compound 'A' (Molecular formula $\text{C}_8\text{H}_8\text{O}$) gives positive 2, 4- DNP test. It gives a yellow precipitate of compound 'B' on treatment with iodine and sodium hydroxide solution. Compound 'A' does not give Tollen's or Fehling's test. On drastic oxidation with potassium permanganate it forms a carboxylic acid 'C' (Molecular formula $\text{C}_7\text{H}_6\text{O}_2$), which is also formed along with the yellow compound in the above reaction. Identify A, B and C and write all the reactions involved.

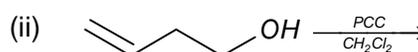
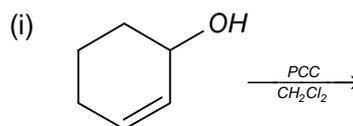
18. Write down functional isomers of a carbonyl compound with molecular formula $\text{C}_3\text{H}_6\text{O}$. Which isomers will react faster with HCN and why? Explain the mechanism of the reaction also. Will the reaction lead to the completion with the conversion of whole reactant into product at reactions conditions? If a strong acid is added to the reaction mixture what will be the effect on concentration of the product and why?

D.P-1

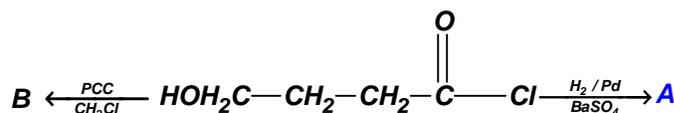
1. Give structure of the following compounds :

- (i) 2-methoxypropionaldehyde
- (ii) 3-hydroxy butanal
- (iii) 2-hydroxy cyclopentanecarbaldehyde
- (iv) 4-oxopentanal
- (v) Di-secbutyl ketone

2. Complete the following reaction by writing down the major product:

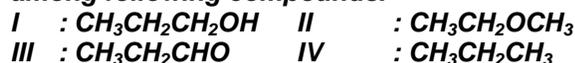


3. Write the structures of compound A and B in the following reaction:



4. What happens when (give equation only)?
 (i) Ethyne is treated with dilute H₂SO₄ in the presence of HgSO₄.
 (ii) propan-2-ol is treated with Cu at 573 K.

5. Give the increasing order of boiling point among following compounds.



6. Write the structure of compound A and B
 $(CH_3)_2C=O \xrightarrow{HCN} A \xrightarrow{H_3O^+} B$

The most reactive compound towards formation of cyanohydrin on treatment with KCN followed by acidification is

- (A) Benzaldehyde (B) p – Nitrobenzaldehyde
 (C) Phenyl acetaldehyde (D) p – Hydroxybenzaldehyde

7. Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reaction:

Benzaldehyde, p – tolualdehyde, p – nitrobenzaldehyde, acetophenone.

D.P-2

- Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer.
- Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?
- Chloroacetic acid has higher pK_a value than acetic acid.
- Give reasons for the following :
 (i) C₆H₅COOH is weaker than formic acid.
 (ii) R - COOH do not give characteristic reaction with > C = O.
 (iii) Carboxylic acids are stronger acids than phenols.
 (iv) Acid amides are weakly basic in nature.

5. Give the chemical test to distinguish between :



- (i) CH₃CHO and CH₃-C-CH₃
 (ii) CH₃CHO and C₆H₅CHO

6. Complete the following reactions and write main products :



7. Arrange the following compounds in an increasing order of their property as indicated:

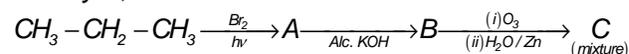
Acetaldehyde Acetone, Methyl tert-butyl ketone (reactivity towards HCN)

8. Arrange the following compounds in an increasing order of their property as indicated:

- (i) Benzoic acid; 3, 4-dinitrobenzoic acid; 4-methoxybenzoic acid (acid strength)
 (ii) CH₃CH₂CH(Br)COOH, CH₃CH(Br)CH₂COH, (CH₃)₂CHCOOH (acid strength)

12. Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer

Identify A, B and C.



13. Which of the following compound gives yellow precipitate with iodine and sodium hydroxide?

- (i) 3-methyl-4-phenyl but-3-en-2-one
 (ii) 1- phenyl ethanone
 (iii) Butanal (iv) Pentan-3-one

D.P-3

1. How will you prepare the following derivatives of acetone?

- (i) 2,4-DNP derivative (ii) Schiff's base
 (iii) Oxime

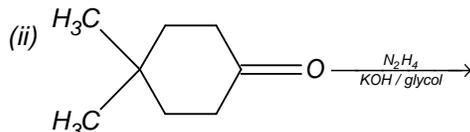
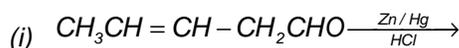
2. For the formation of ethyl acetate from acetic acid and ethanol in presence of sulphuric acid,

the reaction mixture is heated to remove water as fast as it is formed.

3. Monochloroethanoic acid is a weaker acid than dichloroethanoic acid.

4. Name the major product of the following

reactions:



5. Arrange the following illustration in order of increasing acidity

(i) HCOOH , ClCH_2COOH , CH_3COOH

(ii) CH_3COOH , $(\text{CH}_3)_2\text{CHCOOH}$, $(\text{CH}_3)_3\text{CCOOH}$

(iii) ClCH_2COOH , Cl_2CHCOOH , Cl_3CCOOH

(iv) ClCH_2COOH , $\text{CH}_3\text{CH}_2\text{COOH}$, $\text{ClCH}_2\text{CH}_2\text{COOH}$, $(\text{CH}_3)_2\text{CHCOOH}$, CH_3COOH

(v) CH_3COOH , Cl_2CHCOOH , $\text{CH}_3\text{CH}_2\text{COOH}$, Cl_3CCOOH , ClCH_2COOH

Solution:

(i) $\text{CH}_3\text{COOH} < \text{HCOOH} < \text{ClCH}_2\text{COOH}$

(ii) $(\text{CH}_3)_3\text{CCOOH} < (\text{CH}_3)_2\text{CHCOOH} < \text{CH}_3\text{COOH}$

(iii) $\text{ClCH}_2\text{COOH} < \text{Cl}_2\text{CHCOOH} < \text{Cl}_3\text{CCOOH}$

(iv) $(\text{CH}_3)_2\text{CHCOOH} < \text{CH}_3\text{CH}_2\text{COOH} < \text{CH}_3\text{COOH} < \text{ClCH}_2\text{CH}_2\text{COOH} < \text{ClCH}_2\text{COOH}$

(v) $\text{CH}_3\text{CH}_2\text{COOH} < \text{CH}_3\text{COOH} < \text{ClCH}_2\text{COOH} < \text{Cl}_2\text{CHCOOH} < \text{Cl}_3\text{CCOOH}$

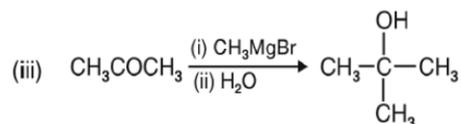
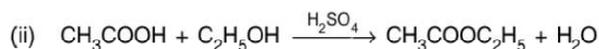
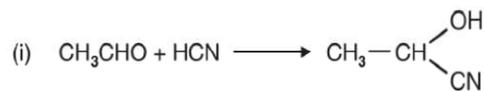
D.P-4

1. Formaldehyde gives Cannizzaro reaction whereas acetaldehyde does not.

2. Chloroacetic acid has lower pka value than acetic acid.

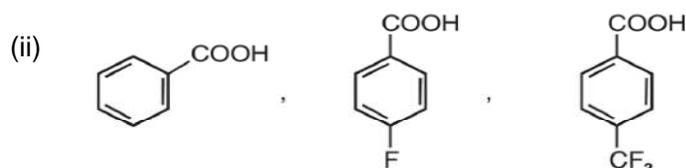
3. An organic compound X has molecular formula $\text{C}_5\text{H}_{10}\text{O}$. It does not reduce Fehling's solution but forms a bisulphate compound. It also gives positive Iodoform test. What are possible structures of X? Explain your reasoning relating structure.

4. Give the reaction mechanism for following reactions :



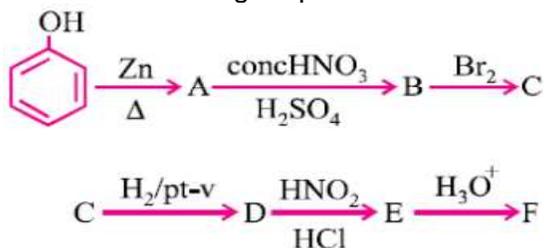
5. Arrange the following acids in the order of increasing acid strength

(i) formic acid, benzoic acid, acetic acid



(iii) $\text{CH}_3\text{CH}_2\text{COOH}$, $\text{C}_6\text{H}_5\text{COOH}$, CH_3COOH , $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$

6. Write the structures of organic compound A to F in the following sequence of reactions :

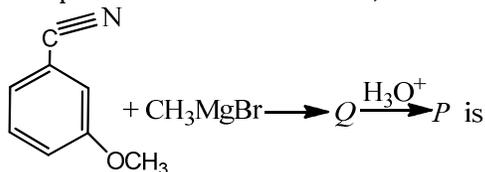


7. An organic compound 'A' ($\text{C}_3\text{H}_6\text{O}$) is resistant to oxidation but forms compound B ($\text{C}_3\text{H}_8\text{O}$). On reduction 'B' reacts with HBr to form the compound 'C'. 'C' with Mg forms Grignard's reagent 'D' which reacts with A to form a product which on hydrolysis gives 'E'. Identify 'A' to 'E'.

8. An organic compound A ($\text{C}_3\text{H}_8\text{O}$) on treatment with copper at 573K gives B. B does not reduce Fehling's reagent but gives a yellow ppt. of compound C with I_2/NaOH . Deduce the structures of A, B and C.

OBJECTIVE QUESTIONS
(Aldehydes, Ketones & Carboxylic Acids)

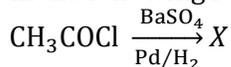
1. The product *P* in the reaction,



[Kerala CEE 2008]

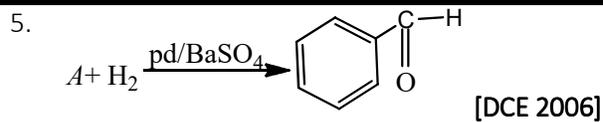
- 1) 2)
3) 4)
5)

2. In the following reaction,



Identify *X* out of the following [J&K CET 2003]

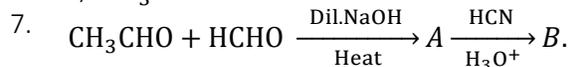
- 1) Acetaldehyde 2) Propionaldehyde
3) Acetone 4) Acetic anhydride
3. Which one of following can be oxidised to the corresponding carbonyl compound? [Manipal 2007]
- 1) 2-hydroxypropane 2) *Ortho*-nitrophenol
3) Phenol 4) 2-methyl-2-hydroxypropane
4. Which of the following gives an aldehyde on dry distillation? [KCET 2011]
- 1) Calcium formate + calcium acetate 2) Calcium acetate + calcium benzoate
3) Calcium acetate 4) Calcium benzoate



- 1) 2)
3) 4)

6. The most suitable reagent for the conversion of primary alcohol into aldehyde with the same number of carbon is [Kerala CEE 2007]

- 1) Acidified $K_2Cr_2O_7$ 2) Acidified $KMnO_4$
3) Alkaline $KMnO_4$ 4) Pyridinium chlorochromate
5) CrO_3

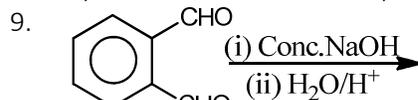


The structure of compound *B* is [RPET 2010]

- 1) 2)
3) 4)

8. Which of the following cannot reduce Fehling solution? [J&K CET 2004]

- 1) $HCOOH$ 2) H_3CCOOH
3) $HCHO$ 4) H_3CCHO



[OJEE 2008]

- 1) 2)
3) 4)

10. Aldehyde with $NH_2 \cdot NH_2$ forms [BCECE 2008]

- 1) Hydrazones 2) Aniline
3) Nitrobenzene 4) None of these

11. Which factor/s will increase the reactivity of $>C=O$ group?

1. Presence of a group with positive inductive effect.

5. CH_3COCH_3
 6. PhCOCH_3
 7. PhCOPh [AIEEE 2006]
 1) $A < B < C < D$ 2) $D < B < C < A$
 3) $D < C < B < A$ 4) $C < D < B < A$
28. The most reactive compound towards formation of cyanohydrin on treatment with HCN followed by acidification is [JCECE 2010]
 1) Benzaldehyde 2) *p*-nitrobenzaldehyde
 3) Phenylacetaldehyde 4) *p*-hydroxybenzaldehyde
29. Which of the following compounds would be the main product of an aldol condensation of acetaldehyde and acetone? [UP SEE 2009]
 1) $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CHO}$ 2) $\text{CH}_3\text{CH}=\text{CHCOCH}_3$
 3) $(\text{CH}_3)_2\text{C}=\text{CH}\cdot\text{CHO}$ 4) $(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$
30. Which of the aldehyde is most reactive? [DCE 2004]
 1) $\text{C}_6\text{H}_5\text{CHO}$ 2) CH_3CHO
 3) HCHO 4) All are equally reactive
31. Which of the following acids has the smallest dissociation constant? [WB JEE 2008]
 1) $\text{CH}_3\text{CHF}\text{COOH}$ 2) $\text{FCH}_2\text{CH}_2\text{COOH}$
 3) $\text{BrCH}_2\text{CH}_2\text{COOH}$ 4) $\text{CH}_3\text{CHBr}\text{COOH}$
32. Which of the following compounds would have the smallest value of pK_a ? [Kerala CEE 2004]
 1) $\text{CHF}_2\text{CH}_2\text{CH}_2\text{COOH}$ 2) $\text{CH}_3\text{CH}_2\text{CF}_2\text{COOH}$
 3) $\text{CH}_2\text{FCH}_2\text{CH}_2\text{COOH}$ 4) $\text{CH}_3\text{CF}_2\text{CH}_2\text{COOH}$
 5) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
33. The correct order of acidic strengths of the carboxylic acids is [DCE 2009]
 1) Formic acid < benzoic acid < acetic acid < formic acid
 2) Formic acid < acetic acid < benzoic acid < formic acid
 3) Acetic acid < formic acid < benzoic acid < formic acid
 4) Acetic acid < benzoic acid < formic acid < acetic acid
34. Identify *D* in the following reaction

$$\text{CH}\equiv\text{CH} + \text{CH}_3\text{MgBr} \xrightarrow{-\text{CH}_4} \text{A} \xrightarrow[\text{(ii) H}_3\text{O}]{\text{(i) CO}_2} \text{B}$$

$$\text{B} \xrightarrow[\text{H}_2\text{SO}_4]{\text{HgSO}_4} \text{C}$$

$$\text{D} \xleftarrow{\text{Tautomerisation}} \text{C}$$
 [Punjab CET 2010]
 1) $\text{HOOC}-\text{CH}_2-\text{COOH}$ 2) $\text{OHC}-\text{CH}_2-\text{COOH}$
 3) $\text{OHC}-\text{CH}_2-\text{CHO}$ 4) $\frac{\text{HO}-\text{CH}}{=\text{CH}-\text{COOH}}$
35. When $\text{CH}_2=\text{CH}-\text{COOH}$ is reduced with

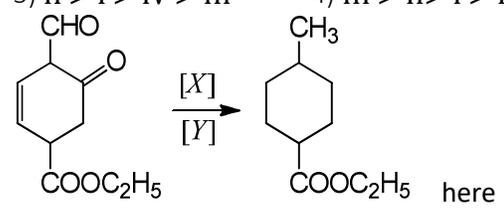
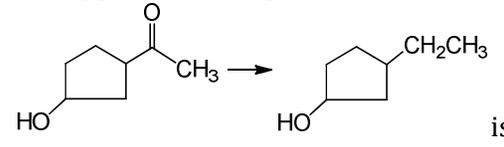
- LiAlH_4 , the compound obtained will be [MP PET 2007, AIEEE 2007, UP SEE 2007]
 1) $\text{CH}_3-\text{CH}_2-\text{COOH}$ 2) $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$
 3) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ 4) $\text{CH}_3\text{CH}_2\text{CHO}$
36. In a set of the given reactions, acetic acid yielded a product *C*.

$$\text{CH}_3\text{COOH} + \text{PCl}_5 \rightarrow \text{A}$$

$$\text{A} \xrightarrow[\text{anhyd. AlCl}_3]{\text{C}_6\text{H}_5} \text{B} \xrightarrow[\text{ether}]{\text{C}_2\text{H}_5\text{MgBr}} \text{C}$$

 Product *C* would be [UP SEE 2007]
 1) $\text{CH}_3\text{CH}(\text{OH})\text{C}_6\text{H}_5$ 2) $\begin{matrix} \text{C}_2\text{H}_5 \\ | \\ \text{CH}_3-\text{C}(\text{OH})\text{C}_6\text{H}_5 \end{matrix}$
 3) $\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_5$ 4) $\text{CH}_3\text{COC}_6\text{H}_5$
37. End product of the following reaction is [MHT CET 2008]

$$\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow[\text{red P}]{\text{Cl}_2} \text{X} \xrightarrow{\text{Alc. KOH}} \text{Y}$$

 1) $\begin{matrix} \text{CH}_3\text{CH}_2\text{COOH} \\ | \\ \text{OH} \end{matrix}$ 2) $\begin{matrix} \text{CH}_2\text{CH}_2\text{COOH} \\ | \\ \text{OH} \\ | \\ \text{CH}_2\text{CHCOOH} \end{matrix}$
 3) $\text{CH}_2=\text{CHCOOH}$ 4) $\begin{matrix} | & | \\ \text{Cl} & \text{OH} \end{matrix}$
38. What will be the order of reactivity of the following carbonyl compounds with Grignard's reagent?
 I: $\begin{matrix} \text{H} \\ | \\ \text{C}=\text{O} \\ | \\ \text{H} \end{matrix}$ II: $\begin{matrix} \text{H} \\ | \\ \text{C}=\text{O} \\ | \\ \text{CH}_3 \end{matrix}$
 III: $\begin{matrix} \text{CH}_3 \\ | \\ \text{C}=\text{O} \\ | \\ \text{CH}_3 \end{matrix}$ IV: $\begin{matrix} (\text{CH}_3)_3\text{C} \\ | \\ \text{C}=\text{O} \\ | \\ (\text{CH}_3)_3\text{C} \end{matrix}$
 1) $\text{I} > \text{II} > \text{III} > \text{IV}$ 2) $\text{IV} > \text{III} > \text{II} > \text{I}$
 3) $\text{II} > \text{I} > \text{IV} > \text{III}$ 4) $\text{III} > \text{II} > \text{I} > \text{IV}$
39. 
 here
 1) H_2/Ni and NaOH 2) H_2/Ni and hydrazine
 3) H_2/Ni , LAH 4) None of these
40. The appropriate reagent for the transformation

 is
 1) $\text{Zn}(\text{Hg})$, HCl 2) NH_2NH_2 , OH^-
 3) H_2/Ni 4) NaBH_4
41. Methyl ethyl ketone can be reduced to *n*-butane

by

- 1) The Meerwein-Ponndroff reduction
 2) The Wolf-Kishner reduction
 3) Mg – Hg, H₂O
 4) All of the above

ANSWER KEY

1)4	2)1	3)1	4)1	5)1
6)4	7)1	8)2	9)2	10)1
11)2	12)4	13)2	14)1	15)2
16)2	17)3	18)1	19)3	20)4
21)1	22)2	23)3	24)1	25)2
26)4	27)3	28)2	29)2	30)3
31)3	32)2	33)1	34)1	35)4
36)2	37)2	38)1	39)3	40)1
41)2				

Assertion and Reason Type-I

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following

choices.

- (i) Assertion and reason both are correct and reason is correct explanation of assertion.
 (ii) Assertion and reason both are wrong statements.
 (iii) Assertion is correct statement but reason is wrong statement.
 (iv) Assertion is wrong statement but reason is correct statement.
 (v) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

42. Assertion : Formaldehyde is a planar molecule.

Reason : It contains *sp*₂ hybridised carbon atom.

43. Assertion : Compounds containing —CHO group are easily oxidised to corresponding carboxylic acids.

Reason : Carboxylic acids can be reduced to alcohols by treatment with LiAlH₄

44. Assertion : The α -hydrogen atom in carbonyl compounds is less acidic.

Reason : The anion formed after the loss of α -hydrogen atom is resonance stabilised.

45. Assertion : Aromatic aldehydes and formaldehyde undergo Cannizaro reaction.

Reason : Aromatic aldehydes are almost as reactive as formaldehyde.

46. Assertion : Aldehydes and ketones, both react with Tollen's reagent to form silver mirror.

Reason : Both, aldehydes and ketones contain a carbonyl group.

Assertion and Reason Type

42. (i) 43. (v) 44. (iv) 45. (iii) 46. (iv)

Assertion and Reason Type-II

- If both Assertion & Reason are True and Reason is the correct explanation of Assertion.
- If both Assertion & Reason are True but Reason is not the correct explanation of Assertion.
- If Assertion is True but Reason is False.
- If both Assertion & Reason are False.

1. **Assertion:** All ketones on reaction with Grignard reagents, followed by hydrolysis yield tertiary alcohols.

Reason: RCHO on reaction with Grignard reagents followed by hydrolysis yield secondary alcohols.

2. **Assertion:** $>C=O$ group is present both in aldehydes and acid derivatives.

Reason: Aldehydes give nucleophilic addition across $>C=O$ bond but esters do not exhibit such reactions.

3. **Assertion:** Aldehydes and ketones do not give nucleophilic substitution reactions.

Reason: Aldehydes and ketones are functional isomers of each other.

4. **Assertion:** Benzoic acid does not undergo Friedal Craft's reaction.

Reason: $-COOH$ group deactivates the benzene ring by its electron withdrawing nature.

5. **Assertion:** Acetic acid does not undergo haloform reaction.

Reason: Acetic acid has no alpha hydrogens.

6. **Assertion:** Benzaldehyde forms two oximes on reacting with NH_2OH .

Reason: The two oximes arise due to geometrical isomerism in compounds having $C=N$ bond.

7. **Assertion:** Formyl chloride cannot be prepared by Rosenmund's reaction.

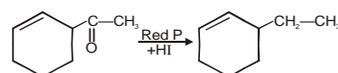
Reason: Formyl chloride is highly unstable and does not exist at room temperature.

8. **Assertion:** Both acid anhydrides and esters hydrolyse in acidic medium to give carboxylic acids.

Reason: Acid anhydrides and esters are functional isomers of each other.

9. **Assertion:** Red P & HI also reduce alcohol to alkane.

Reason: Reaction



is called Clemmenson reduction

10. **Assertion:** Formic acid reduces mercuric chloride.

Reason: Formic acid has reducing aldehydic group.

11. **Assertion:** $(CH_3)_3C-COOH$ does not give HVZ reaction

Reason: It does not have any α -hydrogen.

12. **Assertion:** pK_a of formic acid is less than acetic acid.

Reason: Formic acid is weaker acid than acetic acid.

13. **Assertion:** Lower aldehydes and ketones are soluble in water but the solubility decreases as the molecular mass increases.

Reason: Distinction between aldehydes and ketones can be made by Tollens' reagent.

14. **Assertion:** Formaldehyde is a planar molecule.

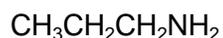
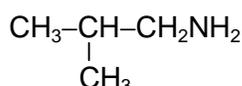
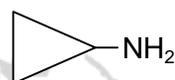
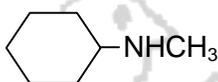
Reason: Carbon atom in formaldehyde is sp^2 -hybridized.

15. **Assertion:** Carbonyl compounds take part in nucleophilic addition reaction.

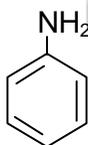
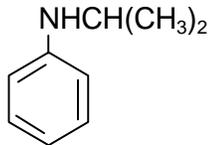
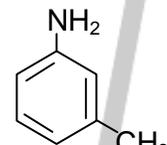
Reason: These reactions are initiated by nucleophilic attack at the electron deficient carbon atom.

ANSWERS

Q :1	2	3	4	5
A :2	2	2	1	3
Q :6	7	8	9	10
A :1	1	3	3	1
Q :11	12	13	14	15
A :1	3	2	1	1

AMINES**Nomenclature****(a) Primary amines:****1-Propanamine**
(n-propylamine)**2-methyl-1-propanamine**
(isobutylamine)**Cyclopropanamine**
(cyclopropylamine)**(b) Secondary amines:****N-methylethanamine**
(Ethylmethylamine)**N-methylcyclohexanamine**
(cyclohexylmethylamine)**N-ethylethanamine**
(Diethylamine)**(c) Tertiary amines:****N-ethyl-N-methyl-1-propanamine**
(Ethylmethylpropylamine)**N, N-dimethylmethanamine**
(Trimethylamine)**N-methyl-N-cyclopropylcyclopentanamine**
(Methylcyclopentylcyclopropylamine)**(d) Arylamines:**

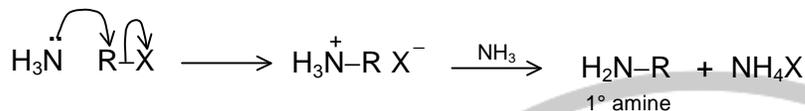
Arylamines have NH_2 group directly attached to the benzene ring. They are named as derivatives of aniline (common name) or benzenamine (IUPAC name).

**Benzenamine**
(Aniline)**N-isopropylbenzenamine**
(N-isopropylaniline)**3-methylbenzenamine**
(m-toluidine)

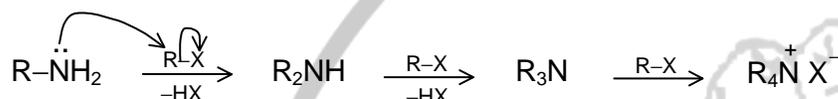
Amines are derivatives of NH_3 . They are represented by general formula $\text{C}_n\text{H}_{2n+3}\text{N}$.

General methods of preparation:**1. Alkylation of NH₃ with alkyl halides or alcohols:**

Alkyl halides undergo nucleophilic substitution reaction by S_N2 mechanism with NH₃ forming primary amines.

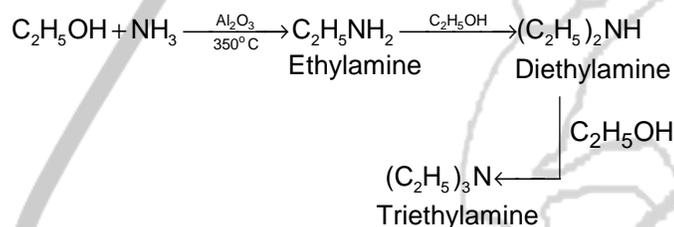


The reaction does not stop at this stage. Primary amine being more basic than ammonia further reacts with alkyl halide forming secondary amine (2°), tertiary amine (3°) and eventually quaternary ammonium salt, if the alkyl halide is present in excess.

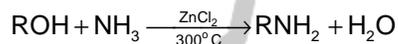
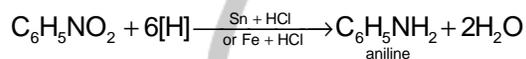
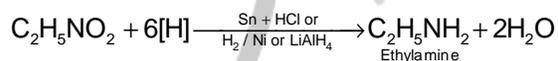
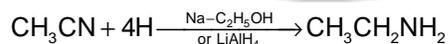


We can make primary amine as the major product by carrying out the reaction with liquid ammonia.

Aryl halides show low reactivity for this reaction.

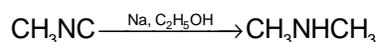
2. By the action of ammonia on alcohol:

This method yields a mixture of 1°, 2°, 3° amines and 4° salts which are separated from each other by means of Hinsberg method, Hofmann method and fractional distillation. However, 1° amines can be prepared in good yield by using excess of ammonia.

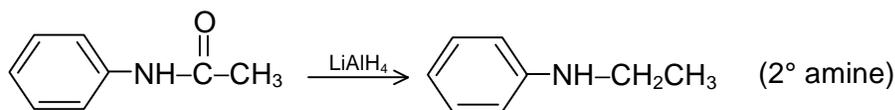
**3. By reduction of nitroalkanes:****4. Mendius reduction of alkyl cyanides:**

Ethylamine

Reduction of alkyl isocyanides with Na/C₂H₅OH gives 2° amines eg.

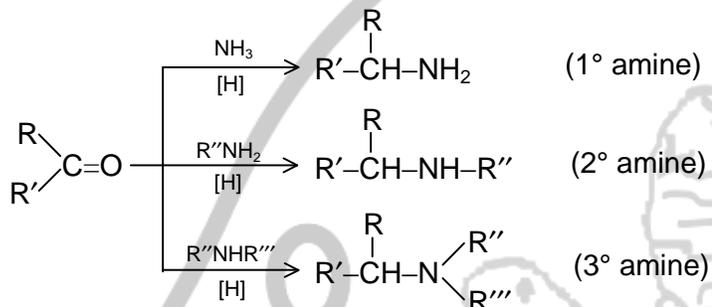


5. By reduction of amides and oximes:

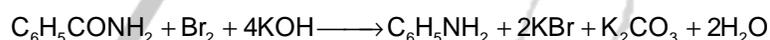
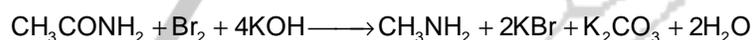


6. Reductive Amination Of Carbonyl Compounds

Aldehydes and ketones are converted to amines through catalytic or chemical reduction in the presence of ammonia or amine. Primary, secondary and tertiary amines can be prepared by this method.

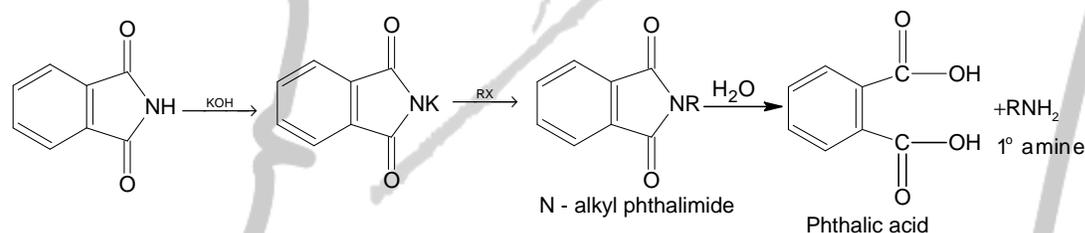


7. By Hofmann bromamide reaction:



8. By Gabriel phthalimide reaction:

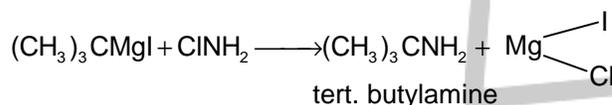
Potassium phthalimide formed after reaction of phthalimide with KOH, on heating with alkyl halide gives N-alkyl phthalimide. This on hydrolysis with 20% hydrochloric acid under pressure gives 1° amine.



The secondary and tertiary alkyl halides are not employed because they undergo elimination reactions also.

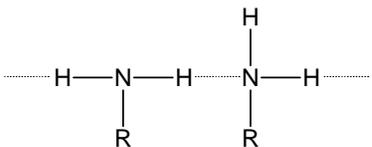
This method is not suitable for preparing aromatic primary amines as aryl halides are not good substrates for nucleophilic substitution.

9. By action of chloramine on Grignard's reagent:



PROPERTIES OF AMINES**PHYSICAL PROPERTIES****Boiling points:**

All amines except tertiary amines are capable of forming intermolecular hydrogen bonds due to the presence of polar N – H bonds.



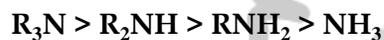
Due to this, amines have higher boiling points than non – polar compounds of comparable molecular mass. Among isomeric amines, 1° amines have highest boiling point due to more extensive H – bonding while 3° amines have the least boiling point due to their inability to form hydrogen bonds.

Solubility:

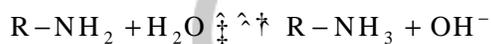
Aliphatic amines of lower molecular mass are soluble in water. With increase in molecular mass, solubility in water decreases, while that in ether increases.

Basic Character of Amines**❑ Aliphatic Amines**

According to Lewis theory, a base is a substance which donates a lone pair of electrons e.g. ammonia, water etc. Like ammonia, amines contain a lone pair of electrons on nitrogen and hence are basic. The basic strength of a base is related to the ease with which it can donate its lone pair of electrons. Primary amine (R – NH₂) has one alkyl group attached to the nitrogen atom. In comparison to NH₃, the electron density of nitrogen atom is more in R – NH₂ due to +I effect of the alkyl group. Thus R – NH₂ is expected to be more basic than NH₃. Going by the same arguments the basic strength of amines is expected to increase with the increase in the number of alkyl groups attached to the nitrogen atom



However, this trend is not observed in aqueous medium. The nitrogen atom in an amine shares its electron pair with H⁺ ion from water to form alkyl ammonium ion,

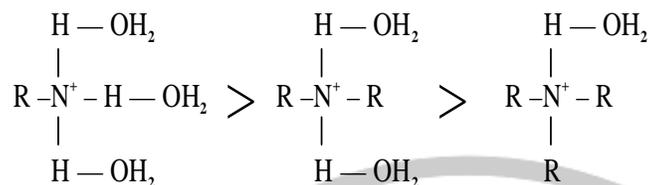


The basic strength of the amine is expressed as equilibrium constant K_b

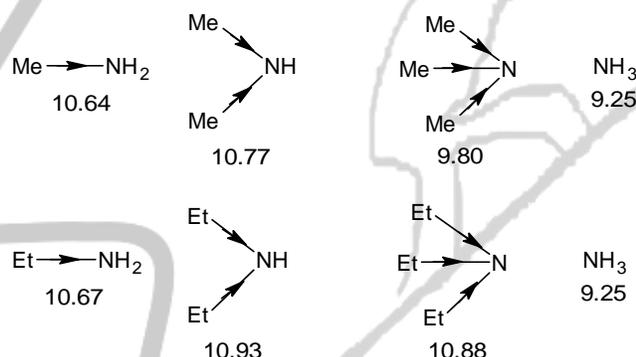
$$K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]}$$

The greater the value of K_b of an amine, the greater is its basicity. Thus, the smaller the pK_b of an amine the stronger will be the base.

The basic strength of an amine in aqueous medium is determined not only on the basis of +I effect of the alkyl groups attached to the nitrogen atom **but also the solvation of alkyl ammonium ion formed by uptake of proton.**

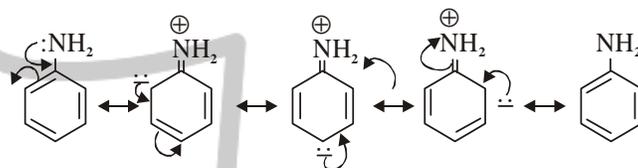


The solvation of alkyl ammonium ion is maximum as it has three H-atoms attached to the nitrogen atom which can form hydrogen bonds with water molecules. It is less in the case of dialkylammonium ion which has two H-atoms attached to the nitrogen atom and still less in the case of trialkyl ammonium ion which has only one H-atom attached to the nitrogen atom. Thus on going along the series $\text{NH}_3 \rightarrow \text{R}-\text{NH}_2 \rightarrow \text{R}_2\text{NH} \rightarrow \text{R}_3\text{N}$, the +I effect of the increasing number of alkyl groups will tend to increase the basic strength but the gradual decrease in the solvation of cation and hence the stabilization of cation will tend to decrease the basic strength. The effect of alkyl dominates till secondary amines. The actual changeover takes place on going from a secondary amine to tertiary amine. Thus, 2° amine becomes more basic in comparison with 3° amine as far as aqueous medium is concerned.



□ Aromatic Amines

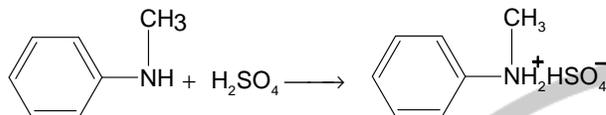
In aromatic amines the nitrogen atom of $-\text{NH}_2$ group is directly attached to the benzene ring. The unshared pair of electrons at the nitrogen is in resonance with the benzene ring and hence not fully available for donation as in the case of aniline



If aniline is to function as a base, it has to use its unshared pair of electrons for donation at the cost of resonance stabilization. Thus aniline is reluctant to function as a base. This is supported by the pK_b values of aniline in comparison to those of ammonia and cyclohexylamine.

CHEMICAL PROPERTIES**Reaction with acids to form salts:**

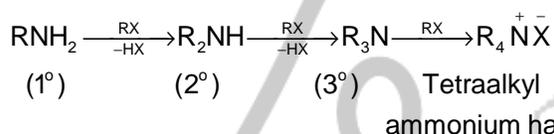
The nitrogen is quadricovalent unielectrovalent in amine salts.



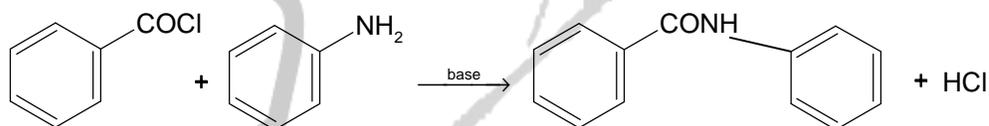
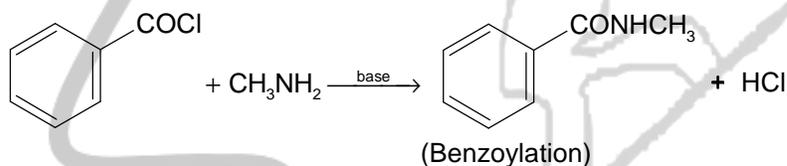
N - methylaniline

Alkylation:

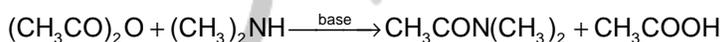
Amines react with R - X to form amines of higher class. In this reaction, the amine acts as nucleophile bringing about nucleophilic substitution of alkyl halides.



These salts give a test for halide ion with AgNO_3 solution.

Acylation and benzoylation of amines to form substituted amides

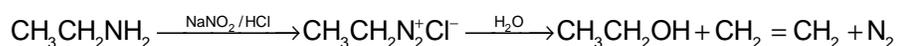
The above reactions are called **Schotten - Baumann reaction**.

**Reaction with HNO_2 ($\text{NaNO}_2 + \text{HCl}$):**

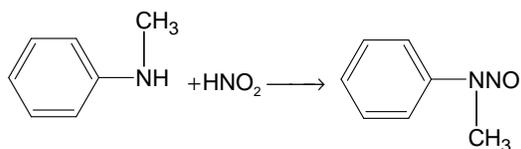
1° amines give diazotization reaction as follows :



1° aliphatic amines also react with HNO_2 to form diazonium salt but due to the absence of delocalization, it is unstable, decompose to yield a mixture of alcohols, **alkenes with the evolution of N_2 gas**.

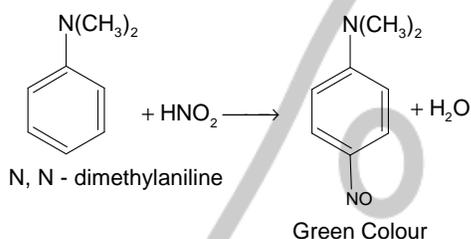
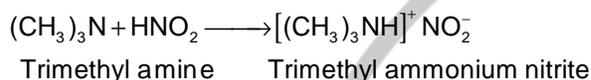


2° amine: Both aliphatic and aromatic 2° amines react with HNO_2 to produce N-nitroso amines that are insoluble in the aqueous solution and separate out as a yellow oily layer.



The nitroso amines on warming with a little phenol and conc. H_2SO_4 produce a red solution which changes to blue with NaOH (This is Liebermann nitroso test for 2° amine and phenol).

3° amine: Aliphatic 3° amines form nitrites while aromatic 3° amines undergo electrophilic substitution.

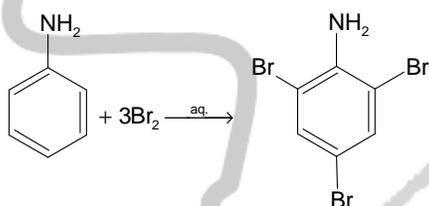


Ring substitution in aromatic amines:

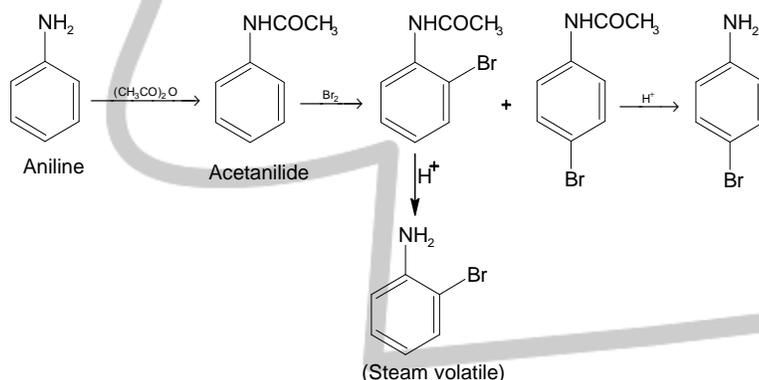
Due to resonance effect $-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$ groups are ortho and para directing for electrophilic attack.

Following reactions clarify the point:

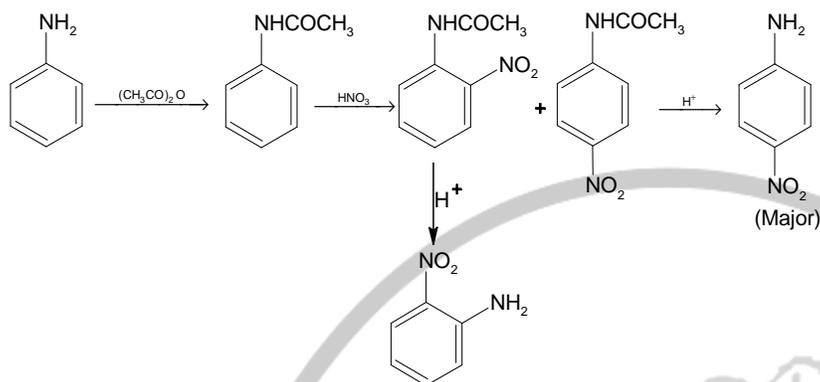
(i) Halogenation:



In order to introduce only one halogen atom, the activating effect of the $-\text{NH}_2$ group must be lowered using acetylation.

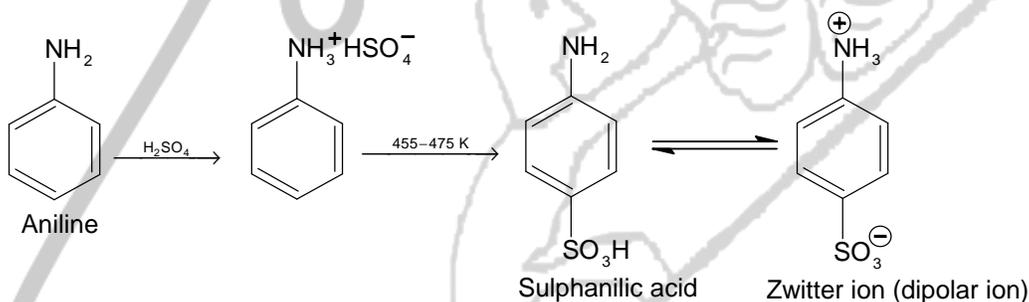


(ii) Nitration: Direct nitration of aniline with nitric acid gives a complex mixture of mono – di and trinitro compounds and oxidation products. If however, NH_2 group is protected by acetylation, main product of nitration is p – nitro derivative.



(iii) Sulphonation:

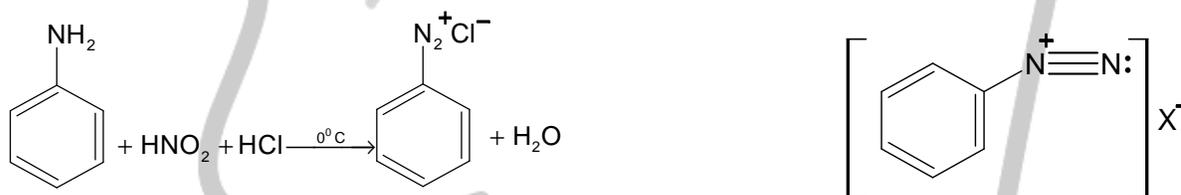
Aniline reacts with conc. H_2SO_4 to form the salt anilinium hydrogen sulphate which on heating at 455 – 475 K gives sulphanilic acid (p – amino benzene sulphonic acid).



Sulphanilic acid exists as Zwitter ion i.e. a dipolar ion which exists in the form of internal salt structure. Such ion has positive as well as negative charge within same molecular structure.

DIAZONIUM SALT:

When primary aromatic amine is treated with nitrous acid in a cool solution, product is unstable compound, known as diazonium salt.



This reaction is known as **diazotisation**. Diazonium salts have the structure

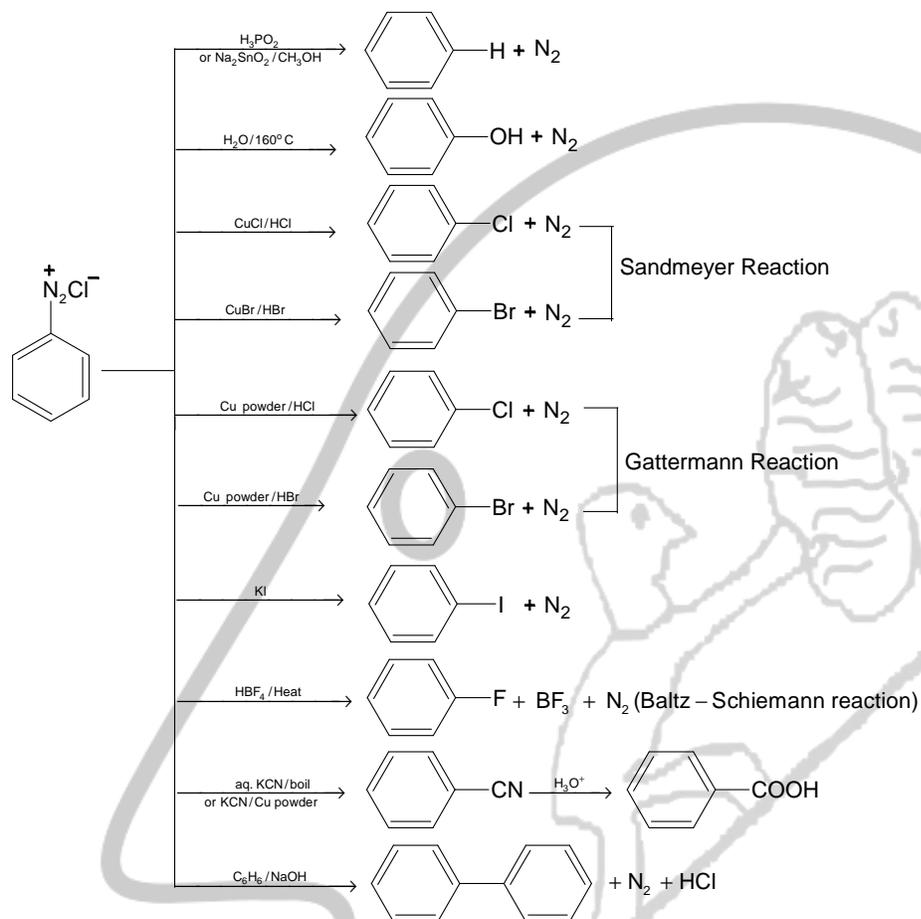
Illustration 28. Why ice cold condition have to be maintained in the diazotisation reaction of aniline?

Solution. Because benzene diazonium chloride is unstable and decomposes to give phenol above 278 K.

Reactions of diazonium salts:

These salts give substitution reactions and coupling reactions as follows:

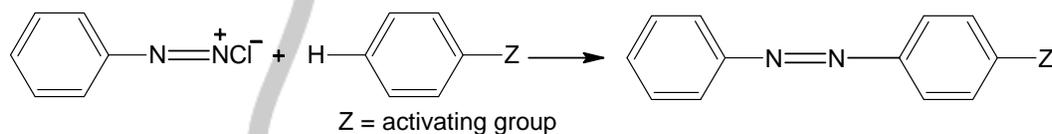
Substitution reactions:



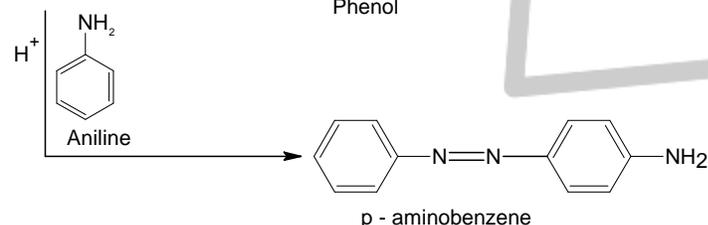
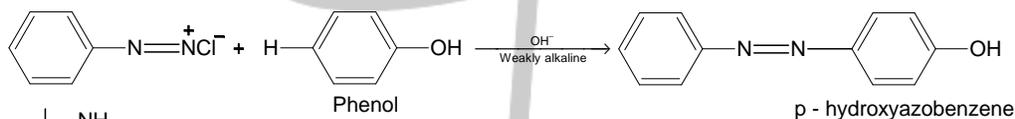
COUPLING REACTIONS

Coupling reactions are electrophilic substitution reactions. Some examples are as follows :

General reaction



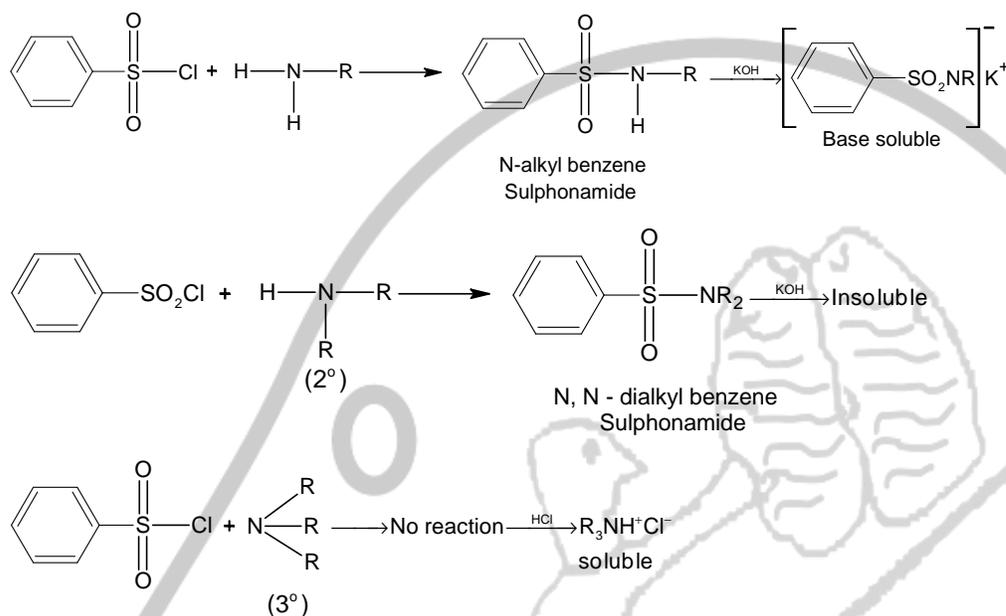
Examples:



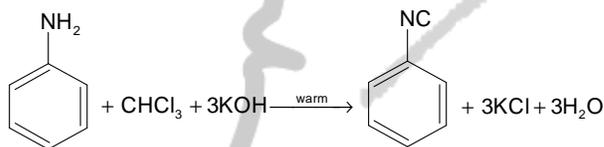
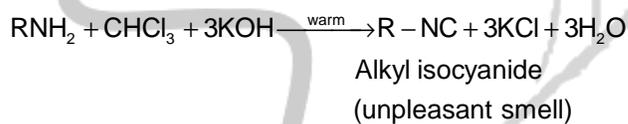
Analysis of Amines:

1. Hinsberg Test:

This test helps to distinguish 1°, 2° and 3° amines. **The Hinsberg's reagent is benzene sulphonyl chloride.**

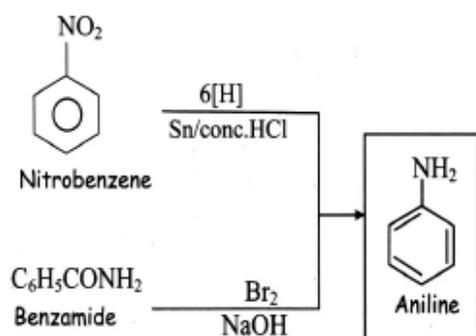
2. Carbylamine test (Isocyanide test):

This test is used to distinguish 1° amines from 2° and 3° amines. This test is given by both 1° aliphatic and 1° aromatic amines.

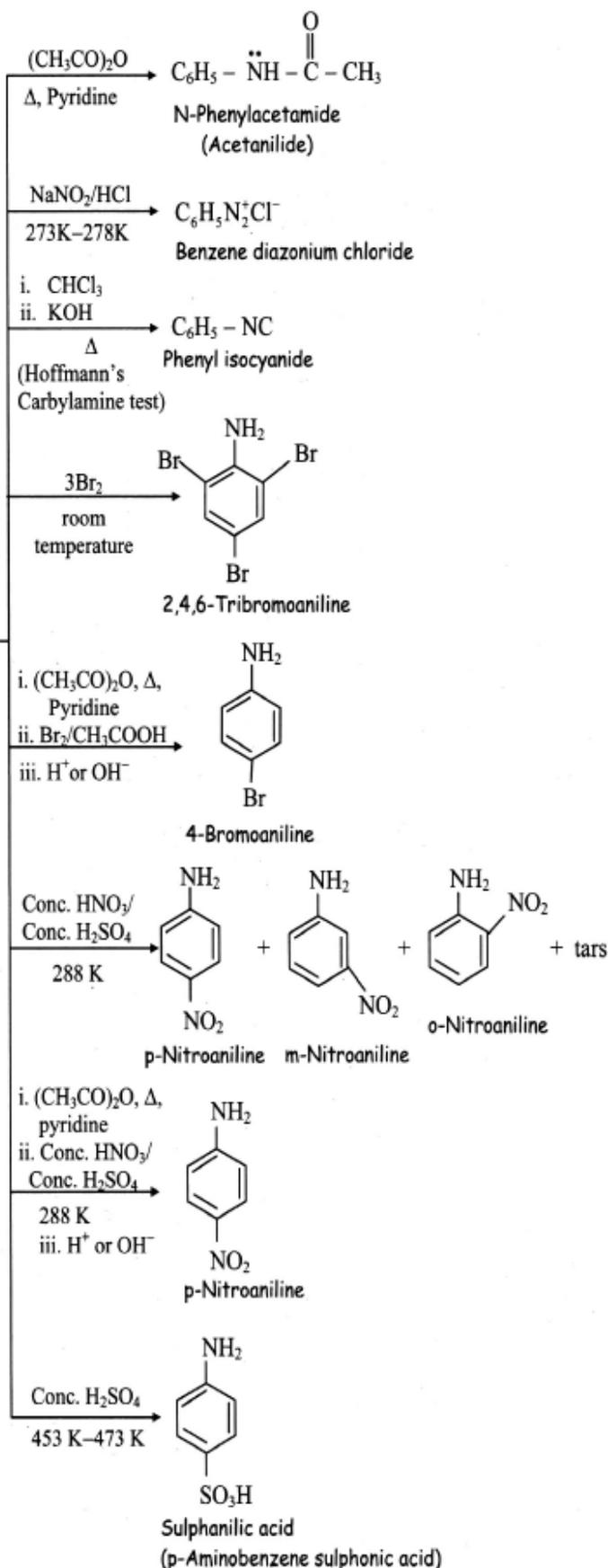


Quick Review

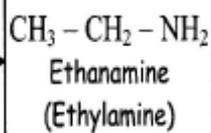
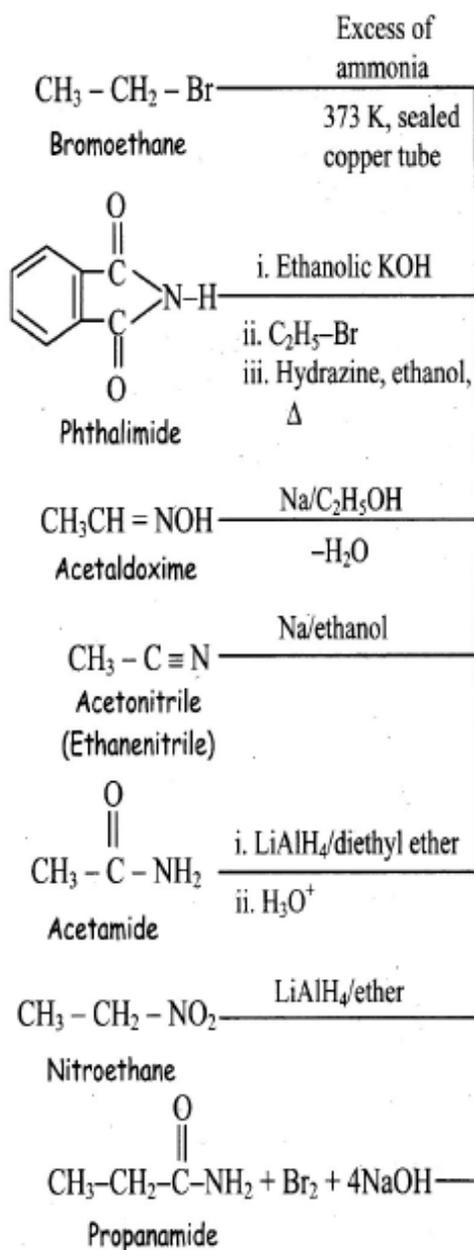
Preparation of aniline:



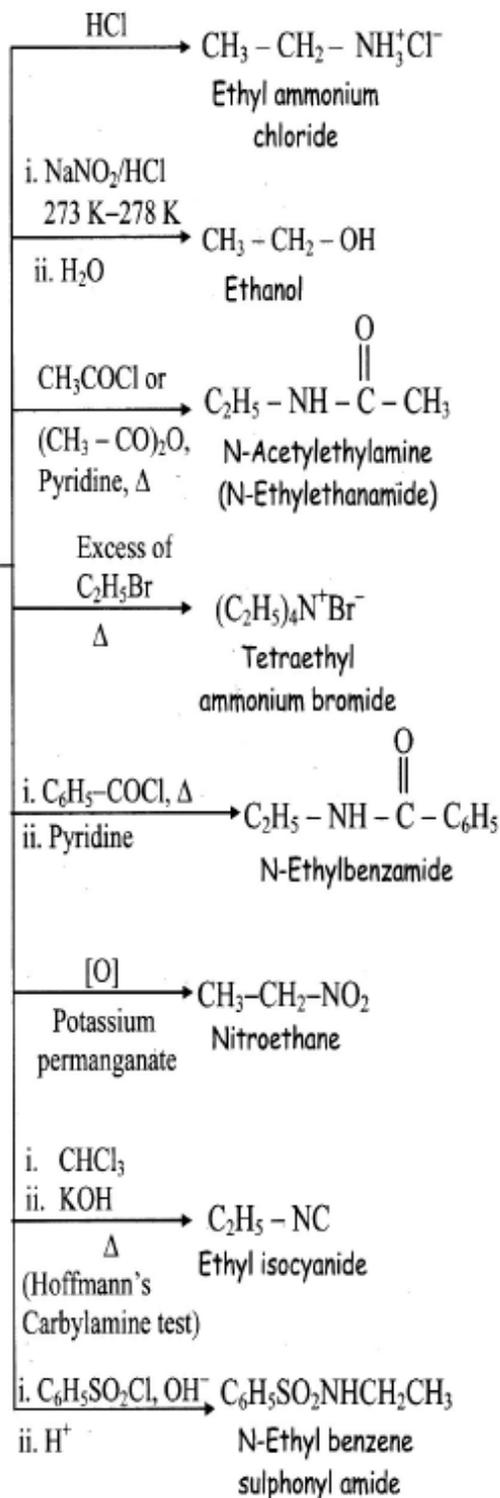
Reactions of aniline:



Preparation of amines:



Reactions of amine:



CH: AMINES
(SUBJECTIVE ASSIGNMENT)

CONCEPTUALS

Q1. The C-N-C bond angle in trimethyl amine is 108°?

Ans. In amines due to the presence of lone pair of e⁻'s the angle is less than tetrahedral angle of 109.5° but due to large size of carbon the angle increase from (107) in ammonia to 108°.

Q2. Alkyl amines are more basic than ammonia?

Ans. The basicity is due to presence of lone pair of e⁻'s but alkyl groups are electron releasing groups so it increases electron density on N atom and makes it more basic.

Q3. Aniline cannot be prepared by Gabriel Phthalamide synthesis?

Ans. As the aryl halide do not undergo nucleophilic substitution with the anion formed by phthalamide.

So it is mainly used for preparation of primary amines only.

Q4. Ethylamine is soluble in water but aniline is not?

Ans. Due to large size of benzene ring, steric hindrance will occur due to which it is less soluble in water as compared to ethylamine.

Q5. Amines have lower b.pt than alcohols of comparable molecular mass.

Ans. Due to less E.N. of nitrogen as compared to oxygen in alcohol, amines form a weaker H-bond and hence they have lower b.pt.

Q6. The order of b.pt is amines is 1° > 2° > 3° Why?

Ans. In 1° amine, more number of H-bonds can be formed as compared to 2° or 3° which increases its b.pt.

Q7. The pK_b value of benzene amines is 9.33 while that of ammonia is 4.75?

Ans. In benzene amine the lone pair of e⁻'s are delocalised due to resonance so it is not available to show basic character and hence it is less basic or its pK_b value is higher than ammonia.

Q8. Aniline does not undergo Friedel-Crafts reaction?

Ans. Because aniline will form salt with aluminium chloride (Lewis acid). Due to this nitrogen acquires positive charge and hence acts as a strong deactivating group for further reaction.

Q9. Aniline readily forms 2, 4, 6-tribromo aniline on reaction with bromine water?

Ans. Due to the highly activating nature of NH₂ group, substitution of Br₂ occurs both at ortho and para positions.

Q10. Sulphanilic acid is soluble in water?

Ans. It is soluble in water because it is capable to form zwitter ion when dissolved in water.

Q11. Methylamine in water reacts with ferric chloride to ppt hydrated ferric oxide.

Ans. Because methylamine in water shows its basic nature and releases OH⁻ ion. The ferric ion will react with OH⁻ ion to form ferric hydroxide and releases Cl⁻ ion.

Q12. Diazonium salts of aromatic amines are more stable than diazonium salt of aliphatic amines?

Ans. The stability of aromatic diazonium salt is due to delocalisation of the charge in benzene ring

Q13. Although amine group is o & p directing in aromatic electrophilic substitution reaction, aniline on nitration also gives a substantial amount of m-nitroaniline?

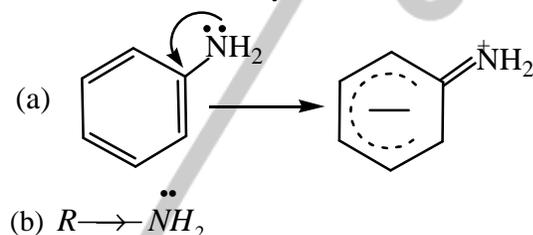
Ans. In strongly acidic medium aniline is protonated to form the anilinium ion which is meta directing. Due to this meta derivative is also formed along with ortho and para derivatives.

14 Acetylation of aniline reduces its activation effect.

Ans. After acetylation of aniline, acetanilide is formed in which due to the presence of $\begin{array}{c} O \\ || \\ -C-CH_3 \end{array}$ group having -I effect, electron density on N-atom decreases and hence, activation effect of aniline gets reduced.

15 CH_3NH_2 is more basic than $C_6H_5NH_2$

Ans. In Aniline, lone pair of electrons of nitrogen is not free for donation because it is involved in resonance. But, in case of methylamine, lone pair of electrons on nitrogen is free for donation. So, aniline is less basic than methylamine.



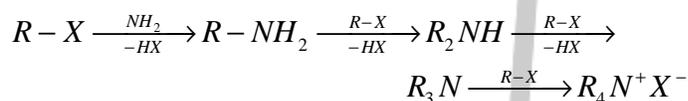
16. Aniline is a weaker base than cyclohexyl amine.

Ans.(i) Aniline is weaker base than cyclohexylamine because of resonance. Due to electromeric effect, the lone pair on nitrogen is attracted by benzene ring.

Hence, Donor tendency of $-\ddot{N}H_2$ group decreases. There is no resonance in cyclohexylamine. Electron repelling nature of cyclohexyl group further increases the donor property of NH_2 group. So, cyclohexylamine is a stronger base.

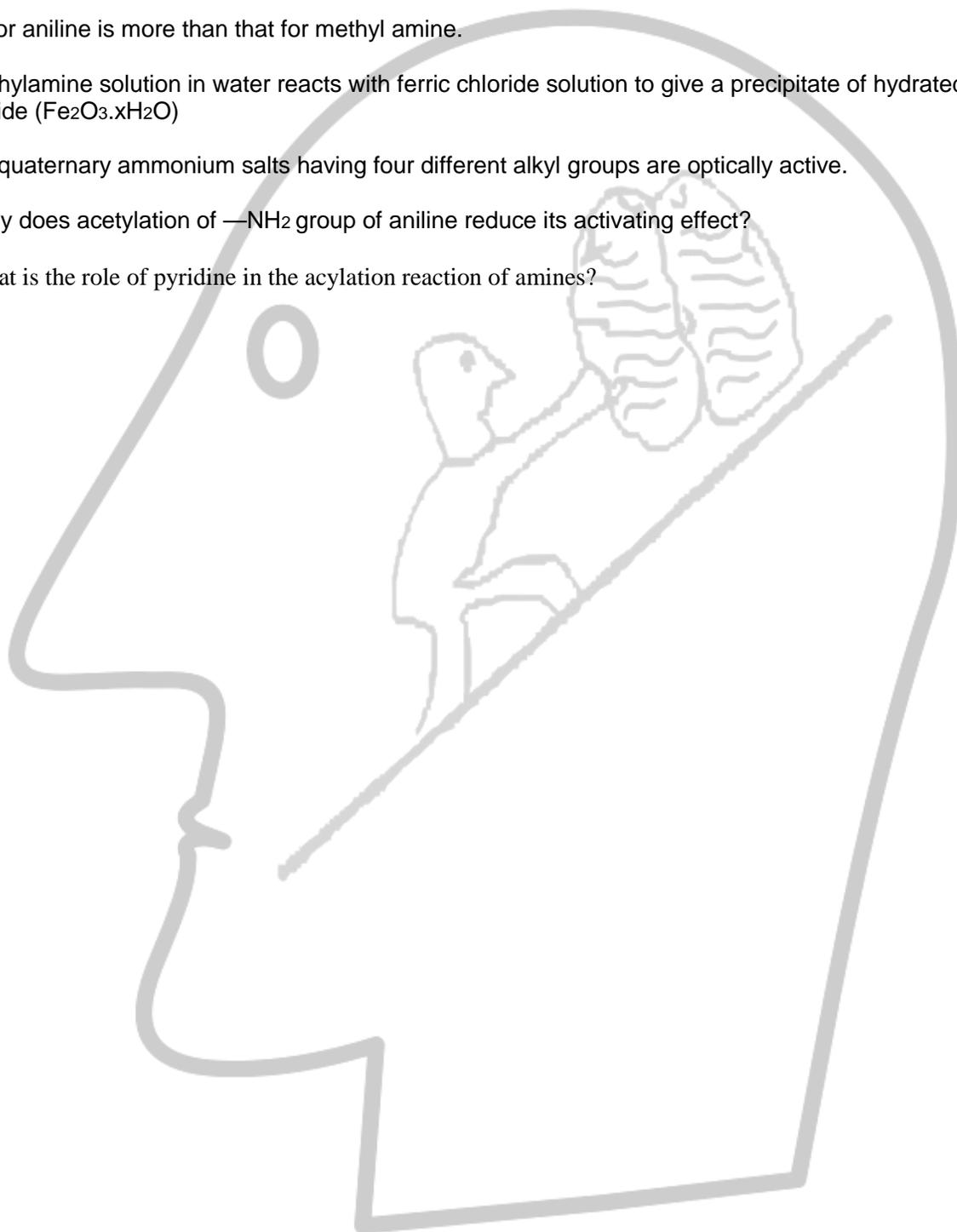
17. It is difficult to prepare pure amines by ammonolysis of alkyl halides.

Ans. The ammonolysis of alkyl halides with ammonia is a nucleophilic substitution reaction in which ammonia acts as a nucleophile by donating the electron pair on nitrogen atom to form primary amine as the initial product. Now, the primary amine can act as a nucleophile and combine with alkyl halide (if available) to give secondary amine and the reaction continues in the same way to form tertiary amine and finally quaternary ammonium salt. Thus, a mixture of products is formed and it is not possible to separate individual amines from the mixture



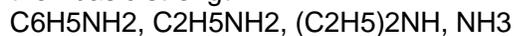
FOR PRACTICE

3. Gabriel phthalimide synthesis is preferred for synthesising primary amines.
4. Why are amines less acidic than alcohols of comparable molecular masses?
5. Why do primary amines have higher boiling point than tertiary amines?
6. Why are aliphatic amines stronger bases than aromatic amines?
7. pK_b for aniline is more than that for methyl amine.
8. Methylamine solution in water reacts with ferric chloride solution to give a precipitate of hydrated iron oxide ($Fe_2O_3 \cdot xH_2O$)
9. the quaternary ammonium salts having four different alkyl groups are optically active.
10. Why does acetylation of $-NH_2$ group of aniline reduce its activating effect?
12. What is the role of pyridine in the acylation reaction of amines?

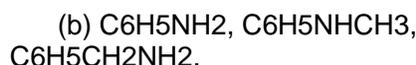
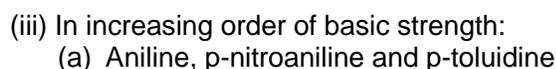
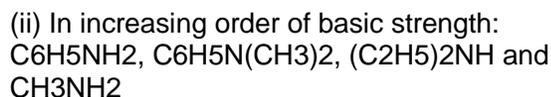
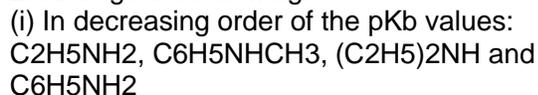


INCREASING/DECREASING ORDER

1. Arrange the following in decreasing order of their basic strength:



2. Arrange the following:



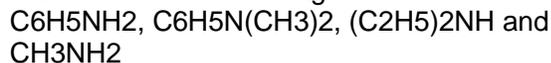
(iv) In decreasing order of basic strength in gas phase:



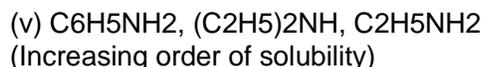
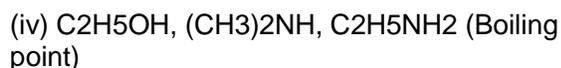
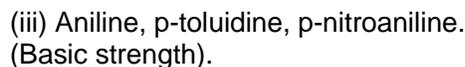
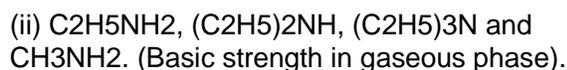
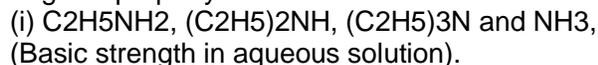
(v) In increasing order of boiling point:
 C_2H_5OH , $(CH_3)_2NH$, $C_2H_5NH_2$

(vi) In increasing order of solubility in water:
 (a) $C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$.

3. Rearrange the following in the increasing order of their basic strength.



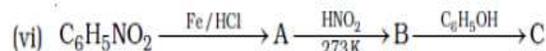
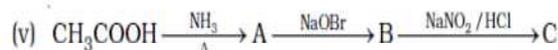
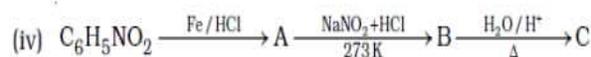
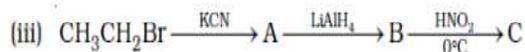
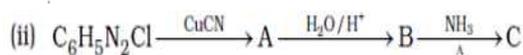
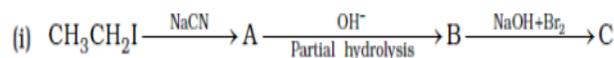
4. Arrange the following in the increasing order of given property indicated.


REACTION COMPLETION

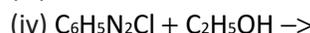
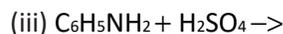
1. Write chemical equations for the following reactions:

- (i) Reaction of ethanolic NH_3 with C_2H_5Cl .
 (ii) Ammonolysis of benzyl chloride and reaction of amine so formed with two moles of CH_3Cl .

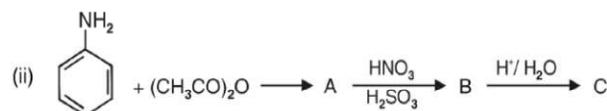
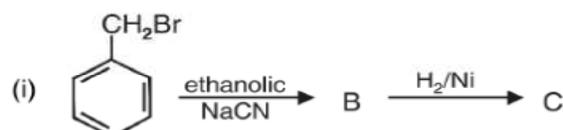
2. Give the structures of A, B and C in the following reactions:



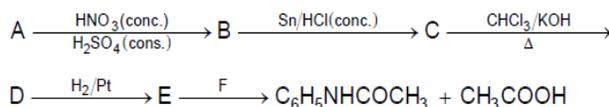
3. Complete the following reactions:



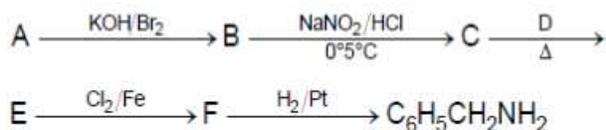
4. Identify the missing reagent/product in the following reactions :



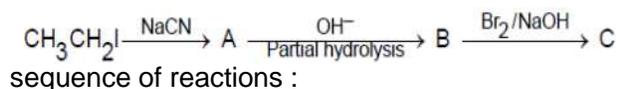
5. Identify A to F.



6. Identify A to F.



7. Write the products formed in the following



PREDICTION

1. An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br₂ and KOH forms a compound 'C' of molecular formula C₆H₇N. Write the structures and IUPAC names of compounds A, B and C.

2. Three isomeric amines A, B and C have the molecular formula C₃H₉N. Compound A on reaction with benzene sulphonyl chloride forms a product which is soluble in NaOH. Compound B on reaction with benzene sulphonyl chloride forms a product which is insoluble in NaOH and compound C does not react with benzene sulphonyl chloride. Identify A, B and C.

[Ans. : (A) CH₃CH₂CH₂NH₂ (B) CH₃CH₂NHCH₃ (C) (CH₃)₃N]

3. An organic compound A (C₂H₃N) is used as a solvent of choice for many organic reactions because it is not reactive in mild acidic and basic conditions. Compound A on treatment with Ni/H₂ forms B. When B is treated with nitrous acid at 273K, ethanol is obtained. When B is warmed with chloroform and NaOH, a foul smelling compound C formed. Identify A, B and C.

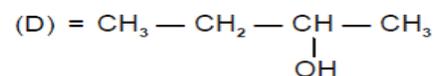
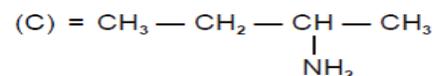
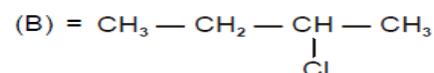
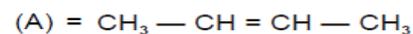
[Ans. : (A) CH₃CN (B) CH₃CH₂NH₂ (C) CH₃CH₂NC

4. An organic compound [A] C₃H₆O₂ on reaction with ammonia followed by heating yields B. Compound B on reaction with Br₂ and alc. NaOH gives compound C (C₂H₇N). Compound

C forms a foul smelling compound D on reaction with chloroform and NaOH. Identify A, B, C, D and write the equations of reactions involved.

[Hint : (A) CH₃CH₂COOH (B) CH₂CH₂CONH₂ (C) CH₃CH₂NH₂ (D) CH₃CH₂NC.]

5. A hydrocarbon 'A', (C₄H₈) on reaction with HCl gives a compound 'B', (C₄H₉Cl), which on reaction with 1 mol of NH₃ gives compound 'C', (C₄H₁₁N). On reacting with NaNO₂ and HCl followed by treatment with water, compound 'C' yields an optically active alcohol, 'D'. Ozonolysis of 'A' gives 2 mols of acetaldehyde. Identify compounds 'A' to 'D'. Explain the reactions involved.



D.P-1

1. Write IUPAC' name of the following compound:



2. Write the structure of 2,4-dinitrochlorobenzene.

3. Gabriel phthalimide synthesis is preferred for synthesising primary amines.

4. Why are amines less acidic than alcohols of comparable molecular masses?

5. Why do primary amines have higher boiling point than tertiary amines?

6. Why are aliphatic amines stronger bases than aromatic amines?

7. pK_b for aniline is more than that for methyl amine.

8. Methylamine solution in water reacts with ferric chloride solution to give a precipitate of hydrated iron oxide (Fe₂O₃.xH₂O)

9. the quaternary ammonium salts having four different alkyl groups are optically active.
 10. Why does acetylation of —NH₂ group of aniline reduce its activating effect?

11. Arrange the following in increasing order of their basic strength:

(i) C₂H₅NH₂, C₆H₅NH₂, NH₃, C₆H₅CH₂NH₂ and (C₂H₅)₂NH

(ii) C₂H₅NH₂, (C₂H₅)₂NH, (C₂H₅)₃N, C₆H₅NH₂

(iii) CH₃NH₂, (CH₃)₂NH, (CH₃)₃N, C₆H₅NH₂, C₆H₅CH₂NH₂.

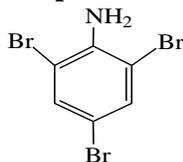
12. What is the role of pyridine in the acylation reaction of amines?

D.P-2

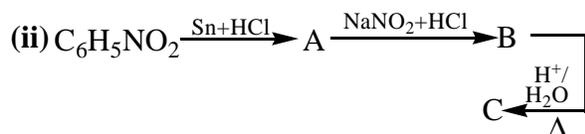
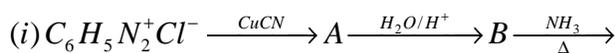
1. Write the IUPAC name of the following compound:



2. Write the IUPAC name of the given compound:



3. Give the structure of A, B, C and C in the following reactions;



D.P-3

1. Write IUPAC name of the following compound:



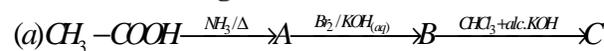
2. Write the structure for *N,N*-ethylmethanamine.

3. How will you convert the following:

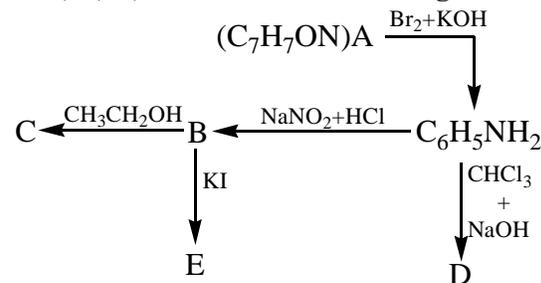
(i) Nitrobenzene into aniline

(ii) Ethanoic acid into methanamine

4. Write the structures of compounds A, B and C in the following reactions:

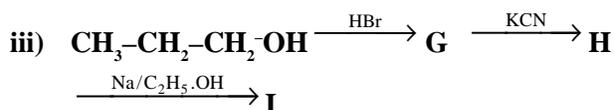
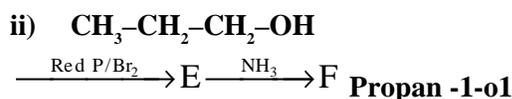
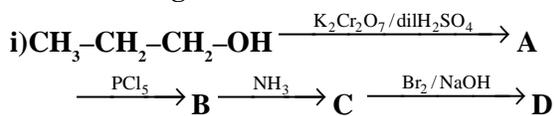


5. An aromatic compound 'A' of molecular formula C₇H₇ON undergoes a series of reaction as shown below. Write the structures of A, B, C, D and E in the following reactions:



6. A colourless substance 'A' (C₆H₇N) is sparingly soluble in water and gives a water soluble compound 'B' on treating with mineral acid. On reacting with CHCl₃ and alcoholic potash 'A' produces an obnoxious smell due to the formation of compound 'C'. Reaction of 'A' with benzenesulphoaryl chloride gives compound 'D' which is soluble in alkali. With NaNO₂ and HCl, 'A' forms compound 'E' which reacts with phenol in alkaline medium to give an orange dye 'F'. Identify compounds 'A' to 'F'.

7. Identify the compounds 'D', 'F' and I in the following series of reactions:



COMPETITION SECTION
OBJECTIVE QUESTIONS
(AMINES)

- Which of the following compounds is soluble in benzene but almost insoluble in water? [EAMCET 2005]
 - C_2H_5OH
 - CH_3CO_2H
 - CH_3CHO
 - $C_6H_5NO_2$
- $$\text{C}_6\text{H}_6 \xrightarrow[\text{H}_2\text{SO}_4]{\text{HNO}_3} A \xrightarrow[\text{FeBr}_3]{\text{Br}_2} B$$

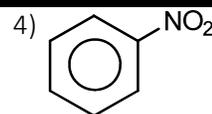
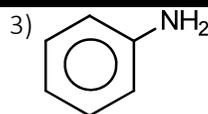
The compound *B* is [OJEE 2008]

 -
 -
 -
 -
- Secondary nitroalkanes can be converted into ketones by using *Y*. Identify *Y* from the following

$$\begin{matrix} R \\ \diagdown \\ \text{CHNO}_2 \\ \diagup \\ R \end{matrix} + Y \longrightarrow \begin{matrix} R \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ R \end{matrix}$$

[VITEEE 2008]

 - Aqueous HCl
 - Aqueous NaOH
 - $KMnO_4$
 - CO
- Which of the following compound reacts with chloroform and a base to form phenyl isocyanide? [MHT CET 2003]
 - Phenol
 - Aniline
 - Benzene
 - Nitrobenzene
- Methyl cyanide gives on hydrolysis [Guj CET 2006]
 - Methyl amine
 - Acetic acid
 - Formic acid
 - Ethyl amine
- Aliphatic nitriles are prepared by the treatment of alkyl halides with [J&K CET 2007]
 - Sodium cyanide
 - Sodium isocyanide
 - Sodium isocyanate
 - Cyanamide
- The compound with foul odour among the following is [J&K CET 2008]
 -
 -



- Final product of hydrolysed alkyl cyanide is [MP PET 2010]
 - $RCOOH$
 - $RCONH_2$
 - $R-C(=NH)-OH$
 - $R-C \equiv N^{\oplus}H$
- Which one of the following does not have sp^2 hybridised carbon? [UP SEE 2007, Jamia Millia Islamia 2007]
 - Acetone
 - Acetic acid
 - Acetonitrile
 - Acetamide
- KCN reacts readily to give a cyanide [J&K CET 2005]
 - Ethyl alcohol
 - Ethyl bromide
 - Bromobenzene
 - chlorobenzene
- Identify *A* and *B* in the reaction given below.

$$\text{Ethane nitrile} \xrightarrow[\text{+2H}_2\text{O, -NH}_3]{\text{Hydrolysis, aq. H}_2\text{SO}_4} A \xrightarrow[\text{-CO}_2]{\text{Decarboxylation, Sodalime, } \Delta} B$$

[Guj CET 2009]

 - Acetic acid, methanol
 - Acetone, methane
 - Ethanoic acid, ethane
 - Ethanoic acid, methane
- Which compound is known as alkyl carbylamines? [Guj CET 2009]
 - $R.CN$
 - $R.NC$
 - $Ar.CN$
 - $Ar.NC$
- $$\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow[\text{(ii) CuCN/H}_3\text{O}^+]{\text{(i) NaNO}_2/\text{HCl}} A; A \text{ is}$$

[OJEE 2007]

 -
 -
 -
 -
- What is '*Z*' in the following reaction?

$$\text{C}_6\text{H}_5\text{NO}_2 \xrightarrow{\text{Sn/HCl}} X \xrightarrow{\text{NaNO}_2} Y \xrightarrow{\text{NaNH}_2} Z$$

[BCECE 2003]

 - Benzoic acid
 - Cyanobenzoic acid
 - Benzamide
 - Aniline

15. $C_5H_{13}N$ reacts with HNO_2 to give an optically active alcohol. The compound is [OJEE 2008]

- 1) Pentan-1-amine
- 2) Pentan-2-amine
- 3) N, N-dimethylpropan-2-amine
- 4) N-methylbutan-2-amine

16.



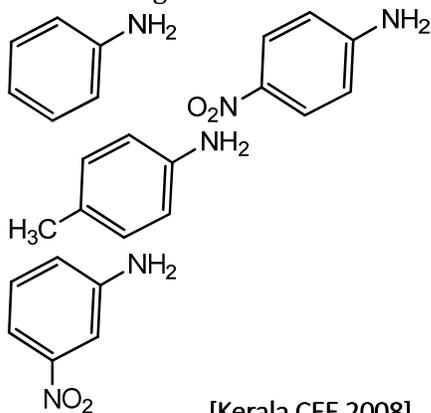
[IIT JEE 2003]

- 1)
- 2)
- 3)
- 4)

17. Which one of the following is most basic? [DCE 2007]

- 1) FCH_2NH_2
- 2) $FCH_2CH_2NH_2$
- 3) $C_6H_5NH_2$
- 4) $C_6H_5CH_2NH_2$

18. The correct order of increasing basic nature of the following bases is



[Kerala CEE 2008]

- 1) $II < V < I < III < IV$
- 2) $V < II < I < III < IV$
- 3) $II < V < I < IV < III$
- 4) $V < II < I < IV < III$
- 5) $II < V < IV < III < I$

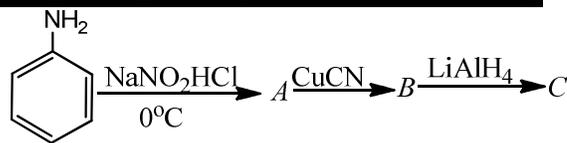
19. The bad smelling substance formed by the action of alcoholic caustic potash on chloroform and aniline is [AMU 2007]

- 1) Nitrobenzene
- 2) Phenyl isocyanide
- 3) Phenyl cyanide
- 4) Phenyl isocyanate

20. Reduction of aniline with acetyl chloride in presence of NaOH produce [BCECE 2007]

- 1) Aniline hydrochloride
- 2) Acetanilide
- 3) *p*-chloroaniline
- 4) A red dye

21. In the reaction sequence



The product 'C' is [AMU 2004]

- 1) Benzonitrile
- 2) Benzaldehyde
- 3) Benzoic acid
- 4) Benzyl amine

22. Decreasing order of basic nature in aqueous solutions [DCE 2007]

- 1) $C_6H_5NH_2 > NH_3 > CH_3NH_2 > (CH_3)_2NH$
- 2) $NH_3 > C_6H_5NH_2 > CH_3NH_2 > (CH_3)_2NH$
- 3) $CH_3NH_2 > NH_3 > C_6H_5NH_2 > (CH_3)_2NH$
- 4) $CH_3NH_2 > (CH_3)_2NH > NH_3 > C_6H_5NH_2$

23. Choose the incorrect statement. [Kerala CEE 2011]

- 1) Primary amines show intermolecular hydrogen bonds.
- 2) Tert-butylamine is primary amine.
- 3) Tertiary amines do not show intermolecular hydrogen bonds.
- 4) Isopropylamine is a secondary amine.

24. Comparing basic strength of NH_3 , CH_3NH_2 and $C_6H_5NH_2$ it may be concluded that [AMU 2009]

- 1) Basic strength remains unaffected
- 2) Basic strength of alkyl amines is lowest
- 3) Basic strength of aryl amines is lowest
- 4) Basic strength of NH_3 is highest

25. Which of the following is strongest base? [Indraprastha CET 2009, CG PET 2009]

- 1) $C_6H_5NH_2$
- 2) $p - NO_2 - C_6H_4NH_2$
- 3) $m - NO_2 - C_6H_4NH_2$
- 4) $C_6H_5CH_2CH_2$

26. Among the amines (A)

$C_6H_5NH_2$, (B) CH_3NH_2 , (C) $(CH_3)_2NH$, (D) $(CH_3)_3N$ the order of basicity is [Kerala CEE 2005]

- 1) $A < B < D < C$
- 2) $D < C < B < A$
- 3) $A < B < C < D$
- 4) $B < C < D < A$
- 5) $D < C < B < A$

27. Why do 2° and 3° amines fail to undergo the carbylamines test? [Guj CET 2010]

- 1) They combine with chloroform to give a stable compound
- 2) They react with alcoholic KOH to give a stable compound
- 3) Their nitrogen atom does not have the required number of hydrogen atoms
- 4) All the given reasons are correct

28. Amino group is *ortho/para*-directing for

- aromatic electrophilic substitution. On nitration of aniline, a good amount of *m*-nitroaniline is obtained. This is due to [DCE 2009]
- In nitration mixture, $-NH_2$ because
- ortho, para*-activity of NH_2 group is completely lost
 - $-NH_3^+$, which is *m*-directing
 - $-NH^+SO_4^-$, which is *m*-directing
 - $-NH_2$ becomes $-NH_2$ becomes
 - $-NH^-NO_2^+$, which is *m*-directing
29. Consider the following reaction,
 $C_6H_5NO_2 \xrightarrow{Sn/HCl} X \xrightarrow{C_6H_5COCl} Y + HCl$
 What is Y? [RPET 2010]
- Acetanilide
 - Benzanilide
 - Azobenzene
 - Hydrazobenzene
30. $CH_3NH_2 + CHCl_3 + KOH \rightarrow$ nitrogen containing compound + KCl + H_2O . Nitrogen containing compound is [IIT JEE 2006]
- $CH_3 - C \equiv N$
 - $CH_3 - NH - CH_3$
 - $CH_3 - \overset{-}{N} \equiv \overset{+}{C}$
 - $CH_3 - \overset{+}{N} \equiv C$
31. Choose the amide which on reduction with $LiAlH_4$ yields a secondary amine [Kerala CEE 2009]
- Ethanamide
 - N-methylethanamide
 - N, N-dimethylethanamide
 - Phenylmethanamide
 - butanamide
32. Primary amine (RNH_2) reacts with nitrous acid to give [MHT CET 2004]
- $RNH_3^+NO_2$
 - ROH
 - ROR
 - None of these
33. In aqueous solutions, the basic strength of amines decreases in the order [JCECE 2010]
- CH_3NH_2
 - $(CH_3)_2NH$
 - $(CH_3)_3N$
 - $(CH_3)_2NH_2$
34. *p*-chloro aniline and anilinium hydrogen chloride can be distinguished by [UP SEE 2003]
- Sandmeyer reaction
 - Carbylamines reaction
 - Hinsberg's reaction
 - $AgNO_3$
35. An organic amino compound reacts with aqueous nitrous acid at low temperature to produce an oily nitrosoamine. The compound is [UP SEE 2008]
- CH_3NH_2
 - $CH_3CH_2NH_2$
 - $CH_3CH_2NHCH_2CH_3$
 - $(CH_3CH_2)_3N$
36. *n*-butylamine (I), diethylamine (II) and N, N-dimethylethylamine (III) have the same molar

- mass. The increasing order of their boiling point is [Kerala CEE 2011]
- III < II < I
 - I < II < III
 - II < III < I
 - II < I < III
 - III < I < II
37. The molecular formula C_3H_9N cannot represent [BCECE 2007]
- 1° amine
 - 2° amine
 - 3° amine
 - Quaternary salt
38. The decreasing order of basic characters of the three amines and ammonia is [MHT CET 2006]
- $NH_3 > CH_3NH_2 > C_2H_5NH_2 > C_6H_5NH_2$
 - $C_2H_5NH_2 > CH_3NH_2 > NH_3 > C_6H_5NH_2$
 - $C_6H_5NH_2 > C_2H_5NH_2 > CH_3NH_2 > NH_3$
 - $CH_3NH_2 > C_2H_5NH_2 > C_6H_5NH_2 > NH_3$
39. The basicity of compounds I, II, III and IV CH_3NH_2 , $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5CH_2NH_2$
- I II III IV
- varies in the order [AMU 2004, Jamia Millia Islamia 2004]
- I > II > III > IV
 - II > I > III > IV
 - III > I > II > IV
 - IV > I > II > III

ANSWER KEY

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

Assertion and Reason Type-II

- If both Assertion & Reason are True and Reason is the correct explanation of Assertion.
- If both Assertion & Reason are True but Reason is not the correct explanation of Assertion.
- If Assertion is True but Reason is False.
- If both Assertion & Reason are False.

- Assertion:** Amides are amphoteric in nature.
Reason: Amides are associated through H-bonding.
- Assertion:** Benzamide and methyl benzoate are derivatives of benzoic acid.
Reason: Benzamide is less easily hydrolysed as compared to methyl benzoate.
- Assertion:** Acetonitrile is another name of ethane nitrile.
Reason: α -H atom of acetonitrile exhibit acidic character.
- Assertion:** Boiling point of trimethyl amine is higher than that of n-propyl amine.
Reason: H-bonding is more extensive in tertiary amines.
- Assertion:** Boiling and melting points of amides are higher than the corresponding acids.
Reason: It is due to strong inter molecular hydrogen bonding in their molecules.
- Assertion:** A mixture of o-nitrophenol and p-nitrophenol can be separated by steam distillation.
Reason: o-nitrophenol is steam volatile but p-nitrophenol is not though both are insoluble in water.
- Assertion:** $C_2H_5O_2N$ shows functional isomerism as well as tautomerism.
Reason: Nitroethane shows tautomerism due to the presence of α -hydrogens and functional isomerism with ethyl nitrite.
- Assertion:** Aniline is a weaker base than benzyl amine.
Reason: In aniline, mesomeric interaction occurs between benzene ring and amino group.

10. Assertion: Urea and thiourea are functional isomers of each other.

Reason: The elements present in thiourea and urea are nitrogen, hydrogen and carbon.

11. Assertion: Methylbromide and silvercyanide react to form methyl isocyanide as major product.

Reason: AgCN has sufficient covalent character.

12. Assertion: Nitroalkanes and alkylnitrites are functional isomers of each other.

Reason: Both alkylnitrites and nitroalkanes give same hydrolytic products.

13. Assertion: Ammonolysis of alkyl halides is not a suitable method for the preparation of pure primary amines.

Reason: Ammonolysis of alkyl halides yields mainly secondary amines.

14. Assertion: The amine product of reaction of alcoholic silver nitrite and ethyl bromide is nitroethane.

Reason: Silver nitrite is predominantly covalent compound.

15. Assertion: Ethanamide (CH_3CONH_2) undergoes dehydration by heating with P_2O_5 .

Reason: ethanamide undergoes dehydration to give nitro compound.

ANSWERS

Q: 1	2	3	4	5
A: 2	2	2	4	1
Q:6	7	8	9	10
A:1	1	1	1	4
Q:11	12	13	14	15
A:1	3	3	1 1	

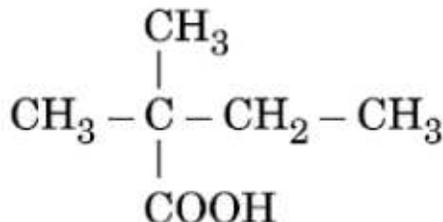
LAST YEARS BOARD QUES.

“ORGANIC CHEMISTRY”**2020****MCQ's**

1. Racemisation occurs in
 (A) SN2 reaction
 (B) SN1 reaction
 (C) Neither SN2 nor SN1 reactions
 (D) SN2 reaction as well as SN1 reaction

2. Peptide linkage is present in
 (A) Carbohydrates (B) Vitamins
 (C) Proteins (D) Rubber

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



- (A) 2,2-Dimethylbutanoic acid
 (B) 2-Carboxyl-2-methylbutane
 (C) 2-Ethyl-2-methylpropanoic acid
 (D) 3-Methylbutane carboxylic acid
4. Out of the following, the strongest base in aqueous solution is
 (A) Methylamine (B) Dimethylamine
 (C) Trimethylamine (D) Aniline
5. Iodoform test is *not* given by
 (A) Hexan-2-one (B) Hexan-3-one
 (C) Ethanol (D) Ethanal
6. Out of the following, the one which is most reactive towards nucleophilic substitution reaction is
 (A) $\text{CH}_2 = \text{CH} - \text{Cl}$ (B) $\text{C}_6\text{H}_5 - \text{Cl}$
 (C) $\text{CH}_3\text{CH} = \text{CH} - \text{Cl}$
 (D) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{Cl}$

COMPREHENSION**PASSAGE-I**

The substitution reaction of alkyl halide mainly occurs by SN1 or SN2 mechanism.

Whatever mechanism alkyl halides follow for the substitution reaction to occur, the polarity of the carbon halogen bond is responsible for these substitution reactions. The rate of SN1 reactions are governed by the stability of carbocation whereas for SN2 reactions steric factor is the deciding factor. If the starting material is a chiral compound, we may end up with an inverted product or racemic mixture depending upon the type of mechanism followed by alkyl halide.

Cleavage of ethers with HI is also governed by steric factor and stability of carbocation, which indicates that in organic chemistry, these two major factors help us in deciding the kind of product formed.

- Predict the stereochemistry of the product formed if an optically active alkyl halide undergoes substitution reaction by SN2 mechanism.
- Write the structures of the products formed when anisole is treated with HI.
- Predict the major product formed when 2-Bromobutane undergoes a reaction with alcoholic KOH.
- Name the instrument used for measuring the angle by which the plane polarised light is rotated.
- Give one use of CHI_3 .

PASSAGE-II

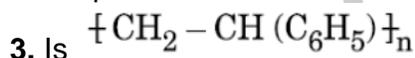
Organic compounds containing amine as functional group are present in a vivid variety of compounds, namely amino acids, hormones, neurotransmitters, DNA, alkaloids, dyes, etc. Drugs including nicotine, morphine, codeine and heroin, etc. which have physiological effects on humans also contain amino group in one form or another. Amines are basic because of the presence of lone pair of electrons on nitrogen. Addition of nitrogen into an organic framework leads to the formation of two families of molecules, namely amines and amides. As chemistry students, we must appreciate the versatility of nitrogen.

1. Give one point of difference between acidic and basic amino acid.
2. What are essential amino acids ?
3. Why are amino acids amphoteric ?
4. Name the linkage formed when carboxyl end of one amino acid condenses with amino end of other amino acid.
5. What are amino acids ?

PASSAGE-III

A large number of simple molecules called monomers combine together by the process of polymerisation to form a macromolecule called polymer. If the repeating structural unit is derived from one type of monomer, the polymer is called homopolymer. If the repeating structural unit is derived from two or more monomers, then the polymer is called copolymer. Homopolymer and copolymer may be formed by addition or condensation reaction. In view of the general awareness and concern for the problems created by the polymeric solid wastes, certain new biodegradable polymers have been developed.

1. Give an example of a natural polymer.
2. Draw the structure of the polymer formed by the polymerisation of monomer chloroprene.



a homopolymer or a copolymer ?

4. Name the polymer used for coating non-stick utensils.
5. Give an example of a biodegradable polymer.

ASSERTION/REASON

- (i) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
- (ii) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is **not** the correct explanation of the Assertion (A).
- (iii) Assertion (A) is correct, but Reason (R) is incorrect statement.
- (iv) Assertion (A) is incorrect, but Reason (R) is correct statement.

1. Assertion (A) : The C – O – H bond angle in alcohols is slightly less than the tetrahedral angle.

Reason (R) : This is due to the repulsive interaction between the two lone electron pairs on oxygen.

2. Assertion (A) : Reactivity of ketones is more than aldehydes.

Reason (R) : The carbonyl carbon of ketones is less electrophilic as compared to aldehydes.

3. Assertion (A) : Sucrose is a non-reducing sugar.

Reason (R) : Sucrose has glycosidic linkage.

4. Assertion (A) : *o*-nitrophenol is a weaker acid than *p*-nitrophenol.

Reason (R) : Intramolecular hydrogen bonding makes *ortho* isomer weaker than *para* isomer.

5. Assertion (A) : Albumin is a globular protein.

Reason (R) : Polypeptide chain coils around to give a straight chain.

6. Assertion (A) : Boiling points of alkyl halides decrease in the order R-I > R-Br > R-Cl > R-F.

Reason (R) : Van der Waals forces decrease with increase in the size of halogen atom.

7. Assertion (A) : Benzaldehyde is less reactive than ethanal towards nucleophilic addition reactions.

Reason (R) : Ethanal is more sterically hindered.

8. Assertion (A) : Alcohols have higher boiling point than alkanes of comparable molecular mass.

Reason (R) : Alcohols have intramolecular hydrogen bond.

ONE WORD

1. Name the disaccharide which on hydrolysis gives two molecules of glucose.

2. Out of $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ and $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Cl}$, which one is more reactive towards $\text{S}_{\text{N}}1$ reaction ?

3. Write an isomer of C_3H_9N which does not react with Hinsberg reagent
4. Name the unit formed by the attachment of a base to 1' position of sugar.

SUBJECTIVE

1. Define the following terms :
 (i) Oligosaccharides
 (ii) Invert sugar
2. What happens when
 (a) Butanone is treated with methyl magnesium bromide and then hydrolysed, and
 (b) Sodium benzoate is heated with soda lime ?
3. Give the structures of A and B in the following sequence of reactions :
- (a) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B$
- (b) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[0^\circ - 5^\circ C]{NaNO_2 + HCl} B$
- (c) $C_6H_5N_2^+Cl^- \xrightarrow[\Delta]{CuCN} A \xrightarrow{H_2O/H^+} B$
4. (a) How will you distinguish between the following pairs of compounds :
 (i) Aniline and Ethanamine
 (ii) Aniline and N-methylaniline
- (b) Arrange the following compounds in decreasing order of their boiling points :
 Butanol, Butanamine, Butane
5. Give the plausible explanation for the following :
 (a) Glucose doesn't give 2,4-DNP test.
 (b) The two strands in DNA are not identical but are complementary.
 (c) Starch and cellulose both contain glucose unit as monomer, yet they are structurally different.
6. (a) Out of t-butyl alcohol and n-butanol, which one will undergo acid catalyzed dehydration faster and why ?
 (b) Carry out the following conversions :
 (i) Phenol to Salicylaldehyde
 (ii) t-butylchloride to t-butyl ethyl ether
 (iii) Propene to Propanol
7. (a) Give the mechanism for the formation of ethanol from ethene.

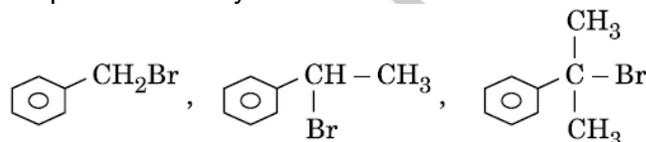
(b) Predict the reagent for carrying out the following conversions :

- (i) Phenol to benzoquinone
 (ii) Anisole to p-bromoanisole
 (iii) Phenol to 2,4,6-tribromophenol

8. Give reasons for the following :

- (a) Bond angle C-O-H in alcohol is slightly less than the tetrahedral angle.
 (b) C - OH bond length in CH_3OH is slightly more than the C - OH bond length in phenol.

9. Justify and arrange the following compounds namely



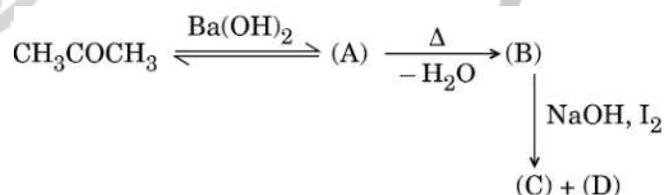
in increasing order of reactivity towards the asked displacement namely :

- (a) S_N1 (b) S_N2

10. Account for the following :

- (a) Aniline is a weaker base compared to ethanamine.
 (b) Aniline does not undergo Friedel-Crafts reaction.
 (c) Only aliphatic primary amines can be prepared by Gabriel Phthalimide synthesis.

11. (a) Complete the following sequence of reactions :



- (i) Identify (A) to (D).
 (ii) Give the IUPAC name of (A).
- (b) How can you distinguish between :
 (i) Ethanol and Propanone, and
 (ii) Benzoic acid and Phenol ?

12. (a) An organic compound 'A' having molecular formula $C_5H_{10}O$ gives negative Tollens' test, forms n-pentane on Clemmensen reduction but doesn't give iodoform test. Identify 'A' and give all the reactions involved.

(b) Carry out the following conversions :

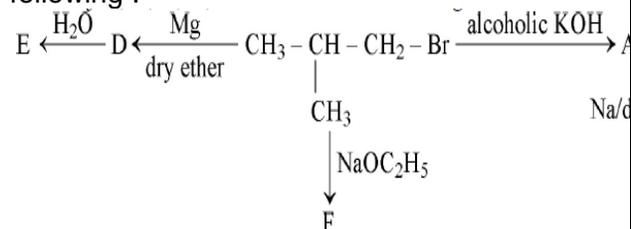
- (i) Propanoic acid to 2-Bromopropanoic acid
 (ii) Benzoyl chloride to benzaldehyde

(c) How will you distinguish between benzaldehyde and acetaldehyde ?

13. How can you convert the following ?

- (i) Phenol to o-hydroxy benzaldehyde.
- (ii) Methanal to ethanol
- (iii) Phenol to phenyl ethanoate.

14. Identify A, B, C, D, E and F in the following :



15. (i) What are the hydrolysis products of DNA ?

(ii) What happens when D-glucose is treated with Bromine water ?

(iii) What is the effect of denaturation on the structure of proteins ?

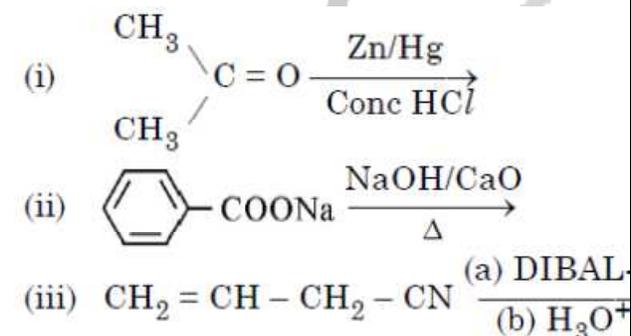
16. (a) Write the products formed when benzaldehyde reacts with the following reagents :

- (i) CH₃CHO in presence of dilute NaOH
- (ii) H₂N – NH
- (iii) Conc. NaOH

(b) Distinguish between following :

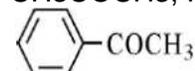
- (i) CH₃ – CH = CH – CO – CH₃ and CH₃ – CH₂ – CO – CH = CH₂
- (ii) Benzaldehyde and Benzoic acid.

17. (a) Write the final products in the following :



(b) Arrange the following in the increasing order of their reactivity

towards nucleophilic addition reaction :



(c) Draw the structure of 2, 4 DNP derivative of acetaldehyde.

18. Give reasons :

- (a) Grignard reagent should be prepared under anhydrous conditions,
- (b) Alkyl halides are immiscible with water although they are polar, and
- (c) Chloroform is stored in dark coloured bottles filled up to the brim.

19. (a) Carry out the following conversions :

(i) Propene to propan-2-ol

(ii) Benzyl chloride to benzyl alcohol

(b) Arrange the following compounds in increasing order of their acidic strength :
4-Methylphenol, Phenol, 4-Nitrophenol

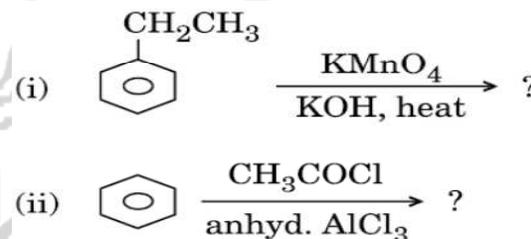
20. Describe a method for the identification of CH₃NH₂, (CH₃)₂NH and (CH₃)₃N. Also write the chemical equations for the reactions involved.

21. (a) Draw the structures of the following derivatives :

(i) 2,4-DNP of benzaldehyde

(ii) Propanone oxime

(b) Complete the following synthesis :



(c) Carboxylic acid is a stronger acid than phenol. Justify.

22. (a) An organic compound 'A' with molecular formula C₄H₈O₂ was hydrolysed with dil. H₂SO₄ to give a carboxylic acid 'B' and an alcohol 'C'. 'C' on dehydration gives ethene and 'C' also on oxidation gives back 'B'. Identify 'A', 'B' and 'C' and write the chemical equations for the reactions involved.

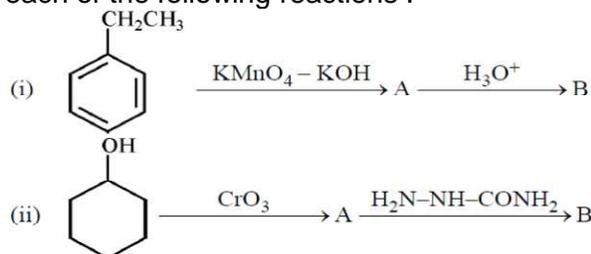
(b) How will you convert ethanal into the following compounds ?

- (i) Ethanol
- (ii) Ethane

2019

1. Arrange the following in increasing order of boiling points :
(CH₃)₃N, C₂H₅OH, C₂H₅NH₂

2. Write structures of compounds A and B in each of the following reactions :



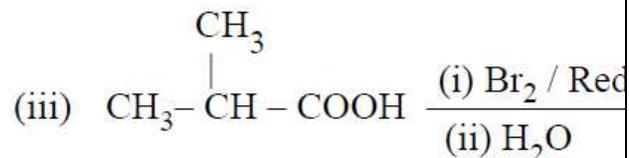
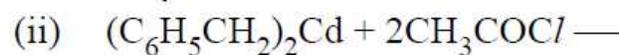
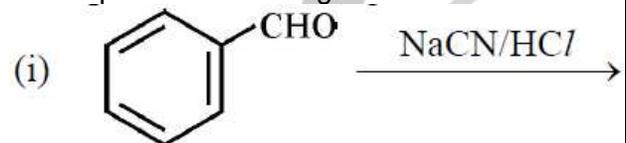
3. (i) Out of (CH₃)₃C-Br and (CH₃)₃C-I, which one is more reactive towards S_N1 and why ?

(ii) Write the product formed when p-nitrochlorobenzene is heated with aqueous NaOH at 443 K followed by acidification.

(iii) Why dextro and laevo – rotatory isomers of Butan-2-ol are difficult to separate by fractional distillation ?

4. An aromatic compound 'A' on heating with Br₂ and KOH forms a compound 'B' of molecular formula C₆H₇N which on reacting with CHCl₃ and alcoholic KOH produces a foul smelling compound 'C'. Write the structures and IUPAC names of compounds A, B and C.

5. Complete the following reactions :

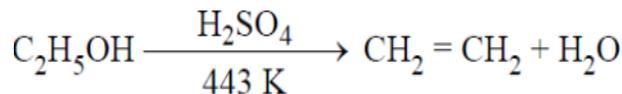


6. Write chemical equations for the following reactions :

- (i) Propanone is treated with dilute Ba(OH)₂.
(ii) Acetophenone is treated with Zn(Hg)/Conc. HCl
(iii) Benzoyl chloride is hydrogenated in presence of Pd/BaSO₄.

7. (a) How do you convert the following :

- (i) Phenol to Anisole
(ii) Ethanol to Propan-2-ol
(b) Write mechanism of the following reaction :



(c) Why phenol undergoes electrophilic substitution more easily than benzene ?

8. (a) Account for the following :

- (i) o-nitrophenol is more steam volatile than p-nitrophenol.
(ii) t-butyl chloride on heating with sodium methoxide gives 2-methylpropene instead of t-butylmethylether.

(b) Write the reaction involved in the following :

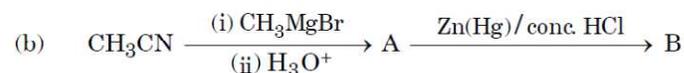
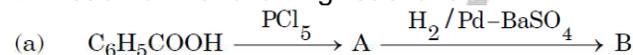
- (i) Reimer-Tiemann reaction
(ii) Friedal-Crafts Alkylation of Phenol

(c) Give simple chemical test to distinguish between Ethanol and Phenol.

9. Arrange the following in decreasing order of basic character :
C₆H₅NH₂, (CH₃)₃N, C₂H₅NH₂

10. Out of Chlorobenzene and Cyclohexyl chloride, which one is more reactive towards nucleophilic substitution reaction and why ?

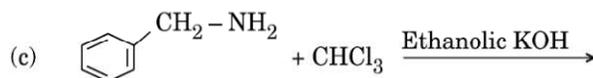
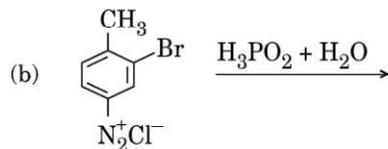
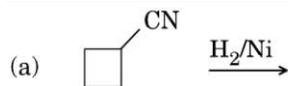
11. Write structures of main compounds A and B in each of the following reactions :



12. Among all the isomers of molecular formula C₄H₉Br, identify

- (a) the one isomer which is optically active.
(b) the one isomer which is highly reactive towards S_N2.
(c) the two isomers which give same product on dehydrohalogenation with alcoholic KOH.

13. Complete the following reactions :



14. How do you convert the following :

- (a) N-phenylethanamide to p-bromoaniline
 (b) Benzene diazonium chloride to nitrobenzene
 (c) Benzoic acid to aniline

15. (a) Give reasons :

- (i) Benzoic acid is a stronger acid than acetic acid.
 (ii) Methanal is more reactive towards nucleophilic addition reaction than ethanal.
 (b) Give a simple chemical test to distinguish between propanal and propanone.

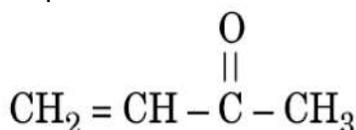
16. (a) Give equations of the following reactions :

- (i) Phenol is treated with conc. HNO_3 .
 (ii) Propene is treated with B_2H_6 followed by $\text{H}_2\text{O}_2/\text{OH}^-$.
 (iii) Sodium t-butoxide is treated with CH_3Cl .
 (b) How will you distinguish between butan-1-ol and butan-2-ol ?
 (c) Arrange the following in increasing order of acidity :
 Phenol, ethanol, water

17. (a) How can you obtain Phenol from (i) Cumene, (ii) Benzene sulphonic acid, (iii) Benzene diazonium chloride ?

- (b) Write the structure of the major product obtained from dinitration of 3-methylphenol.
 (c) Write the reaction involved in Kolbe's reaction.

18. Write the IUPAC name of the following compound :



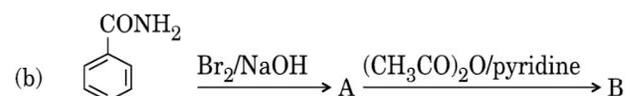
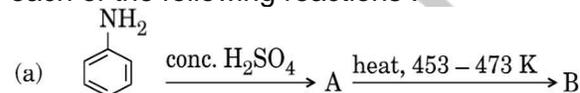
19. Arrange the following in increasing order of their acidic character :

Benzoic acid, Phenol, Cresol

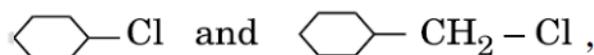
20. Account for the following :

- (a) Gabriel phthalimide synthesis is not preferred for preparing aromatic primary amines.
 (b) On reaction with benzene sulphonyl chloride, primary amine yields product soluble in alkali whereas secondary amine yields product insoluble in alkali.

21. Write structures of compounds A and B in each of the following reactions :

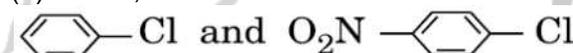


22. (a) Out of ,



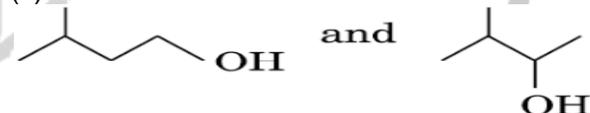
which one is more reactive towards $\text{S}_{\text{N}}2$ reaction and why ?

(b) Out of , which one is more



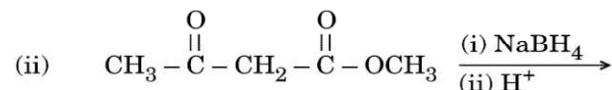
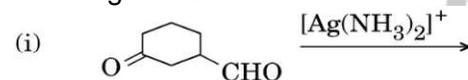
reactive towards nucleophilic substitution reaction and why ?

(c) Out of

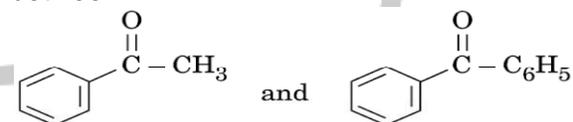


, which one is optically active and why ?

23. a) Predict the main product of the following reactions :



(b) Give a simple chemical test to distinguish between



(c) Why is alpha (α) hydrogen of carbonyl compounds acidic in nature ?

24. (a) Write the main product formed when propanal reacts with the following reagents :
 (i) 2 moles of CH₃OH in presence of dry HCl
 (ii) Dilute NaOH
 (iii) H₂N – NH₂ followed by heating with KOH in ethylene glycol

(b) Arrange the following compounds in increasing order of their property as indicated :
 (i) F – CH₂COOH, O₂N – CH₂COOH, CH₃COOH, HCOOH — acid character
 (ii) Acetone, Acetaldehyde, Benzaldehyde, Acetophenone — reactivity towards addition of HCN

2014

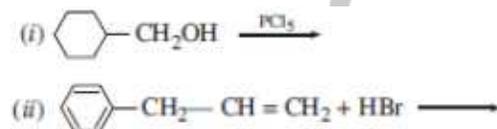
1. Identify the chiral molecule in the following pair:



2. The conversion of primary aromatic amines into diazonium salts is known as _____ .
 3. Write the structure of p-methylbenzaldehyde.
 4. Write the equations involved in the following reactions:
 (i) Reimer-Tiemann reaction
 (ii) Williamson synthesis

5. Write the mechanism of the following reaction:
 CH₃CH₂OH $\xrightarrow{\text{HBr}}$ CH₃CH₂Br + H₂O

6. (a) Draw the structures of major monohalo products in each of the following reactions:



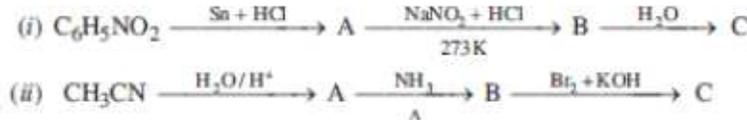
(b) Which halogen compound in each of the following pairs will react faster in SN₂ reaction?

- (i) CH₃Br or CH₃I
 (ii) (CH₃)₃C–Cl or CH₃–Cl

7. Account for the following:
 (i) Primary amines (R-NH₂) have higher boiling point than tertiary amines (R₃N).
 (ii) Aniline does not undergo Friedel–Crafts reaction.
 (iii) (CH₃)₂NH is more basic than (CH₃)₃N in an aqueous solution.

OR

Give the structures of A, B and C in the following reactions:



8. (a) Write the products formed when CH₃CHO reacts with the following reagents:

- (i) HCN
 (ii) H₂N–OH
 (iii) CH₃CHO in the presence of dilute NaOH

(b) Give simple chemical tests to distinguish between the following pairs of compounds:

- (i) Benzoic acid and Phenol
 (ii) Propanal and Propanone

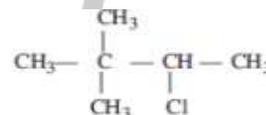
OR

(a) Account for the following:
 (i) Cl–CH₂COOH is a stronger acid than CH₃COOH.
 (ii) Carboxylic acids do not give reactions of carbonyl group.
 (b) Write the chemical equations to illustrate the following name reactions:
 (i) Rosenmund reduction
 (ii) Cannizzaro's reaction
 (c) Out of CH₃CH₂–CO–CH₂–CH₃ and CH₃CH₂–CH₂–CO–CH₃, which gives iodoform test?

9. Write the structure of 4-chloropentan-2-one.
 10. Write the structure of 2-hydroxybenzoic acid.

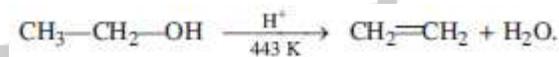
2013

11. Write the IUPAC name of the following compound:



12. Rearrange the following compounds in the increasing order of their boiling points:
 CH₃–CHO, CH₃–CH₂–OH, CH₃–CH₂–CH₃

13. Write the structure of n-methylethanamine.
 14. Explain the mechanism of the following reaction:



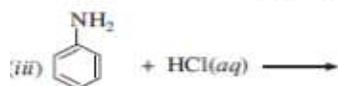
15. Give reasons for the following:
 (i) Ethyl iodide undergoes SN₂ reaction faster than ethyl bromide.
 (ii) (±) 2–Butanol is optically inactive.

(iii) C–X bond length in halobenzene is smaller than C–X bond length in CH₃–X.

16. Write the equations involved in the following reactions:

- (i) Reimer-Tiemann reaction
 (ii) Williamson's ether synthesis

17. Complete the following reactions:



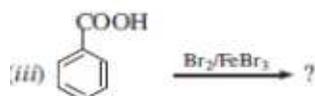
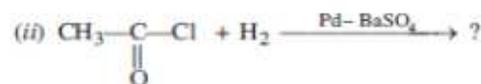
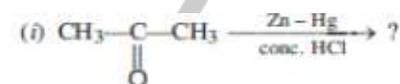
18. (a) How will you convert the following:

- (i) Propanone to Propan-2-ol
 (ii) Ethanal to 2-hydroxy propanoic acid
 (iii) Toluene to benzoic acid
 (b) Give simple chemical test to distinguish between:

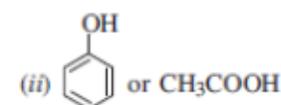
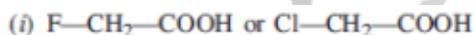
- (i) Pentan-2-one and Pentan-3-one
 (ii) Ethanal and Propanal

OR

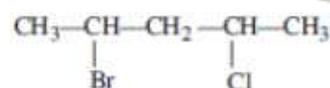
(a) Write the products of the following reactions:



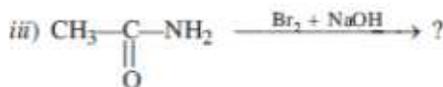
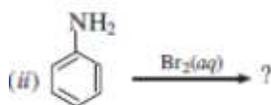
(b) Which acid of each pair shown here would you expect to be stronger?



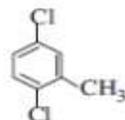
19. Write the IUPAC name of the following compound:



20. Write the main products of the following reactions:

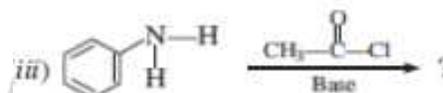
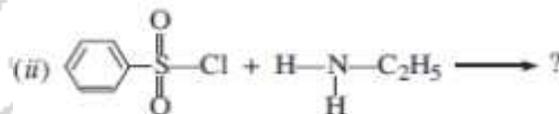
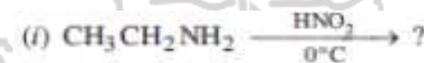


21. Write the IUPAC name of the following compound:



22. Write the structure of prop-2-en-1-amine.

23. Write the main products of the following reactions:



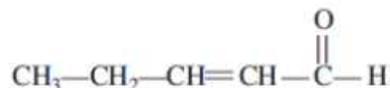
24. Ethanol is soluble in water. Why?

25. Write the structure of 2-aminotoluene.

2012

26. What happens when bromine attacks $\text{CH}_2\text{-CH-CH}_2\text{-C(CH}_3)_2$?

27. Write the IUPAC name of the following:



28. Explain the mechanism of acid catalysed hydration of an alkene to form corresponding alcohol.

29. Explain the following behaviours:

- (i) Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses.
 (ii) Ortho-nitrophenol is more acidic than ortho-methoxyphenol.

30. Describe the following, giving the relevant chemical equation in each case:

- (i) Carbylamine reaction
 (ii) Hoffmann's bromamide reaction

31. Answer the following questions:

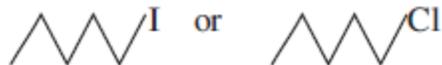
(i) What is meant by chirality of a compound?

Give an example.

(ii) Which one of the following compounds is more easily hydrolysed by KOH and why?

$\text{CH}_3\text{CHClCH}_2\text{CH}_3$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$

(iii) Which one undergoes $\text{S}_\text{N}2$ substitution reaction faster and why?



32.(a) Write a suitable chemical equation to complete each of the following transformations:

(i) Butan-1-ol to butanoic acid

(ii) 4-Methylacetophenone to benzene-1, 4-dicarboxylic acid.

(b) An organic compound with molecular formula $\text{C}_9\text{H}_{10}\text{O}$ forms 2,4-DNP derivative, reduces Tollen's reagent and undergoes Cannizzaro's reaction. On vigorous oxidation it gives 1,2-benzenedicarboxylic acid. Identify the compound.

OR

(a) Give chemical tests to distinguish between

(i) Propanol and propanone

(ii) Benzaldehyde and acetophenone

(b) Arrange the following compounds in increasing order of their property as indicated:

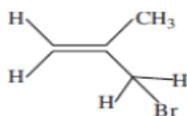
(i) Acetaldehyde, Acetone, Methyl tert-butyl ketone (reactivity towards HCN)

(ii) Benzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)

(iii) $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$, $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$, $(\text{CH}_3)_2\text{CHCOOH}$ (acid strength)

33. Write the IUPAC name of $\text{Ph}-\text{CH}=\text{CH}-\text{CHO}$.

34. Write the IUPAC name of the following:



2015

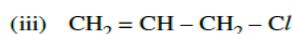
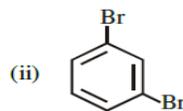
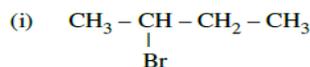
35. Write the IUPAC name of the following :
 $\text{CH}_3 - \text{CH}_2 - \text{CHO}$

36 Arrange the following in increasing order of basic strength

Aniline, p-Nitroaniline and p-Toluidine

37. Write the mechanism of acid dehydration of ethanol to yield ethene.

38. Give the IUPAC names of the following compounds :



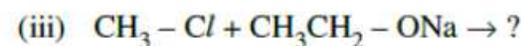
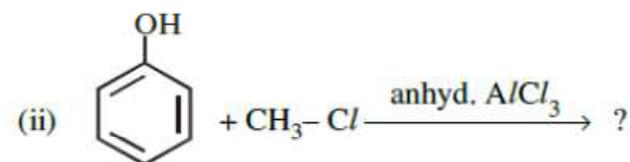
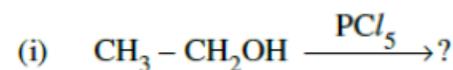
39. How are the following conversions carried out ?

(i) Benzyl chloride to Benzyl alcohol

(ii) Ethyl magnesium chloride to Propan-1-ol

(iii) Propene to Propan-2-ol

40. Write the major product in the following equations :



41.(a) Draw the structures of the following :

(i) p-Methylbenzaldehyde

(ii) 4-Methylpent-3-en-2-one

(b) Give chemical tests to distinguish between the following pairs of compounds :

(i) Benzoic acid and Ethyl benzoate.

(ii) Benzaldehyde and Acetophenone.

(iii) Phenol and Benzoic acid.

42. Draw the structures of the following derivatives :

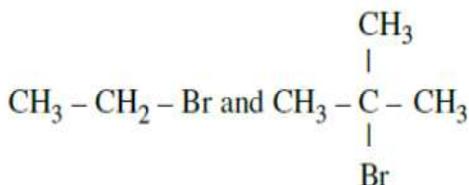
(i) Propanone oxime

(ii) Semicarbazone of CH_3CHO

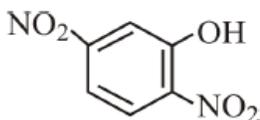
43. How will you convert ethanal into the following compounds ? Give the chemical equations involved.

- (i) $\text{CH}_3 - \text{CH}_3$
 (ii) $\text{CH}_3 - \underset{\text{OH}}{\text{CH}} - \text{CH}_2 - \text{CHO}$
 (iii) $\text{CH}_3\text{CH}_2\text{OH}$

44. Which would undergo $\text{S}_\text{N}2$ reaction faster in the following pair and why ?

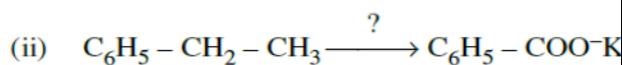
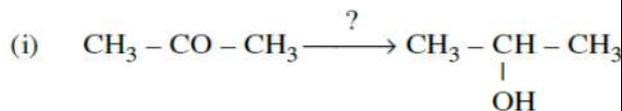


45. Write the IUPAC name of the given



compound :

46. Name the reagents used in the following reactions :

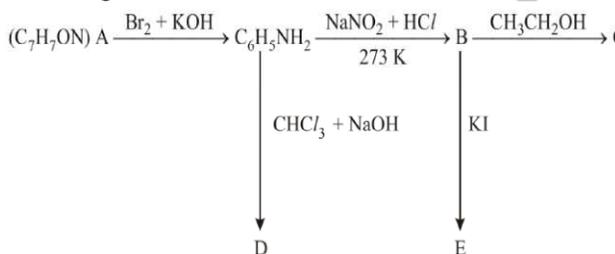


47. Write the structure of an isomer of compound $\text{C}_4\text{H}_9\text{Br}$ which is most reactive towards $\text{S}_\text{N}1$ reaction.

48. Give reasons :

- (a) n-Butyl bromide has higher boiling point than t-butyl bromide.
 (b) Racemic mixture is optically inactive.
 (c) The presence of nitro group ($-\text{NO}_2$) at o/p positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.

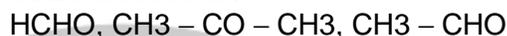
49. An aromatic compound 'A' of molecular formula $\text{C}_7\text{H}_7\text{ON}$ undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions :



50. Write the structures of main products when aniline reacts with the following reagents :

- (i) Br_2 water (ii) HCl
 (iii) $(\text{CH}_3\text{CO})_2\text{O}$ / pyridine

51. Arrange the following in the decreasing order of their reactivity towards nucleophilic addition reaction :



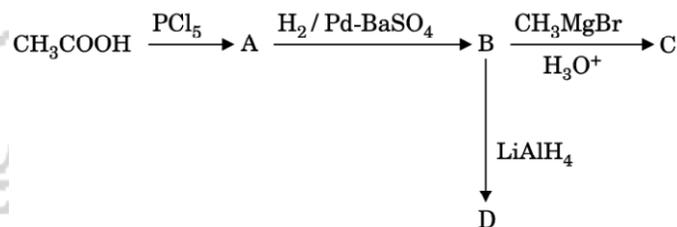
52. Give a simple chemical test to distinguish between the following pairs of compounds : $\text{C}_6\text{H}_5\text{CHO}$ and $\text{C}_6\text{H}_5 - \text{CO} - \text{CH}_3$

53. Write the structure of 4-chloropentan-2-one.

54. Distinguish between the following :

- (i) $\text{CH}_3 - \text{CO} - \text{CH}_2 - \text{CH}_3$ and $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CHO}$
 (ii) Ethanal and ethanoic acid

55. Write the structures of A, B, C, and D in the following reactions :



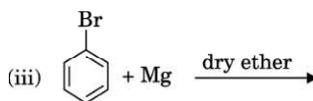
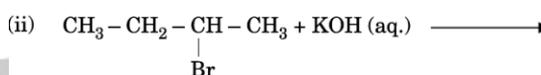
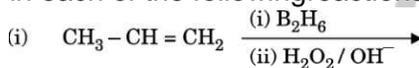
56. Give reasons for the following :

- (i) Aniline does not undergo Friedel-Crafts reaction.
 (ii) p-methylaniline is more basic than p-nitroaniline.
 (iii) Acetylation of $-\text{NH}_2$ group is done in aniline before preparing its ortho and para compounds.

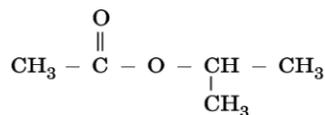
57. How do you convert the following :

- (i) Phenol to 2-hydroxyacetophenone
 (ii) Ethyl chloride to methoxy ethane
 (iii) Acetone to 2-methylpropan-2-ol

58. Write the structures of the major product in each of the following reactions :



59. Name the alcohol that is used to make the following ester and also name this compound :



60. Write the structures of the following organic halogen compounds :

- (i) p-Bromochlorobenzene
(ii) 1-Chloro-4-ethylcyclohexane

61. (i) Arrange the following compounds in an increasing order of basic strength :

$\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$ and CH_3NH_2

(ii) Arrange the following compounds in a decreasing order of pK_b values :

$\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{NHCH}_3$, $(\text{C}_2\text{H}_5)_2\text{NH}$ and $\text{C}_6\text{H}_5\text{NH}_2$

62. Give a chemical test to distinguish between each of the following pairs of compounds :

- (i) Ethylamine and Aniline
(ii) Aniline and Benzylamine

63. How are the following conversions carried out ?

- (i) Propene \rightarrow Propan-2-ol
(ii) Ethylmagnesium chloride \rightarrow Propan-1-ol
(iii) Benzyl chloride \rightarrow Benzyl alcohol

64. Write the IUPAC names of the following compounds :

- (i) $\text{CH}_3\text{CO}(\text{CH}_2)_4\text{CH}_3$
(ii) $\text{Ph} - \text{CH} = \text{CH} - \text{CHO}$

65. Describe the following conversions in not more than two steps :

- (i) Ethanol to 3-Hydroxybutanal
(ii) Benzoic acid to m-Nitrobenzyl alcohol
(iii) Propanone to Propene

66. Draw the structures of the following compounds

- (i) 4-Chloropentan-2-one
(ii) p-Nitropropiophenone

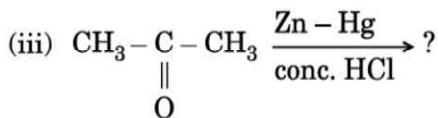
67. Give tests to distinguish between the following pairs of compounds :

- (i) Ethanal and Propanal
(ii) Phenol and Benzoic acid
(iii) Benzaldehyde and Acetophenone

68. Draw the structures of the following compounds

- (i) 4-chloropentan-2-one
(ii) But-2-en-1-al

69. Write the product(s) in the following :



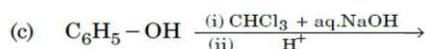
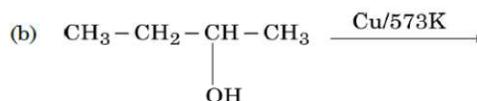
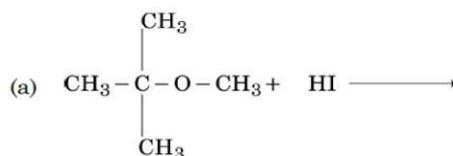
2016

70. Arrange the following in the increasing order of their boiling point :

$\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_2\text{H}_5\text{OH}$, $(\text{CH}_3)_3\text{N}$

71. Give a simple chemical test to distinguish between the following pair of compounds : $(\text{CH}_3)_2\text{NH}$ and $(\text{CH}_3)_3\text{N}$

72. Write the final product (s) in each of the following reactions :



73. Give reasons for the following :

(i) Aniline does not undergo Friedel-Crafts reaction.

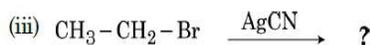
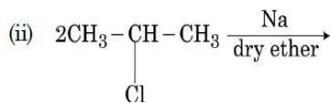
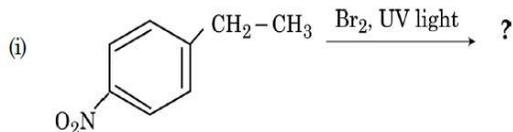
(ii) $(\text{CH}_3)_2\text{NH}$ is more basic than $(\text{CH}_3)_3\text{N}$ in an aqueous solution.

(iii) Primary amines have higher boiling point than tertiary amines.

74. How do you convert :

- (i) Chlorobenzene to biphenyl
(ii) Propene to 1-iodopropane
(iii) 2-bromobutane to but-2-ene

75. Write the major product(s) in the following :

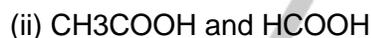
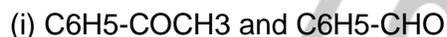


76. Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction :



77. Why carboxylic acid does not give reactions of carbonyl group ?

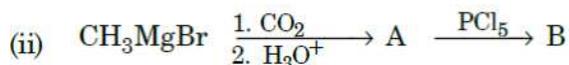
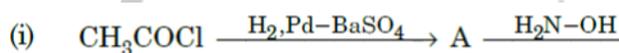
78. Distinguish between :



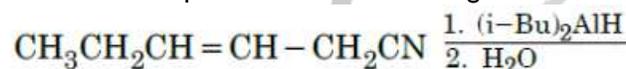
79. Arrange the following in the increasing order of their boiling points :



80. Write the structures of A and B in the following reactions :

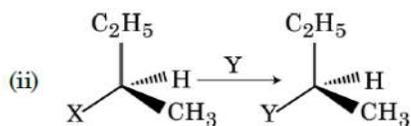
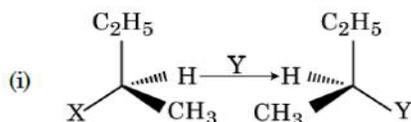


81. Write the product in the following reaction



82. A and B are two functional isomers of compound $\text{C}_3\text{H}_6\text{O}$. On heating with NaOH and I_2 , isomer B forms yellow precipitate of iodoform whereas isomer A does not form any precipitate. Write the formulae of A and B.

83. Which of the following reactions is $\text{S}_{\text{N}}1$

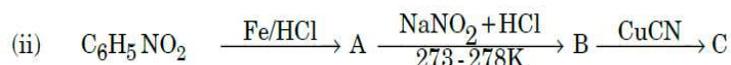
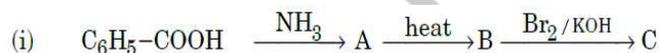


type ?

Write the IUPAC name of the given compound :

84. An organic compound 'X' having molecular formula $\text{C}_4\text{H}_8\text{O}$ gives orange-red ppt. with 2,4-DNP reagent. It does not reduce tollens reagent but gives yellow ppt. of iodoform on heating with NaOI . Compound X on reduction with LiAlH_4 gives compound Y which undergoes dehydration reaction on heating with conc. H_2SO_4 to form But-2-ene. Identify the compounds X and Y.

85. Complete the following reactions :



86. How do you convert :

(i) Chlorobenzene to toluene

(ii) But-1-ene to But-2-ene

(iii) Ethanol to Ethyl iodide

87. What happens when :

(i) n-butyl chloride is treated with alcoholic KOH .

(ii) 2-chloropropane is treated with sodium in the presence of dry ether.

(iii) Chlorobenzene is treated with CH_3Cl in the presence of anhydrous AlCl_3 .

88. Write the chemical equations involved in the above reactions.

89. What happens when :

(i) Phenol reacts with conc. HNO_3 .

(ii) Salicylic acid reacts with $(\text{CH}_3\text{CO})_2\text{O}/\text{H}^+$.

(iii) Ethyl chloride reacts with NaOCH_3 .

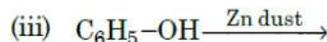
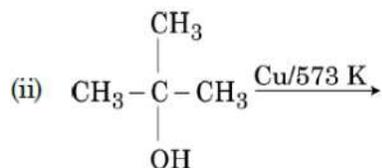
90. Write the chemical equations involved in the above reactions.

91. Distinguish between :

(i) Ethanol and Phenol

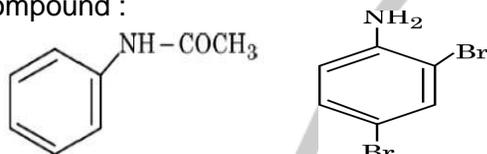
(ii) Propan-2-ol and 2-methylpropan-2-ol

92. Write the product(s) in each of the following reactions :



93. Out of $CH_2=CH-CH_2Cl$ and $CH_3-CH_2-CH_2Cl$, which is more reactive towards $SN1$ reaction ?

94. Write the IUPAC name of the given compound :



95. How do you convert

- (i) Toluene to benzaldehyde
(ii) Ethanoyl chloride to ethanol

96. What happens when :

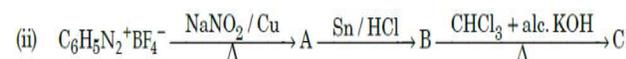
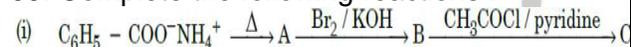
- (i) 2, 4, 6 - trinitrochlorobenzene is treated with warm water.
(ii) 2-chlorobutane is treated with alcoholic KOH.
(iii) ethyl chloride is treated with Na metal in presence of dry ether.

97. Write the equation involved in the above reactions.

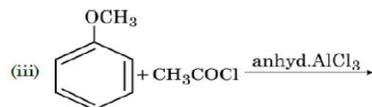
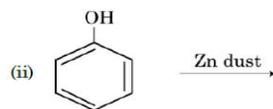
98. Give reasons for the following :

- (a) Aldehydes ($R-CHO$) are more reactive than ketones ($R-CO-R$) towards nucleophilic addition reaction.
(b) Benzaldehyde does not undergo aldol condensation reaction.
(c) Benzoic acid does not give Friedal-Crafts reaction.

99. Complete the following reactions :



100. Write the product(s) in each of the following reactions :



101. Write the mechanism of the following reaction :



102. Write equations of the following reactions :

- (i) Bromine in CS_2 with phenol
(ii) Treating phenol with chloroform in the presence of aq. NaOH
(iii) Anisole reacts with HI

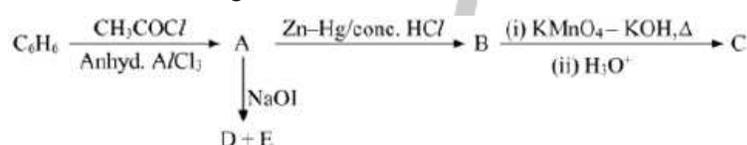
103. Distinguish between :

- (i) Ethanol and Diethyl ether
(ii) Propanol and t-butyl alcohol

104. Given reasons:

- (i) C-Cl bond length in chlorobenzene is shorter than C-Cl bond length in CH_3-Cl .
(ii) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
(iii) $SN1$ reactions are accompanied by racemization in optically active alkyl halides.

105. a) Write the structures of A, B, C, D and E in the following reactions:



(b) Draw the structure of the semicarbazone of ethanal.

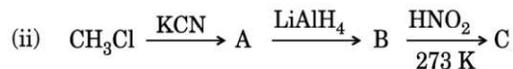
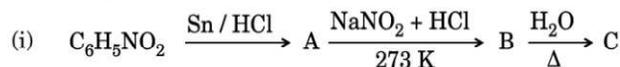
(c) Why pKa of $F-CH_2-COOH$ is lower than that of $Cl-CH_2-COOH$?

(d) How can you distinguish between propanal and propanone?

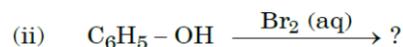
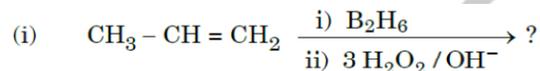
106. Write the structures of main products when benzene diazonium chloride ($C_6H_5N_2^+Cl^-$) reacts with the following reagents :

(i) HBF_4 / Δ (ii) Cu / HBr

107. Write the structures of A, B and C in the following reactions :



108. Predict the products of the following reactions :



109. How do you convert the following :

(i) Benzoic acid to Benzaldehyde

(ii) Ethyne to Ethanal

(iii) Acetic acid to Methane

110. (a) Why are alkyl halides insoluble in water ?

(b) Why is Butan-1-ol optically inactive but Butan-2-ol is optically active ?

(c) Although chlorine is an electron withdrawing group, yet it is *ortho*-, *para*-directing in electrophilic aromatic substitution reactions. Why ?

111. Which would undergo $\text{S}_\text{N}2$ reaction faster in the following pair and why ?
 $\text{CH}_3 - \text{CH}_2 - \text{Br}$ and $\text{CH}_3 - \text{CH}_2 - \text{I}$

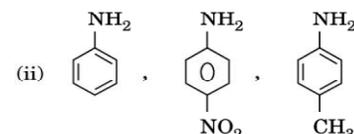
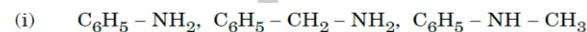
112. How do you convert the following :

(i) Phenol to anisole

(ii) Propan-2-ol to 2-methylpropan-2-ol

(iii) Aniline to phenol

113. Arrange the following in increasing order of their basic strength :



114. Give reasons for the following :

(i) Phenol is more acidic than ethanol.

(ii) Boiling point of ethanol is higher in comparison to methoxymethane.

(iii) $(\text{CH}_3)_3\text{C} - \text{O} - \text{CH}_3$ on reaction with HI gives CH_3OH and $(\text{CH}_3)_3\text{C} - \text{I}$ as the main products and not $(\text{CH}_3)_3\text{C} - \text{OH}$ and CH_3I .

115. How do you convert the following :

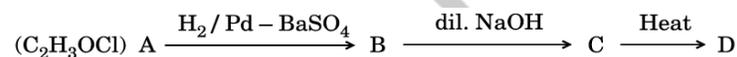
(i) $\text{C}_6\text{H}_5\text{CONH}_2$ to $\text{C}_6\text{H}_5\text{NH}_2$

(ii) Aniline to phenol

(iii) Ethanenitrile to ethanamine

116. (a) A compound 'A' of molecular formula $\text{C}_2\text{H}_3\text{OCl}$ undergoes a series of reactions as shown below. Write the structures of A, B, C and D

in the following reactions :



117. Distinguish between the following :

(i) $\text{C}_6\text{H}_5 - \text{COCH}_3$ and $\text{C}_6\text{H}_5 - \text{CHO}$

(ii) Benzoic acid and methyl benzoate

(c) Write the structure of 2-methylbutanal.

118. (a) Write the structures of the main products when acetone ($\text{CH}_3 - \text{CO} - \text{CH}_3$) reacts with the following reagents :

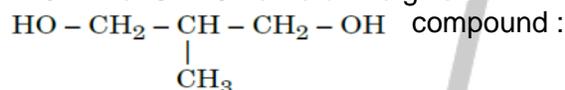
(i) $\text{Zn} - \text{Hg} / \text{conc. HCl}$ (ii) $\text{H}_2\text{N} - \text{NHCONH}_2 / \text{H}^+$ (iii) CH_3MgBr and then H_3O^+

(b) Arrange the following in the increasing order of their boiling points :

 $\text{C}_2\text{H}_5\text{OH}$, $\text{CH}_3 - \text{CHO}$, $\text{CH}_3 - \text{COOH}$

(c) Give a simple chemical test to distinguish between the following pair of compounds :
 $\text{CH}_3\text{CH}_2\text{CHO}$ and $\text{CH}_3\text{CH}_2\text{COCH}_3$

119. Write IUPAC name of the given



120. Write the main products when

(i) n-butyl chloride is treated with alcoholic KOH .

(ii) 2, 4, 6-trinitrochlorobenzene is subjected to hydrolysis.

(iii) methyl chloride is treated with AgCN .

121. How do you convert the following :

(i) Prop-1-ene to 1-fluoropropane

(ii) Chlorobenzene to 2-chlorotoluene

(iii) Ethanol to propanenitrile

122. Give reasons for the following :

(i) o-nitrophenol is more acidic than o-methoxyphenol.

(ii) Butan-1-ol has a higher boiling point than diethyl ether.

(iii) $(\text{CH}_3)_3\text{C} - \text{O} - \text{CH}_3$ on reaction with HI gives $(\text{CH}_3)_3\text{C} - \text{I}$ and $\text{CH}_3 - \text{OH}$ as the main products and not $(\text{CH}_3)_3\text{C} - \text{OH}$ and $\text{CH}_3 - \text{I}$.

123. Arrange the following :

- (i) $\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_2\text{H}_5\text{OH}$, $(\text{CH}_3)_3\text{N}$ – in the increasing order of their boiling point
 (ii) Aniline, p-nitroaniline, p-methylaniline – in the increasing order of their basic strength

124. Arrange the following compounds in increasing order of their property as indicated :

- (i) CH_3COCH_3 , $\text{C}_6\text{H}_5\text{COCH}_3$, CH_3CHO (reactivity towards nucleophilic addition reaction)
 (ii) $\text{Cl} - \text{CH}_2 - \text{COOH}$, $\text{F} - \text{CH}_2 - \text{COOH}$, $\text{CH}_3 - \text{COOH}$ (acidic character)

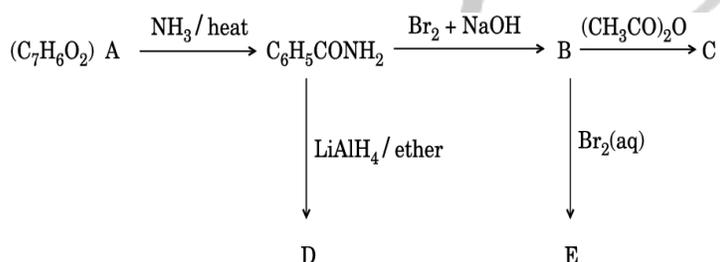
125. How can the following conversions be carried out :

- (i) Aniline to bromobenzene
 (ii) Chlorobenzene to 2-chloroacetophenone
 (iii) Chloroethane to butane

126. What happens when

- (i) chlorobenzene is treated with $\text{Cl}_2/\text{FeCl}_3$,
 (ii) ethyl chloride is treated with AgNO_2 ,
 (iii) 2-bromopentane is treated with alcoholic KOH ?

127. An aromatic compound 'A' of molecular formula $\text{C}_7\text{H}_6\text{O}_2$ undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions :



128. Arrange the following in the increasing order of their basic character in an aqueous solution :

$\text{C}_2\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $(\text{C}_2\text{H}_5)_3\text{N}$

129. Give a simple chemical test to distinguish between the following pair of compounds :

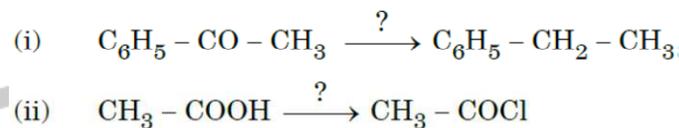
$\text{C}_6\text{H}_5 - \text{NH}_2$ and $\text{C}_6\text{H}_5 - \text{NH} - \text{CH}_3$

130. Arrange the following compounds in increasing order of their property as indicated :

(i) CH_3CHO , $\text{C}_6\text{H}_5\text{CHO}$, HCHO (reactivity towards nucleophilic addition reaction)

(ii) 2,4-dinitrobenzoic acid, 4-methoxybenzoic acid, 4-nitrobenzoic acid (acidic character)

131. Write the reagents used in the following reactions :



132. How do you convert the following :

- (i) Prop-1-ene to Propan-2-ol
 (ii) Bromobenzene to 2-bromoacetophenone
 (iii) 2-bromobutane to But-2-ene

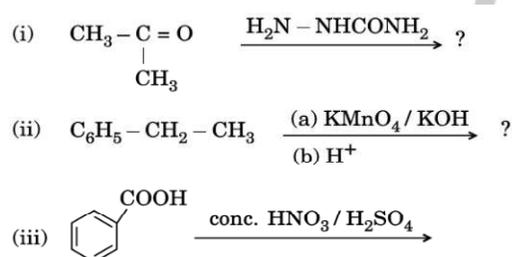
133. What happens when

- (i) ethyl chloride is treated with NaI in the presence of acetone,
 (ii) chlorobenzene is treated with Na metal in the presence of dry ether,
 (iii) methyl chloride is treated with KNO_2 ?
 Write chemical equations in support of your answer.

134. Give reasons for the following :

- (i) p-nitrophenol is more acidic than pmethylphenol.
 (ii) Bond length of $\text{C} - \text{O}$ bond in phenol is shorter than that in methanol.
 (iii) $(\text{CH}_3)_3\text{C} - \text{Br}$ on reaction with sodium methoxide ($\text{Na}^+ - \text{OCH}_3$) gives alkene as the main product and not an ether.

135. Predict the products of the following reactions :



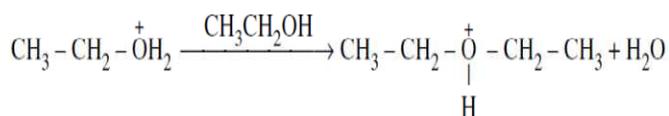
(b) Give simple chemical tests to distinguish between the following pairs of compounds :

- (i) Ethanol and Phenol
- (ii) Propanol and 2-methylpropan-2-ol

16. (a) Write the formula of reagents used in the following reactions :

- (i) Bromination of phenol to 2,4,6-tribromophenol
 - (ii) Hydroboration of propene and then oxidation to propanol.
- (b) Arrange the following compound groups in the increasing order of their property indicated :
- (i) p-nitrophenol, ethanol, phenol (acidic character)
 - (ii) Propanol, Propane, Propanal (boiling point)

(c) Write the mechanism (using curved arrow notation) of the following reaction :



Write the structure of 2,4 dinitrochlorobenzene.

Write IUPAC name of the following compound : $\text{CH}_3\text{NHCH}(\text{CH}_3)_2$

2017 (FOREIGN)

1. Write the IUPAC name of the following compound : $\text{C}_6\text{H}_5 - \text{CH}_2 - \text{CH}_2 - \text{OH}$
2. Among the isomers of pentane (C_5H_{12}), write the one which on photochemical chlorination yields a single monochloride.
3. Do the following conversions in not more than two steps :
 - (a) Propene to Acetone
 - (b) Propanoic acid to 2-hydroxypropanoic acid
4. Give reasons :
 - (a) Propanone is less reactive than ethanal towards nucleophilic addition reactions.

(b) $\text{O}_2\text{N} - \text{CH}_2 - \text{COOH}$ has lower pKa value than CH_3COOH .

(c) $(\text{CH}_3)_2\text{CH} - \text{CHO}$ undergoes aldol condensation whereas $(\text{CH}_3)_3\text{C} - \text{CHO}$ does not.

5. What happens when

- (a) $(\text{CH}_3)_3\text{C} - \text{OH}$ is treated with Cu at 573 K,
 - (b) Anisole is treated with CH_3Cl / anhydrous AlCl_3 ,
 - (c) Phenol is treated with Zn dust ?
- Write chemical equations in support of your answer.

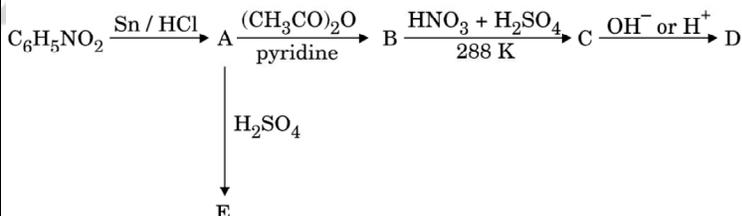
6. (a) Write the structures of the main products when benzene diazonium chloride reacts with the following reagents :

- (i) CuCN
- (ii) $\text{CH}_3 - \overset{\text{CH}_3}{\underset{\text{C}_2\text{H}_5}{\text{C}}} - \underset{\text{OH}}{\text{CH}} - \text{CH}_3$
- (iii) Cu / HCl

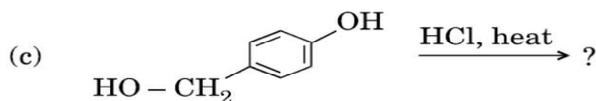
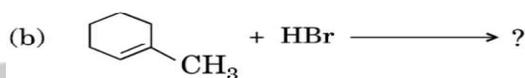
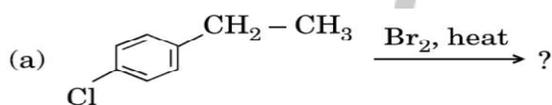
(b) Arrange the following in the increasing order of their basic strength : CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

(c) Write one chemical test to distinguish between Aniline and Ethyl amine.

7. Write the structures of A, B, C, D and E in the following reactions :



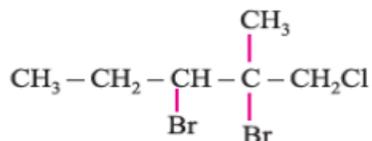
8. Draw the structures of the major monohalo product for each of the following reactions :



2018

1. Out of chlorobenzene and benzyl chloride, which one gets easily hydrolysed by aqueous NaOH and why ?

2. Write the IUPAC name of the following :



3. How do you convert the following ?

- (a) Ethanal to Propanone
(b) Toluene to Benzoic acid

4. Account for the following :

- (a) Aromatic carboxylic acids do not undergo Friedel-Crafts reaction.
(b) pK_a value of 4-nitrobenzoic acid is lower than that of benzoic acid.

5. (a) Identify the chiral molecule in the following pair :



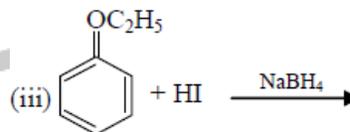
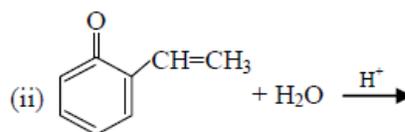
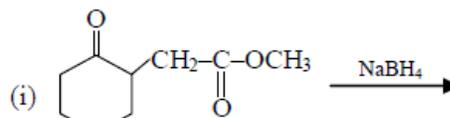
- (b) Write the structure of the product when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.
(c) Write the structure of the alkene formed by dehydrohalogenation of 1-bromo-1-methylcyclohexane with alcoholic KOH

6. (A), (B) and (C) are three non-cyclic functional isomers of carbonyl compound with molecular formula $\text{C}_4\text{H}_8\text{O}$.

Isomers (A) and (C) give positive Tollens' test whereas isomer (B) does not give Tollens' Test but gives positive Iodoform test. Isomers (A) and (B) on reduction with Zn(Hg)/cons.HCl give the same product (D).

- (a) Write the structures of (A), (B), (C) and (D)
(b) Out of (A), (B) and (C) isomers, which one is least reactive towards addition of HCN ?

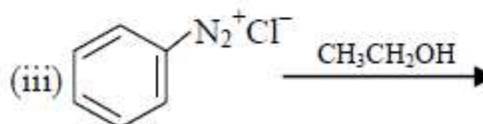
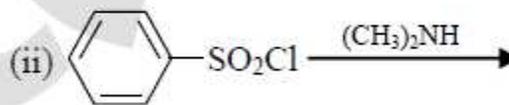
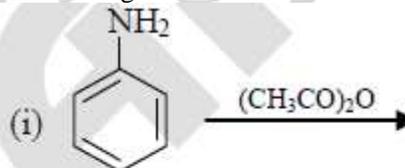
7. Write the structures of the main products in the following reactions :



8. (a) Write the reactions involved in the following,

- (i) Hofmann bromamide degradation reaction
(ii) Diazotisation
(iii) Gabriel phthalimide synthesis
(b) Give reasons :
(i) $(\text{CH}_3)_2\text{NH}$ is more basic than $(\text{CH}_3)_3\text{N}$ in an aqueous solution
(ii) Aromatic diazonium salts are more stable than aliphatic diazonium salts.

9. (a) Write the structures of the main products of the following reactions :



- (b) Give a simple chemical test to distinguish between Aniline and N,N-dimethylaniline.
(c) Arrange the following in the increasing order of their pK_b values. :
 $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{NHCH}_3$

2018(COMPTT.)

1. An aromatic organic compound 'A' with molecular formula C_8H_8O gives positive DNP and iodoform tests. It neither reduces Tollens' reagent nor does it decolourise bromine water. Write the structure of 'A'.

2. Predict the major product formed when sodium ethoxide reacts with tert. Butyl chloride.

3. Which one of the following compounds is more reactive towards S_N2 reaction and why?
 $CH_3CH(Cl)CH_2CH_3$ or $CH_3CH_2CH_2Cl$

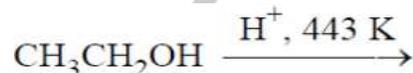
4. Write the product(s) formed when

(i) 2-Bromopropane undergoes dehydrohalogenation reaction.

(ii) Chlorobenzene undergoes nitration reaction.

(iii) Methylbromide is treated with KCN.

5. (i) Complete the following reaction and suggest a suitable mechanism for the reaction :



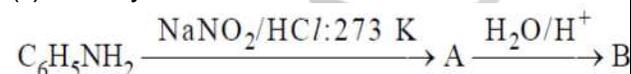
(ii) Why ortho-Nitrophenol is steam volatile while para-Nitrophenol is less volatile ?

6. Do as directed :

(i) Arrange the following compounds in the increasing order of their basic strength in aqueous solution :

CH_3NH_2 , $(CH_3)_3N$, $(CH_3)_2NH$.

(ii) Identify 'A' and 'B' :



(iii) Write equation of carbylamine reaction.

7. Give reasons :

(a) HCHO is more reactive than CH_3CHO towards addition of HCN.

(b) pK_a of O_2N-CH_2-COOH is lower than that of CH_3-COOH .

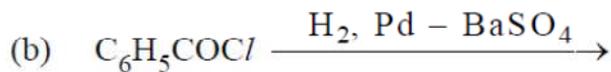
(c) Alpha hydrogen of aldehydes & ketones is acidic in nature.

8. Give simple chemical tests to distinguish between the following pairs of compounds :

(a) Ethanal and Propanal

(b) Pentan-2-one and Pentan-3-one

Write structure of the product(s) formed :



9. How will you bring the following conversions in not more than two steps :

(a) Propanone to propene

(b) Benzyl chloride to phenyl ethanoic acid