CBSE

CLASS XI TERM - I

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GENERAL ORGANIC CHEMISTRY

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BASIC PRINCIPLES & TECHNIQUES IN ORGANIC CHEMISTRY (GOC)

Introduction

'The branch of chemistry dealing with these compounds, which are widely distributed in nature and play an important role in our daily lives', is called organic chemistry.

In earlier period of development of chemistry, compounds were classified as follows

1. **Organic compounds** derived from 'living matter' (plants and animals).
2. **Inorganic compounds** prepared from 'non-living matter' (mineral sources).

Berzelius, a Swedish chemist proposed the mistaken notion that a '**vital force**' present in living matter was essential for the synthesis of organic compounds. However, the synthesis of urea an organic compound present in urine, from **ammonium cyanate**, an inorganic compound by **Frederic Wohler** in 1828 effectively destroyed the myth of organic compounds being associated with a 'vital force'.

$$\underset{\text{Ammonium Chloride}}{NH_4Cl} + \underset{\text{Potassium Cyanate}}{KCNO} \xrightarrow{\Delta} \underset{\text{Ammonium Cyanate}}{NH_4CNO} + \underset{\text{Potassium Chloride}}{KCl}$$

$$\underset{\text{Ammonium Cyanate}}{NH_4CNO} \xrightarrow{\text{Heat}} \underset{\text{Urea}}{NH_2CONH_2}$$

Soon afterwards the pioneering work of Herman Kolbe who synthesized acetic acid and of Berthelot who synthesized methane showed conclusively that organic compounds are essentially the compounds formed by carbon with itself and other elements and that they can be synthesized in a laboratory as easily as inorganic compounds.

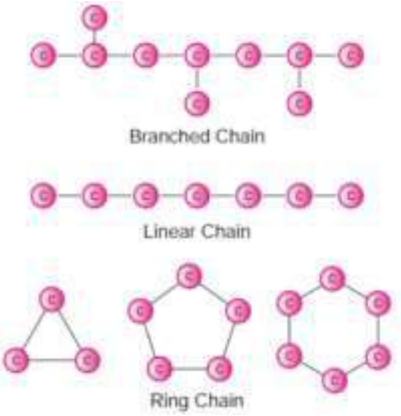
$$\underset{\text{Acetaldehyde}}{CH_3-CHO} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3-COOH}$$

(First organic compound synthesized from its elements)

The chemistry of hydrocarbons and their derivatives constitutes organic chemistry.

The **number of organic compounds available today is more compare to total inorganic compounds** of all elements except carbon. This is due to unique **catenation** property of Carbon.

Some properties of Carbon

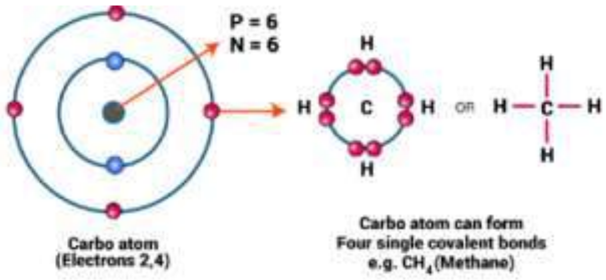


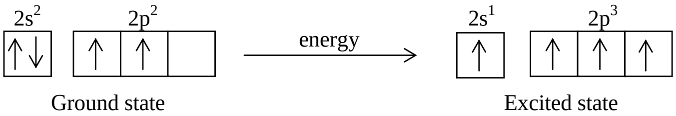
- **Catenation:** is **the property of an element where a large number of its own atoms join together through covalent bonds**. Due to which it forms single as well as multiple covalent bonds with other carbon atoms. It is further supplemented by the fact that **it also forms covalent bonds with atoms of other elements like hydrogen, oxygen, nitrogen, Sulphur, phosphorus and halogens** in a variety of ways (i.e., single and multiple bonds).

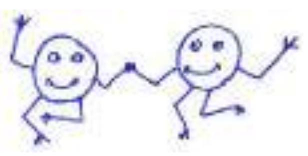
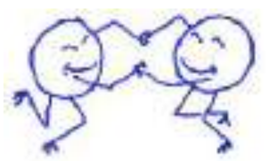
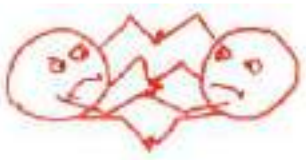
  This property gives a scope for the Chemists to synthesize new compounds.

- **Tetravalency of carbon atom**

The atomic number of carbon is 6 and it has four electrons in its valence shell. In order to acquire a stable noble gas configuration, it can share its 4 electrons with the electrons of its atom or electrons of other atoms to form **four covalent bonds**. The bonds can be sigma(σ) or pi(π).





Alkanes → C_nH_{2n+2}	Alkenes→C_nH_{2n}	Alkynes→C_nH_{2n-2}	
			

As per Lewis theory, Carbon can easily form tetra-bonds with other carbon atoms & other atoms. C-C, C=C, C≡C exists in nature but not Carbon-Carbon tetrabonds.

Carbon can form single, double or triple bond (covalent). When a single bond is formed between carbon atoms (or any atoms), energy is released. Changing the molecule's electron arrangement to make a double bond releases more energy, but not as much as when the first bond was made. Making a triple bond again releases energy, but again to a lesser degree. However, when a fourth bond is attempted, the overcrowded electrons between the atoms resist the change so strongly that it releases little, if any, energy. This arrangement is therefore unstable, so a quadruple bond will be essentially impossible.

- **Hybridization in carbon compounds**

Hybridization is defined as intermixing of degenerate orbitals (orbitals at nearly same energy) to produce entirely equivalent number of new orbitals of same energy, identical shapes and symmetrically disposed in planes. The orbitals formed are called hybrid orbitals.

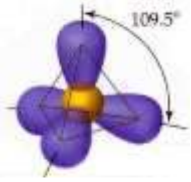
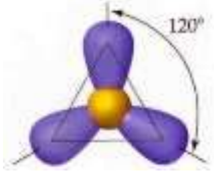
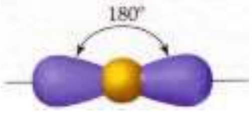
- The orbitals of an isolated atom can undergo hybridization.
- Numbers of hybrid orbitals generated are equal to number of contributing atomic orbitals.
- The hybrid orbitals orient in the space providing definite geometry to molecule or ion.
- Like atomic orbital, a hybrid orbital cannot have more than two electrons of opposite spins. In diamond carbon is sp^3 hybridized and in graphite carbon is sp^2 hybridized.

  There are three types of hybridization,

(i) **sp^3 hybridization** (contain saturated organic compounds with only single covalent bonds)

(ii) **sp^2 hybridization** (here organic compounds having carbon atoms linked by double bonds)

(iii) **sp hybridization** (here organic compounds having carbon atoms linked by a triple bonds).

Type of hybridization	sp^3	sp^2	sp
Number of orbitals used	1s and 3p	1s and 2p	1s and 1p
Number of unused p-orbitals	Nil	One	Two
Bond	Four -σ	Three -σ, One -π	Two -σ, Two -π
Bond angle	109.5°	120°	180°
Geometry	Tetrahedral 	Trigonal planar 	Linear 
% s-character	25 or 1/4	33.33 or 1/3	50 or 1/2

Prediction of hybridization- It can be done by two methods,

(i) First Method: In this method hybridization can be known by the number of π – bonds present on that particular atom.

Number of π- bond/s	0	1	2
Type of hybridization	sp^3	sp^2	sp

(i) $\begin{array}{ccccc} & & & O & \\ & & & \| & \\ CH_3- & CH= & CH- & C- & CH_3 \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ sp^3 & sp^2 & sp^2 & sp^2 & sp^3 \end{array}$	**(ii)** $\begin{array}{ccc} CH_2= & C= & CH_2 \\ \downarrow & \downarrow & \downarrow \\ sp^2 & sp & sp^2 \end{array}$
(iii) $\begin{array}{cccccc} CH_3- & CH= & CH- & CH_2- & C\equiv & N \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ sp^3 & sp^2 & sp^2 & sp^3 & sp & sp \end{array}$	**(iv)** $\begin{array}{cccc} HC\equiv & C- & CH= & CH_2 \\ \downarrow & \downarrow & \downarrow & \downarrow \\ sp & sp & sp^2 & sp^2 \end{array}$

(ii) Second Method (Electron pair method): The hybridized state of an atom of a molecule or an ion or radical can be predicted by calculating number of orbitals or electron pairs involved in hybridization (H) which is evaluated as follows.

H = (number of σ bonds formed with adjected atom/s + number of lone pairs of electrons

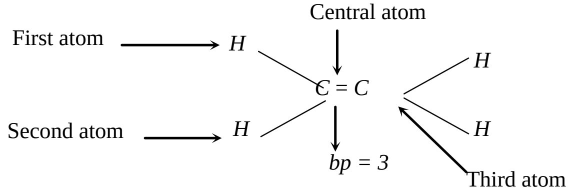
ep = bp + lp;

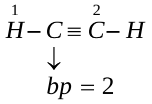
where, ep = electron pair present in hybrid orbitals,

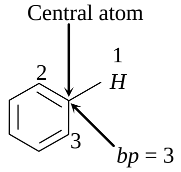
bp = bond pair present in hybrid orbitals

Number of bp = Number of atoms attached to the central atom of the species (do not include π electron pairs).

Value of H	2	3	4
Hybridization	sp	sp^2	sp^3
Structure	linear	trigonal planar	tetrahedral







Number of lp's can be determined as follows,

(a) If C has π- bonds or positive charge or odd electron, than lp on C will be zero.

(b) If carbon has negative charge, then lp will be equal to one.

Example:

$$CH_2=\overset{\oplus}{C}H \quad bp=2,\ lp=0,\ ep=2, sp$$

$$CH\equiv\overset{\ominus}{C} \quad bp=1,\ lp=1,\ ep=2, sp$$

$$CH_2=\overset{\ominus}{C}H \quad bp=2,\ lp=1,\ ep=3, sp^2$$

$$CH_2=\overset{\bullet}{C}(CH_3)-CH_3 \quad bp=3,\ lp=0,\ ep=3, sp^2$$

$$CH_3-\overset{\ominus}{C}H-CH_3 \quad bp=3,\ lp=1,\ ep=4, sp^3$$

Pitfall - It may be noted that, the hybridized state of a heteroatom containing lone pair electrons or carbanion or free radical bonded in conjugation with multiple bond/s is sp^2. For example, hybridized state of allylic or benzylic carbanions or free radicals or atoms of aromatic ring is sp^2.

Problem 1: How many sigma (σ) and pi (π) bonds are present in each of the following molecules? a) $CH_2 = C = CH_2$ b) $CH_3 - CH = CH - C \equiv C - CH_3$

Solution: Every single bond is a σ bond; every double bond contains one σ–bond and one π–bond while every triple bond consists of one σ– and two π–bonds. Thus

a) $\sigma_{C-C}: 2, \sigma_{C-H}: 4, \pi_{C-C}: 2$ b) $\sigma_{C-C}: 5, \sigma_{C-H}: 8, \pi_{C-C}: 3$

Problem 2: Predict the shape of each of the following molecules.

a) $HC \equiv CH$ b) CH_3Cl c) $H_2C = O$

Solution: sp^3 hybridization can always be correlated to tetrahedral shape, sp^2 to trigonal planar and sp to linear. Thus,

a) sp hybridized carbon atoms, linear

b) sp^3 hybridized carbon, tetrahedral

c) sp^2 hybridized carbon, trigonal planar

Applications of hybridization

(i) Size of the hybrid orbitals: Since s- orbitals are closer to the nucleus than p-orbitals, it is reasonable to expect that greater the s-character of an orbital the smaller it is. Thus, the decreasing order of the size of the three hybrid orbitals is opposite to that of the decreasing order of s orbital character in the three hybrid orbitals. $sp^3 > sp^2 > sp$

(ii) Electro negativity of different orbitals

(a) Electro negativity of s-orbital is maximum.

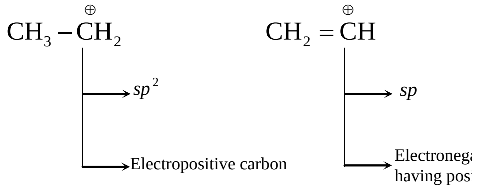
(b) Electro negativity of hybrid orbital $\propto$ % s-character in hybrid orbitals

Orbital	sp	sp^2	sp^3
% s -character	50	33.33	25

$\xrightarrow{\hspace{10cm}}$

s-character in decreasing order and electronegativity in decreasing order

Thus sp-hybrid carbon is always electronegative in character and sp^3-hybrid carbon is electropositive in character. sp^2-hybrid carbon can behave as electropositive (in carbocation) as well as electronegative (in carbanion) in character.



$CH_3-\overset{\oplus}{C}H_2$ $\quad$ $CH_2=\overset{\oplus}{C}H$

(c) Electro negativities of hybrid & unhybrid orbitals in decreasing order is as follows

$$\underrightarrow{\;s > sp > sp^2 > sp^3 > p\;}$$

% s-character and electronegativity in decreasing order.

(iii) Bond length in hydrocarbons, % of s orbital character $\propto \dfrac{1}{C-C\,\text{bond length}} \propto \dfrac{1}{C-H\text{ bond length}}$

Bond type (C – H)	**Bond length**	**Bond type (C – C)**	**Bond length**
sp^3-s (alkanes)	1.112Å	sp^3-sp^3(alkanes)	1.54 Å
sp^2-s (alkenes)	1.103Å	sp^2-sp^2(alkenes)	1.34Å
$sp-s$ (alkynes)	1.08Å	$sp-sp$(alkynes)	1.20Å

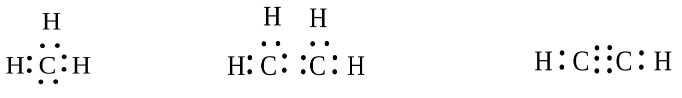
(iv) Bond strength in hydrocarbons: The shorter is the bond length, the greater is the compression between atomic nuclei and hence greater is the strength of that bond.

Bond type(C – H)	Bond energy **(kcal/mole)**	**Bond type (C – C)**	**Bond energy (kcal/mole)**
sp^3-s (in alkanes)	104	sp^3-sp^3(in alkanes)	80 – 90
sp^2-s (in alkene)	106	sp^2-sp^2 (in alkenes)	122 – 164
sp-sp (in alkynes)	121	sp-sp (in alkynes)	123 – 199

Structural representation of Organic Compounds

Structural formula (structure) is the sequence in which different atoms constituting the molecule are bonded to one anoOther. Structures of molecules of organic compounds can be described in various ways. The most common types of representations are:

1) Lewis structure (or electron dot structure) Here dots are used to represent all of the valence electrons of all the bonded atoms in the molecule:



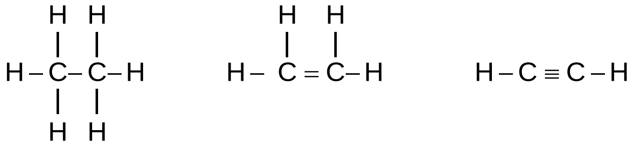
Ethene Ethyne

Writing dot structure is **tedious and time-consuming**. The other representations are more convenient and are, therefore, more often used.

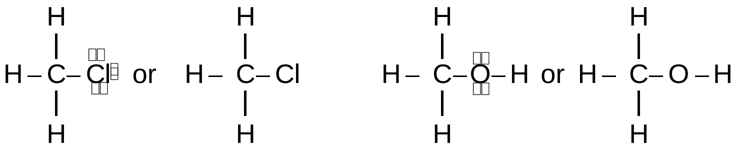
2) Dash structural formula The Lewis structure can be simplified by representing a shared electron pair by a 'stick' (dash, –) between the bonded atoms. When there is one dash between two atoms, the atoms are said to be bonded by a single covalent bond. A double covalent bond, in which two pairs of electrons are shared, is shown by two dashes between the atoms. A triple bond is represented by three dashes between the atoms.

The valence electrons that are not included in covalent bonds are called **nonbonding electrons (lone pairs)**. These are assigned to specific atoms and are represented by dots drawn next to the symbols for these atoms.

Lone pair of electrons on hetero atoms (e.g. oxygen, nitrogen, sulphur, phosphorus, halogens) may or may not be shown. Such structural formulae which focus only on the valence electrons involved in bond formation are called **complete structural formulae**.



Ethane Ethene Ethyne



Methyl chloride Methyl alcohol

chloromethane methanol

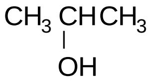
3) Condensed structural formula Complete structural formulae can be shortened by leaving out some or all of the covalent bonds and by denoting the number of identical groups attached to an atom by a subscript. The resulting description of the molecule is called a condensed structural formula. Thus,

CH_3CH_3	$H_2C=CH_2$	$HC\equiv CH$	CH_3CH_2Cl
or	or	or	or
C_2H_6	C_2H_4	C_2H_2	C_2H_5Cl
Ethane	Ethene	Ethyne	Ethyl Chloride

$CH_3CH_2CH_2OH$	$CH_3CH_2CH_2CH_2CO_2H$
or	or
$CH_3(CH_2)_2OH$	$CH_3(CH_2)_3CO_2H$
Methanol	Pentanoic acid

Condensed structural formulae are easier to write than dash formulae. In condensed formulae all of the hydrogen atoms that are attached to a particular carbon are usually written immediately after the carbon. In fully condensed formulae, all of the atoms that are attached to the carbon are usually written immediately after that carbon, listing hydrogens first.

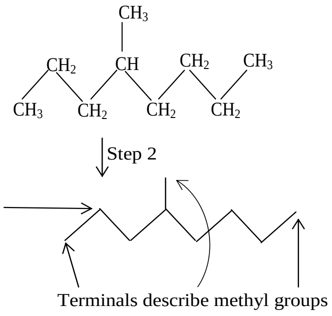
For example, the condensed formula for isopropyl alcohol can be written in four different ways:



$\underset{\underset{OH}{|}}{CH_3CHCH_3}$ $CH_3CH(OH)CH_3$ $\underbrace{CH_3CHOHCH_3 or (CH_3)_2CHOH}_{condensedformulae}$

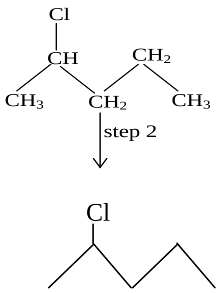
4) Bond-line structural formula: For further simplification only lines are used to represent the structures of organic molecules. Here carbon and hydrogen atoms are not shown. The lines denoting the carbon – carbon bonds are drawn in a zig – zag fashion. The only atoms especially written are the hetero atoms (oxygen, nitrogen etc). They are neither carbon nor hydrogen bonded to carbon. The termini describe methyl (CH_3 –) groups (unless denoted otherwise by a functional group). The line junctions indicate carbon atoms bonded to suitable number of hydrogens needed to satisfy the covalency of the carbon atoms: Thus The bond-line representation is the quickest of all to write because it shows only the carbon skeleton.

a) $CH_3CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH_3 \xrightarrow{\text{step 1}}$

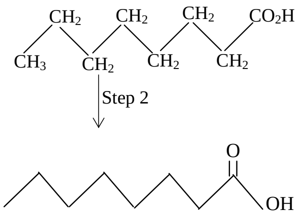


Line junctions denote carbon atoms

b) $CH_3CHClCH_2CH_2CH_3 \xrightarrow{\text{step1}}$

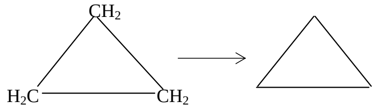


c) $CH_3(CH_2)_6CO_2H \xrightarrow{\text{step1}}$

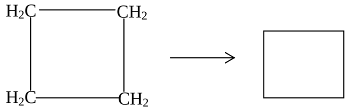


Ring or cyclic compounds - An organic compound in which carbon atoms are not bonded in chain but are bonded in closed structures called rings are known as **cyclic compounds**. Such a compound containing one or more rings is represented by drawing the suitable ring (polygon) without indicating the carbon and hydrogen atoms. The corner of the polygon denotes a carbon atom and its sides represent a carbon – carbon bond. An atom or a group of atoms (other than hydrogen) bonded to the carbon is however shown in the structure.

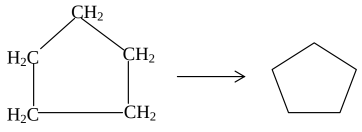
Bond-line formulae of some cyclic compounds are:



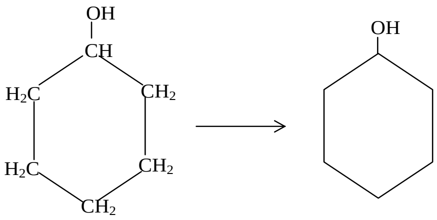
Cyclopropane



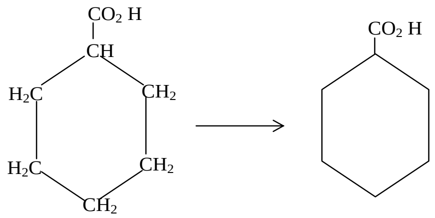
Cyclobutane



Cyclopentane



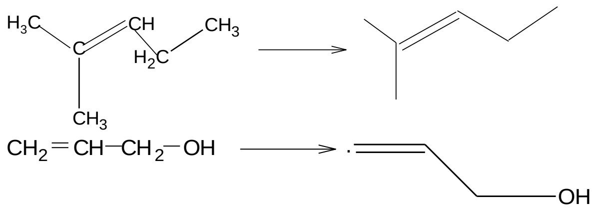
Cyclohexanol



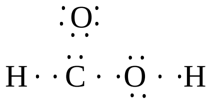
Cyclohexane carboxylic acid

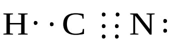
Multiple bonds are also indicated in bond-line formulae.

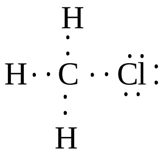
For example:



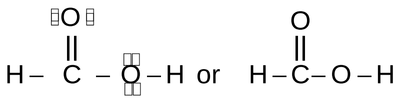
Exp 1: Convert each of the following Lewis structures into complete structural formulae:

a) 

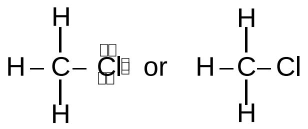
b) 

c) 

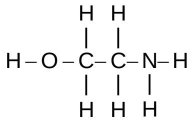
Solution: Use the dash to represent the shared electron pair.

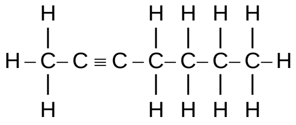
a) 

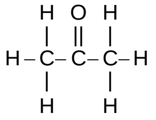
b) H - C ≡ N: or H - C ≡ N

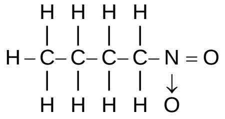
c) 

Exp2: Convert each of the complete structural formulae into condensed formulae.

a) 

b) 

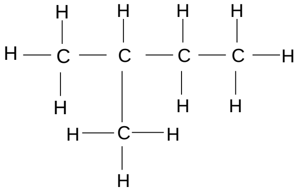
c) 

d) 

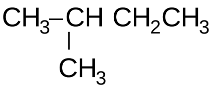
Solution: Omitting some or all of the dashes and indicating the number of identical groups by a subscript we get

a) $HO(CH_2)_2NH_2$ b) $CH_3C \equiv C(CH_2)_3CH_3$ c) H_3CCOCH_3 d) $CH_3(CH_2)_3NO_2$

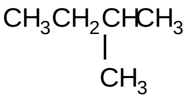
Exp 3: Write the condensed structural formulae for the compound that follows in different ways.



Solution:



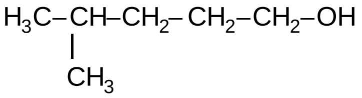
$CH_3\text{–}\underset{\displaystyle CH_3}{CH}\ CH_2CH_3$ or $CH_3CH(CH_3)CH_2CH_3$ or



$CH_3CH_2\underset{\displaystyle CH_3}{CH}CH_3$

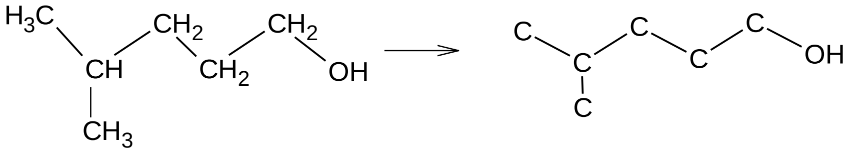
or $(CH_3)_2CHCH_2CH_3$ or $CH_3CH_2CH(CH_3)_2$

Exp 4: Write the bond-line formula for

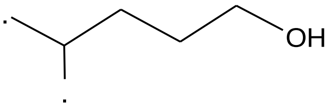


$H_3C\text{–}\underset{\displaystyle CH_3}{CH}\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}OH$

Solution: First, outline the carbon skeleton, including the OH group as follows:



Thus, the bond-line formula is

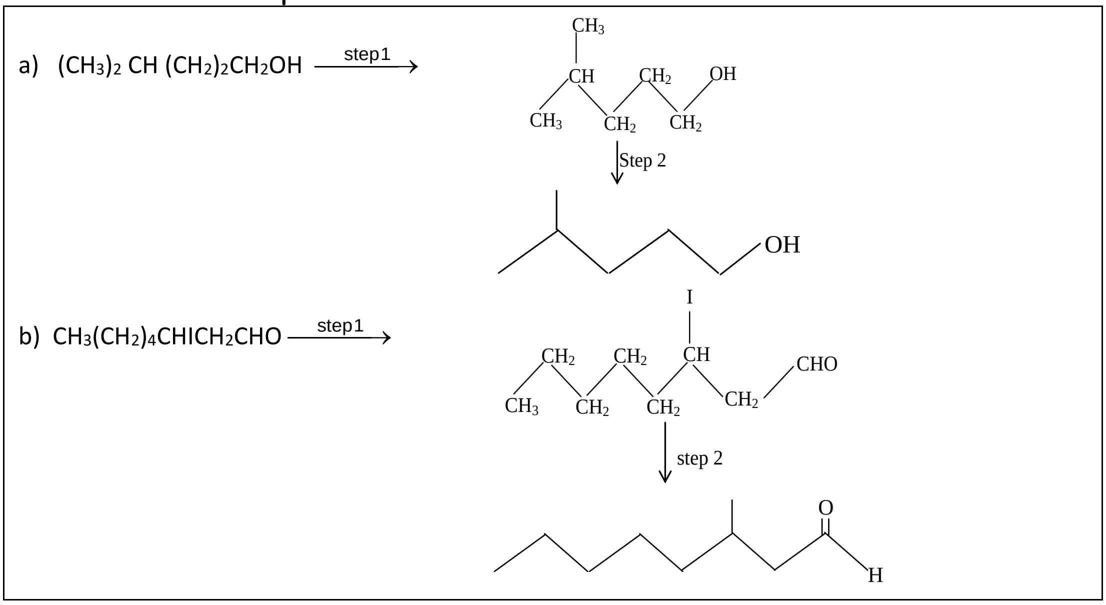


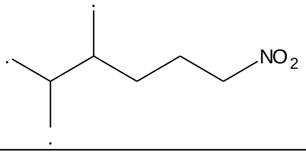
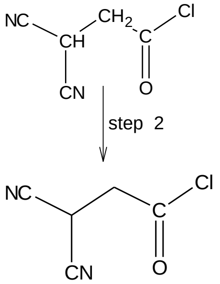
Exp 5: For following condensed formulae write the corresponding bond-line formula.

a) $(CH_3)_2CH(CH_2)_2CH_2OH$ b) $CH_3(CH_2)_4CHICH_2CHO$

c) $(CH_3)_2CHCH_3CH(CH_2)_3NO_2$ d) $(CN)_2CHCH_2COCl$

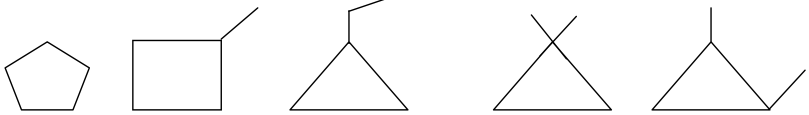
Solution: In bond-line formula carbon and hydrogen atoms except those that are part of the functional groups are not shown. We show only the carbon skeleton. The number of hydrogen atoms necessary to fulfill the carbon atoms' valences is assumed to be present, but we do not write them in. Other atoms (e.g., Cl, O, N) are written in. Each intersection of two or more lines and the end of a line represent a carbon atom unless some other atom is written in.



c) $(CH_3)_2CHCH_3CH(CH_2)_3NO_2 \xrightarrow{\text{step 2}}$	
d) $(CN)_2CHCH_2COCl \xrightarrow{\text{step1}}$	

Exp 6: Draw all possible bond-line formulae for a cyclic compound, C_5H_{10}.

Solution: Start with the maximum number of carbon atoms in the ring and move towards the ring of 3 carbon atoms. Explore all sorts of possibilities on this route:

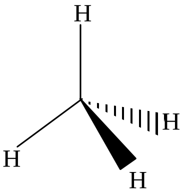


Three-dimensional representation of organic molecules

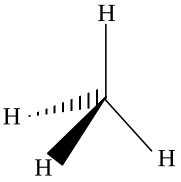
None of the formulae that we have described so far conveys any information about how the atoms of a molecule are arranged in space. Shape or the three-dimensional (3-D) structure of organic molecules can be described on a paper (two-dimensional) by exploring certain conventions. For instance, by using solid  and dashed wedge  formula the 3-D image of an organic molecule can be perceived on a two-dimensional paper.

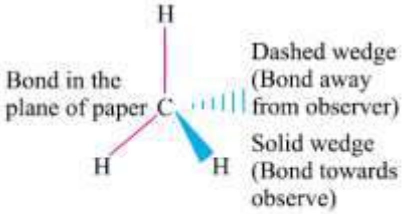
In solid-wedge and dashed-wedge description the **solid-wedge denotes a bond projecting out of the plane of the paper towards the viewer**. The dashed-wedge depicts the bond projecting behind the plane of the paper and going away from the viewer. Both the wedges are drawn in such a way that the broad end of the wedge is near the viewer. The other two bonds lying in the plane of the paper are shown by using a normal line (—).

Let's consider the wedge- and dashed-wedge representation of methane (CH_4) molecule:



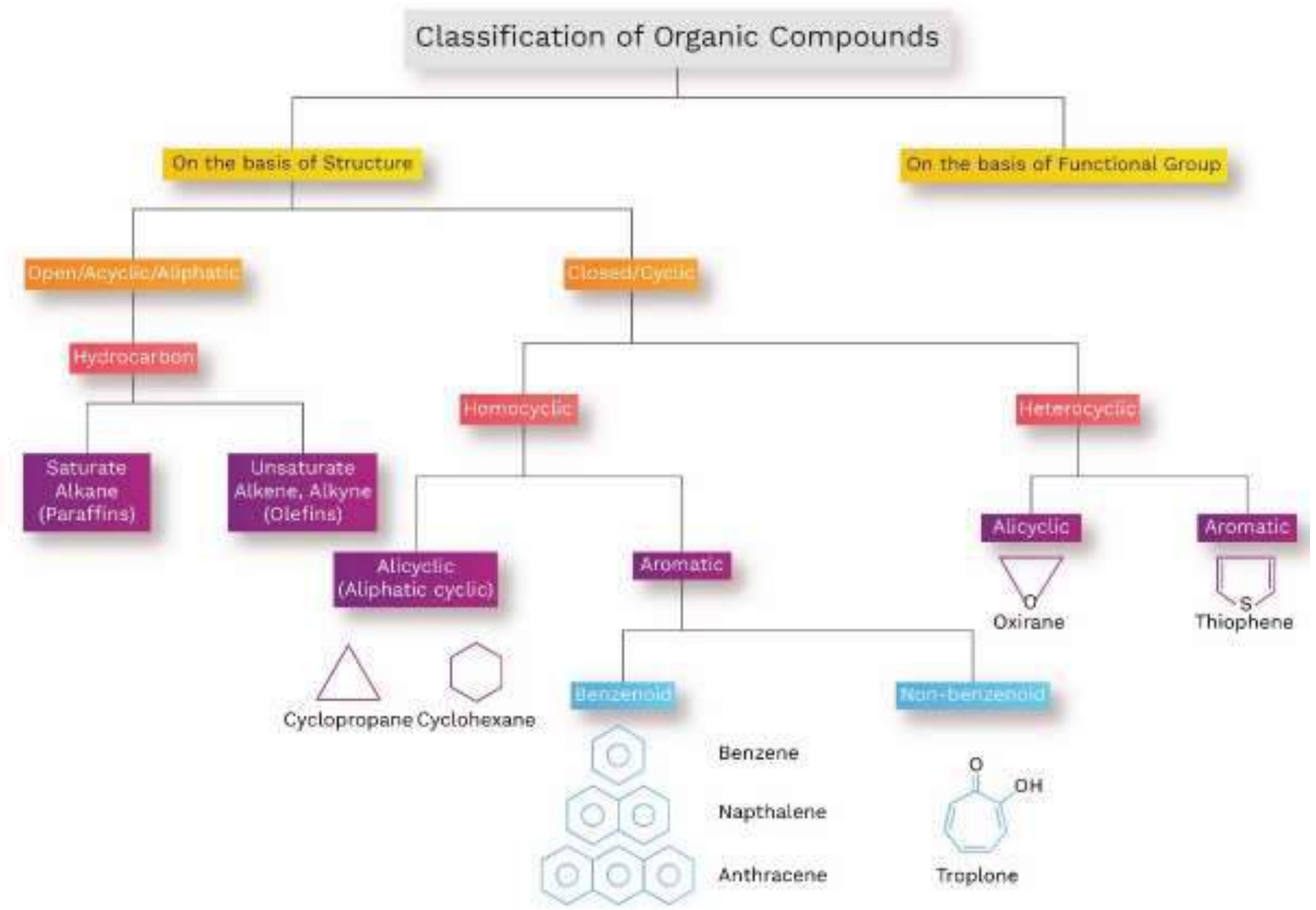
or





The two carbon-hydrogen bonds represented by normal lines are in the plane of paper, whereas the carbon-hydrogen bond represented with a solid wedge is aimed to be in front of the plane of paper. The hydrogen bonded to carbon by dashed wedge is intended to be behind the plane of paper. Note that the carbon atom is lying in the plane of paper. Wedge and dashed-wedge formulae are an important tool for clearly showing three dimensions.

Classification of organic compounds



The compounds with C and H are called **hydrocarbons**. Organic compounds are considered as the derivatives of hydrocarbons obtained by replacing H-atoms by other atoms or groups. Based on C - skeleton, organic compounds divided as below,

1. Acyclic compounds - **The open chain organic compounds are called acyclic compounds. The carbon chains may be linear or branched.**

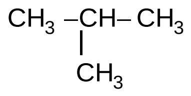
The open chain compounds are classified into **two groups**.

a. **Saturated compounds**: Open chain compounds in which carbon atoms of parent chain are bonded with single bonds are called saturated acyclic compounds.

Example:

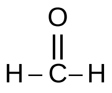
$CH_3CH_2CH_2CH_3$

n–Butane



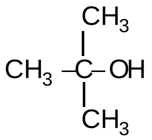
$CH_3-CH(CH_3)-CH_3$

Isobutane



$H-\overset{\overset{O}{\|}}{C}-H$

Formaldehyde



$CH_3-C(CH_3)_2-OH$

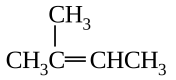
tert-Butyl alcohol

b. **Unsaturated compounds**: The open chain organic compounds in which parent chain contains one or more carbon-carbon double bonds or triple bonds are called unsaturated acyclic compounds.

$CH_2{=}CH_2$ ethylene

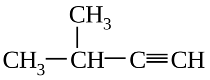
$CH_3CH{=}CH_2$ propene

$CH_3CH{=}CHCH_3$ 2-butene



$CH_3C(CH_3){=}CHCH_3$

2-methyl-2-butene



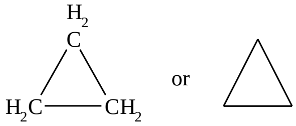
$CH_3-CH(CH_3)-C\equiv CH$

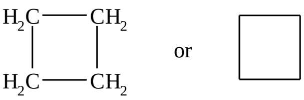
2-methyl-1-butyne

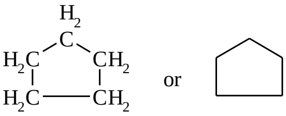
2. **Cyclic Compounds – Here carbon atoms are linked by covalent bonds to form ring structures are called cyclic compounds. Depending upon the constituents of ring, these compounds are further classified into two groups.**

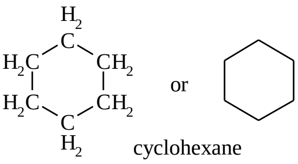
A. **Carbocyclic compounds (Homocyclic compounds):** The cyclic compounds containing only carbon atoms in their ring are called carbocyclic compounds. They are further divided into two groups.

- **Alicyclic compounds:** The carbocyclic compounds which resemble with aliphatic compounds in most of their properties are called alicyclic compounds.

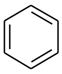

cyclopropane

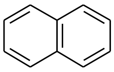

cyclobutane

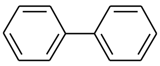

cyclopentane

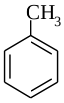

cyclohexane

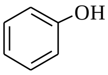
Aromatic compounds: Benzene is the parent aromatic hydrocarbon. The organic compounds containing one or more isolated or fused benzene rings and their functionalized derivatives are called aromatic compounds or **benzenoid compound**.

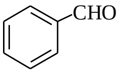

benzene


naphthalene

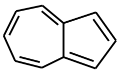

diphenyl

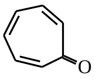

toluene


phenol


benzaldehyde

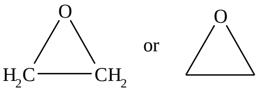
The aromatic compounds which resemble benzene in most of their properties are called **non-benzenoid aromatic compounds**.

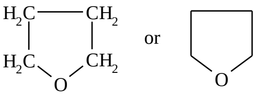

azulene

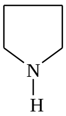

tropolone

- **Heterocyclic compounds:** The cyclic compounds containing one or more heteroatoms (atom other than C it may be O, N, S, etc.,) in their ring are called *heterocyclic compounds*. Depending upon their chemical behaviors, they are further classified into two groups.

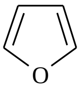
i. **Alicyclic heterocyclic compounds:** The aliphatic cyclic compounds containing one or more hetero atoms in their ring are called *alicyclic heterocyclic compounds*.

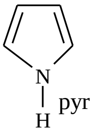

oxirane (ethylene oxide)
or epoxide

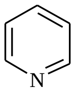

tetrahydrofuran (THF)

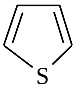

pyrrolidine

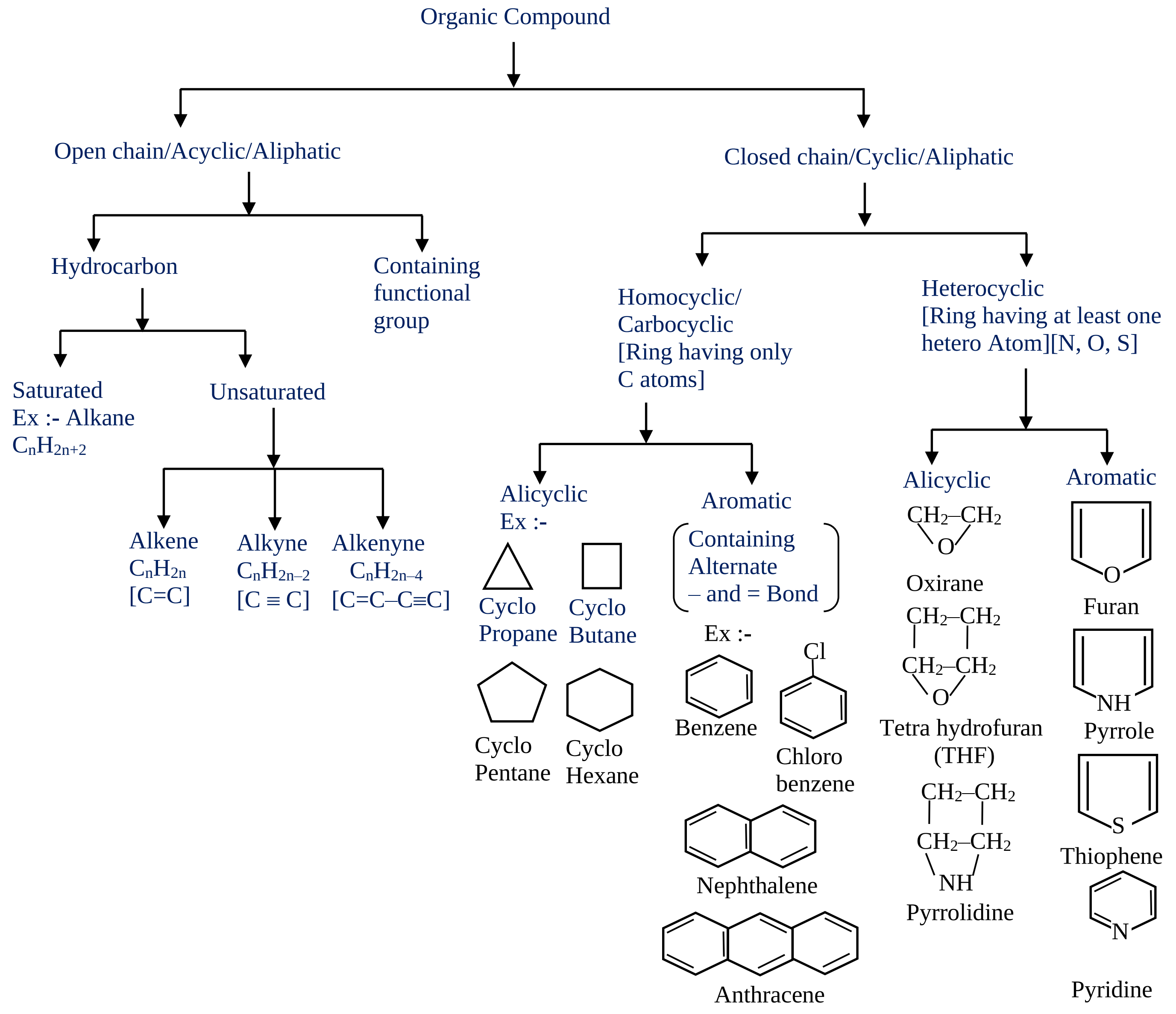
ii. **Aromatic heterocyclic compounds:** The aromatic cyclic compounds containing one or more hetero atoms in their molecules are called aromatic heterocyclic compounds.


furan


pyrrole


pyridine

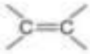
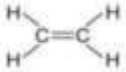
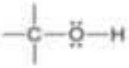
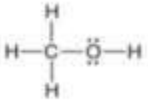
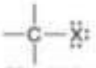
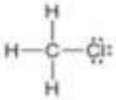
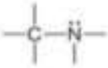
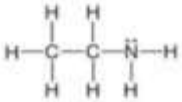
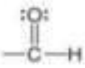
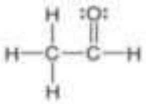
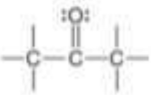
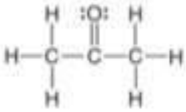
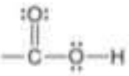
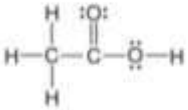
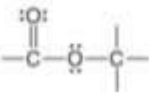
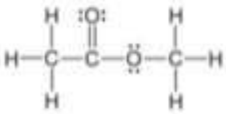
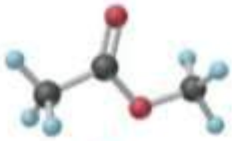
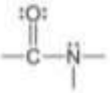
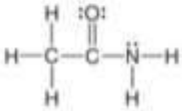
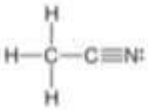

thiophene



Functional groups: is defined as **"an atom or group of atoms present in a molecule which decides the chemical properties of the organic compounds".**

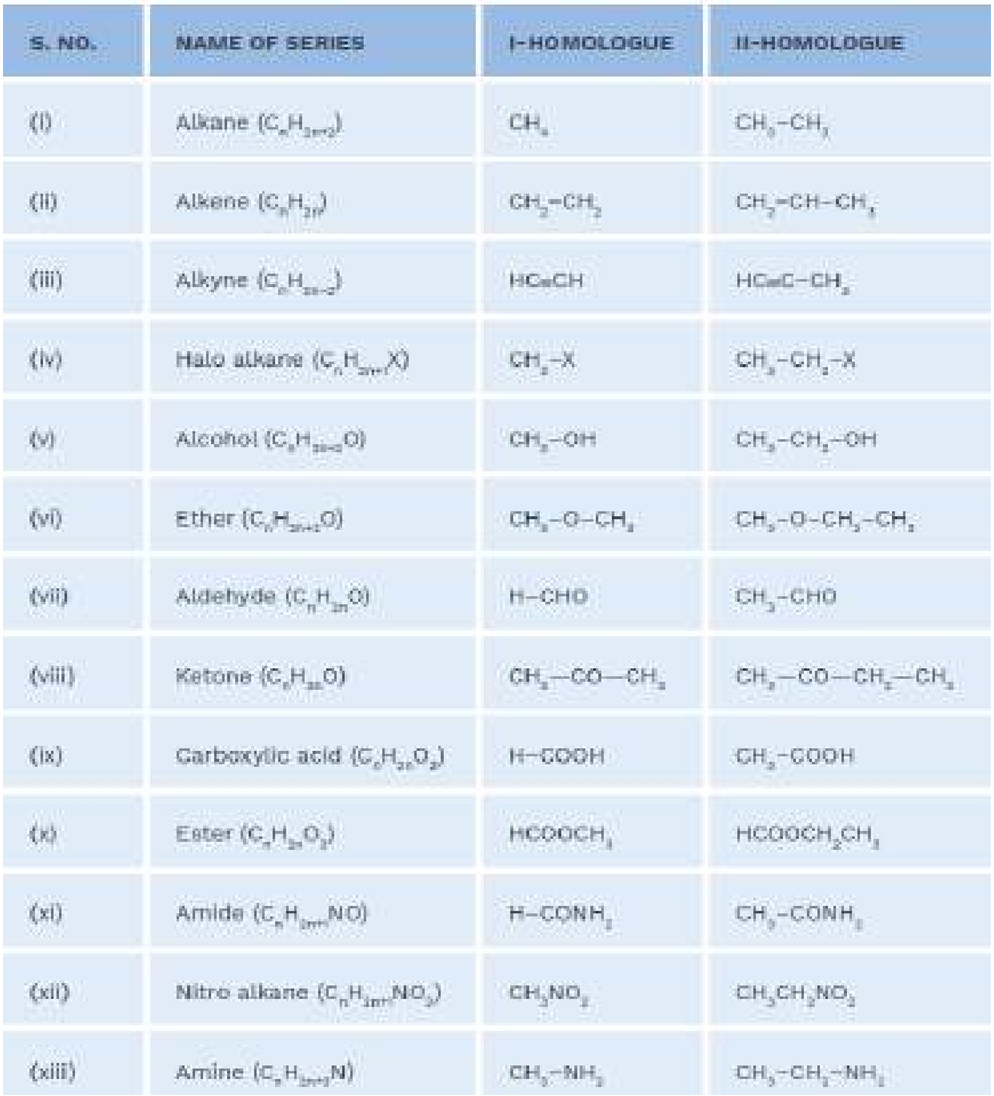
Double and triple bonds are also considered as functional groups.

The organic compounds are further classified into different classes depending upon the nature of functional group. Classification of organic compounds based on functional group is summarized in the table.

Functional Group	Compound Type	Prefix or Suffix of Name	Example		
			Lewis Structure	Ball-and-Stick Model	Systematic Name (Common Name)
	alkene	-ene			ethene (ethylene)
$-C\equiv C-$	alkyne	-yne	$H-C\equiv C-H$		ethyne (acetylene)
	alcohol	-ol			methanol (methyl alcohol)
 (X = halogen)	haloalkane	halo-			chloromethane (methyl chloride)
	amine	-amine			ethanamine (ethylamine)
	aldehyde	-al			ethanal (acetaldehyde)
	ketone	-one			2-propanone (acetone)
	carboxylic acid	-oic acid			ethanoic acid (acetic acid)
	ester	-oate			methyl ethanoate (methyl acetate)
	amide	-amide			ethanamide (acetamide)
$-C\equiv N:$	nitrile	-nitrile			ethanenitrile (acetonitrile, methyl cyanide

Homologous Series

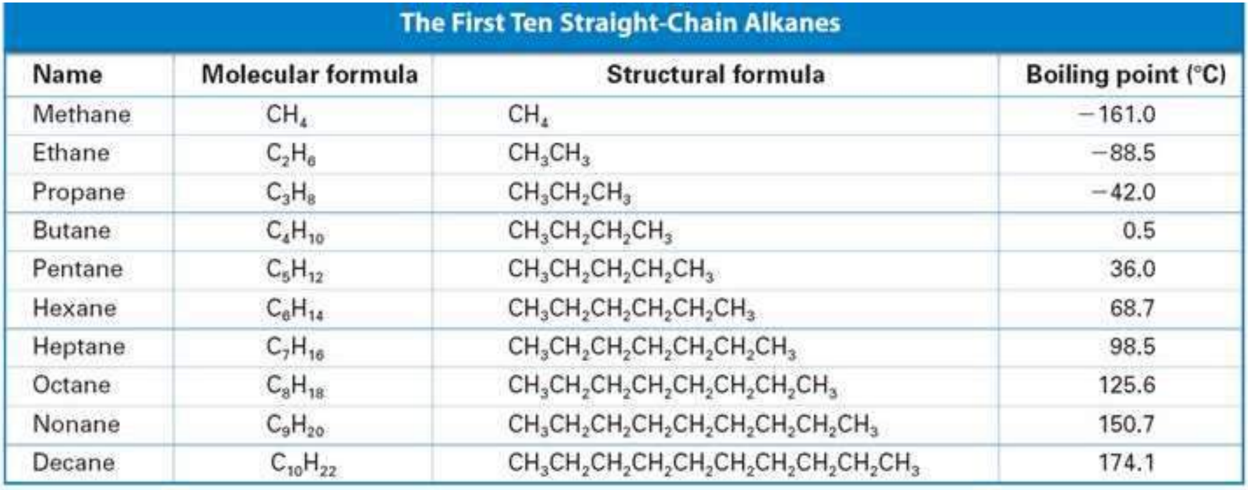
A series of structurally related organic compounds with same functional group can be represented by a general formula and differ by —CH_2 group is called homologous series. The individual members of such series are called homologue and this phenomenon is known as homology.



S. NO.	NAME OF SERIES	I-HOMOLOGUE	II-HOMOLOGUE
(i)	Alkane (C_nH_{2n+2})	CH_4	CH_3-CH_3
(ii)	Alkene (C_nH_{2n})	$CH_2=CH_2$	$CH_2=CH-CH_3$
(iii)	Alkyne (C_nH_{2n-2})	$HC\equiv CH$	$HC\equiv C-CH_3$
(iv)	Halo alkane ($C_nH_{2n+1}X$)	CH_3-X	CH_3-CH_2-X
(v)	Alcohol ($C_nH_{2n+2}O$)	CH_3-OH	CH_3-CH_2-OH
(vi)	Ether ($C_nH_{2n+2}O$)	CH_3-O-CH_3	$CH_3-O-CH_2-CH_3$
(vii)	Aldehyde ($C_nH_{2n}O$)	$H-CHO$	CH_3-CHO
(viii)	Ketone ($C_nH_{2n}O$)	$CH_3-CO-CH_3$	$CH_3-CO-CH_2-CH_3$
(ix)	Carboxylic acid ($C_nH_{2n}O_2$)	$H-COOH$	CH_3-COOH
(x)	Ester ($C_nH_{2n}O_2$)	$HCOOCH_3$	$HCOOCH_2CH_3$
(xi)	Amide ($C_nH_{2n+1}NO$)	$H-CONH_2$	CH_3-CONH_2
(xii)	Nitro alkane ($C_nH_{2n+1}NO_2$)	CH_3NO_2	$CH_3CH_2NO_2$
(xiii)	Amine ($C_nH_{2n+3}N$)	CH_3-NH_2	$CH_3-CH_2-NH_2$

Characteristics of a homologous series are as follows.

- Each homologues series can be represented by general molecular formula.
  Exp - General molecular formula of alkane is C_nH_{2n+2}. Molecular formula $C_nH_{2n}O_2$ represents alkanoic acids (carboxylic acids) and alkyl-alkanoates (esters).
- All members of a given homologous series (homologues) possess the same functional group.
- The successive members of a homologous series differ by a —CH_2— group or by mass units.
- Homologues of a homologous series can be prepared by general methods.
- The physical properties such as boiling point, melting point, density, etc., of the members of a homologues series show a regular gradation with increase in molecular mass.



The First Ten Straight-Chain Alkanes

Name	Molecular formula	Structural formula	Boiling point (°C)
Methane	CH_4	CH_4	−161.0
Ethane	C_2H_6	CH_3CH_3	−88.5
Propane	C_3H_8	$CH_3CH_2CH_3$	−42.0
Butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	0.5
Pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	36.0
Hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	68.7
Heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	98.5
Octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	125.6
Nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	150.7
Decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	174.1

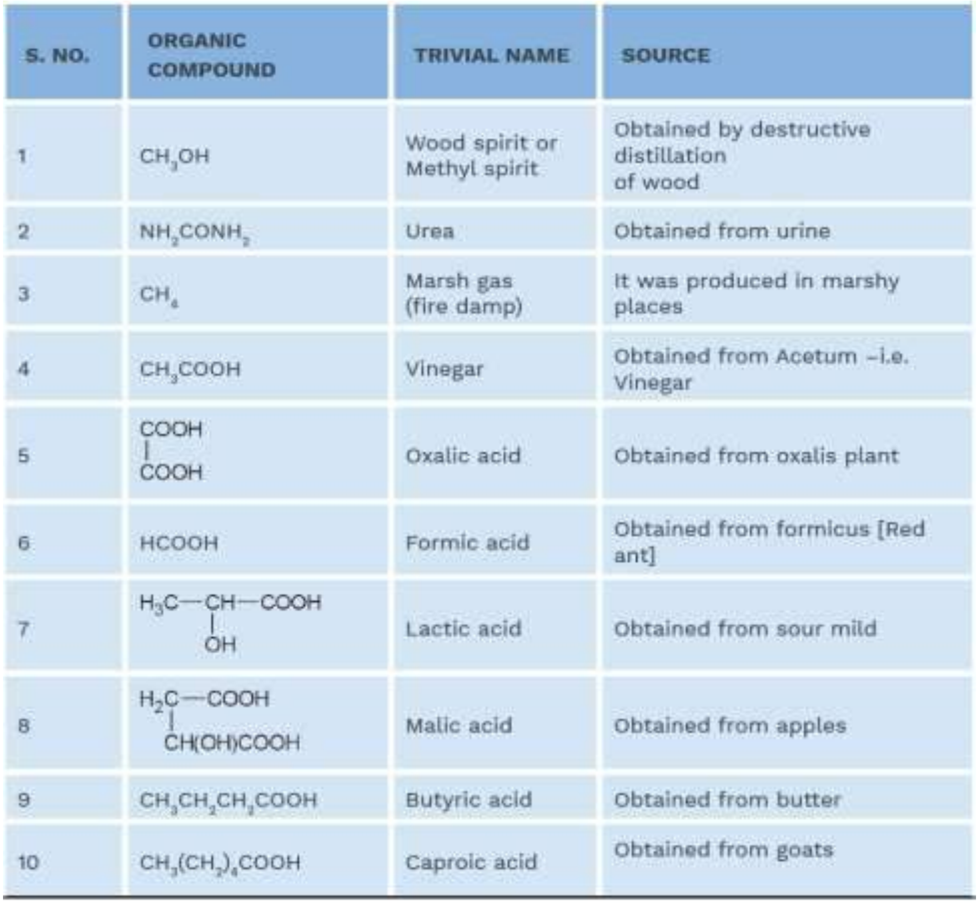
- Chemical properties of the members of a homologous series are similar though the first homologue may vary considerably from the rest of the homologues.

Nomenclature of Organic Compounds

The nomenclature deals with the naming of millions of organic compounds. The following systems are employed.

1. Trivial system (common system)

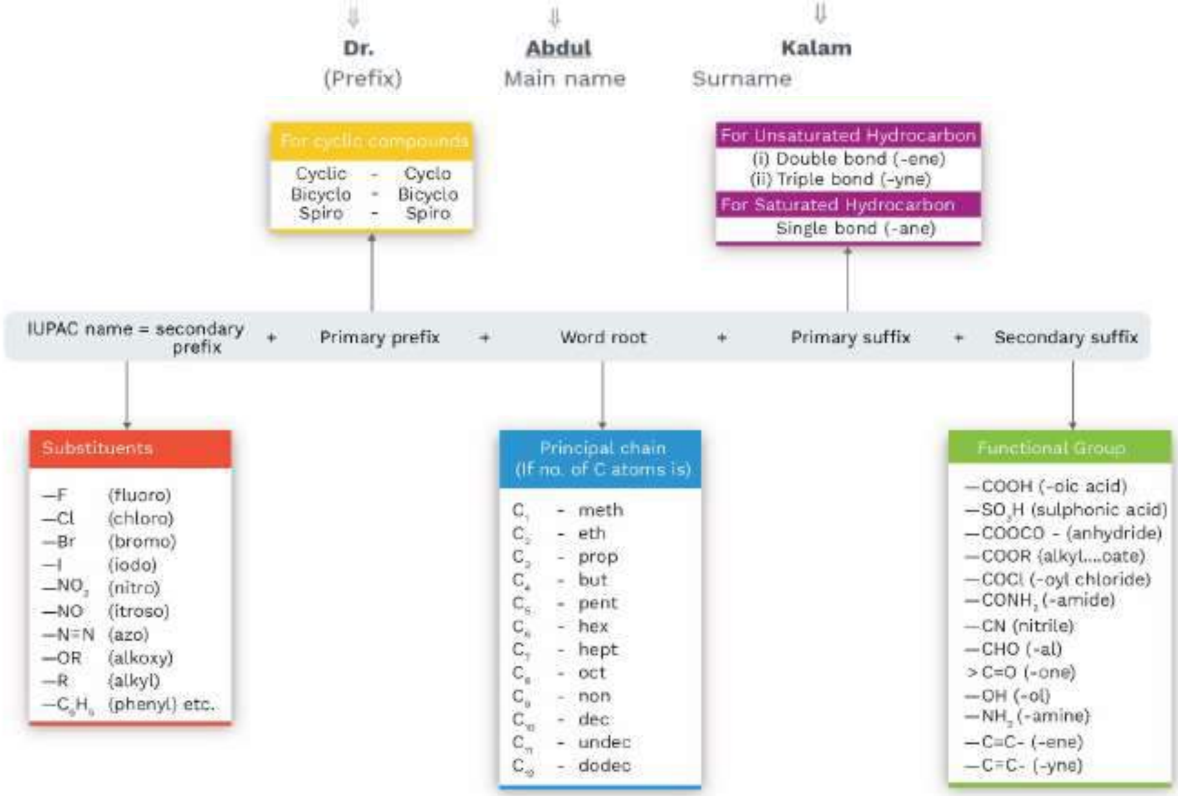
It is the oldest system of naming organic compounds. In the early stages of the development of organic chemistry, organic compounds were named after the source from which they were first isolated. Generally, the names chosen had Latin or Greek roots. The following illustrations justify the statement.



S. NO.	ORGANIC COMPOUND	TRIVIAL NAME	SOURCE
1	CH_3OH	Wood spirit or Methyl spirit	Obtained by destructive distillation of wood
2	NH_2CONH_2	Urea	Obtained from urine
3	CH_4	Marsh gas (fire damp)	It was produced in marshy places
4	CH_3COOH	Vinegar	Obtained from Acetum –i.e. Vinegar
5	COOH | COOH	Oxalic acid	Obtained from oxalis plant
6	HCOOH	Formic acid	Obtained from formicus [Red ant]
7	$H_3C-\underset{\underset{OH}{\vert}}{CH}-COOH$	Lactic acid	Obtained from sour mild
8	$\underset{\underset{CH(OH)COOH}{\vert}}{H_2C}-COOH$	Malic acid	Obtained from apples
9	$CH_3CH_2CH_2COOH$	Butyric acid	Obtained from butter
10	$CH_3(CH_2)_4COOH$	Caproic acid	Obtained from goats

2. **IUPAC System -** Saturated hydrocarbons are the parent compounds and other organic compounds as their derivatives obtained by substituting one or more hydrogen atoms with functional groups. IUPAC name of any organic compound may consist of three parts. ***"prefix-root word-suffix"***.

IUPAC system for naming is something that is very similar to addressing a person with his complete designation.



a. Root word – is assigned to organic molecule based on the number of carbon atoms present in the main parent chain

No. of C atoms	Root word	Molecular formula	Molecular structure	IUPAC name
1	Meth	CH_4	CH_4	Methane
2	Eth	C_2H_6	CH_3CH_3	Ethane
3	Prop	C_3H_8	$CH_3CH_2CH_3$	Propane
4	But	C_4H_{10}	$CH_3(CH_2)_2CH_3$	Butane
5	Pent	C_5H_{12}	$CH_3(CH_2)_3CH_3$	Pentane
6	Hex	C_6H_{14}	$CH_3(CH_2)_4CH_3$	Hexane
7	Hept	C_7H_{16}	$CH_3(CH_2)_5CH_3$	Heptane
8	Oct	C_8H_{18}	$CH_3(CH_2)_6CH_3$	Octane
9	Non	C_9H_{20}	$CH_3(CH_2)_7CH_3$	Nonane
10	dec	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	Decane
11	Undec			
12	dodec			

b. Suffix – is based on the **nature of bonds and functional group** present in the molecules. It is of 2 types,

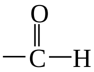
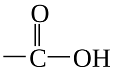
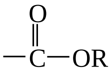
- **Primary suffix:** A primary suffix is added next to the root word to indicate whether the parent chain is saturated or unsaturated.

Type of carbon chain	**root word**	**primary suffix**	**generic name**
Saturated (C-C single bonds)	alk	ane	alkane
Unsaturated [C=C bond]	alk	ene	alkene
Unsaturated [–C≡C–]	alk	yne	alkyne

Note: A carbon-carbon double bond or triple bond must be included in parent chain even if it contains less number of carbon atoms.

- **Secondary suffix** added next to the primary suffix to indicate the presence of a functional group in organic compounds which determines the class of organic compounds.

Secondary suffix of a few **functional groups** are given.

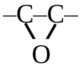
Functional group	**Structure**	**Secondary suffix**	**Class of organic compounds**
Hydroxyl	-OH	- ol	Alcohols
Aldehydic	 $-\overset{O}{\overset{\parallel}{C}}-H$	- al	Aldehydes
Ketonic	$>C=O$	- one	Ketones
Carboxy	 $-\overset{O}{\overset{\parallel}{C}}-OH$	-oic acid	Carboxylic acids
Ester	 $-\overset{O}{\overset{\parallel}{C}}-OR$	alkylalkanote	Esters
Amino	$-NH_2$	- amine	Amines

Note - While adding the secondary suffix, the letter 'e' of the primary suffix (i.e., ane, ene and yne) is dropped if the secondary suffix begins with a vowel (a, e, i, o or u). It is retained if secondary suffix begins with a consonant.

C. Prefix (substituent)

All the groups which are not names in parent chain and functional groups are called as substituents. Its name placed before the root word.

Exp – Alkyl group, halo atoms, nitro group

Substituents group	**Prefix**
$-CH_3$	Methyl
$-C_2H_5$	Ethyl
$-NO_2$	Nitro
-Cl	Chloro
-OR	Alkoxy
	Epoxy
-NO	Nitroso

Alkyl groups – derived from an alkane, by removing a hydrogen atom bonded to carbon. These groups are named simply by dropping –ane from the name of the corresponding alkane and replacing it by **–yl**. R is a general symbol, general formula for an alkyl group is C_nH_{2n+1}, because it contains one less hydrogen atom than the parent alkane, C_nH_{2n+2}.

Alkane	Alkyl group	Abbreviation
Methane, CH_4	Methyl, CH_3–	Me–
Ethane, CH_3CH_3	Ethyl, CH_3CH_2– or C_2H_5–	Et –
Propane, $CH_3CH_2CH_3$	n - propyl, $CH_3CH_2CH_2$– Isopropyl, $CH_3\underset{\vert}{C}HCH_3$	n-Pr - or Pr - i-Pr–
n-Butane, $CH_3CH_2CH_2CH_3$	n-Butyl, $CH_3CH_2CH_2CH_2$– sec - Butyl, $CH_3CH_2\underset{\vert}{C}HCH_3$	n-Bu– or Bu– s-Bu–
Isobutane, $CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_3$	Isobutyl, $CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_2$ tert-Butyl, $CH_3–\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}–$	i-Bu– t-Bu–

Among the alkyl groups **we encounter the problem of isomerism**.

- While only one alkyl group can be derived from methane (the methyl, CH_3–)
- Ethane (the ethyl, CH_3CH_2–)
- Two or more alkyl groups can be derived from higher alkanes.

Exp - (1) From **propane (C_3H_8)**, two alkyl groups can be derived. **Removal of one of the hydrogens from one of the end carbon atoms** gives an alkyl group that is called the propyl group or **n-propyl group**.

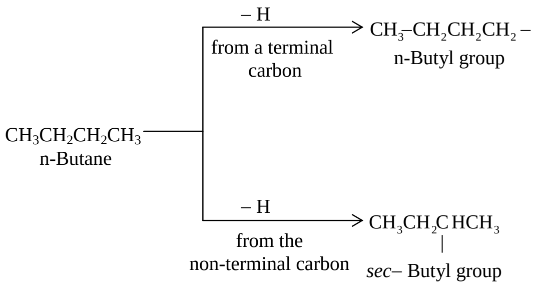
$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow[\text{from end carbon}]{-H} \underset{\text{Propyl}}{CH_3CH_2CH_2-} \quad \text{or n – Propyl}$$

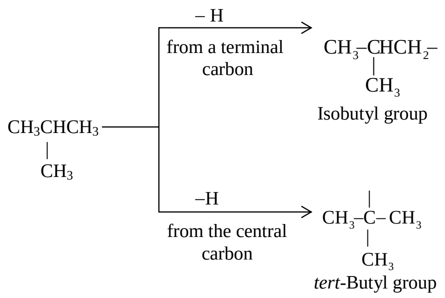
Removal of one of the hydrogens from the middle carbon atom gives an alkyl group that is called the **isopropyl group**.

$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow[\text{from middle carbon}]{-H} \underset{\text{Isopropyl}}{CH_3\underset{\vert}{C}HCH_3}$$

Both these alkyl groups contain the propane chain, but differ in the point of attachment of the group to the rest of the molecule.

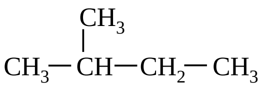
(2) There are four butyl groups, two derived from the straight-chain **n-butane**, and two derived from the branched-chain isobutane. These are given the designations: **n–** (normal), **sec–** (secondary), **iso–** and **tert–** (tertiary) as shown below:





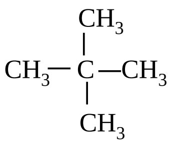
$$CH_3-CH_2-CH_2-CH_2-CH_3$$

n-pentane



$$CH_3-\overset{\overset{CH_3}{\vert}}{C}H-CH_2-CH_3$$

iso-pentane



$$CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-CH_3$$

neo-pentane

An alkyl group is described as,

- **primary** if the carbon at the point of attachment is bonded to only one other carbon,
- as **secondary** if bonded to two other carbons,
- **tertiary** if bonded to three other carbons. Thus, if R is any hydrocarbon radical, the different kinds of alkyl groups are

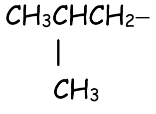
RCH_2–	R_2CH–	R_3C–
Primary	Secondary	Tertiary

Problem 1: Classify each of the following alkyl groups as primary, secondary or tertiary: Butyl, Isopropyl, Isobutyl, sec-Butyl and tert-Butyl.

Solution: Primary alkyl group is RCH_2 –

$CH_3CH_2CH_2CH_2$–

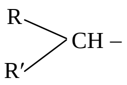
Butyl

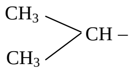


$\underset{\displaystyle CH_3}{CH_3\overset{}{C}HCH_2}$–

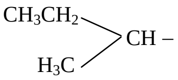
Isobutyl

Secondary alkyl group is



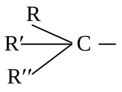


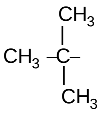
Isopropyl



sec - Butyl

Tertiary alkyl group is





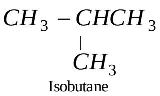
$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-$$

(tert-Butyl)

Prefix n-(normal) is used for those alkanes in which all the carbon atoms form a continuous chain with no branching.

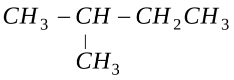
$$\underset{n-\text{Butane}}{CH_3CH_2CH_2CH_3}\ ; \qquad \underset{n-\text{Pentane}}{CH_3CH_2CH_2CH_2CH_3}$$

Prefix iso is used for those alkanes in which one methyl group is attached to the next-to-end carbon atom (second last) of the continuous chain.



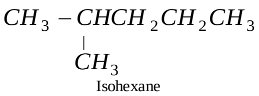
$$CH_3-\underset{\displaystyle CH_3}{C}HCH_3$$

Isobutane



$$CH_3-\underset{\displaystyle CH_3}{CH}-CH_2CH_3$$

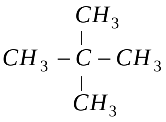
Isopentane



$$CH_3-\underset{\displaystyle CH_3}{C}HCH_2CH_2CH_3$$

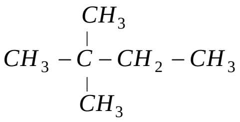
Isohexane

Prefix neo is used for those alkanes which have two methyl groups attached to the second last carbon atom of the continuous chain.



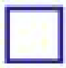
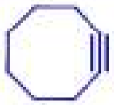
$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-CH_3$$

Neopentane



$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-CH_2-CH_3$$

Neohexane

Compound	2° prefix	1° prefix	Word root	1° suffix	2° suffix	IUPAC name
$CH_3CH_2CH_3$	–	–	prop	ane	–	Propane
$CH_3–CH = CH_2$	–	–	prop	ene	–	Propene
$CH_3–C \equiv CH$	–	–	prop	yne	–	Propyne
$HC \equiv CH$	–	–	eth	yne	–	Ethyne
	–	cyclo	but	ane	–	Cyclobutane
	–	cyclo	but	ene	–	Cyclobutene
	–	cyclo	oct	yne	–	Cyclooctyne

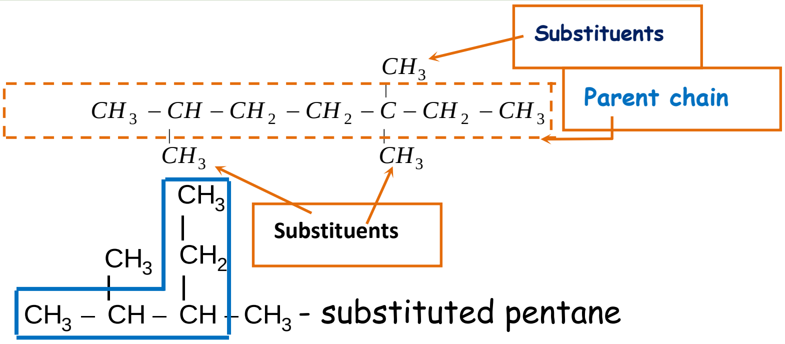
Rules for naming of open chain Organic compound.

Rule 1 - Longest chain rule (root word rule)

The **continuous carbon chain containing maximum carbon atoms including the function group is selected**. It is called the ***parent chain***. For one to four carbon atoms of the parent chain, special root words are used but for chains of five or more carbon atoms *Greek number roots* are employed.

The generic root word for any parent chain is **'alk'**.

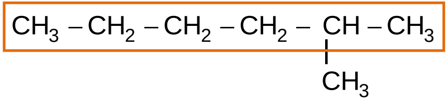
Priority order: Functional group > Multiple bond (= or ≡) > Substituent



$$CH_3-CH(CH_3)-CH_2-CH_2-C(CH_3)_2-CH_2-CH_3$$

- substituted pentane

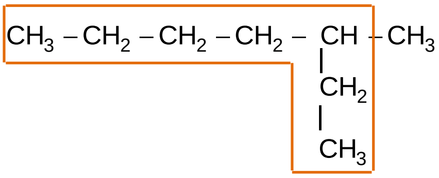
Similarly, the following hydrocarbon will be regarded as a substituted hexane because the longest continuous carbon chain (parent chain/ root chain) contains six carbon atoms.



$$CH_3-CH_2-CH_2-CH_2-CH(CH_3)-CH_3$$

Substituted hexane

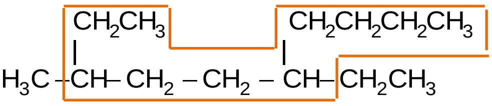
$CH_3(CH_2)_3CHCH_3CH_2CH_3 \rightarrow$



$$CH_3-CH_2-CH_2-CH_2-CH(CH_2CH_3)-CH_3$$

Substituted heptane

$CH_3CH_2CHCH_3(CH_2)_2CHC_2H_5(CH_2)_3CH_3 \rightarrow$



$$H_3C-CH(CH_2CH_3)-CH_2-CH_2-CH(CH_2CH_2CH_2CH_3)-CH_2CH_3$$

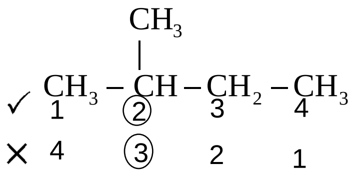
substituted decane

Note:

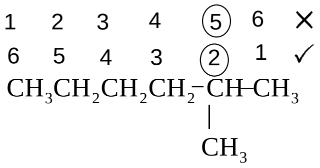
- **If two different chains of equal length are possible, the chain with maximum number of side chains or alkyl groups is selected.**
- **Number used to specify the position of the substituents is called locant.**

Rule 2 - Lowest sum rule (rule of locant)

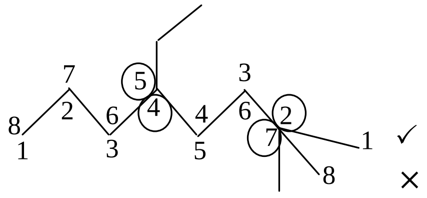
Parent carbon chain is numbered using Arabic numerals 1, 2, 3, 4, 5..... in such a way that functional group or substituents containing carbon receive least number.

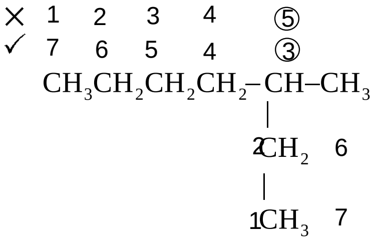


$CH_3-CH(CH_3)-CH_2-CH_3$

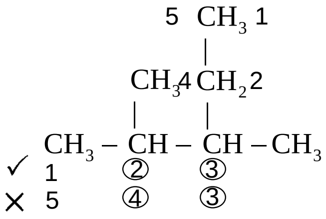


$CH_3CH_2CH_2CH_2-CH(CH_3)-CH_3$

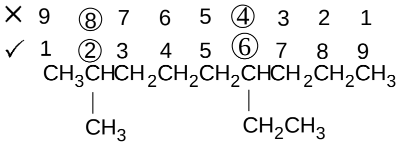




$CH_3CH_2CH_2CH_2-CH(CH_2CH_3)-CH_3$

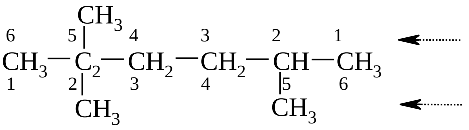


$CH_3-CH(CH_3)-CH(CH_2CH_3)-CH_3$



$CH_3CH(CH_3)CH_2CH_2CH_2CH(CH_2CH_3)CH_2CH_2CH_3$

☛ When the parent chain contains two or more substituents, the numbering is done from the end where the sum of the locants is least.

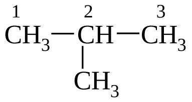


$CH_3-C(CH_3)_2-CH_2-CH_2-CH(CH_3)-CH_3$

(2 + 5 + 5 = 12, wrong)

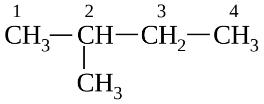
(2 + 2 + 5 = 9, correct)

☛ **Parent chain with one substituent:** Prefix the name of the substituent to the root word of parent chain and indicate its position. The name of the substituent is separated from its locant by a *hyphen* (-). Name of the organic compound is written as *one word*.



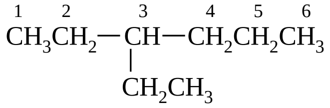
$CH_3-CH(CH_3)-CH_3$

2-methylpropane



$CH_3-CH(CH_3)-CH_2-CH_3$

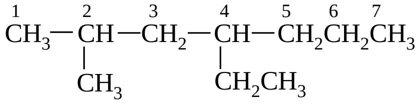
2-methylbutane



$CH_3CH_2-CH(CH_2CH_3)-CH_2CH_2CH_3$

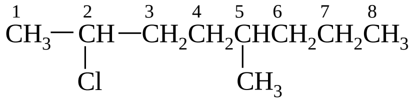
3-ethylhexane

☛ **Naming of different substituents**: When two or more different substituents are present on the parent chain, they are named in *alphabetical order* along with their appropriate locants.



$CH_3-CH(CH_3)-CH_2-CH(CH_2CH_3)-CH_2CH_2CH_3$

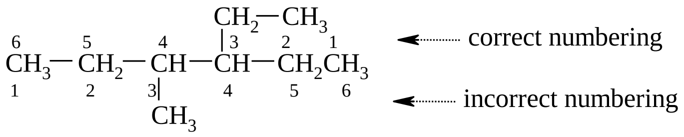
4-ethyl-2-methylheptane



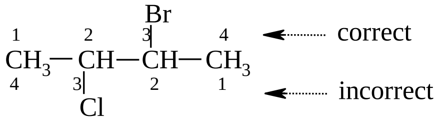
$CH_3-CH(Cl)-CH_2CH_2CH(CH_3)CH_2CH_2CH_3$

2-chloro-5-methyloctane

☛ **Numbering of different substituents at equivalent positions**: If two different alkyl or halo groups are present at equivalent positions, the numbering of the parent chain is done in such a way that the substituent which comes first in the alphabetical order gets the lower number.



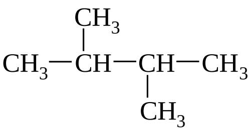
3-ethyl-4-methylhexane (NOT 3-methyl-4-ethylhexane)



$$CH_3-CH(Cl)-CH(Br)-CH_3$$

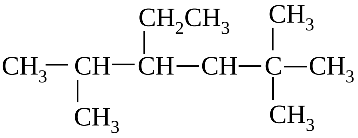
2-bromo-3-chlorobutane (NOT 3 - chloro-2-bromobutane)

☛ **Presence of the same substituent more than once:** If the same substituent occurs more than once, the prefixes *di, tri, tetra* are prefixed to the name of the substituent. It may be noted that the position and name of the substituent are separated by a *hyphen (-)* whereas the numerals representing the positions of the substituents are separated by *commas*.



$$CH_3-CH(CH_3)-CH(CH_3)-CH_3$$

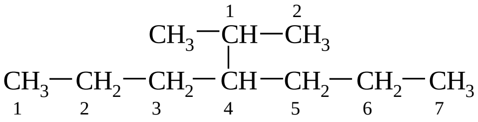
2, 3-dimethylbutane



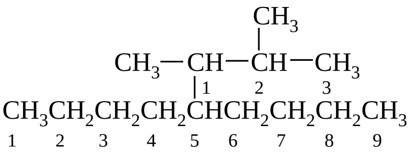
$$CH_3-CH(CH_3)-CH(CH_2CH_3)-CH_2-C(CH_3)_2-CH_3$$

4-ethyl-2,2,5-trimethylhexane

☛ **Naming a complex substituent:** In case the substituent on the parent chain is complex (i.e., it has a branched chain), it is named as a substituted alkyl group by numbering the carbon atom of this group attached to the parent chain as 1. Name of complex substituent is enclosed in bracket to avoid confusion with the numbers of parent chain.



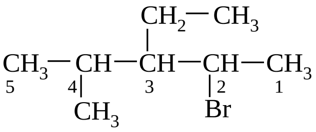
4-(1-methylethyl)heptane



5-(1, 2-dimethylpropyl)nonane

If same complex substituent occurs more than once on the parent chain, prefixes *bis, tris, tetrakis*, etc., are used before the name of the complex substituent.

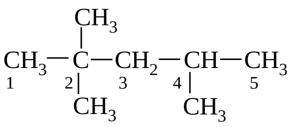
The application of IUPAC rules to the structure of a molecule to arrive at IUPAC name is illustrated as follows.



$$\overset{5}{CH_3}-\overset{4}{CH}(CH_3)-\overset{3}{CH}(CH_2CH_3)-\overset{2}{CH}(Br)-\overset{1}{CH_3}$$

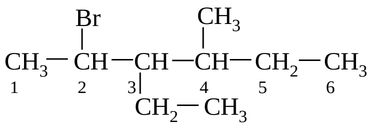
- Parent chain has 5 carbon atoms, and it has more number of substituents. The root word is *'pent'*.
- Primary suffix is *'ane'*
- Sum of locants is 9, the substituent which comes first in alphabetical order gets the lower number.
- Prefixes to the rootword are bromo, ethyl and methyl. Hence, IUPAC name is
- "2-bromo-3-ethyl-4-methylpentane"
-

A few examples are given below:



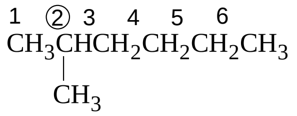
$CH_3-C(CH_3)_2-CH_2-CH(CH_3)-CH_3$

2,2,4-trimethylpentane



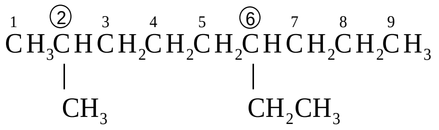
$CH_3-CH(Br)-CH(CH_2CH_3)-CH(CH_3)-CH_2-CH_3$

2-bromo-3-ethyl-4-methylhexane



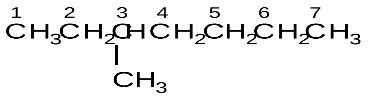
$CH_3CH(CH_3)CH_2CH_2CH_2CH_3$

2–Methylhexane



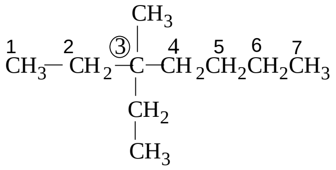
$CH_3CH(CH_3)CH_2CH_2CH_2CH(CH_2CH_3)CH_2CH_2CH_3$

6-Ethyl-2-methylnonane



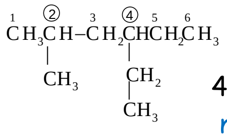
$CH_3CH_2CH(CH_3)CH_2CH_2CH_2CH_3$

3–Methylheptane



$CH_3-CH_2-C(CH_3)(CH_2CH_3)-CH_2CH_2CH_2CH_3$

3-Ethyl-3-methylheptane

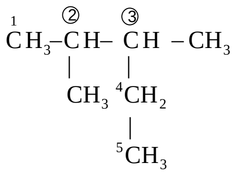


$CH_3CH(CH_3)-CH_2CH(CH_2CH_3)CH_2CH_3$

4-Ethyl-2-methylhexane

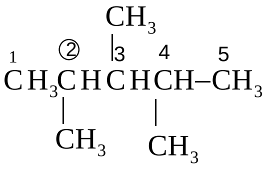
not

2-Methyl-4–ethylhexane because ethyl comes before methyl alphabetically



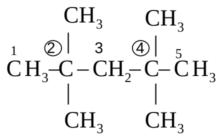
$CH_3-CH(CH_3)-CH(CH_2CH_3)-CH_3$

2, 3 – Dimethylpentane



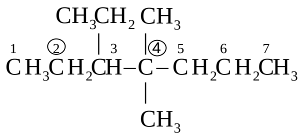
$CH_3CH(CH_3)CH(CH_3)CH(CH_3)-CH_3$

2, 3, 4 – Trimethylpentane



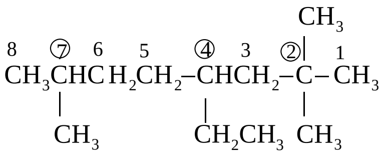
$CH_3-C(CH_3)_2-CH_2-C(CH_3)_2-CH_3$

2, 2, 4, 4 – Tetramethylpentane



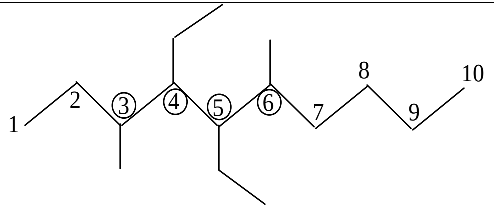
$CH_3CH_2CH(CH_2CH_3)-C(CH_3)_2-CH_2CH_2CH_3$

3 – Ethyl – 4, 4 – dimethylheptane

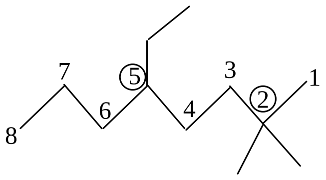


$CH_3CH(CH_3)CH_2CH_2-CH(CH_2CH_3)CH_2-C(CH_3)_2-CH_3$

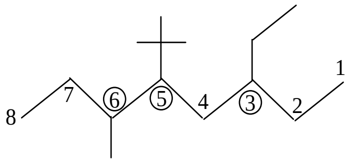
4 – Ethyl – 2, 2, 7– trimethyloctane



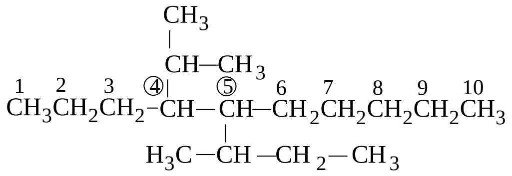
4,5–Diethyl–3, 6-dimethyldecane



5-Ethyl–2, 2–dimethyloctane
(“di” not considered in alphabetical ordering)

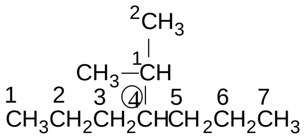


5–(1, 1-Dimethylethyl)–3–ethyl-6-methyloctane
(“di” is being part of substituent name)

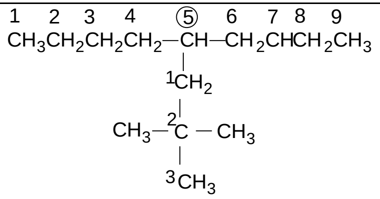


$CH_3CH_2CH_2-CH(CH(CH_3)CH_3)-CH(CH(CH_3)CH_2CH_3)-CH_2CH_2CH_2CH_2CH_3$

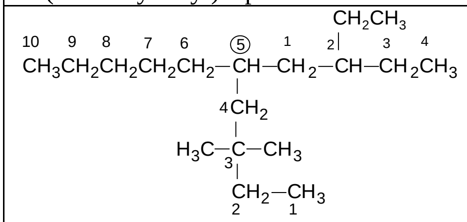
5–sec–Butyl– 4–isopropyldecane



4 – Isopropylheptane
or
4–(1–Methylethyl)heptane



5-(2, 2–Dimethylpropyl)nonane



5–(2–Ethylbutyl)–3, 3–dimethyldecane

N.B. Longest chain selected has maximum number of side chains.

Naming of organic compounds containing a functional group

Prefix and suffix names of a few common functional groups and their **decreasing order of priority** are given in the table.

Group	Prefix name	Suffix name	Class of organic compounds
–COOH	–	-oic acid	Carboxylic acids
–COOR	–	alkyl....oate	Esters
–COX	–	-oyl halide	Acid halides
$-CONH_2$	carbamoyl	-amide	Amides
–CHO	formyl	-al	Aldehydes
–CO	oxo	-one	Ketones
–OH	hydroxyl	-ol	Alcohols
$-NH_2$	amino	-amine	Amines
$>C=C<$	–	-ene	Alkenes
$-C\equiv C-$	–	-yne	Alkynes
–X (halogen)	halo	–	Alkyl halides
$-NO_2$	nitro	–	Nitroalkanes
–OR	alkoxy	–	Ethers

It may be noted that the groups —R, —OR, $—NO_2$, —X, etc. are considered as substituents and are indicated as prefixes.

1. **Longest chain-** The parent chain is the one which has functional group directly attached to it, even if it violates the longest chain rule.
2. **Numbering of parent chain-**The numbering should be done in such a way that the carbon linking to the functional group gets the lowest number even if it violates the lowest sum rule or locant rule.

When the functional group itself contains carbon atom, then that carbon atom is assigned as number 1.

3. **Naming of compounds with polyfunctional group-** If there is more than one functional group present in a compound, then one of the functional group is chosen as the principal functional group (secondary suffix) and the remaining functional groups are treated as (substituents) subordinate functional groups.

The functional group with higher priority in the sequence given below is termed as principal functional group.

$–COOH > –SO_3H > –COOR$ (ester) $> –COCl$ (acylhalide) $> –CONH_2$ (amide) $> –C \equiv N$ (nitriles) $> –CH = O$ (aldehyde)$> > C = O$ (keto) $> –OH$ (alcohol) $> –NH_2$ (amine) $> > C = C$ (alkene) $> –C \equiv C –$ (alkyne)

KNOWLEDGE BUILDER

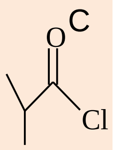
1. When the names of two or more substituents are composed of Identical Words

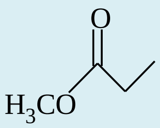
The priority of citation is given to the substituent which has the first cited point of difference with in the complex substituent.

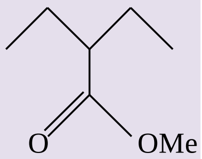
2. Poly-functional compounds containing more than two like-functional groups

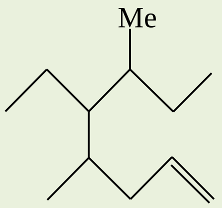
According to the latest convention (1993 recommendation for IUPAC nomenclature), if an unbranded carbon chain is directly linked to more than two like-functional groups, then the organic compound is named as a derivative of the parent alkane which does not include the carbon atoms of the functional groups.

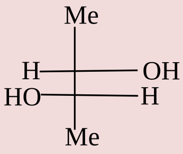
1. **Write the correct IUPAC names of the following bond line formula**:

(i)


(ii)


(iii)


(iv)


(v)


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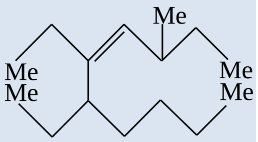

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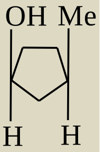

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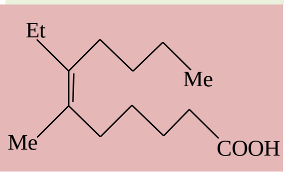

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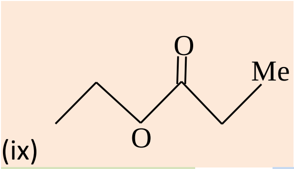
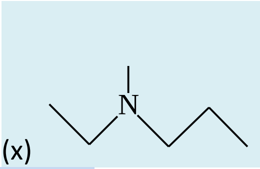


(x)


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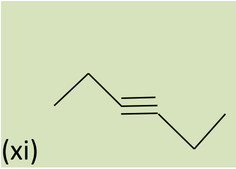
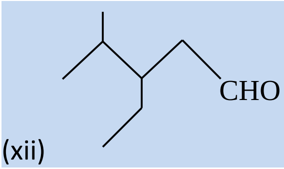


(xii)


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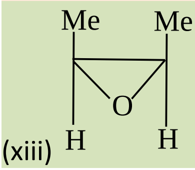
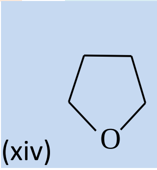


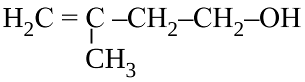
(xiv)


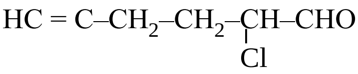
Answers

(i) 2-Methylpropanoyl chloride
(ii) Methyl propanoate
(iii) Methyl 2-ethylbutanoate
(iv) 5-Ethyl-4, 6-dimethyloct-1-ene
(v) Butane-2,3-diol
(vi) 5,6-Diethyl-3-methylundec-4-ene
(vii) 3-Methyl cyclopentam-1-ol
(viii) 7-Ethyl-6-methylundec-6-cnoic acid
(ix) Ethyl propanoate
(x) N-Ethyl-N-methyl propan-1-amine
(xi) Hex-3-yne
(xii) 3-Ethyl-4-methylpentanal
(xiii) 2,3-Dimethyloxirane
(xiv) Tetrahydrofuran

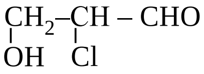
2. Write the IUPAC names of the following compounds:

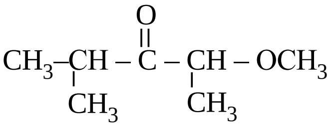
(i) $HOH_2C-CH=CH-CH_2OH$

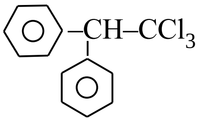
(ii)

$H_2C=\underset{CH_3}{\underset{|}{C}}-CH_2-CH_2-OH$

(iii)

$HC=C-CH_2-CH_2-\underset{Cl}{\underset{|}{CH}}-CHO$

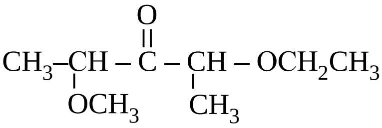
(iv) $CH_3COCOOH$

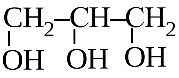
(v)

$\underset{OH}{\underset{|}{CH_2}}-\underset{Cl}{\underset{|}{CH}}-CHO$

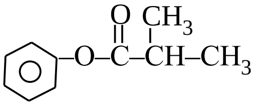
(vi)

$CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-\underset{CH_3}{\underset{|}{CH}}-OCH_3$

(vii)


(viii) $C_6H_5-CH=CH-COOH$

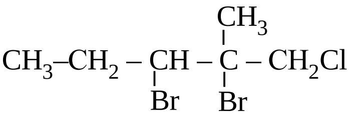
(ix)

$CH_3-\underset{OCH_3}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-\underset{CH_3}{\underset{|}{CH}}-OCH_2CH_3$

(x)

$\underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$

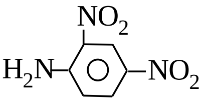
(xii)


(xiii) $[(CH_3)_2CH]_3COH$

(xiv) $(CH_3)_3COH$

(xv)

$CH_3-CH_2-\underset{Br}{\underset{|}{CH}}-\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-CH_2Cl$

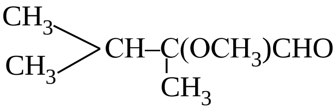
(xvi) $CH_3CH_2CH(CHO)CH_2COOH$

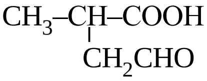
(xvii)


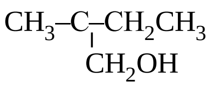
3. Write correct IUPAC names of the following polyfunctional compounds:

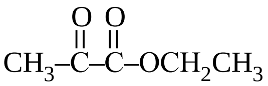
(i) $CH_2=CH-CH_2Cl$

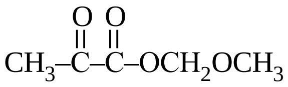
(ii) $CH_3CH\ CHCH_2OH$

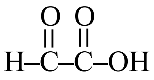
(iii)

$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-\underset{CH_3}{\underset{|}{C}}(OCH_3)CHO$

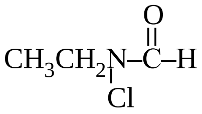
(iv)

$CH_3-\underset{CH_2CHO}{\underset{|}{CH}}-COOH$

(v) 
$\mathrm{CH_3{-}\underset{CH_2OH}{\underset{|}{C}}{-}CH_2CH_3}$

(vi) 
$\mathrm{CH_3{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OCH_2CH_3}$

(vii) 
$\mathrm{CH_3{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OCH_2OCH_3}$

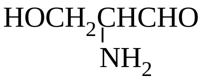
(viii) 
$\mathrm{H{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OH}$

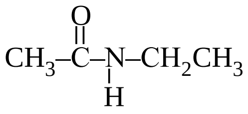
(ix) 
$\mathrm{CH_3CH_2\underset{Cl}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}H}$

(x) $\mathrm{CH_3CH_2CHCH_2CN}$

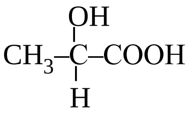
4. Write IUPAC names of the following compounds:

(i) $\mathrm{CH_3OCH_2CH_2CH_2OC_2H_5}$

(ii) 
$\mathrm{HOCH_2\underset{NH_2}{\underset{|}{C}}HCHO}$

(iii) 
$\mathrm{CH_3{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{\underset{|}{N}}{-}CH_2CH_3}$

(iv) $\mathrm{HC{=}C{-}CH{=}CH{-}CH_3}$

(v) 
$\mathrm{CH_3{-}\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}{-}COOH}$

Answers

1. (i) –C = N> –C– > –OH (ii) $\mathrm{–SO_3H > –COCl > –CHO}$
(i) $\mathrm{–COOR > –CONH_2 > –CHO}$

2. (i) But-2-ene-1, 4-diol
(ii) 3-Methyl-but-3-en-l-ol
(iii) 2-Chlorohex-5-yn-l-al
(iv) 2-Ketopropanoic acid
(v) 2-Chloro-3-hydroxypropanal
(vi) 2-Methoxy-4-methylpentan-3-one
(vii) 1,1,1-Trichloro-2,2-diphenylethane
(viii) 3-Phenylprop-2-en-l-oic acid
(ix) 2-Ethoxy-4-methoxypentan-3-one
(x) Propane 1,2,3-triol
(xi) 2-Methoxybenezoic acid
(xii) Phenyl 2-methylpropanoate
(xiii) 2,4-Dimethyl-3-(1-nethylethyl) pentan-3-ol
(xiv) 2-Methylpropan-2-ol
(xv) 2,3-Dibromo-1-chloro-2-methylpentane
(xvi) 3-Formylpentanoic acid
(xvii) 2,4-Dinitro benezamine

3. (i) 3-chloroprop-1-ene
(ii) butane-1,2,3-triol
(iii) 2-Methoxy-2,3-dimethylbutanal
(iv) 3-Formyl-2-methylproanoic acid
(v) 2-Ethyl-3-hydroxy-2-methyl propanal
(vi) Ethyl-(2-oxo) propanoate
(vii) 1-Methoxy-2-3,-butanedione
(viii) Formylmethanoic acid
(ix) N-Chloro-N-ethyl methanamide
(x) 2-Ethyl-butane-1,4-dinitrile

4. (i) 1-Ethoxy-3-methoxypropane
(ii) 2-Amino-3-hydroxypropanal
(iii) N-Ethyl ethanamide
(iv) Pent-3-en-1-yne
(v) 2-Hydroxypropanoic acid

Nomenclature of substituted benzene compounds

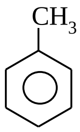
Benzene is a six membered cyclic compound with alternate single and double bonds. It is represented in any one of the following ways:

(i) Naming of monosubstituted benzene

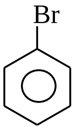
It is derived by adding the name of the substituent with the word benzene.

Substituent + benzene → substituted benzene

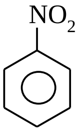
Example:



methylbenzene

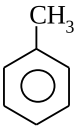
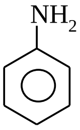
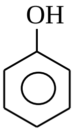
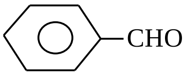
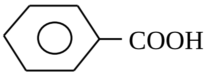
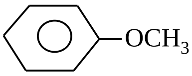


bromobenzene



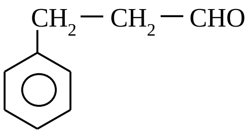
nitrobenzene

Special names of some monosubstituted benzene compounds

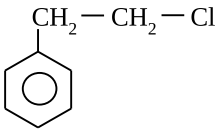
Molecular formula	Structural formula	IUPAC name	Special name
$C_6H_5CH_3$		methylbenzene	Toluene
$C_6H_5NH_2$		benzenamine	Aniline
C_6H_5OH		phenol	Phenol
C_6H_5CHO		Benzene Carbaldehyde	Benzaldehyde
C_6H_5COOH		Benzene Carboxylic acid	Benzoic acid
$C_6H_5OCH_3$		methoxybenzene	Anisole

If the functional group is attached to the carbon chain connected to benzene ring, then benzene ring is considered as substituent and is prefixed before the root word as phenyl.

Example:



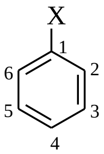
3-phenylpropanal



2-phenylchloroethane

(ii) Naming of disubstituted benzene

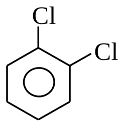
(a) If the substituents are same: In such case, the relative position of the substituents must be indicated by adding the symbols o – (1, 2) ; m – (1, 3) ; p – (1, 4).



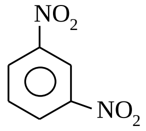
o-ortho : positions 2, 6
m-meta : positions 3, 5
p-para : positions 1, 4

In the trivial system of nomenclature, the terms ortho(o), meta(m) and para(p) are used as prefixes to indicate the relative positions 1, 2-; 1, 3 and 1, 4-respectively.

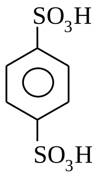
Example:



1,2-dichlorobenzene
(or) o-dichlorobenzene

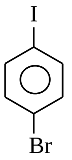


1,3-dinitrobenzene
(or) m-dinitrobenzene

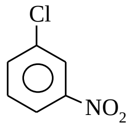


1,4-benzenedisulphonic acid
(p-benzenedisulphonic acid)

(b) If the two substituents are different, they are named in the alphabetical order.

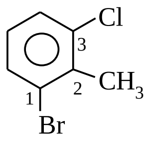


1-bromo-4-iodobenzene
(or) p-bromoiodobenzene

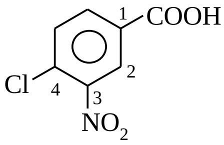


1-chloro-3-nitrobenzene
(or) m-chloronitrobenzene

(c) If there are more than two substituents: The numbering is done in such a way that it satisfies the lowest sum rule.



1-bromo-3-chloro-2-methylbenzene



4-chloro-3-nitrobenzoic acid

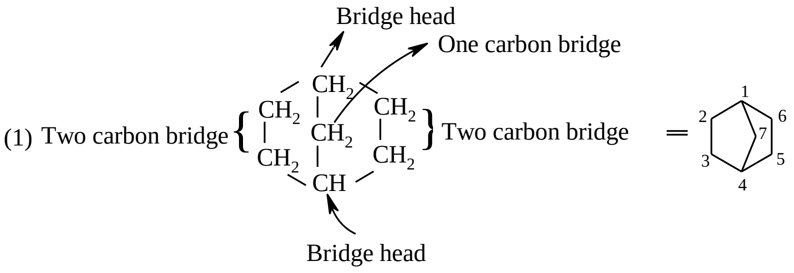
Nomenclature of Bicyclo compounds

(i) Bicyclo compounds contain two fused rings with the help of a bridge. We use the name of the alkane corresponding to the total number of carbon atoms as the base name. The carbon atoms common to both the rings are called bridge heads, and each bond or chain of atoms connecting the bridgehead atoms called a bridge.

(ii) While naming the bi-cycloalkane we write an expression between the word bicyclo and alkane (in square bracket), that denotes the number of carbon atoms in each bridge. The numerals are written in descending order and the numbers are separated by a point.

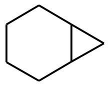
(iii) If substituents are present, we number the bridged ring system beginning at one bridge head, proceeding first along the longest bridge to the other bridge head, then along the second next longest bridge back to first bridge head. The shortest bridge is numbered in the last.

Example:



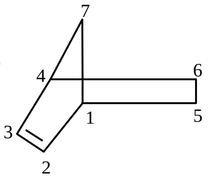
Bicyclo [2, 2, 1] heptane
It's common name is norborane

(2)



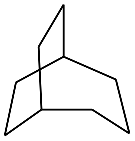
Biyclo [4.1.0] heptane

(3)



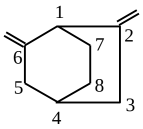
Bicyclo [2.2.1] hept-2-ene

(4)



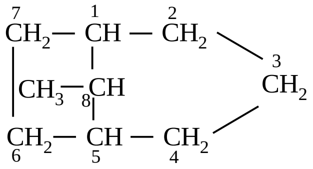
Bicyclo [3.2.2] nonane

(5)

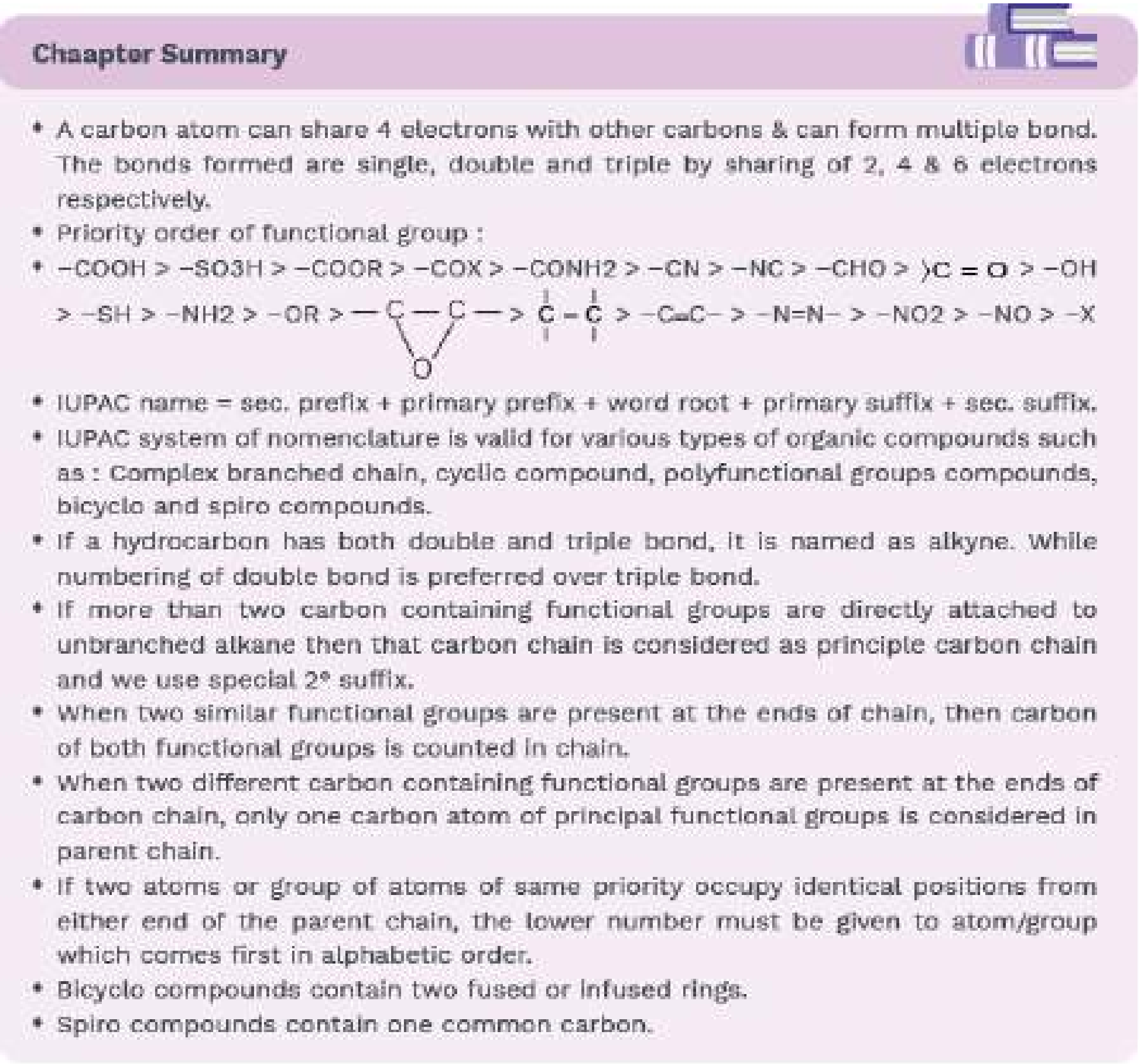


Bicyclo [2.2.2] octa-2,6-dione

(6)



8-Methylbicyclo [3.2.1] octane



Chaapter Summary

- A carbon atom can share 4 electrons with other carbons & can form multiple bond. The bonds formed are single, double and triple by sharing of 2, 4 & 6 electrons respectively.
- Priority order of functional group :
- $-COOH > -SO3H > -COOR > -COX > -CONH2 > -CN > -NC > -CHO > \rangle C = O > -OH > -SH > -NH2 > -OR > -\underset{O}{C-C}- > \overset{|}{\underset{|}{C}} = \overset{|}{\underset{|}{C}} > -C \equiv C- > -N=N- > -NO2 > -NO > -X$
- IUPAC name = sec. prefix + primary prefix + word root + primary suffix + sec. suffix.
- IUPAC system of nomenclature is valid for various types of organic compounds such as : Complex branched chain, cyclic compound, polyfunctional groups compounds, bicyclo and spiro compounds.
- If a hydrocarbon has both double and triple bond, it is named as alkyne. While numbering of double bond is preferred over triple bond.
- If more than two carbon containing functional groups are directly attached to unbranched alkane then that carbon chain is considered as principle carbon chain and we use special 2° suffix.
- When two similar functional groups are present at the ends of chain, then carbon of both functional groups is counted in chain.
- When two different carbon containing functional groups are present at the ends of carbon chain, only one carbon atom of principal functional groups is considered in parent chain.
- If two atoms or group of atoms of same priority occupy identical positions from either end of the parent chain, the lower number must be given to atom/group which comes first in alphabetic order.
- Bicyclo compounds contain two fused or infused rings.
- Spiro compounds contain one common carbon.

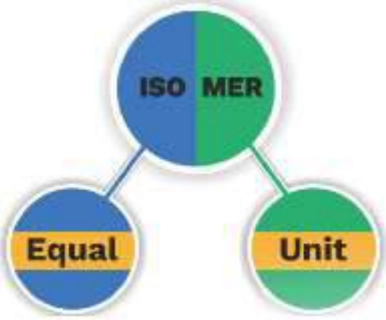
Isomerism

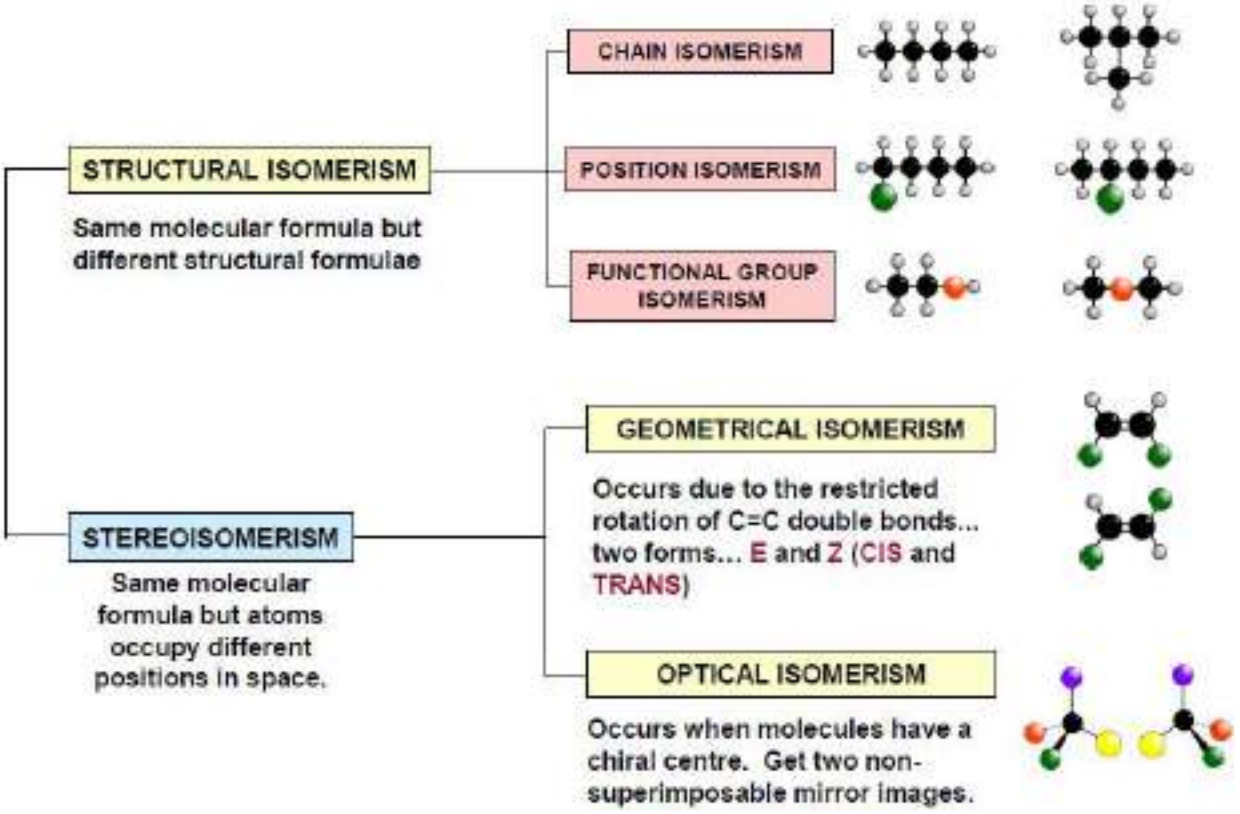
The existence of two or more compounds with the same molecular formula but different physical and chemical properties is known as **isomerism** and the molecules themselves called as isomers.

The term was given by Berzelius. The difference in properties of the two isomers is due to difference in the arrangement of atoms within their molecules.

Concept Ladder

Isomerism is resultant factor of thermodynamic system "entropy".





Isomerism is mainly classified into structural isomerism and stereoisomerism.

1. Structural isomerism

It is due to the differences in structures of the isomers. Structural isomerism is further classified into 5 types.

(i) Chain isomerism (nuclear isomerism)

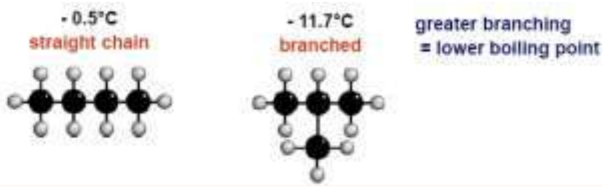
Compounds with **same molecular formula but differ in the arrangement and number of carbon atoms** within the molecule are called *chain isomers* and the phenomenon as chain isomerism.

DIFFERENCES BETWEEN CHAIN ISOMERS

Chemical properties- Isomers show similar chemical properties because the same functional group is present.

Physical Properties- such as density and boiling point show trends according to the of the degree of branching

Boiling Point of straight chain isomers have higher values than branched ones the greater the degree of branching the lower the boiling point branching decreases the effectiveness of intermolecular forces less energy has to be put in to separate the molecules

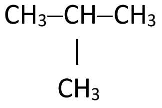


For example,

(i) Butane (C_4H_{10}) has two isomers – normal butane and *iso*butene. One isomer has a straight chain and the other has a branched chain.

$CH_3–CH_2–CH_2–CH_3$

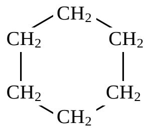
n–butane



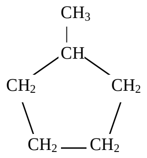
$CH_3–\underset{\underset{CH_3}{|}}{CH}–CH_3$

isobutane

(ii) cyclohexane and methylcyclopentane are nuclear isomers.



cyclohexane

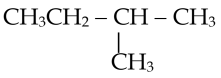


methylcyclopentane

(iii) C_5H_{12} has three chain isomers.

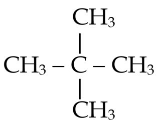
$CH_3CH_2CH_2CH_2CH_3$

n–pentane



$CH_3CH_2 - \underset{\underset{CH_3}{|}}{CH} - CH_3$

Isopentane



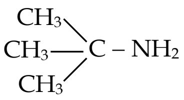
$CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - CH_3$

neopentane

(iv) $C_4H_9NH_2$ also shows two chain isomers.

$CH_3CH_2CH_2CH_2NH$

n–butylamine

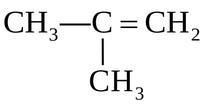


tert.butylamine

Solve 1- How many chain isomers does butane have?

$CH_3—CH_2CH_2 = CH_2$

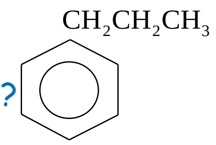
n – Butylene (1 – Butene)



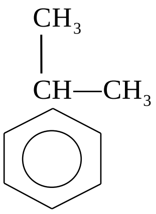
$CH_3—\underset{\underset{CH_3}{|}}{C} = CH_2$

Isobutylene (2-Methylpropene)

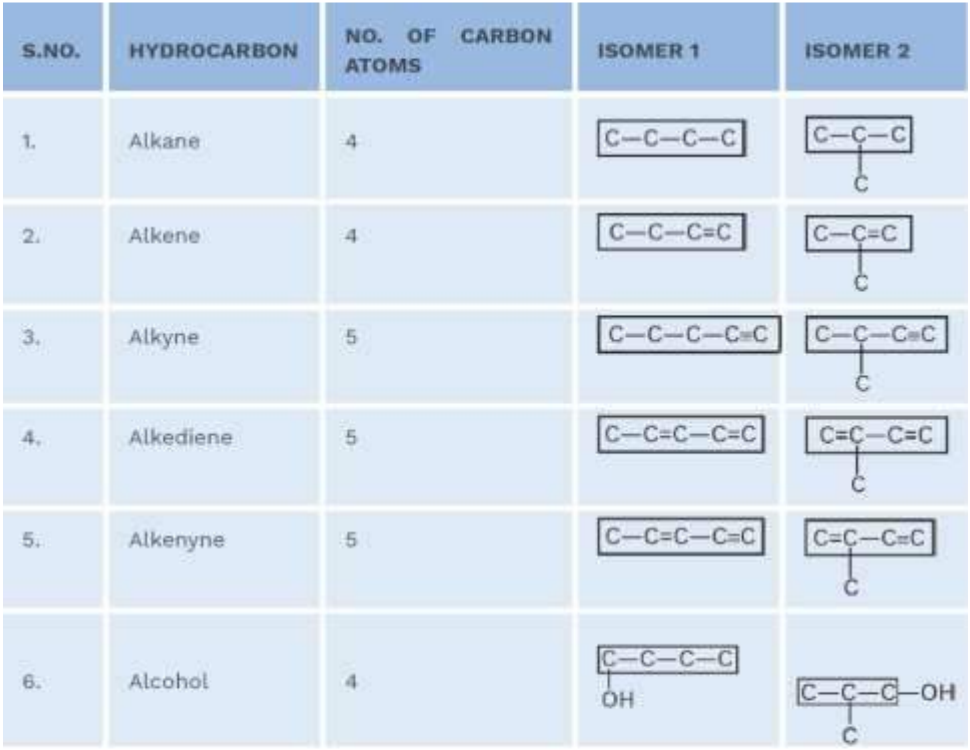
Solve 2 - How many chain isomers does propyl benzene have?



n – Propylbenzene



Isopropylbenzene

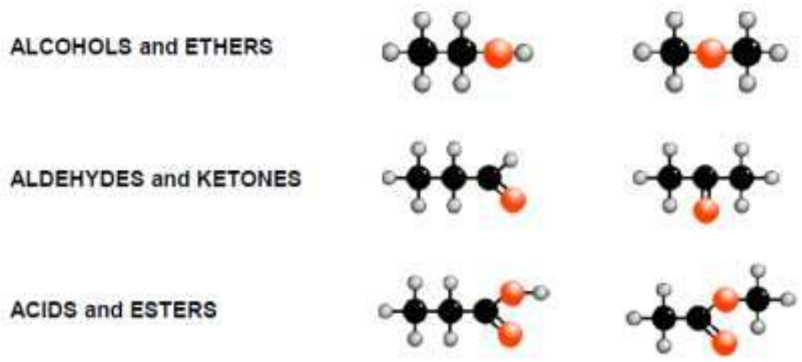


S.NO.	HYDROCARBON	NO. OF CARBON ATOMS	ISOMER 1	ISOMER 2
1.	Alkane	4	C—C—C—C	C—C—C │ C
2.	Alkene	4	C—C—C=C	C—C=C │ C
3.	Alkyne	5	C—C—C—C≡C	C—C—C≡C │ C
4.	Alkediene	5	C—C=C—C=C	C=C—C=C │ C
5.	Alkenyne	5	C—C=C—C≡C	C=C—C≡C │ C
6.	Alcohol	4	C—C—C—C │ OH	C—C—C—OH │ C

(ii) Functional isomerism

Compounds with same molecular formula but differ in functional groups are called functional isomers and the phenomenon is known as functional isomerism.

For example



- Diethyl ether butyl alcohol both has the molecular formation C_4H_6O, but contains different functional groups.

  $C_2H_5-O-C_2H_5$ $\quad$ C_4H_9-OH

  diethyl ether $\quad$ butyl alcohol

  Thus, functional group in diethyl ether is $(-O-)$, while is butyl alcohol it is $(-OH)$.

- Acetone and propionaldehyde both with the molecular formula C_3H_6O are functional isomers.

  $CH_3-CO-CH_3$ $\quad$ CH_3-CH_2-CHO

  acetone $\quad$ acetaldehyde

  In acetone the functional group is $(-CO-)$, while in acetaldehyde it is $(-CHO)$

- Cyanides are isomeric with isocyanides;

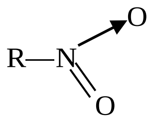
  RCN $\quad$ RNC

  Alkyl cyanide $\quad$ Alkyl isocyanide

- Carboxylic acids are isomeric with esters.

CH_3CH_2COOH	CH_3COOCH_3
Propanoic acid	Methyl ethnoate

- Nitroalkanes are isomeric with alkyl nitrites:



Nitroalkane

$R—O—N=O$

Alkyl nitrite

- Sometimes a double bond containing compound may be isomeric with a triple bond containing compound. This also is called as functional isomerism. Thus, butyne is isomeric with butadiene (molecular formula C_4H_6).

$CH_3-CH_2C\equiv CH$	$CH_2=CH-CH=CH_2$
1 - Butyne	1, 3 - Butadiene

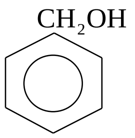
- Unsaturated alcohols are isomeric with aldehydes. Thus,

$CH_2=CH-OH$	CH_3CHO
Vinyl alcohol	Acetaldehyde

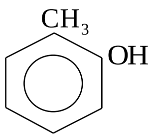
- Unsaturated alcohols containing three or more carbon atoms are isomeric to aldehydes as well as ketones:

$CH_2=CH-CH_2OH$	CH_3CH_2CHO	CH_3COCH_3
Allyl alcohol	Propionaldehyde	Acetone

- Aromatic alcohols may be isomeric with phenols

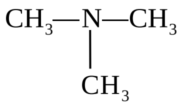


Benzyl alcohol



$o-$Cresol

- Primary, secondary and tertiary amines of same molecular formula are also the functional isomers.

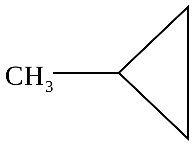
$CH_3CH_2CH_2NH_2$	$CH_3-NH-C_2H_5$	 $CH_3—\underset{\underset{CH_3}{\vert}}{N}—CH_3$
n-propylamine (1°)	Ethylmethyla min (2°)	Trimethylamine$(3°)$

- Alkenes are isomeric with cycloalkanes:

$CH_3CH_2CH=CH_2$

Butene

Cyclobutane



Methycyclopropane

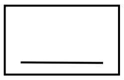
- Such isomers in which one is cyclic and other is open chain are called ring-chain isomers. Alkynes and alkadienes are isomeric with cycloalkanes.

$CH_3CH_2C\equiv CH$

$1-$Butyne

$CH_2=CH—CH=CH_2$

$1,3-$Butadinene



Cyclobutene

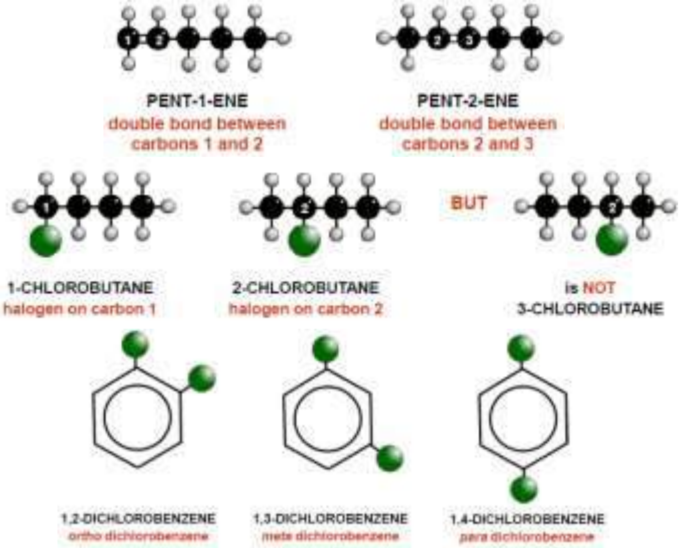
(iii) Position isomerism

Compounds which have the same structure (arrangement) of carbon chain (carbon skeleton) but differ in the position of the multiple bond or the functional group are called position isomers and the phenomenon is known as position isomerism.

Thus the following compounds can exhibit position isomerism:

(a) Alkenes (b) Alkynes (c) Arenes d) Alkyl halides
(e) Aryl halides (f) Alcohols (g) Amines and h) Nitro compounds

a) Alkenes containing four or more carbon atoms can exhibit position isomerism due to the difference in the position of double bond on the same carbon skeleton, For example:



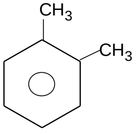
i) $CH_3CH_2CH = CH_2$ $CH_3CH = CHCH_3$
But-1-ene But-2-ene
ii) $CH_3CH_2CH_2CH = CH_2$ $CH_3CH_2CH = CHCH_3$
Pent-1-ene Pent-2-ene
iii) $CH_3CH_2CH_2CH = CH_2$ $CH_3CH_2CH_2CH = CHCH_3$
Hex-1-ene Hex-2-ene
$CH_3CH_2CH = CHCH_2CH_3$
Hex-3-ene

b) Alkynes containing four or more carbon atoms can exhibit position isomerism due to the difference in the position of triple bond on the same carbon skeleton. For example:

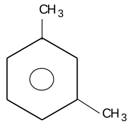
i) $CH_3CH_2\,C \equiv CH$ $CH_3C \equiv CCH_3$
But-1-yne But-2-yne
ii) $CH_3CH_2CH_2C \equiv CH$ $CH_3CH_2C \equiv CCH_3$
Pent-1-yne Pent-2-yne

c) Arenes containing eight or more carbon atoms exhibit position isomerism due to the difference in the position of alkyl groups on the benzene ring. For example:

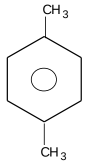
i)



o – Xylene

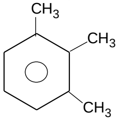


m – Xylene

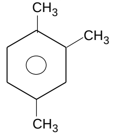


p – Xylene

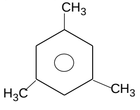
ii)



1, 2, 3 – Trimethyl benzene
(hemimellitene)



1,2,4– Trimethylbenzene
(pseudocumene)



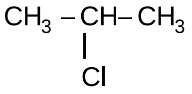
1, 3, 5 – Trimethylbenzene
(mesitylene)

d) Alkyl halides containing three or more carbon atoms can exhibit position isomerism due to the difference in the position of halogen atom on the same carbon skeleton. For example

i) C_3H_7Cl has two position isomers:

$CH_3CH_2CH_2Cl$

1 – Chloropropane



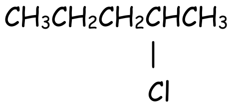
$CH_3-\underset{\underset{\displaystyle Cl}{|}}{CH}-CH_3$

2 – Chloropropane

ii) n – Pentane on monochlorination gives three isomeric chloropentanes:

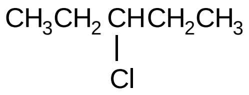
$CH_3CH_2CH_2CH_2CH_2Cl$

1 – Chloropentane



$CH_3CH_2CH_2\underset{\underset{\displaystyle Cl}{|}}{CH}CH_3$

2 – Chloropentane



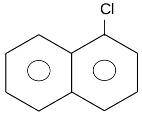
$CH_3CH_2\underset{\underset{\displaystyle Cl}{|}}{CH}CH_2CH_3$

3 – Chloropentane

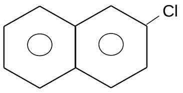
Polyhalogen derivatives containing two or more carbon atoms can also exhibit position isomerism. For example:

CH_3CHCl_2	1, 1 – Dichloroethane	$ClCH_2CH_2Cl$	1, 2 – Dichloroethane

e) Aryl halides containing two or more benzene rings can exhibit position isomerism due to the difference in the position of halogen atom. For example:

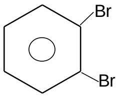


1 – Chloronaphthalene

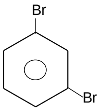


2 – Chloronaphthalene

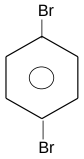
Polyhalogen compounds containing just one benzene ring can also exhibit position isomerism. For example:



1, 2 – Dibromobenzene



1, 3 – Dibromobenzene



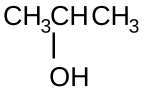
1, 4 – Dibromobenzene

f) Alcohols containing three or more carbon atoms exhibit position isomerism due to the difference in the position of functional group (–OH). For example :

i) The molecular formula C_3H_8O represents two isomeric alcohols:

$CH_3CH_2CH_2OH$

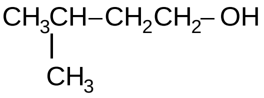
Propan-1-ol



$CH_3\underset{\underset{\displaystyle OH}{|}}{CH}CH_3$

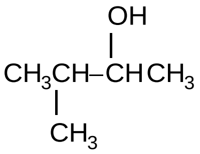
Propan-2-ol

ii) Four monohydric alcohols differing in the position of – OH group can be derived from isopentane:



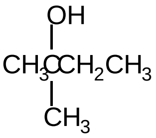
$CH_3\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2CH_2-OH$

3 – Methylbutan-1-ol



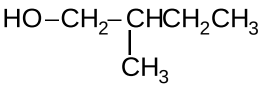
$CH_3\underset{\underset{\displaystyle CH_3}{|}}{CH}-\overset{\overset{\displaystyle OH}{|}}{CH}CH_3$

3 – Methylbutan-2-ol



$CH_3\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_2CH_3$

2 – Methylbutan-2-ol



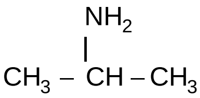
$HO-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}CH_2CH_3$

2 – Methylbutan-1-ol

g) Primary amines (RNH_2) containing three or more carbon atoms can exhibit position isomerism due to the difference in the position of amino group on the same carbon skeleton. For example:

$CH_3CH_2CH_2NH_2$

1 – Aminopropane



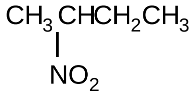
$CH_3-\overset{\overset{\displaystyle NH_2}{|}}{CH}-CH_3$

2 – Aminopropane

h) Nitro compounds (RNO_2) containing three or more carbon atoms can exhibit position isomerism due to the difference in the position of nitro group on the same carbon skeleton. For example:

$CH_3CH_2CH_2CH_2NO_2$

1-Nitrobutane



$$CH_3\underset{\displaystyle NO_2}{\underset{|}{C}}HCH_2CH_3$$

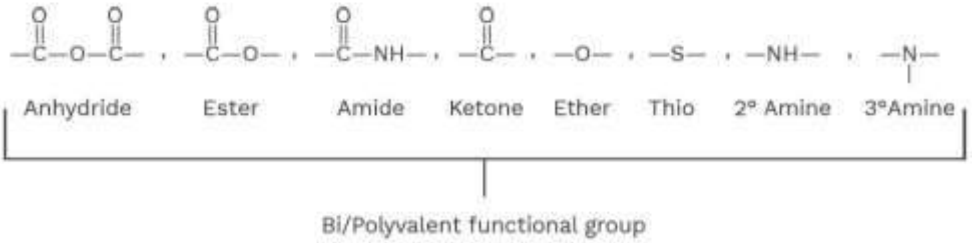
2-Nitrobutane

(iv) Metamerism

Here two or more different compounds having the same molecular formula but **different number and arrangement of carbon atoms on either side of the functional group** is called metamerism. Such compounds are known as metamers.

Metamerism is never possible in compounds possessing the univalent functional group.

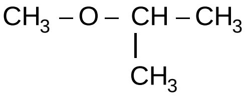
Metamerism is due to the difference in the nature of alkyl groups attached to the same polyvalent functional group such as $-\underset{\underset{O}{\|}}{C}-, -\ddot{O}-, -\ddot{\underset{..}{S}}-, -\ddot{N}H-, -\underset{|}{\ddot{N}}-$ and $-\underset{\underset{O}{\|}}{C}-O-$.



Metamerism is exhibited by compounds of the same homologous series.

a) **Ethers, R–O–R′,** exhibit metamerism due to difference in the nature of the alkyl groups attached to the oxygen atom. Thus, the molecular formula, $C_4H_{10}O$, represents the following metamers:

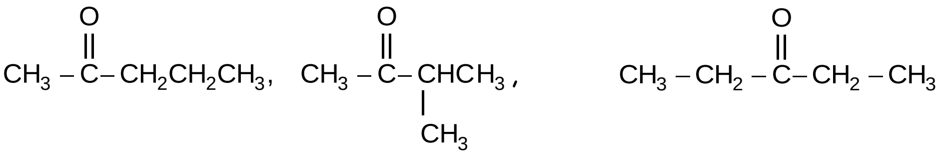
$CH_3CH_2-O-CH_2CH_3$



$$CH_3-O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

$CH_3-O-CH_2CH_2CH_3$

b) **Ketones,** $R-\overset{\displaystyle O}{\overset{\|}{C}}-R'$, exhibit metamerism due to the difference in the nature of the alkyl groups attached to the carbonyl group. Thus, the molecular formula, $C_5H_{10}O$, represents the following metamers:



$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2CH_2CH_3,\quad CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3,\quad CH_3-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-CH_3$$

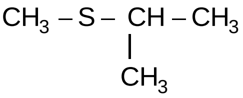
Did You Know

Ketones shows position isomerism as well as metamerism but preferentially it is considered position isomerism.

c) **Thioethers**, R–S–R′, exhibit metamerism due to the difference in the nature of the alkyl groups attached to the sulphur atom. Thus, the molecular formula, $C_4H_{10}S$, represents the following metamers:

$CH_3-S-CH_2CH_2CH_3$

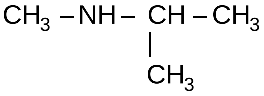
$CH_3-CH_2-S-CH_2-CH_3$



$$CH_3-S-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

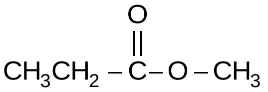
d) Secondary and tertiary amines exhibit metamerism due to the difference in the nature of the alkyl groups attached to the – NH – group and the $-\overset{|}{N}-$ atom respectively. Thus the molecular formula, $C_4H_{11}N$, represents the following metamers:

$CH_3CH_2-NH-CH_2CH_3$ $CH_3-NH-CH_2CH_2CH_3$

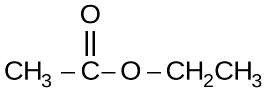


$CH_3-NH-\underset{\underset{CH_3}{|}}{CH}-CH_3$

e) Esters, $R-\overset{\overset{O}{\|}}{C}-O-R'$, exhibit metamerism due to the difference in the nature of the alkyl groups attached to the $-\overset{\overset{O}{\|}}{C}-O-$ group. Thus, the following esters are metamers:



$CH_3CH_2-\overset{\overset{O}{\|}}{C}-O-CH_3$



$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2CH_3$

Note- If same polyvalent functional group is present in two or more organic compounds, then instead of chain or position isomerism, treat the phenomenon as metamerism.

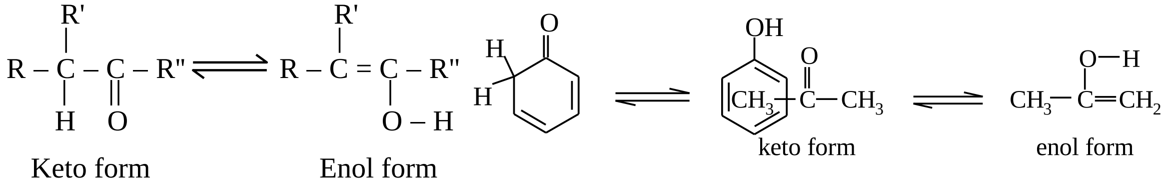
(i) Pentan – 2- one and pentan – 3- one are metamers and not position isomers. They can be included in position isomerism, if metamerism is not mentioned.

(ii) Similarly, pentan – 2- one and 3 – methylbutan-2-one are metamers and not chain isomers. Metamers may be considered as position isomers. For instance, pentan – 2- one and penta-3-one may be regarded as position isomers as well as metamers.

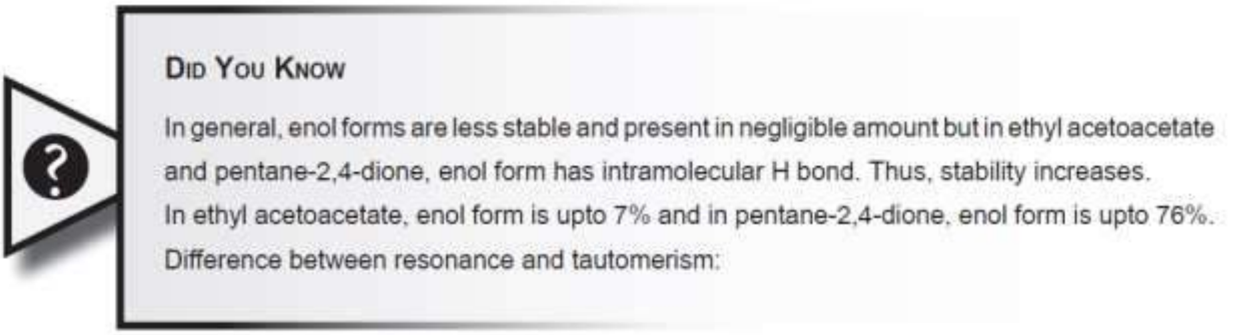
(v) Tautomerism

Here a single compound exists in two readily interconvertible structures that differ in position of hydrogen atom. Tautomer exhibits dynamic equilibrium with each other.

A very common form of tautomerism is that between a carbonyl compound containing an α - hydrogen and its enol form. This type of isomerism is also known as **keto–enol isomerism**.



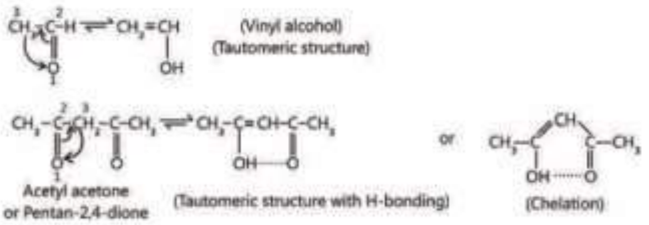
The **percentage of enol form increases** in the order simple **aldehydes and ketones < β–keto esters < β–diketones < β–diketones having phenyl group < phenols**. This increase in the enol content is due to the fact that the enol form of the above type of compounds is increasingly stabilized by resonance and hydrogen bonding than the corresponding keto form.



DID YOU KNOW

In general, enol forms are less stable and present in negligible amount but in ethyl acetoacetate and pentane-2,4-dione, enol form has intramolecular H bond. Thus, stability increases.
In ethyl acetoacetate, enol form is upto 7% and in pentane-2,4-dione, enol form is upto 76%.
Difference between resonance and tautomerism:

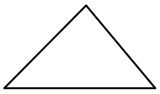
Table 14.1: Difference between Tautomerism and Resonance

Tautomerism	Resonance
1. Being a real concept, tautomers are definite compounds, which can be separated and characterized by suitable methods.	1. Being a hypothetical concept, the resonating structures are the imaginary structures of the same compound which cannot be isolated.
2. There is a simultaneous shift of an H atom and π-bond, taking place at 1, 3-positions (1, 3-shift). For example: 	2. In resonance, position of atoms or nuclei are fixed.
3. Tautomeric forms have different functional groups	3. Resonating structures have the same functional group.
4. Tautomeric forms have no effect on bond lengths.	4. Resonance affects the bond length.
5. These structures are obtained by delocalisation of σ- and π-bond.	5. These structures are obtained by the delocalisation of π or non-bonding e's or both.
6. Tautomers are interconvertible, indicating the dynamic nature. Thus, it is represented by $\rightleftharpoons$.	6. These structures are not interconvertible, i.e. not dynamic in equilibrium with each other. Thus, it is represented by $\leftrightarrow$.
7. Tautomerism does not contribute for the structure stabilization.	7. Resonance causes a low energy which in turn gives stability to the molecule.

(vi) Ring – chain isomerism

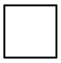
The phenomenon of existence of two or more compounds having the same molecular formula but possessing open chain and closed chain (cyclic structure) is called ring – chain isomerism. This type of isomerism arises due to different modes of linking of carbon atoms. Thus ring-chain isomers possess open chain or closed chain structures as illustrated by the following examples:

i) Two ring-chain isomers are possible corresponding to the molecular formula C_3H_6:

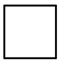
$CH_3CH=CH_2$ and 

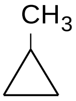
Propene Cyclopropane

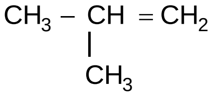
ii) Six pairs of ring-chain isomers are possible for the molecular formula C_4H_8:

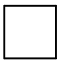
$CH_3CH_2CH=CH_2$ and 

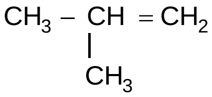
$CH_3CH_2CH=CH_2$ and 

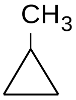
$CH_3CH=CHCH_3$ and 

$CH_3CH=CHCH_3$ and 

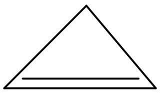


$\underset{CH_3}{CH_3-\overset{|}{C}H=CH_2}$ and 



$\underset{CH_3}{CH_3-\overset{|}{C}H=CH_2}$ and 

iii) The molecular formula C_3H_4 represents the two ring – chain isomers:

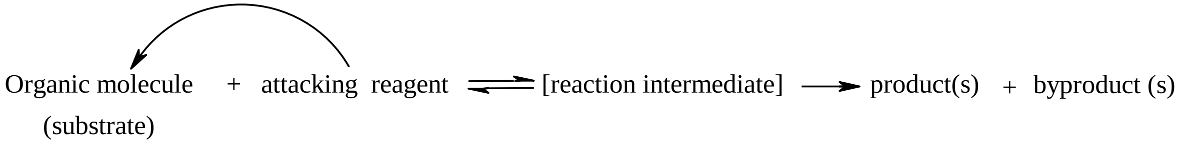
$CH_3-C\equiv CH$ and 

Ring chain isomerism, can be included in functional isomerism, if not considered separately.

Concepts in organic reaction mechanism

The organic reactions involve the breaking of covalent bonds in the reacting molecules and formation of new bonds to give product molecules

The organic molecule which reacts with attacking reagent is called **substrate**. In multistep organic reactions, substrate react with reagent and leads to the formation of one or more **reaction intermediates**. The general reaction path involving the formation of one reaction intermediate is depicted as follows.



Organic molecule + attacking reagent ⇌ [reaction intermediate] → product(s) + byproduct (s)

(substrate)

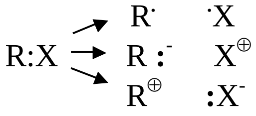
Substrate + Reagent ⟶ Intermediate ⟶ Products

(Transition state)

Fission or Cleavage of covalent bond

The fission of covalent bond can take place in two ways depending on **the nature of covalent bond, nature of attacking reagent and conditions of the reaction**.

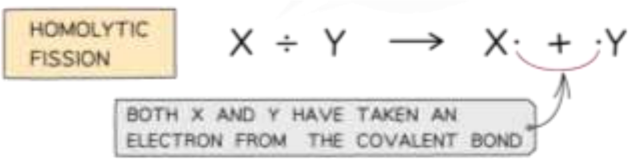
Like other chemical reactions, organic reactions are also a process of bond breaking and bond making. A covalent bond between two atoms can be broken in essentially the following ways:



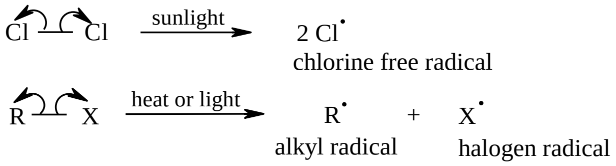
$$R{:}X \rightarrow \begin{cases} R^{\cdot} & {}^{\cdot}X \\ R{:}^{-} & X^{\oplus} \\ R^{\oplus} & {:}X^{-} \end{cases}$$

1) Homolytic cleavage (Homolytic fission)

"In this type of fission bond breaks symmetrically and each fragment formed gets an odd electron from the shared bond pair electrons". This cleavage results in the formation of specie(s) with unshared electron called **free radicals**. It is also known as **free radical cleavage** or **non-polar bond fission**. The homolytic fission of a sigma (σ) bond is shown as follows.



$$A-B \longrightarrow A^{\bullet} + B^{\bullet}$$



The free radicals contain unpaired electron (with odd number of electrons), **electrically neutral and paramagnetic**.

The conditions favorable for homolytic cleavage are

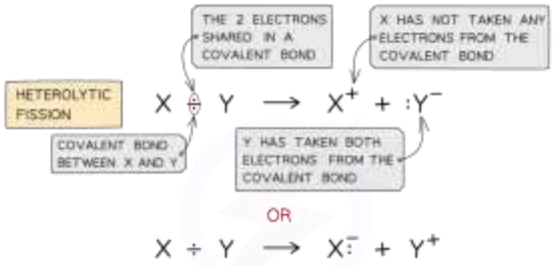
- The difference in **electro negativity between A and B is less or zero.**
- Homolysis takes place in **gaseous phase** or in the presence of **non polar solvents**(CCl_4, CS_4), **peroxide**, **UV light**, **high temperature** (≥500^0C), **electricity** and free radical.

2) Heterolytic cleavage (Heterolytic fission)

In this type of cleavage, covalent bond breaks asymmetrically & one of the two species gets both the electrons and other loses resulting in the formation of ions. Heterolytic cleavage results in formation of electron deficient and electron rich fragments.

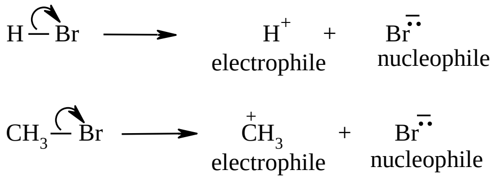
It is also known as ionic cleavage or polar bond or ionic fission.

The electron deficient fragment is called **electrophile** while electron rich fragment is known as **nucleophile**. In case of organic compounds, if positive charge is present on the carbon then cation is termed as **carbocation**. If negative charge is present on the carbon then anion is termed as **carbanion**. The heterolytic fission is shown below



$A\text{-}B \longrightarrow A^{-}: + B^{+}$ [Electronegativity of A is greater than B]

$A\text{-}B \longrightarrow A^{+} + B^{-}:$ [Electronegativity of B is greater than A]



Both electrophile and nucelophile contain even number of electrons, influenced by strong electrical field as they possess positive or negative charge and they are **diamagnetic**.

- The factor which favors heterolysis is **greater difference of electro negativities** between A and B.
- The energy required for heterolysis is always greater than that for homolysis due to electrostatic forces of attraction between ions.
- Low temperature
- Polar nature of substrate and attacking reagent
- Presence of acid or base catalyst

Reaction intermediates

Highly reactive, short lived and energetic intermediate formed in multistep organic reactions by the action of reagent on substrate and readily transformed into product(s) is called reaction intermediate.

The important reaction intermediates are free radicals, carbocations, carbanions, carbenes, benzyne and nitrenes.

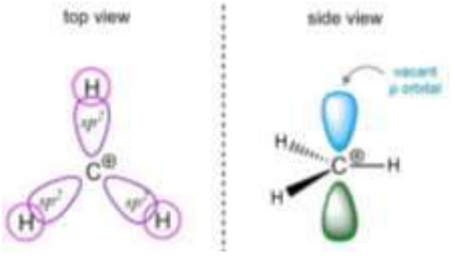
(i) Carbocations or Carbonium ions

A reaction intermediate formed by heterolytic fission of a covalent bond which contains one positively charged carbon with three bond pair electrons (sextext of electrons) is called carbocation.

For example,

$CH_3^+, CH_3CH_2^+, (CH_3CH_2)_2CH^+, (CH_3)_3C^+$ etc.

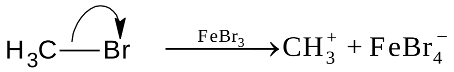
$$-\overset{|}{\underset{|}{C}}-X \longrightarrow -\overset{|}{\underset{|}{C^+}} + \ddot{X}^-$$



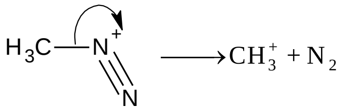
Formation of carbocations:

(i) $(CH_3)_3CCl \longrightarrow (CH_3)_3C^+ + Cl^-$ (Heterolytic fission)

(ii) $CH_3-OH \xrightarrow{H^+} CH_3-OH_2^+$ (Protonation)



$H_3C-Br \xrightarrow{FeBr_3} CH_3^+ + FeBr_4^-$ (Abstraction of halide ion by Lewis acid)



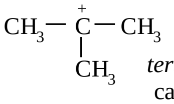
$H_3C-\overset{+}{N}\equiv N \longrightarrow CH_3^+ + N_2$ (Removal of N_2 from diazonium cation)

The carbocations are classified into different groups depending upon the nature of carbon bearing the positive charge. Alkyl carbocations may **be primary (1°), secondary (2°) or tertiary (3°) carbocations**.

$\overset{+}{C}H_3$ methyl carbocation (1°)

$CH_3-\overset{+}{C}H_2$ ethyl carbocation (1°)

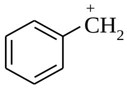
$CH_3-\overset{+}{C}H-CH_3$ *iso* propyl carbocation (2°)



$CH_3-\overset{+}{\underset{CH_3}{C}}-CH_3$ *tertiary* butyl carbocation (3°)

$CH_2=\overset{+}{C}H$ vinyl carbocation

$CH_2=CH-\overset{+}{C}H_2$ allyl carbocation



beznyl carbocation

Structure of carbocation: The carbocations are electron deficient and contain six electrons (three bond pair electrons). In strong electrical field, carbocations move towards cathode. The carbocations have trigonal planar structure and the positively charged carbon in sp^2 hybridized.

Rate of formation of carbocations:

More stable carbocation forms at faster rate as compared to less stable carbocation.

For example,

(i) $R-CH_2-Cl \longrightarrow R-CH_2^+ + Cl^-$

(ii) $R_3C-Cl \longrightarrow R_3C^+ + Cl^-$

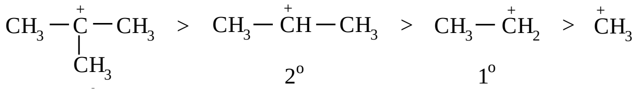
A tertiary carbocation is more stable, the *transi*tion state of tertiary carbocation is lower in energy than *transi*tion state of primary carbocation. As a result, a tertiary carbocation will form more rapidly than primary carbocation.

Stability of carbocations:

- Electron deficient carbocations are stabilized by **electron releasing group**. **Participation of empty p-orbital in lateral overlap with completely filled orbital** is the major contributing factor for stability to stability in which positive charge is delocalized.

Alkyl group directly bonded to the positively charged carbon stabilize the carbocations due to inductive and hyperconjugation effects. The dispersal of the positive charge due to hyperconjugation stabilize the carbocation. The observed order of carbocation stability is

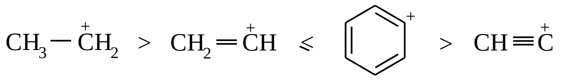
$$(C_6H_5)_3C^+ > (C_6H_5)_2CH^+ > C_6H_5CH_2^+ > CH_2 = CH - CH_2^+ > 3° > 2° > 1° > CH_3^+$$



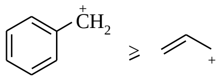
$$CH_3-\overset{+}{C}(CH_3)-CH_3 > \underset{2°}{CH_3-\overset{+}{C}H-CH_3} > \underset{1°}{CH_3-\overset{+}{C}H_2} > \overset{+}{C}H_3$$

- The reaction intermediates are highly reactive, usually **order of reactivity of such intermediates is reverse that of its stability**. Therefore, order of reactivity of carbocations follows the sequence: $\overset{+}{C}H_3 > 1° > 2° > 3°$
- **Electron attractors** (–I effect) increases the postive charge on carbon atom and thus reduces the stability of carbocation, e.g.$O_2N - CH_2 - CH_2^+$, $Cl - CH_2 - CH_2^+$.]
- Carbocation are **sp^2 hybridized and have trigonal planar structure**, so the **attacking species can approach both from top and bottom.**
- **Hybridized state of carbon:**

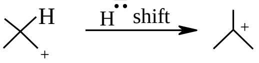
Higher the s-character, lesser the stability. The order of stability is



- **Resonance:** The greater the delocalization of positive charge of carbocations, higher is the stability. The stability of benzyl carbocation is comparable with allyl carbocation as resonance energies is nearly the same



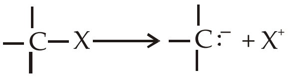
- Carbocations, undergo rearrangement forming more stable carbocations.

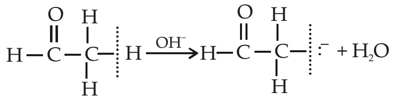


(ii) Carbanions

A reaction intermediate formed by heterolytic fission of a covalent bond which results negatively charged carbon with eight electrons in its valence shell is called carbanion.

The heterolytic cleavage of a covalent bond as indicated in the following reactions gives carbanions.





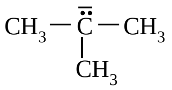
For example, $CH_3^-, CH_3CH_2^-, (CH_3)_2CH^-, CH_2^-CHO$ etc.

Formation of carbanion:

(i) $CH_3 - CHO + OH^- \xrightarrow{base} CH_2^- - CHO + H_2O$

(ii) $C_2H_5O^- + CH_3 - COOC_2H_5 \longrightarrow CH_2^- - COOC_2H_5 + C_2H_5OH$

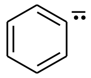
The carbanions are classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the nature of carbon bearing negative charge.



tertiarybutyl carbanion (3°)

$CH_2=\bar{\ddot{C}}H$

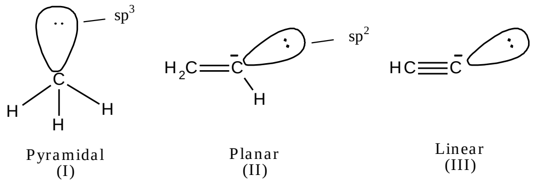
vinyl carbanion (1°)



phenyl carbanion

Structure of carbanion: The carbanions are electron rich with complete octate configuration. Shape of alkyl carbanion is usually **pyramidal** like ammonia when carbon atom carrying the negative charge is sp^3 hybridised.

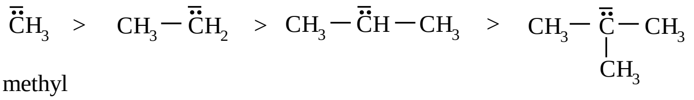
In contrast, carbnions which are stabilised by resonance are **planar** and carbon atom carrying negative charge is **sp^2 hybridised**. The vinyl carbanion, phenyl carbanion and cyclopentadiene carbanion are sp^2 hybridised where as acetylide carbanion is sp hybridised.



Stability order III > II > I

Stability of carbanions:

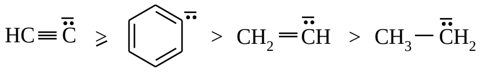
- Alkyl group bonded to negatively charged carbon increases the intensity of negative charge due to +I effect and destabilize the carbanion. The order of stability of alkyl carbanions is:



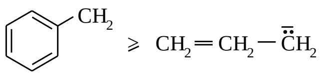
$$\bar{\ddot{C}}H_3 > CH_3-\bar{\ddot{C}}H_2 > CH_3-\bar{\ddot{C}}H-CH_3 > CH_3-\underset{CH_3}{\underset{|}{\bar{\ddot{C}}}}-CH_3$$

methyl carbanion 1° 2° 3°

- The order of **reactivity of carbanions is reverse that of its stability**. Therefore, order of reactivity of carbanions follows the sequence: $3^o > 2^o > 1^o > \ddot{C}H_3$
- **Higher the s character greater the stability** of carbanion. Order of stability is



- **Resonance:** Greater the delocalisation of negative charge by resonance, higher the stability. The stability of benzyl carbanion is comparable with allyl carbanions.

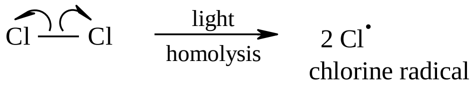


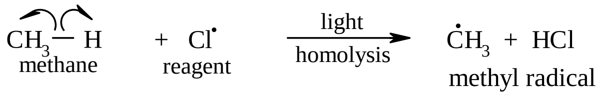
(iii) Free radicals

A reaction intermediate formed by the homolytic cleavage of a covalent bond which contains an unpaired electron is called free radical.

The homolytic cleavage is favored for nonpolar covalent bond. Such cleavage for bond is initiated by the action of heat, light or a reagent.

For example, $\dot{C}H_3, CH_3\dot{C}H_2, (CH_3)_2\dot{C}H, CH_2=CH-\dot{C}H_2, C_6H_5\dot{C}H_2$ etc.

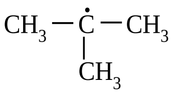




Depending upon nature of carbon atom carrying the unpaired electron, free radicals are also classified as primary (1°), secondary (2°) and tertiary (3°) free radicals.

$\dot{C}H_3$ $\quad CH_3-\dot{C}H_2$ $\quad CH_3-\dot{C}H-CH_3$

methyl radical (1°) ethyl radical (1°) *iso* propyl radical (2°)

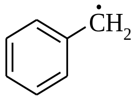


$$CH_3-\overset{\displaystyle CH_3}{\underset{|}{\dot{C}}}-CH_3$$

tertiary butyl radical (3°)

$CH_2=CH-\dot{C}H_2$

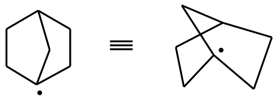
allyl radical (1°)



benzyl radical (1°)

Structure of free radical: The free radicals are electron deficient since they contain seven electrons on carbon atom. They are electrically neutral and paramagnetic. The structure of alkyl radical is not known with certainty. For alkyl radicals two possible structures have been proposed. The first is a planar sp^2 hybridised radical similar to a carbocation. The second one is a pyramidal sp^3 hybridised radical similar to a carbanion.

- Resonance stabilised free radicals such as allyl radicals and benzyl radicals are planar sp^2 hybridised.
- The bridge head free radicals are pyramidal (sp^3-hybridised) because they cannot assume planar geometry due to angle strain. Further, the free radicals in which carbon is bonded to highly electronegative atoms are pyramidal.

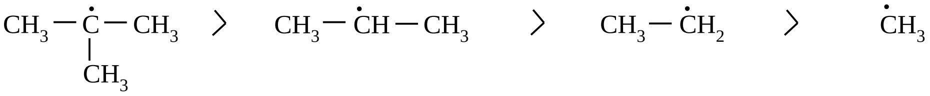


bridge head radical (sp^3-hybridised)

$\dot{C}F_3$

trifluoromethyl radical
(sp^3-hybridised)

Stability of free radicals: The relative stability of alkyl free radicals is explained on the basis of hyperconjugation and inductive effects. Greater the number of alkyl groups attached to the carbon atom carrying unpaired electron, higher the delocalisation and hence more stable is the alkyl radical. The order of stability of a few alkyl radicals is given below



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\dot{C}}}-CH_3 > CH_3-\dot{C}H-CH_3 > CH_3-\dot{C}H_2 > \dot{C}H_3$$

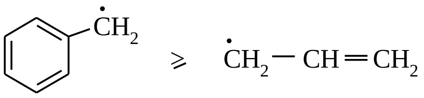
t-butyl radical (3°) *iso* propyl radical (2°) ethyl radical (1°) methyl radical (1°)

The order of stability of free radicals on the basis of resonance inductive effect is as follows:

$$(C_6H_5)_3C^{\bullet} > (C_6H_5)_2CH^{\bullet} > C_6H_5^{\bullet} > CH_2=CHCH_2^{\bullet} > 3° > 2° > 1° > CH_3^{\bullet}$$

Like carbocations and carbanions, free radicals are highly reactive and short-lived intermediates because of the strong tendency of the carbon atom carrying the unpaired electron to acquire one more electron from an atom or a group to complete its octate. The reactivity of alkyl radical is reverse the order of stability $\dot{C}H_3 > 1° > 2° > 3°$

The allyl and benzyl radicals are stabilised by resonance. The stability of allyl and benzyl radicals is comparable.



$$C_6H_5\dot{C}H_2 \geqslant \dot{C}H_2-CH=CH_2$$

The allyl or benzyl radicals are more stable than alkyl radicals.

The reactions involving free radicals are

(i) catalysed by light, heat etc.
(ii) proceed in vapour phase or in non-polar solvents.
(iii) autocatalytic.

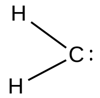
(iv) Carbenes

They are neutral and highly reactive species generally obtained by successive elimination of an electrophile and a nucleophile from the same carbon atom (α-elimination). The carbon atom of carbene has six electrons in valence shell, out of which two constitute unshared electrons and two bond pair electrons. So they are divalent carbon species containing two unshared electrons and electrically neutral.

Carbenes exist in two possible forms

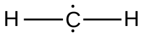
(i) Singlet
(ii) Triplet

(i) Singlet



sp^2 hybridized
Two electrons are in same orbital (spin paired)

(ii) Triplet

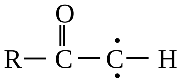


sp hybridized
Two electrons are in two different orbitals (spin free)

$\mathrm{H-\underset{\cdot}{\dot{C}}-H}$ carbene

$\mathrm{R-\underset{\cdot}{\dot{C}}-H}$ alkyl carbene

$\mathrm{Cl-\underset{\cdot}{\dot{C}}-H}$ chloro carbene



$\mathrm{R-\overset{\overset{O}{\|}}{C}-\underset{\cdot}{\dot{C}}-H}$

acyl carbene

$\mathrm{Cl-\underset{\cdot}{\dot{C}}-Cl}$ dichloro carbene

	Free Radical	Carbocation	Carbanion
(1) Lone pair	0	0	1
(2) Bond pair	3	3	3
(3) Unpaired e^-	1	×	×
(4) Bond Angle	120º	120º	107º
(5) Hybridisation	sp^2	sp^2	sp^3
(6) Shape	Trigonal planar	Trigonal planer	Pyramidal
(7) Magnetic property	Paramagnetic	Diamagnetic	Diamagnetic
(8) Stability order (As per inductive effect)	3º > 2º > 1º	3º > 2º > 1º	1º > 2º > 3º
(9) e^- rich/deficient/poor	ED(Deficient)	ED	ER(Rich)
(10) Reactivity order	1º > 2º > 3º	1º > 2º > 3º	3º > 2º > 1º
(11) +I/-I (stabilized)	+I	+I	

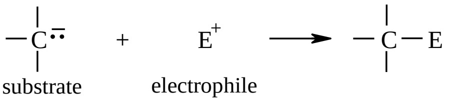
Attacking Reagents

The organic reactions proceed by the attack of highly reactive reagents on the substrate molecule. These reagents are called attacking reagents which may be electron deficient or electron rich. They are classified into two groups.

Electrophiles

The electron deficient molecules or positively charged ions which are capable of accepting an electron pair from substrate molecule are called electrophiles.

These species act as Lewis acids and attack the electron rich centre of the organic molecules.



They are of following types,

(i) Positively charged: The species having a positive charge, e.g.

$H^+, CH_3^+, NO_2^+, H_3O^+, NO^+, Br^+, CH_3CO^+$ etc .

(ii) Neutral: The molecules containing electron deficient atom (i.e. Lewis acids) e.g. $:CH_2$, $AlCl_3$, BF_3, $ZnCl_2$, $FeCl_3$, SO_3, etc.

(ii) Ambident: Molecules with 2 electrons deficient centers,

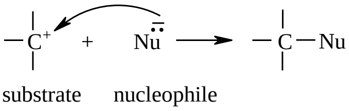
e.g. α, β-unsaturated carbonyl compounds.

It may be noted that **all the positively charged species do not act as electrophiles**. The positively charged species which can accept an electron pair can act as electrophiles. The positively charged ions such as $H_3\overset{+}{O}$, $\overset{+}{N}H_4$, $N\overset{+}{a}$, $C\overset{2+}{a}$, etc. do not act as electrophile as they cannot accept electron pair, since all the ions have an octet configuration.

Nucleophiles

The molecules or negatively charge ions which are capable of donating an electron pair to electron deficient centre of the substrate are called nucleophiles.

These species act as Lewis bases & attack on electron deficient centre of organic molecule.



The common examples of nucleophiles are given below:

(i) Negatively charged: The species having a negative charge, e.g. Cl^-, Br^-, OH^-, CN^-, NO_2^- etc.

(ii) Neutral: The molecules having an unshared pair of electrons (i.e. Lewis base),

$$\text{e.g. } \ddot{N}H_3,\ R-\ddot{N}H_2,\ R_2-\ddot{N}H, H_2\ddot{\underset{..}{O}}, R-\ddot{\underset{..}{O}}-H \quad etc.$$

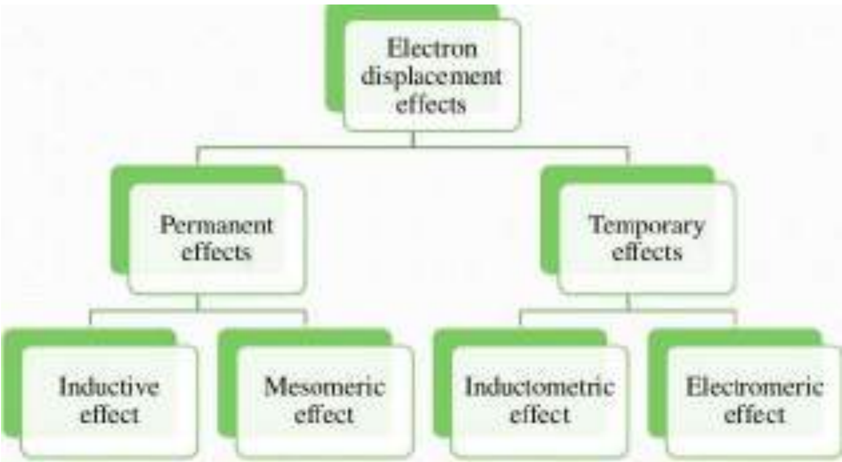
(iii) Ambident: The molecule with two electron rich centres, e.g. $^-C\equiv\ddot{\underset{..}{N}}, N=\ddot{O}$, $\ddot{O}\leftarrow\ddot{N}-\ddot{O}$ etc.

Comparison between Nucleophiles and electrophiles

Nucleophiles	Electrophiles
• Electron rich, donate electron pair, generally anions.	• Electron deficient, accept electron pair, generally cations
• Act as Lewis bases	• Act as Lewis acids
• Attack an region of low electron density of substrate	• Attack on region of high electron density of substrate
• They are represented by a general symbol ($N\ddot{u}$)	• They can be represented by a general symbol (E^+)

Electron Displacement Effects in Covalent Bonds

The electron pair displacement in organic molecules takes place under the influence of a hetero atom/group or by the attacking reagent. The displacement or shift of electron pair in the organic molecule under the influence of substituent makes the molecule permanently polar.



(i) Inductive effect (I effect)

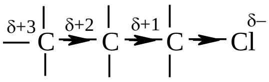
The inductive effect is defined as **"the permanent displacement of sigma (σ) bond pair of electrons towards more electronegative atom or group and as a result molecule becomes permanently polar"**.

Larger the displacement of σ bond pair electrons greater the polarity. Consider the carbon chain in which terminal carbon is bonded to a chlorine atom. Since chlorine is more electronegative bond pair of electrons are displaced towards chlorine.

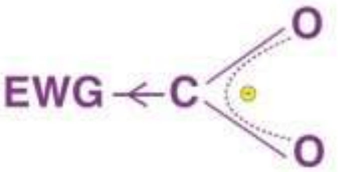
C – C – C – C is non polar

$$C^{\delta\delta\delta\delta^+} \longrightarrow C^{\delta\delta\delta^+} \longrightarrow C^{\delta\delta^+} \longrightarrow C^{\delta^+} \longrightarrow X^{\delta^-}$$

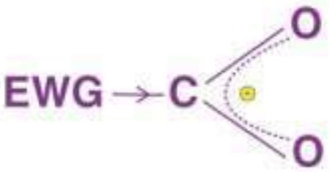
$$C^{\delta\delta\delta\delta^-} \longleftarrow C^{\delta\delta\delta^-} \longleftarrow C^{\delta\delta^-} \longleftarrow C^{\delta^-} \longleftarrow Y^{\delta^+}$$



$-\overset{\delta+3}{C} \rightarrow \overset{\delta+2}{C} \rightarrow \overset{\delta+1}{C} \rightarrow \overset{\delta-}{Cl}$ order of intensity of I effect $\delta_{+3} << \delta_{+2} < \delta_{+}$



EWG stabilises the (COO) and increases the acidity



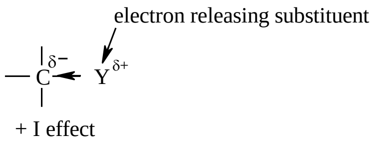
EDG stabilises the (COO) and decreases the acidity

There are two types of Inductive effect,

a. **Positive inductive effect (+I effect)**

Here **substituent (Y) releases electron pair away from itself**. In other words, σ **bond pair of electrons are displaced away from the substituent towards the C-chain**.

When **less electronegative atom is attached to carbon atom** (i.e. electron donating group), the inductive effect is called + I effect.

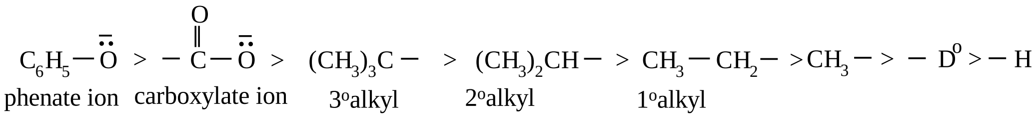


$$\overset{\delta\delta\delta-}{C_3} \leftarrow \overset{\delta--}{C_2} \leftarrow \overset{\delta-}{C_1} \leftarrow \overset{\delta+}{Z}$$

Electronegativity of Y or Z is less than carbon atom, so the Y or Z group releases electron and gets a partial positive charge (i.e. δ^+) and induces a partial negative charge (i.e. δ^-) on C_1. As we move along the chain from C_1 to C_3, the partial negative charge decreases.

The examples of electron donating group are **$(CH_3)_3C$, $(CH_3)_2CH$, CH_3CH_2, CH_3** etc.

The order of electron releasing or releasing ability of substituent is given below.



$$\underset{\text{phenate ion}}{C_6H_5-\ddot{\bar{O}}} > \underset{\text{carboxylate ion}}{-\overset{\overset{O}{\|}}{C}-\ddot{\bar{O}}} > \underset{3^o\text{alkyl}}{(CH_3)_3C-} > \underset{2^o\text{alkyl}}{(CH_3)_2CH-} > \underset{1^o\text{alkyl}}{CH_3-CH_2-} > CH_3- > -D^o > -H$$

+ I power in decreasing order with respect to the reference *H*

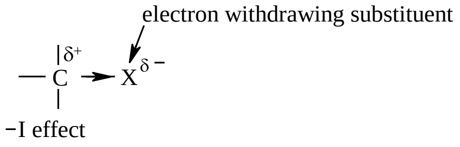
b. Negative inductive effect (–I effect)

Here, **the sigma bond pair of electrons are displaced towards electron withdrawing substituent (X) or away from the carbon chain**.

More electronegative atom is attached to carbon atom (i.e. electron withdrawing group), the inductive effect is called – I effect.

The examples of electron withdrawing group $\overset{+}{N}R_3,\ NO_2,\ F,\ Cl,\ I,\ OH\ etc.$

$$\overset{\delta\delta\delta+}{C_3} \rightarrow \overset{\delta\delta+}{C_2} \rightarrow \overset{\delta+}{C_1} \rightarrow \overset{\delta-}{Z}$$



Order of electron withdrawing ability (–I effect) of a few substituents is given below.

$$\underrightarrow{\overset{\oplus}{N}H_3 > NO_2 > CN > SO_3H > CHO > CO > COOH > COCl > COOR > CONH_2 > F > Cl > Br > I > OH > OR > NH_2 > C_6H_5 > H}$$

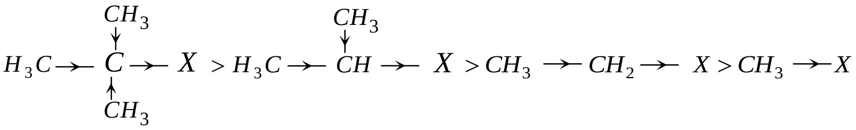
–I power of groups in decreasing order with respect to the reference *H*

Applications of inductive effect:

(i) Magnitude of $+^{ve}$ and $-^{ve}$ charges: can be compared by + I or – I groups present in it.

- Magnitude of $+ve$ charge $\propto \dfrac{1}{+\text{I power of the group}} \propto -I$ power of the group.
- Magnitude of $-ve$ charge $\propto \dfrac{1}{-\text{I power of the group}} \propto +I$ power of the group.

(ii) Reactivity of alkyl halide: + I effect of methyl group enhances – I effect of the halogen atom by repelling the electron towards tertiary carbon atom.



$$H_3C\rightarrow \overset{\overset{CH_3}{\downarrow}}{\underset{\underset{CH_3}{\uparrow}}{C}} \rightarrow X > H_3C \rightarrow \overset{\overset{CH_3}{\downarrow}}{CH} \rightarrow X > CH_3 \rightarrow CH_2 \rightarrow X > CH_3 \rightarrow X$$

Tertiary > Secondary > Primary > Methyl

(iii) Relative strength of the acids:

(a) Any group or atom showing +I effect decreases the acid strength as it increases the negative charge on the carboxylate ion which holds the hydrogen firmly. Alkyl groups have + I effect. Thus, acidic nature is, $\underrightarrow{HCOOH > CH_3COOH > C_2H_5COOH > C_3H_7COOH > C_4H_9COOH}$

+I effect increases, so acid strength decreases

Formic acid, having no alkyl group, is the most acidic among these acids.

(b) The group or atom having – I effect increases the acid strength as it decreases the negative charge on the carboxylate ion. Greater is the number of such atoms or groups (having – I effect), greater is the acid strength.

Thus, acidic nature is, $\underset{\text{Trichloro acetic acid}}{CCl_3COOH} > \underset{\text{Dichloro acetic acid}}{CHCl_2COOH} > \underset{\text{Monochloro acetic acid}}{CH_2ClCOOH} > \underset{\text{Acetic acid}}{CH_3COOH}$

$$\xleftarrow{\hspace{12cm}}$$

(– Inductive effect increases, so acid strength increases)

(c) Strength of aliphatic carboxylic acids and benzoic acid

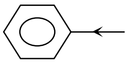
$$\underset{\substack{\uparrow \\ +I\,group}}{R} \rightarrow COOH \qquad \underset{\substack{\uparrow \\ -I\,group}}{C_6H_5} \leftarrow COOH$$

Hence benzoic acid is stronger acid than aliphatic carboxylic acids but exception is formic acid. Thus, $HCOOH > C_6H_5COOH > RCOOH$

$$\xrightarrow{\hspace{8cm}}$$

Acid strength in decreasing order

As compared to water, phenol is more acidic (–I effect) but methyl alcohol is less acidic (+I effect).



$\underset{Phenol}{\leftarrow OH} > \underset{Water}{H-OH} > \underset{Methyl\ alcohol}{CH_3 \rightarrow OH}$

(vi) Relative strength of the bases (Basic nature of $-NH_2$)

The difference in base strength in various amines can be explained on the basis of inductive effect. The +I effect increases the electron density while –I effect decreases it. The amines are stronger bases than NH_3 as the alkyl groups increase electron density on nitrogen due to + I effect while $ClNH_2$ is less basic due to –I effect. "So more is the tendency to donate electron pair for coordination with proton, the more is basic nature, i.e., more is the negative charge on nitrogen atom (due to +I effect of alkyl group), the more is basic nature". Thus, the basic nature decreases in the order; $\underset{\text{Diethyl amine}}{(C_2H_5)_2NH} > \underset{\text{Ethyl amine}}{CH_3CH_2NH_2} > \underset{\text{Methyl amine}}{CH_3NH_2} > \underset{\text{Ammonia}}{NH_3} > \underset{\text{Chloro amine}}{ClNH_2}$

The order of basicity is as given below;

Alkyl groups (R–)	Relative base strength
CH_3	$R_2NH > RNH_2 > R_3N > NH_3$
C_2H_5	$R_2NH > RNH_2 > NH_3 > R_3N$
$(CH_3)_2CH$	$RNH_2 > NH_3 > R_2NH > R_3N$
$(CH_3)_3C$	$NH_3 > RNH_2 > R_2NH > R_3N$

(vii) Basicity of alcohols: The decreasing order of base strength in alcohols is due to +I effect of alkyl groups. $\underset{(3^o)}{(CH_3)_3COH} > \underset{(2^o)}{(CH_3)_2CHOH} > \underset{(1^o)}{CH_3CH_2OH} > CH_3OH$

(viii) Stability of carbonium ion: +I effect tends to decrease the (+ve) charge and –I effect tends to increases the +ve charge on carbocation.

$$(CH_3)_3C^{\oplus} > (CH_3)_2CH^{\oplus} > CH_3CH_2^{\oplus} > CH_3^{\oplus}$$

(ix) Stability of carbanion: Stability of carbanion increases with increasing – I effect.

$$CH_3^- > CH_3CH_2^- > (CH_3)_2CH^- > (CH_3)_3C^-$$

(x). Dipole moment: Inductive effect produces dipole moment in a molecule. As this effect increases (electronegativity difference increases) the dipole moment also increases.

$$\underset{1.648\ D}{CH_3-I} < \underset{1.79\ D}{CH_3-Br} < \underset{1.83\ D}{CH_3-Cl}$$

(ii) Resonance effect (R–effect) or Mesomeric effect

"The permanent polarity produced in the molecule by the shift of pi(π) or lone pair electrons in the conjugate system creating electron deficient and electron rich centres called resonance effect (R–effect).

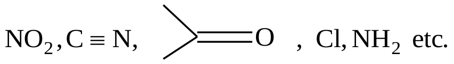
The conditions required for M or R effect:

1. Molecule should be unsaturated with conjugated system (presence of alternate single and double bond or heteroatom containing one or more lone pair electrons linked to multiple bonded atom) of double bond.

1,3-butadiene, aniline, phenol, nitrobenzene, etc. In such systems, π or lone pair electrons are delocalised and the molecule develops polarity.

2. Negative charge is in conjugation with double (or multiple) bond.
3. Lone pair of electrons in conjugation with double bond.

The reactivity of compounds is affected by the presence of groups like

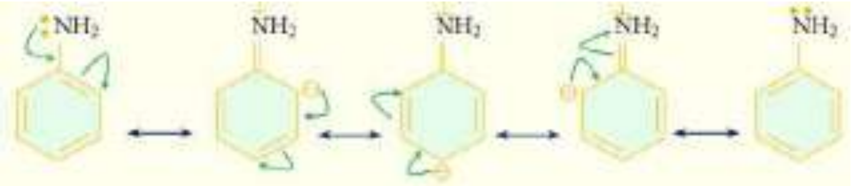


$NO_2, C\equiv N, >C{=}O, Cl, NH_2$ etc.

The movement of π electrons from one end to the other end of the chain through a conjugated system of double bond is observed in resonance effect. It is a permanent effect.

Depending upon the direction of shift of electron pair in conjugate system, R–effect is classified into two types.

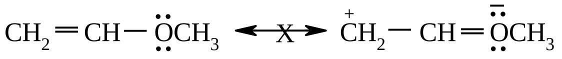
a. **Positive resonance effect (+R effect / +M effect):** In this effect, of electron pair (π or lone pair) moves away from the substituent or towards the conjugate system. The **+R effect** in aniline as shown below.



Substituents exert only +R effect as follows, $-Cl, -Br, -I, -\ddot{N}H_2, -NR_2, -OH, -OR, -SH, -OCH_3, -\underset{\cdot\cdot}{\ddot{S}}R$

The substituent which exerts +R effect are called **electron releasing groups**.

The resonance effect in which resonance structure violates the octate rule should not be considered. For example, structure (II) cannot be considered as resonance structure since it violates the octate rule because oxygen has 10 electrons in the valence shell.

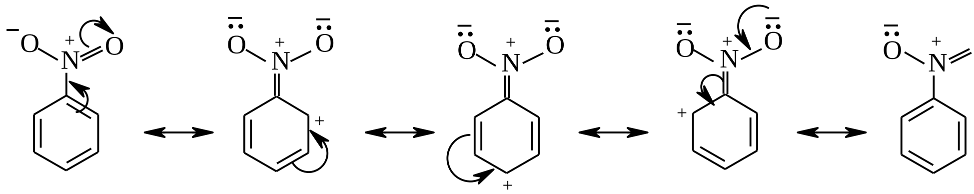


$$\underset{\text{I}}{CH_2=CH-\underset{\cdot\cdot}{\ddot{O}}CH_3} \xleftrightarrow{\times} \underset{\text{II}}{\overset{+}{C}H_2-CH=\underset{\cdot\cdot}{\ddot{O}}CH_3}$$

I

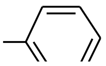
II

b. **Negative resonance effect (–R effect / –M effect):** isthe shift of π or lone pair electrons is towards the substituent attached to the conjugate system. The electron displacement depicted in nitrobenzene represents –R effect.



Substituents, which exert –R effect are given below. $-NO_2, -C\equiv N, -\overset{O}{\overset{||}{C}}-, -CHO, -COOH, -SO_3H, -COOR$

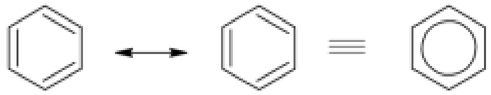
The substituent which exert –R effect is called **electron withdrawn group**. Resonance effect provides explanation to least reactivity of haloalkenes and aryl halides towards nucleophilic substitution reactions, acidic nature of phenols and carboxylic acids, mechanism of electrophilic substitution reactions of benzene.

Substituents like $-\ddot{N}=O$,  (phenyl) etc. exert both +R and –R effects.

➢ Resonance

- Delocalization of p-electrons in conjugation is known as resonance.
- When one structure is not sufficient to explain each and every property (chemical & physical) then, a different structure has been drawn which is known as **Resonating Structure** (canonical structure).
- All these structures contribute to the formation of a Real structure, known as Resonating Hybrid.

or



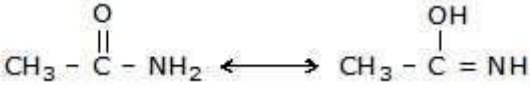
(Actual Structure)

(resonating structures) (Resonance hybrid)

Condition for showing resonance:

(i) Molecule should be planar, nearly planar or a part of it is planar

(ii) Molecule should possess conjugated system.

Note: 

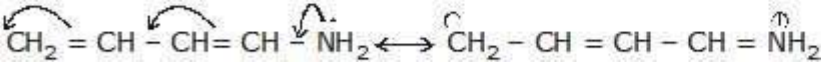
$$CH_3-\overset{O}{\overset{||}{C}}-NH_2 \longleftrightarrow CH_3-\overset{OH}{\overset{|}{C}}=NH$$

They are not resonating structures rather they are **tautomers**.

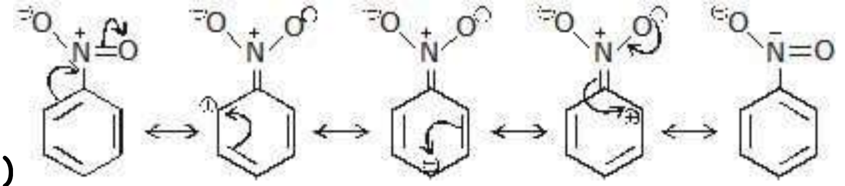
➢ Resonating Structure

- Hypothetical structure existing on paper.
- The energy difference b/w different resonating structure is very small.
- All R.S. contribute towards the formation of resonance hybrid (Their contribution may be different).
- A single R.S. can't explain each & every property of that particular compound.

Q. Draw the resonating structures:

Sol. (i) 

$$CH_2=CH-CH=CH-\ddot{N}H_2 \longleftrightarrow \overset{\ominus}{C}H_2-CH=CH-CH=\overset{\oplus}{N}H_2$$

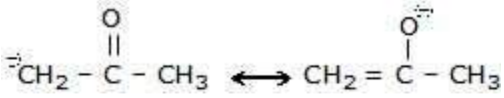
(ii) 

- **Resonance hybrid:** It is a real structure that explains all the properties of a compound formed by the contribution of different R.S.
  It has got maximum stability as compared to any R.S.
- **Resonance Energy:** It is the difference b/w theoretical value of H.O.H & experimental value. Or it can be defined as the difference b/w more stable R.S. & R. H.
  The more resonance energy, the more stable will be the molecule.
  Resonance energy is an absolute term.

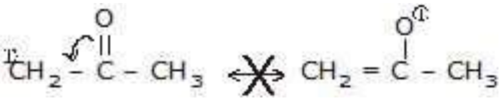
Note: Cyclohexane is thermodynamically more stable than benzene, even though the resonance energy of benzene is more.

Contribution of different R. S. towards resonance hybrid:

- Non-polar R.S. contributes more than polar R.S.
  Example: (a) $CH_2 = CH - CH = CH_2$ **(b)** $CH_2\text{-}CH = CH - CH_2$ **(c)** $CH_2 - CH = CH - CH_2$
  Order of stability of given R.S. ⇒ a > b = c
- Polar R. S. with complete octet will contribute more as compared with the one with an incomplete octet
  $CH_3 - CH\ \ - OCH_3$ (Incomplete octet) $\longleftrightarrow$ $CH_3 - CH = :O - CH_3$ (Complete octet)
- In polar R. S. the -ve charge should be on more electro - ve atom & +ve charge should be on more electro +ve atom.
  Example:

(a) 

$\overset{-}{C}H_2-\overset{\overset{O}{\|}}{C}-CH_3 \longleftrightarrow CH_2=\overset{\overset{O^-}{|}}{C}-CH_3$ (more stable)

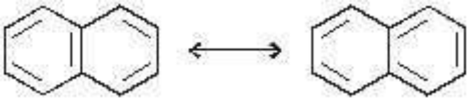
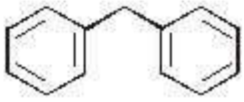
(b) 

$\overset{+}{C}H_2-\overset{\overset{O}{\|}}{C}-CH_3 \not\longleftrightarrow CH_2=\overset{\overset{O^+}{|}}{C}-CH_3$ (less stable)

- Compound with more covalent bonds will contribute more.
- Unlike charges should be closer to each other whereas like charges should be isolated.
- Extended conjugation contributes more than cross conjugation.

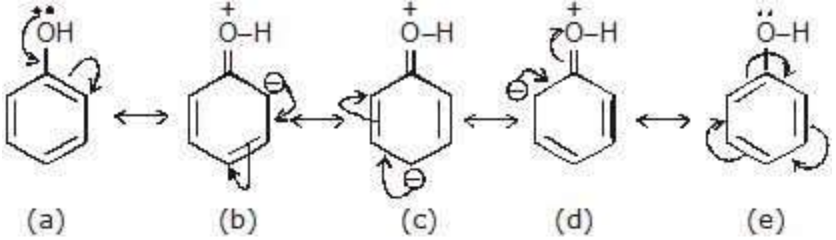
Example:  <  (Cross conjugation < Extended conjugation)

➢ Fries Rule:

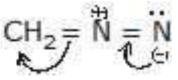
- Compounds with **more benzenoid structures are more stable.**
- As the Resonance energy is greater than those in which lesser no. of benzenoid structures are present.
- R. E. is  < 
- If a double bond is participating in resonance then it will acquire a partial single bond character as a result of which bond length increases & bond strength decreases.
- If a single bond is involved in resonance then it will acquire partial double bond character. As a result of which bond length decreases & bond strength increase.

Q. Find the order of Stability in the following:

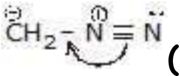
(i)



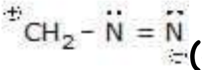
(ii) (a)



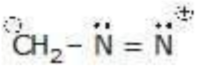
(b)



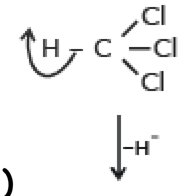
(c)

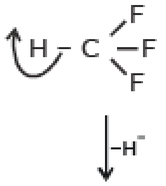


(d)

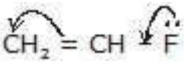


(iii)





(iv) (a)



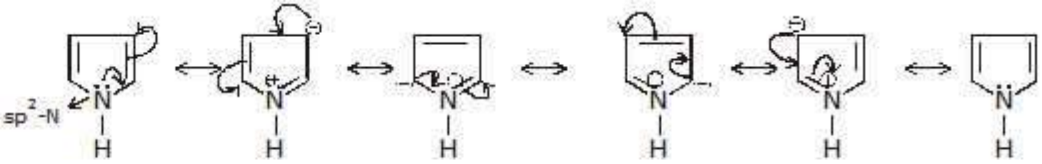
(b) $CH_2 - CH = F$

Sol. (i) a = e > b = d > c

(ii) a > b > c > d, c and are in complete

(iii) $+CCl3 < +CF_3$, due to back bonding in $+CF_3$

(iv) a > b (stability)



Note:

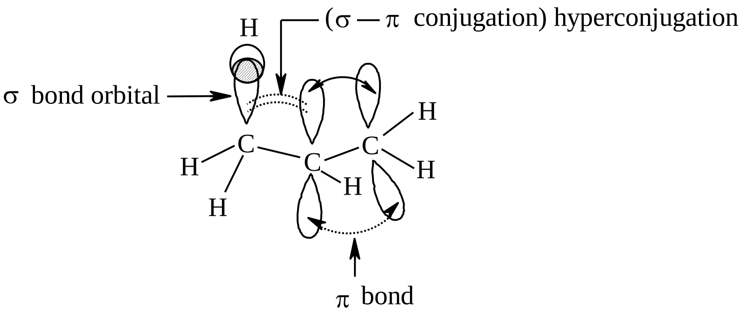
When lone pair, as well as a double bond, is present in some atom then only p bond will be participating in resonance. Whereas lone pair remains sp^2 hybridized orbital. When an atom has two or more than two lone pairs then only one lone pair will participate in resonance and the other one remains in sp^2 hybridized orbital.

(iii) Hyperconjugation (No bond resonance)

The phenomenon of hyperconjugation is also known as **Baker-Nathan effect** as it was proposed by Baker and Nathan. The hyperconjugation effect is much **weaker compared to resonance effect**, yet it is quite useful is explaining **relative stability, physical and chemical properties** of organic molecules.

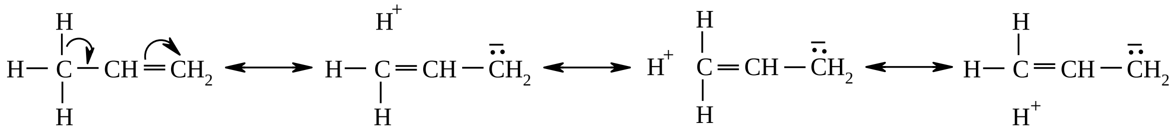
This effect is extension of resonance in which C–H sigma (σ) bond pair electrons are involved in delocalization. **It is a permanent effect in which electron releasing alkyl group bonded to unsaturated system in which delocalization of electrons takes place through overlap between C–H sigma (σ) orbital and Pi(π) bond orbital or vacant p-orbital** is known as hyperconjugation.

The hyperconjugation is a stabilizing interaction. The delocalization of electrons by hyperconjugation in propene molecule is depicted as in figure



Orbital diagram showing hyperconjugation in propene

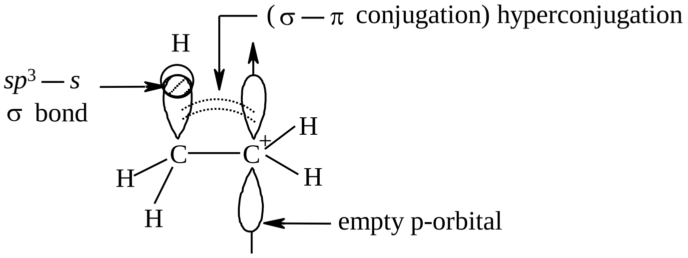
Propene molecule may be regarded as the resonance hybrid of the following hyperconjugative structures (I - IV).



(I) (II) (III) (IV)

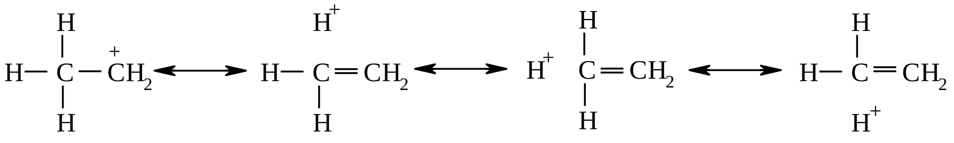
Since there is no bond between carbon and hydrogen atoms in these structures (II -IV), hyperconjugation is also called **no bond resonance**. It may be noted that although a free proton (H^+) has been shown in the above structures, it is still bound firmly to the π- cloud and hence is not free to move.

Hyperconjugation effect in carbocations, let us take an example of ethyl carbocation $(CH_3-\overset{+}{C}H_2)$, in which the positively charged carbon atom has an empty p orbital. One of the C–Hα σ bond orbital of methyl group align in the plane of empty p orbital and this bond pair electrons delocalise into the empty p-orbital as shown in figure.



Orbital diagram showing hyperconjugation in ethylcarbocation

The overlap of completely filled C–H σ bond orbital with empty p-orbital of carbocation causes dispersion of positive charge and stabilize the carbocation. The ethyl carbocation is resonance hybrid of following contributing structures.



(I) (II) (III) (IV)

In general, **larger the number of α-hydrogen atoms of alkyl groups attached to a positively charged carbon atom greater the stability of carbocations.**

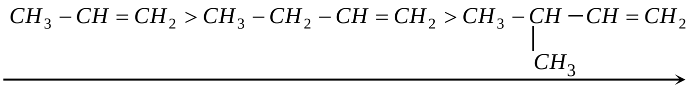
Applications of hyperconjugation effect:

1. **Stability of alkenes: Larger the number of hyperconjugative structures higher the delocalization of electron pairs and greater the stability of alkene.** Number of hyperconjugative structures is equal to number of α-hydrogen atoms plus one.

More number of methyl groups attached to double bonded carbon atom more would be the stability of alkene.

$CH_2 = CH_2$	<	$CH_3 - CH = CH_2$	<	$(CH_3)_2\,C = CH_2$
No hyperconjugation structures		3 hyperconjugation structures		6 hyperconjugation structures

This order of stability is because of greater number of hyperconjugative contributing structures causing larger delocalisation of π-electrons solve and hence accounts for higher stability of alkene.



$$CH_3-CH=CH_2 > CH_3-CH_2-CH=CH_2 > CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2$$

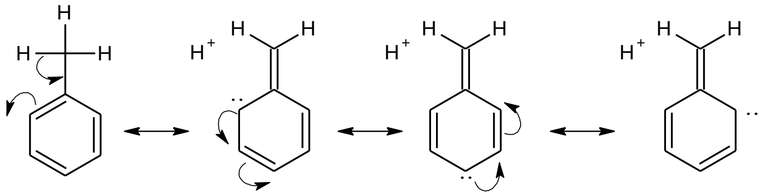
Stability in decreasing order

2. **Stability of carbonium ions:** More, number of hyperconjugation structures of the carbocation more will be its stability.

tert–butyl	>	isopropyl	>	ethyl
9 hyperconjugation structures		6 hyperconjugative structures		3 hyperconjugation structures

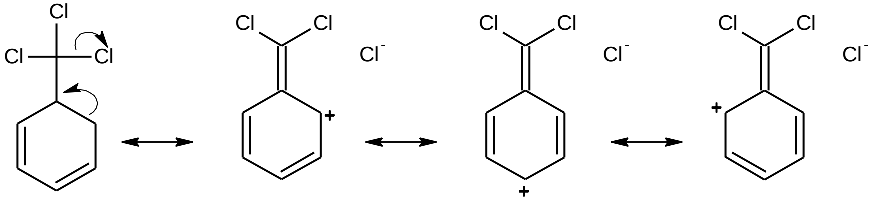
3. **Bond lengths:** The bond length in a molecule change if there is hyperconjugation. In $C^3H_3-C^2H=C^1H_2$, the C^1–C^2 bond length is found to be more than 1.34 $\dot{A}$ (normal C = C bond length) while the C^2–C^3 bond distance is less than 1.54 $\dot{A}$ (normal C – C bond length).

4. **Directive influence of the group:** +M effect of methyl group in toluene is due to hyperconjugation.



Due to hyperconjugation, there are nine different structures having negative charge at ortho and para positions. Hence, + M effect of alkyl group attached to benzene ring follows the order: **methyl > ethyl > isopropyl > tert – butyl.**

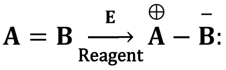
In the same way, the meta directing influence and deactivating effect of $-CCl_3$ group in benzotrichloride can be explained on the basis of hyperconjugation as follows,



Due to low electron density at ortho and para positions, the meta position becomes point of high electron density, hence electrophilic substitution takes place in meta position.

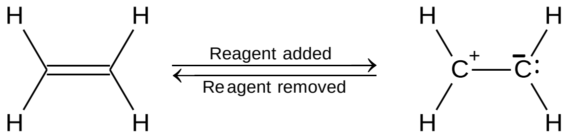
(iv) Electromeric effect (E effect)

The complete transfer or shift of π electron pair of a multiple bond to one of the bonded atoms during the attack of positively or negativity attacking agents. As soon as the reagent is removed, the molecule reverts back to original position.



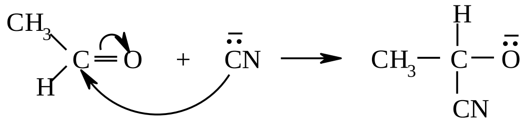
$$A = B \xrightarrow[\text{Reagent}]{E} \overset{\oplus}{A} - \overset{-}{B}:$$

Temporary polarization of the substrate molecule at the site of multiple bonds, by complete shift of an π electron pair from one atom to the other under the influence of attacking reagents.



Depending upon the direction of displacement, E effect is also of two types.

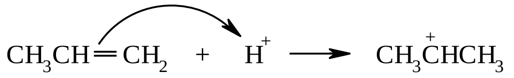
- **–E effect**: An attacking reagent is said to have –E effect when the **direction of π electron pair transfer of multiple bond is away from the attacking reagent**.



acetaldehyde; (-E effect)

The –E effect operates during nucleophilic addition reaction of aldehydes and ketones.

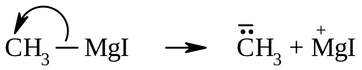
- **+E effect:** An attacking reagent is said to have +E effect when the **direction of π electron pair transfer of a multiple bond is towards the attacking reagent**.



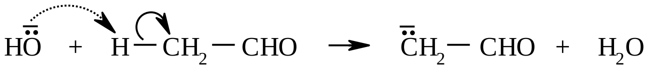
$CH_3CH{=}CH_2 + \overset{+}{H} \longrightarrow CH_3\overset{+}{C}HCH_3$

Propene ; (+E effect) isopropyl carbocation

The +E effect is observed during electrophilic addition reaction of alkenes and alkynes

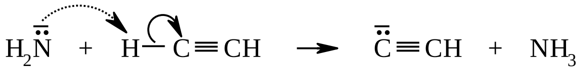


$CH_3 - MgI \longrightarrow \ddot{C}H_3 + \overset{+}{M}gI$



$H\ddot{O} + H - CH_2 - CHO \longrightarrow \ddot{C}H_2 - CHO + H_2O$

ethanal ethanal carbanion



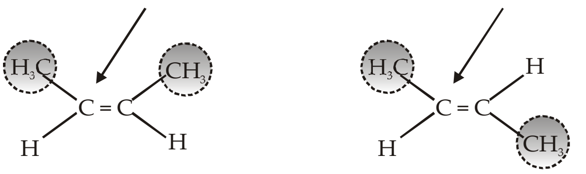
$H_2\ddot{N} + H - C \equiv CH \longrightarrow \ddot{C} \equiv CH + NH_3$

amide acetylide ion

Steric Hindrance or Steric Strain

When two atoms are closer to each other than the sum of their van der Waal's radii they repel each other due to spatial crowding. Steric hindrance or steric strain refers to non-bonded repulsive interactions between atoms which arise when the atoms come too close due to the shape of the molecule. The repulsion arises due to nuclear-nuclear and electron-electron repulsive forces which start dominating the attractive forces. Molecules with steric strain are relatively less stable than those having no strain or less strain.

For example, in cis-but-2-ene steric hindrance is present because the two methyl groups are quite close to each other wheras in trans-but-2-ene no steric hindrance is there because the two methyl groups on the opposite sides.



cis-But-2-ene (Sterically hindered molecule, less stable)

trans-But-2-ene (No Steric hindrance, more stable)

Steric factors have great influence on orientation and reactivity of organic molecules in various reactions.

Types of Organic Reactions

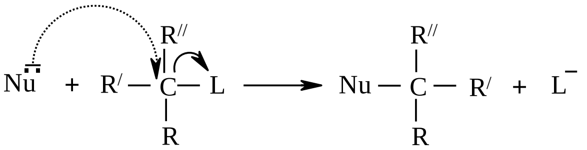
I. Substitution reaction

The reactions in which an atom or a group in a molecule is replaced by another are called substitution reactions. The incoming group gets attached to the same carbon atom to which leaving group was attached. The substituting species may be a nucleophile, an electrophile or a free radical.

$$A - B + X - Y \longrightarrow A - X + B - Y$$

(i) Nucleophilic substitution (S_N) reactions

The substitution reactions which are brought about by the attack of nucleophile $(Nu)^{\ddot{}}$ are called nucleophilic substitution reactions.



$$\ddot{Nu} + R^{/} - \overset{R^{//}}{\underset{R}{C}} - L \longrightarrow Nu - \overset{R^{//}}{\underset{R}{C}} - R^{/} + L^{-}$$

[$\ddot{Nu}$ = attacking reagent; L = leaving group]

The common examples of S_N reactions are as follows.

$$R{-}CH_2{-}X + NaOH \xrightarrow{\text{aqueous}} R{-}CH_2{-}OH + X^{-}\ (X = Cl, Br, I)$$

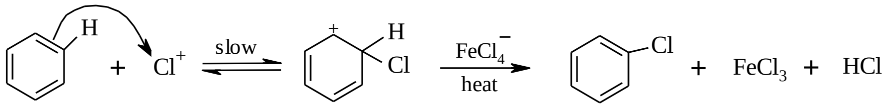
$$R{-}CH_2{-}X + KCN \xrightarrow{\text{alcohol}} R{-}CH_2CN + X^{-}$$

$$R{-}CH_2OH + SOCl_2 \longrightarrow R{-}CH_2Cl + HCl + SO_2$$

(ii) Electrophilic substitution (S_E) reactions

The substitution reactions which are brought about by the attack of an electrophile are called electrophilic substitution reactions. The substitution reactions of aromatic compound such as chlorination, nitration of benzene are representatives of S_E reactions.

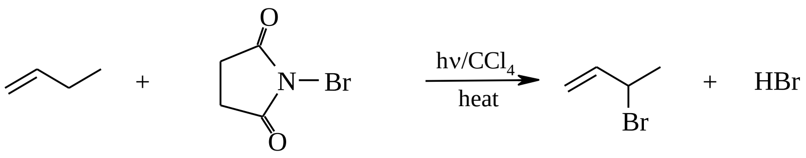
- **Chlorination:** $Cl_2 + FeCl_3 \rightarrow FeCl_4^{-} + Cl^{+}$



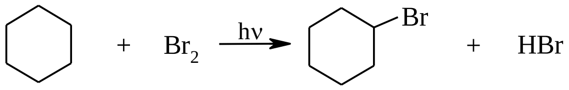
(iii) Free radical substitution

The substitution reactions which are brought about by the attack of free radical are called free radical substitution reactions. The chlorination of aliphatic hydrocarbons in presence of diffused sunlight is common example of free radical substitution.

$$CH_4 + Cl_2 \xrightarrow{\text{sunlight}} CH_3Cl + HCl$$



N-bromosuccinamide(NBS)



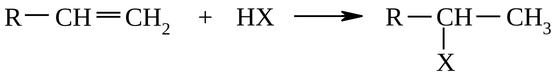
II. Addition reaction

"An addition reaction is defined as one in which an unsaturated molecule combines with reagent (addendum) to give a single saturated or nearly saturated compound". If one π bond is broken then two σ bonds are formed. A few examples for different types of addition reactions are given below

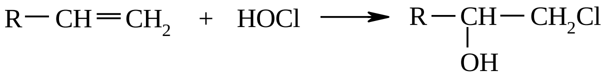
$$A = B + X–Y \longrightarrow X–A–B–Y$$

(i) Electrophilic addition reactions

The addition of common reagents like $X_2 (X = \text{Cl, Br or I})$, HX, H_2O, HOCl, etc to alkenes and alkynes are common examples of electrophilic addition reaction. The addition of unsymmetrical molecules like HX, H_2O, HOCl, etc. to unsymmetrical alkenes or alkynes takes place according to Markownikoffs' rule.



$$R-CH=CH_2 + HX \longrightarrow R-\underset{X}{\underset{|}{CH}}-CH_3$$

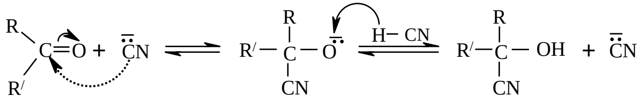


$$R-CH=CH_2 + HOCl \longrightarrow R-\underset{OH}{\underset{|}{CH}}-CH_2Cl$$

(ii) Nucleophilic Addition Reactions

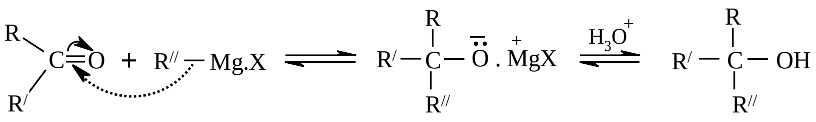
The electron deficient carbonyl group of aldehydes or ketones is easily attacked by nucleophile which can supply an electron pair. Thus the addition reactions of carbonyl compounds initiated by nucleophile and known as nucleophilic addition reactions.

Addition of hydrogen cyanide

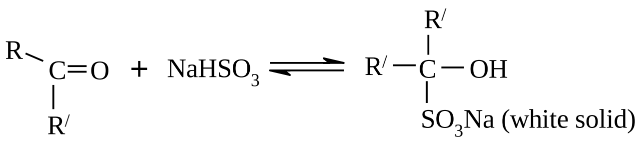


R'=H or alkyl (–CH_3, –CH_2CH_3, etc.) or aryl (C_6H_5–) or aralkyl ($C_6H_5CH_2$–)

Addition to Grignard reagent



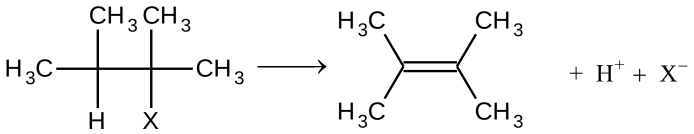
Addition of sodium bisulphite



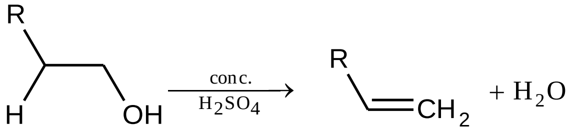
$$\begin{matrix} & & R' \\ & & | \\ R\diagdown C=O + NaHSO_3 \rightleftharpoons & R'- & C-OH \\ | & & | \\ R' & & SO_3Na \text{ (white solid)}\end{matrix}$$

III. Elimination reactions

The loss of atoms or group from adjacent carbon atoms (one in the form of a nucleophile and other in the form of an electrophile) resulting in the formation of an unsaturated compound is known as elimination reaction.



[Note: If these two groups or atoms are removed from adjacent carbon atoms, then it is known as β □ elimination reaction.]



The elimination reactions are two types, β-elimination reactions and α-elimination reactions

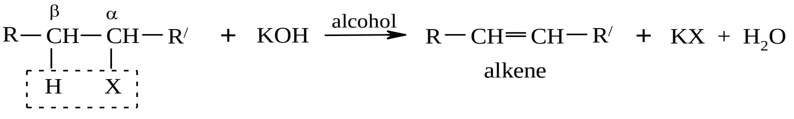
(i) β-elimination reactions

This type of reaction involves loss of two atoms or groups from vicinal (adjacent) carbon atoms resulting in the formation of a π bond. Thus, it is the reverse of addition reactions. The most familiar example of

β-elimination reactions are dehydrohalogenation reactions of alkylhalides, dehalogenation of dihaloalkanes, dehydration of alcohols, pyrolysis of esters, Hofmann elimination of quaternary ammonium hydroxide.

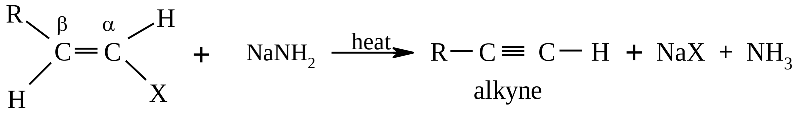
Dehydrohalogenation

When alkylhalides are treated with alcoholic potassium hydroxide solution or sodamide the corresponding alkenes are formed with the elimination of hydrogen halide.



$$R-\underset{H}{\overset{\beta}{CH}}-\underset{X}{\overset{\alpha}{CH}}-R' + KOH \xrightarrow{\text{alcohol}} \underset{\text{alkene}}{R-CH=CH-R'} + KX + H_2O$$

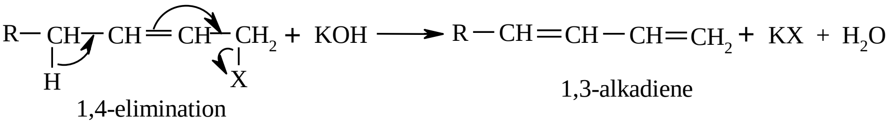
β-elimination



β-elimination

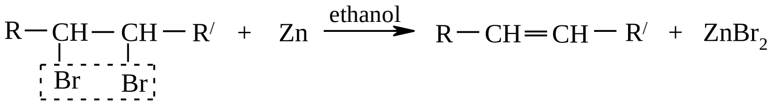
(i) Sodamide ($NaNH_2$) is stronger dehydrohalogenating agent.

(ii) An example of 1,4-elimination (δ-elimination) is



Dehalogenation

The dehalogenation involves the removal of halogen molecule (X_2) from vicinal dihalide by heating with zinc dust in alcoholic medium.

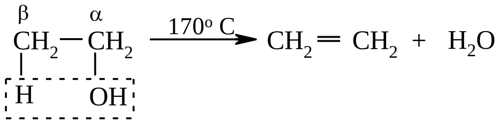


$$R-\underset{Br}{CH}-\underset{Br}{CH}-R' + Zn \xrightarrow{\text{ethanol}} R-CH=CH-R' + ZnBr_2$$

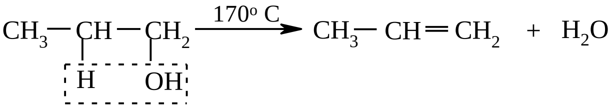
β -elimination

Dehydration of alcohols

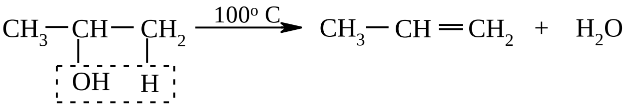
When alcohols are heated with dehydrating agent like concentrated sulphuric acid, the corresponding alkenes are formed with the elimination of water (β-elimination). The reaction is called dehydration of alcohols.



$$\overset{\beta}{\underset{H}{CH_2}}-\overset{\alpha}{\underset{OH}{CH_2}} \xrightarrow{170^o\,C} CH_2=CH_2 + H_2O$$

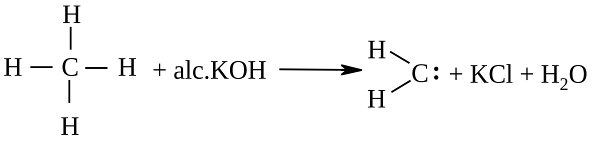


$$CH_3-\underset{H}{CH}-\underset{OH}{CH_2} \xrightarrow{170^o\,C} CH_3-CH=CH_2 + H_2O$$



$$CH_3-\underset{OH}{CH}-\underset{H}{CH_2} \xrightarrow{100^o\,C} CH_3-CH=CH_2 + H_2O$$

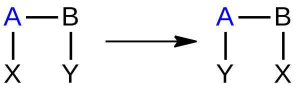
(ii) **α-elimination:** It involves loss of two atoms from same atom resulting in the formation of reaction intermediates like carbine

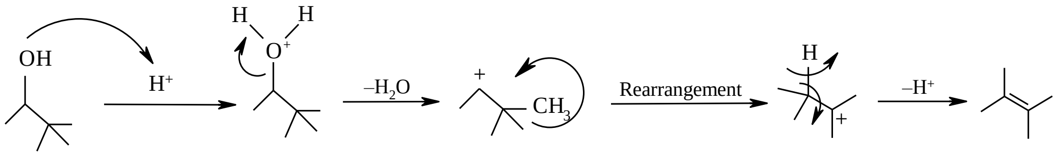


$$H-\overset{H}{\underset{H}{C}}-H + \text{alc.KOH} \longrightarrow H_2C: + KCl + H_2O$$

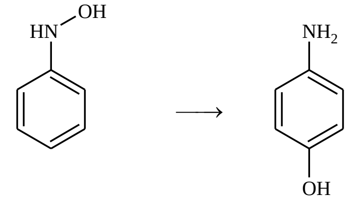
IV. Rearrangement reactions

The reactions which proceed by a rearrangement or reshuffling of atoms or groups in the molecule to produce a structural isomer of the original substance are called rearrangement reactions.



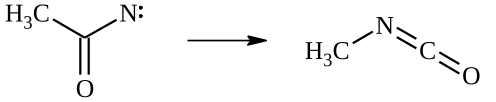


(i)



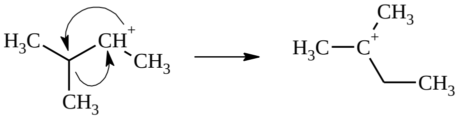
Phenyl hydroxylamine p – aminophenol

(ii)



acetyl nitrene methyl isocyanate

(iii)



sec – carbocation tert – carbocation

Purification and Characteristics of Organic Compounds

The study of organic compounds starts with the characterization of the compound and the determination of its molecular structure. The procedure generally employed for this purpose consists of the following steps:

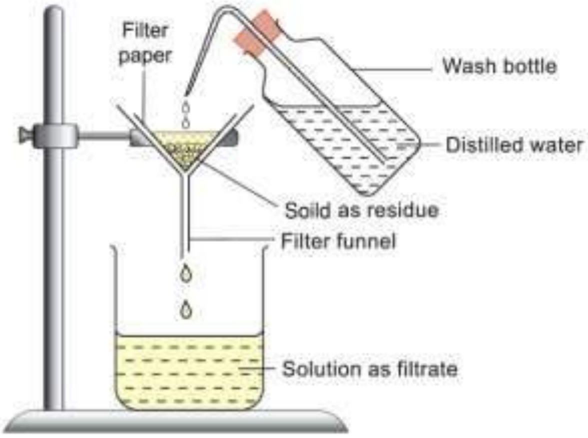
(1) Purification of organic compounds
(2) Qualitative analysis of organic compounds
(3) Quantitative analysis of organic compounds
(4) Determination of molecular mass of organic compounds
(5) Calculation of Empirical formula and Molecular formula of organic compounds

(1) Purification of organic compounds: A large number of methods are available for the purification of substances. The choice of method, however, depends upon the nature of substance (whether solid or liquid) and the type of impurities present in it. Following methods are commonly used for this purpose,

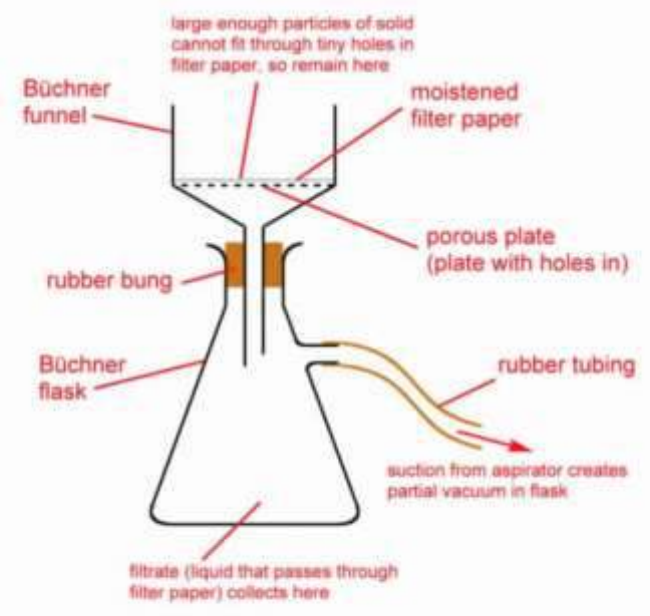
(i) Filtration

The process of filtration is used to separate insoluble solid component of a mixture from the soluble components in a given solvent.

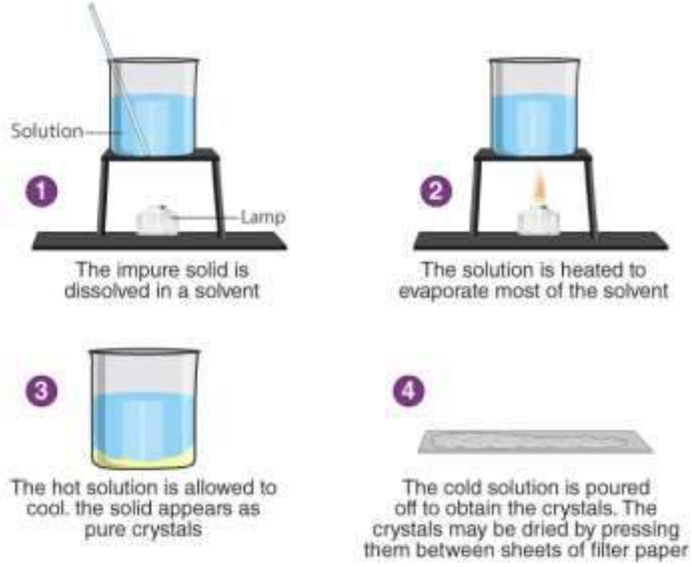
Exp- It is used to separate a mixture of Naphthalene and Urea using a water as solvent. Urea dissolves in water while Naphthalene remains insoluble. Upon filtration, naphthalene remains on the filter paper while urea is recovered from the filtrate by evaporating water.



Filtration is very slow and takes along time. In such cases, filtration is carried out under reduced pressure using a Buchner funnel and water suction pump.



(ii) Crystallization



① The impure solid is dissolved in a solvent

② The solution is heated to evaporate most of the solvent

③ The hot solution is allowed to cool. the solid appears as pure crystals

④ The cold solution is poured off to obtain the crystals. The crystals may be dried by pressing them between sheets of filter paper

The method is based on the difference in the solubilities of the compound and the impurities in a suitable solvent. Pure compound crystallises out from the solution and highly soluble impurities remain in the solution. Impure organic compounds like glucose, urea, cinnamic acid, etc are purified. Fractional crystallisation is used for the separation of a mixture of two compounds which are soluble in the same solvent but to a different extent.

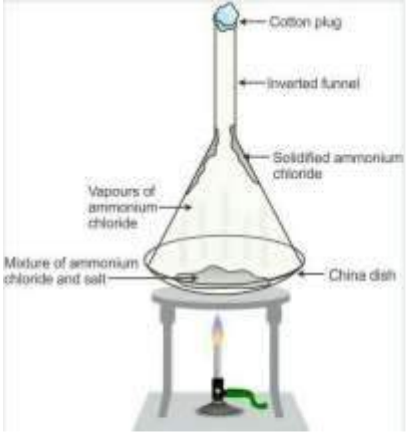
Ex: Separation of sugar and salt.

(ii) Sublimation is the process of direct conversion of a solid into the gaseous state on heating without passing through the intervening liquid state and vice versa on cooling.

$$\text{Solid} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \text{Vapour}$$

Only those substances whose vapour pressure becomes equal to the atmospheric pressure much before their respective melting points are capable of undergoing sublimation.

There exists an equilibrium between the solid and its vapours.



Camphor, naphthalene, anthracene, iodine, benzoic acid, salicylic acid, NH_4Cl, $HgCl_2$, etc are purified by sublimation.

(iii) Distillation- Distillation is a method used to separate constituents of a liquid mixture which differ in their boiling points.

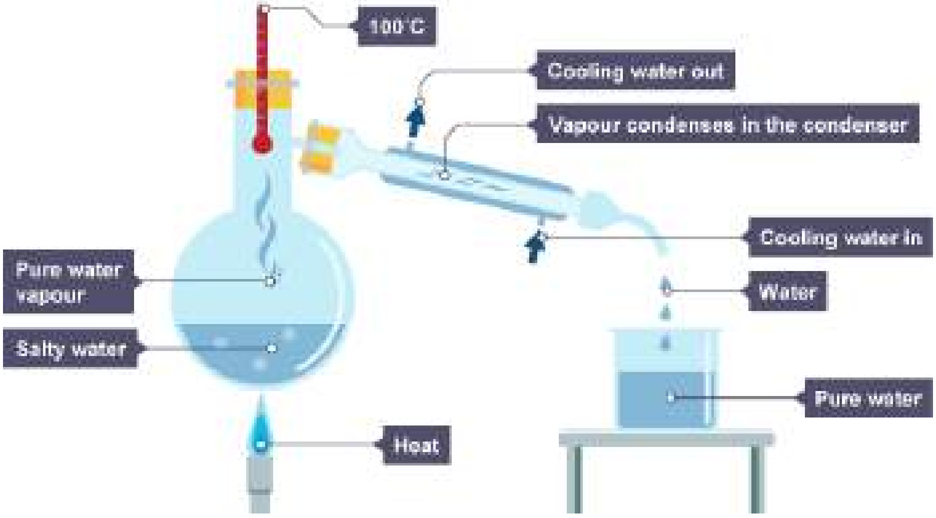
Distillation is a process which involves two steps:

Vapourisation: Liquid is converted into vapours.

Condensation: Vapours are condensed again into liquid.

Depending upon the difference in the boiling points of the constituent liquids, different types of distillation methods are employed.

- **Simple distillation:** Simple distillation is applied only for volatile liquids which boil without decomposition at atmospheric pressure and contain non-volatile impurities.

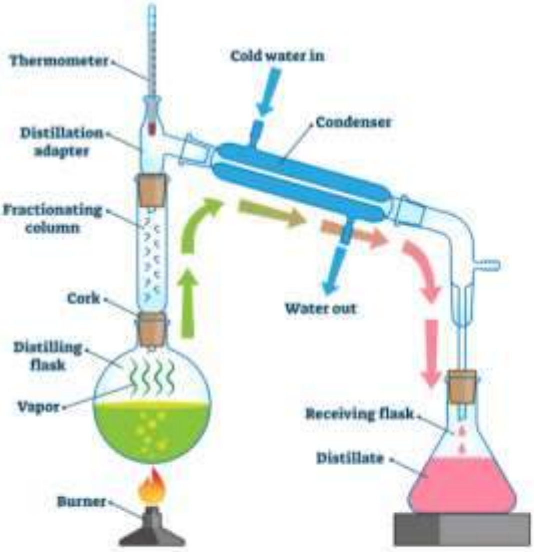


This method can also be used for separating liquids having sufficient difference in their boiling points. For example,

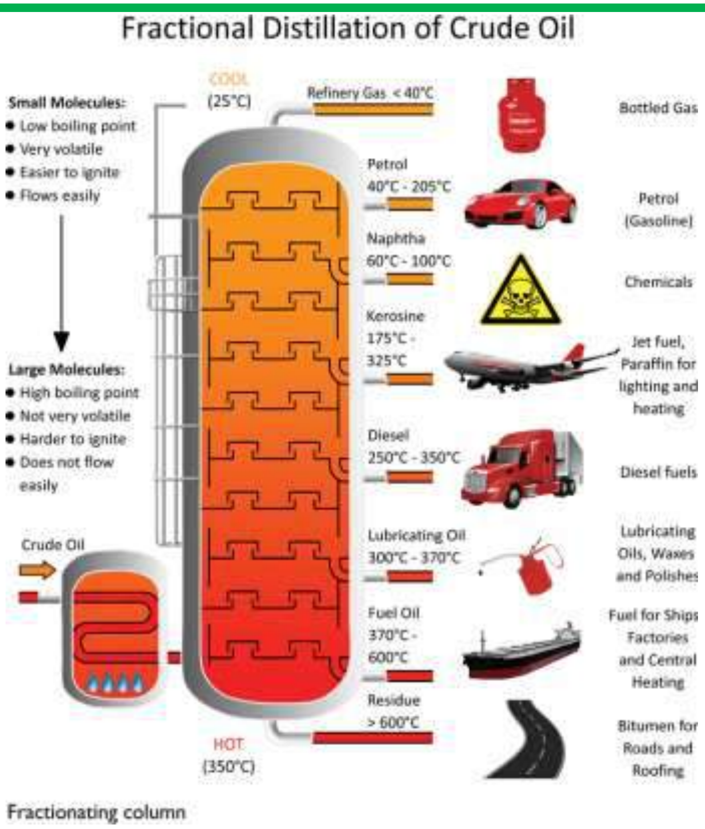
(i) benzene (boiling point 353 K) and aniline (boiling point 475 K)
(ii) chloroform (boiling point 334 K) and aniline (boiling point 457 K)
(iii) ether (boiling point 308 K) and toluene (boiling point 383 K)

Nitrobenzene prepared in the laboratory can also be purified by distillation.

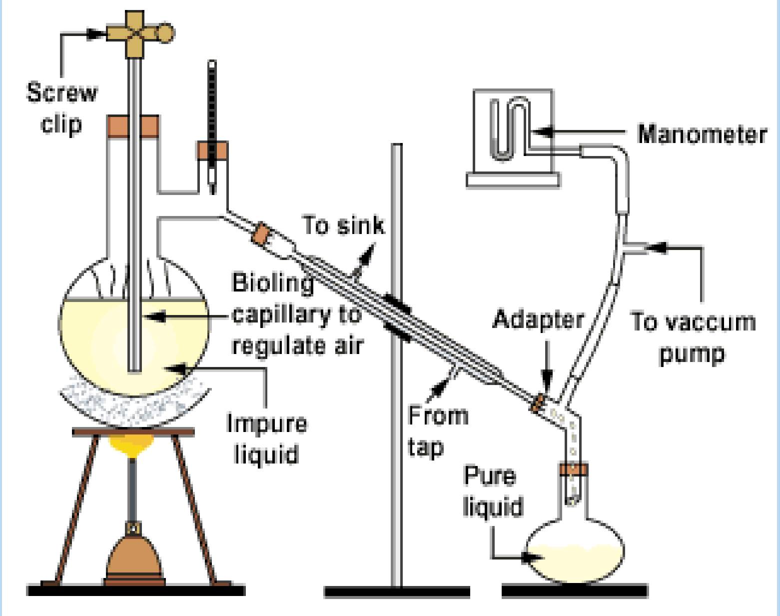
- **Fractional distillation:** This method is used for the separation of two or more volatile liquids from a liquid mixture which has boiling points close to each other. Liquids forming a constant boiling mixture (azeotropic mixture) such as rectified spirit cannot be separated by this method.



Fractional distillation is used these days in industries, especially, in the **distillation of petroleum, coal tar and crude alcohol**. A mixture of methanol (boiling point 338 K) and propanone (boiling point 330 K) or a mixture of benzene and toluene may be separated by fractional distillation.


Fractional Distillation of Crude Oil

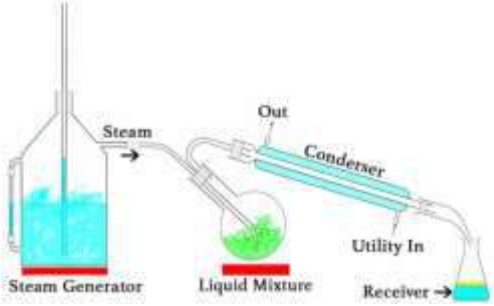
- **Distillation under reduced pressure (Vacuum distillation):** The compounds, which decompose at a temperature below their normal boiling points, cannot be purified by distillation under ordinary atmospheric pressure.



Distillation under reduced pressure

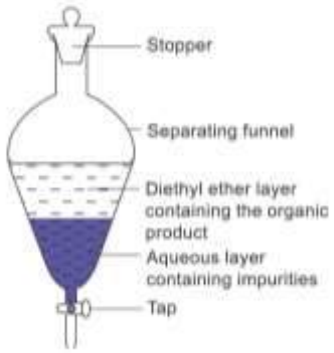
Glycerin is one such compound which decomposes at its boiling point. The pressure is reduced by suction pump and the distillation is carried out at lower temperature as glycerine can be distilled at 453 K (normal boiling point 563 K) under a pressure of 10-12 mm. Cane juice can also be concentrated by this method. This technique can be used to separate glycerol from spent lye in soap industry.

- **Steam distillation:** This method is used to purify the organic compounds which
  - ❖ Are volatile in steam but are immiscible with water.
  - ❖ Possess high vapour pressure at the boiling point of water.
  - ❖ Contain nonvolatile impurities.



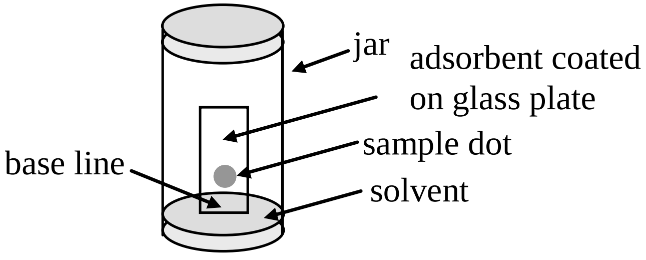
The compound to be purified is distilled with steam and impurities being nonvolatile remains in mother liquor. For example, o- nitrophenol (volatile) and p-nitrophenol (non volatile) are separated by this method.

(iv) Differential extraction (or solvent extraction): The process of separation of an organic compound (solid or liquid) from its aqueous solution by shaking with a suitable organic solvent is termed as **solvent extraction**. This method is employed for non-volatile compounds. For example, benzoic acid is extracted from its aqueous solution using benzene as solvent.

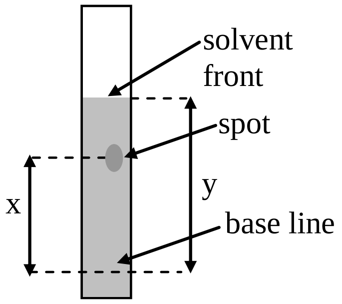


(v) Chromatography

Chromatography is the technique of separating the components of mixture in which the separation is achieved by the differential movement of individual components through a stationary phase under the influence of a mobile phase.



Thin layer chromatography chromatogram being developed



Developed chromatogram

$$R_f = \frac{\text{Distance moved by the substance form base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

Depending upon the nature of the stationary phase (either a solid or a liquid tightly bound on a solid support) and the nature of the mobile phase (either a liquid or a gas), different types of chromatographic techniques are followed.

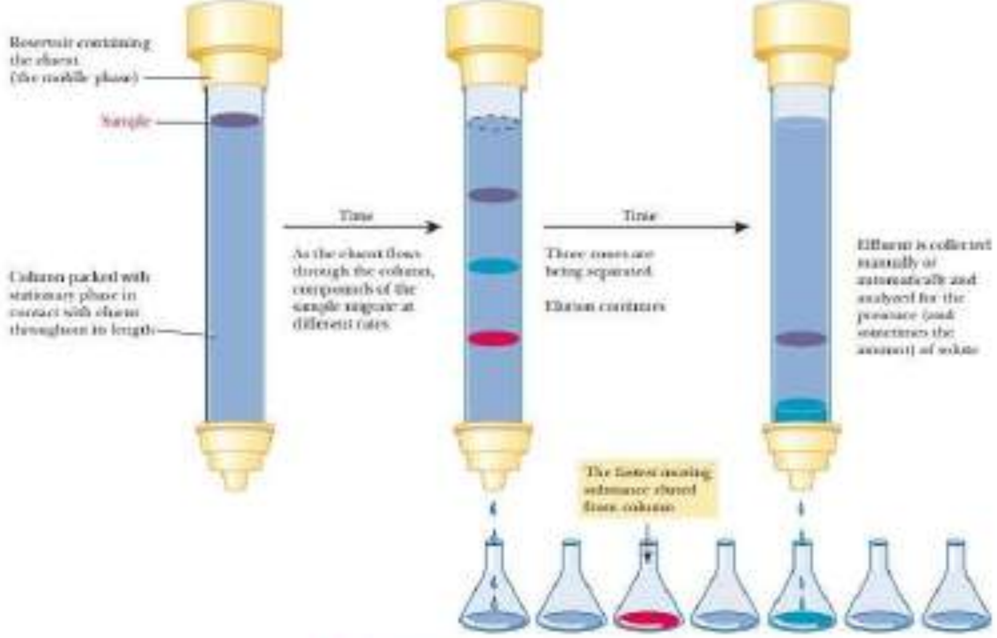
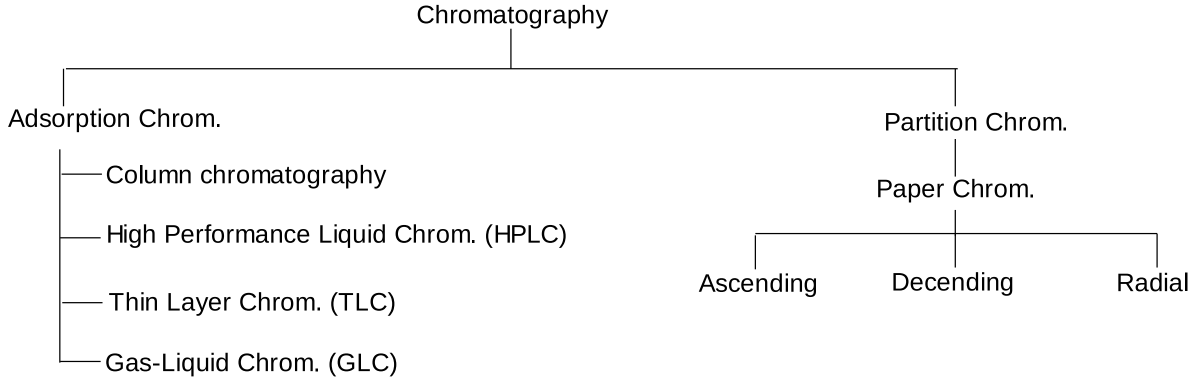


FIGURE 5.2 **Column chromatography.** A sample containing several components is applied to the column. The various components travel at different rates and can be collected individually.



Type of chromatography	**Stationary phase**	**Mobile phase**	**Application**
Column/adsorption	Solid	Liquid	Large scale separation
Thin layer chromatography (TLC	Solid	Liquid	Qualitative analysis
High performance liquid chromatography (HPLC)	Solid	Liquid	Qualitative analysis and also for separation
Gas liquid chromatography(GLC	Liquid	Gas	Qualitative analysis and also for separation
Proper chromatography	Liquid	Liquid	Qualitative analysis and also for separation

The various components on the developed TLC plate are identified through their retardation factor, i.e., R_f **values**.

$$R_f = \frac{\text{distance moved by the substance from base line}}{\text{distance moved by the solvent from base line}}$$

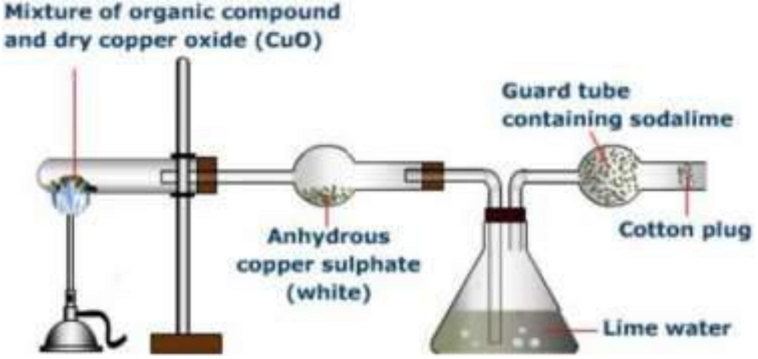
A component with highest value of R_f elute first. A component with greater tendency to adsorb on solid has lesser the R_f value.

2. Qualitative Analysis (Detection of Elements)

The qualitative analysis of an organic compound involves the detection of all the elements present in it. Carbon and hydrogen are generally present in all organic compounds. Other elements which may be present in organic compounds are oxygen, nitrogen, sulphur, halogens, phosphorus, etc. These elements are detected by the following tests.

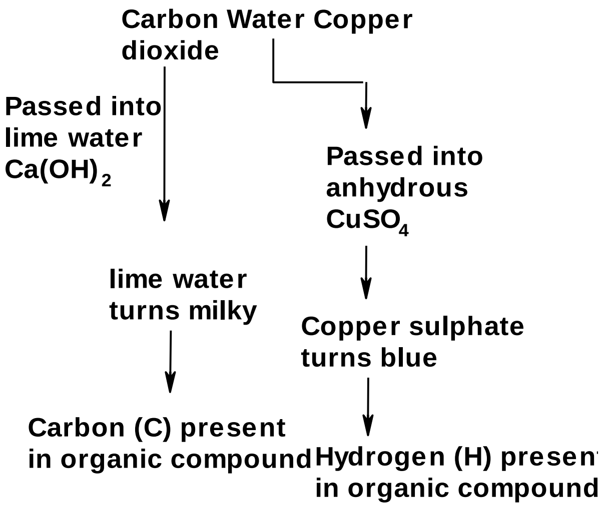
Detection of Carbon and Hydrogen by Copper oxide test

Principle Organic compounds undergo oxidation in the presence of a suitable oxidizing agent. In this process, carbon is oxidized to CO_2 and hydrogen is oxidized to water.



Procedure The compound is intimately mixed with dry cupric oxide. The mixture is strongly heated in a hard glass test tube fitted with a cork and a delivery tube. The liberated gases are passed into lime water.

$$\text{Organic compound} + CuO \xrightarrow{\triangle} CO_2 + H_2O + Cu$$



$$\underset{organic compound}{[C]} + 2CuO \xrightarrow{heat} CO_2 + 2Cu$$

$$CO_2 + \underset{\text{lime water}}{Ca(OH)_2} \longrightarrow \underset{\text{(milky)}}{CaCO_3} + H_2O$$

$$\underset{organic compound}{[2H]} + CuO \xrightarrow{heat} H_2O + Cu$$

$$\underset{(white)}{CuSO_4} + 5H_2O \longrightarrow \underset{(blue)}{CuSO_4.5H_2O}$$

Detection of Nitrogen, Halogen and Sulphur by Lassaigne's test

Principle This is the most reliable test for the detection of nitrogen, sulphur, halogens etc. In this method sodium fusion extract of organic compound is prepared. In this fusion process, carbon and nitrogen present in the organic compounds get converted into cyanide ion (CN^-), sulphur (S) into sulphide ion S^{2-} and halogens (X) into halide ion (X^-). By testing for radicles, presence of these elements can be find.

Preparation of Sodium fusion extract

A piece of Na metal taken in a fusion tube and heated. Na melts to form shining globule. Organic compound added to it and heated to red hot. Red hot tube is now dropped into water taken in a porcelain dish. The contents are heated to concentrate the solution. Solution is then filtered. The filtrate is called sodium fusion extract.

Test for nitrogen

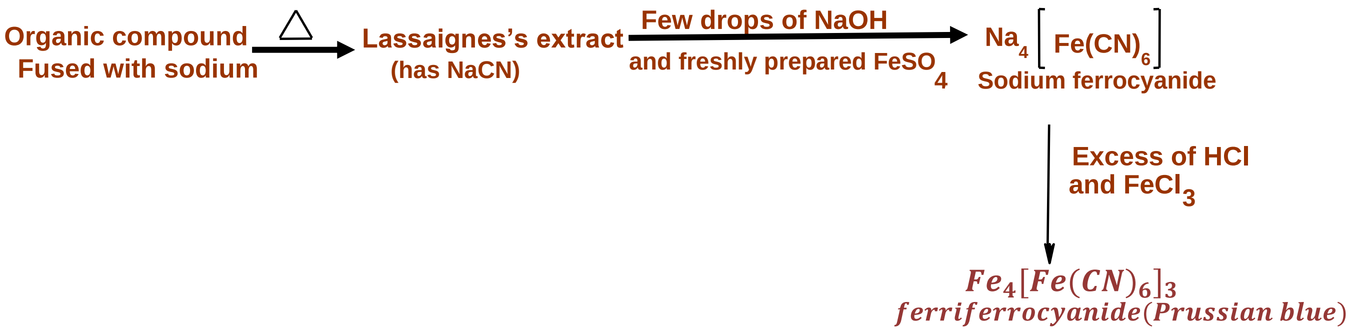
Ferrous sulphate are added to the sodium fusion extract. The mixture is boiled and cooled. It is acidified with hydrochloric acid and a few drops of ferric chloride solution are added. Sodium cyanide in the filtrate reacts with ferrous sulphate to give sodium ferrocyanide. It further reacts with ferric chloride to give a blue coloured solution of ferric ferrocyanide.

$$\underset{organic\ compound}{[C,N]} + Na \xrightarrow{fuse} NaCN$$

$$FeSO_4 + 2NaCN \longrightarrow Fe(CN)_2 + Na_2SO_4$$

$$Fe(CN)_2 + 4NaCN \longrightarrow \underset{sodiumferrocyanide}{Na_4[Fe(CN)_6]}$$

$$3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow \underset{ferriferrocyanide(\textbf{Prussian blue})}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$



Note- If organic compound contains N and S, sodium thiocyanate is formed in sodium extract which gives blood red colouration with $FeCl_3$ due to the formation of ferric thiocyanate.

$$\underset{\textbf{organiccompound}}{\boldsymbol{[C,N,S]}} + \boldsymbol{Na} \xrightarrow{fuse} \boldsymbol{NaCNS}$$

$$\boldsymbol{NaCNS + FeCl_3 \longrightarrow \underset{ferric\ sulpho\ cyanide(Prussian\ blue)}{Fe(CNS)Cl_2} + NaCl}$$

Test for Sulphur

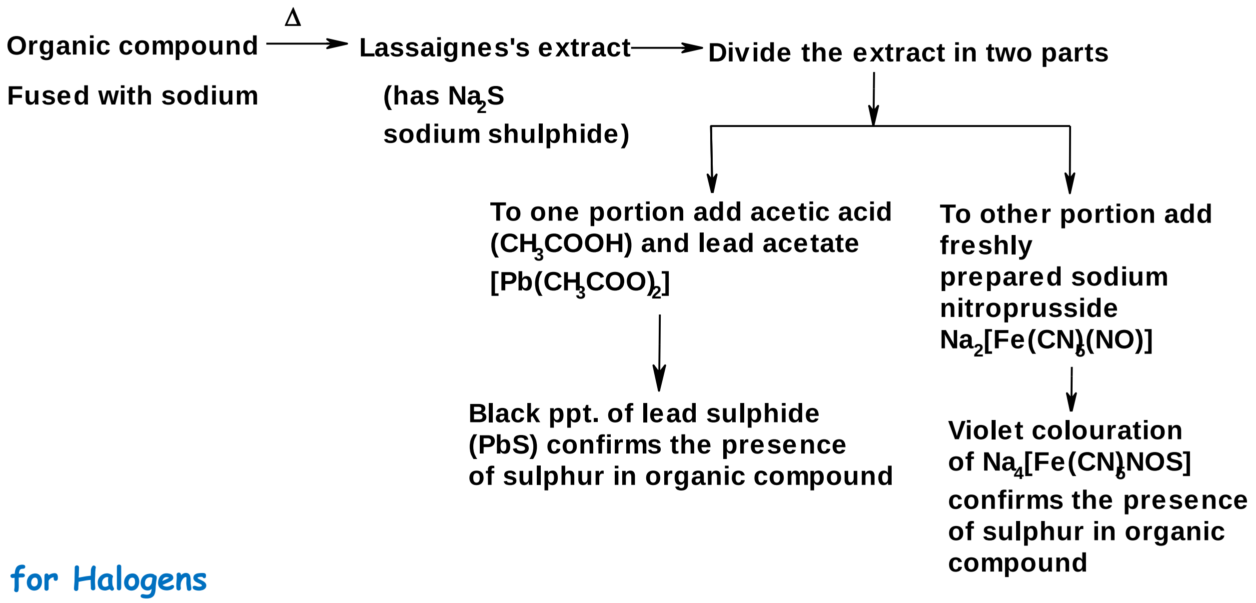
Lead acetate test: Second part of the filtrate is treated with excess of acetic acid and lead acetate solution. A black precipitate of lead sulphide is formed.

$$\underset{(oforganiccompound)}{[S]} + 2Na \xrightarrow{fuse} Na_2S$$

$$Na_2S + Pb(CH_3COO)_2 \longrightarrow 2CH_3COONa + \underset{blackprecipitate}{PbS\downarrow}$$

Sodium nitroprusside test: To the sodium fusion extract, a few drops of sodium nitroprusside are added. The appearance of **violet or purple colour** indicates the presence of sulphur.

$$Na_2S + \underset{\text{Sodium nitroprusside}}{Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\substack{sodium\ sulpho\ nitro\ prusside \\ \text{(Purple)}}}{Na_4[Fe(CN)_5NO.S]} \quad \text{or} \quad \underset{\substack{\text{Sodium thionitroprusside} \\ \text{(Violet)}}}{Na_3[Fe(ONSNa)(CN)_5]}$$



Test for Halogens

Silver nitrate test A portion of the stock solution is boiled with dil. HNO$_3$, cooled and silver nitrate is added.

A white precipitate soluble in ammonium hydroxide shows the presence of *chlorine. A pale yellow precipitate* slightly soluble in ammonium hydroxide shows the presence of *bromine. A yellow precipitate* insoluble in ammonium hydroxide shows the presence of *iodine.*

$$NaX + AgNO_3 \xrightarrow{HNO_3} \underset{ppt}{AgX\downarrow}$$

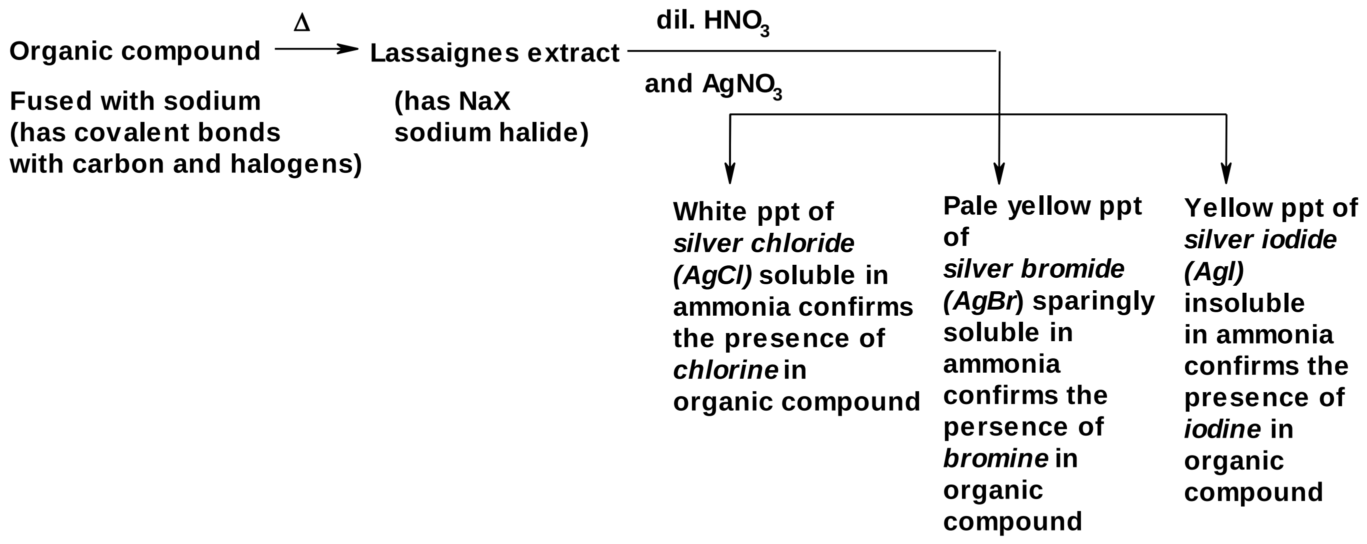
$$NaCl + AgNO_3 \longrightarrow \underset{white\ ppt}{AgCl\downarrow} + NaNO_3$$

$$NaBr + AgNO_3 \longrightarrow \underset{pale\ yellow\ ppt}{AgBr\downarrow} + NaNO_3$$

$$NaI + AgNO_3 \longrightarrow \underset{yellow\ ppt}{AgI\downarrow} + NaNO_3$$

Note: During the detection of halogens, the sodium fusion extract is boiled with nitric acid in order to expel the N and S as HCN and H$_2$S.

When AgNO$_3$ added cyanide gives white ppt, sulphide gives black ppt and interfere with observation.



White ppt of *silver chloride (AgCl)* soluble in ammonia confirms the presence of *chlorine* in organic compound

Pale yellow ppt of *silver bromide (AgBr)* sparingly soluble in ammonia confirms the persence of *bromine* in organic compound

Yellow ppt of *silver iodide (AgI)* insoluble in ammonia confirms the presence of *iodine* in organic compound

Note: Beilstein's test: Beilstein's test is used to detect the halogen in an organic compound. A copper wire is heated in a Bunsen flame till no colour is imparted to the flame. The copper wire is dipped in the given organic compound and exposed to the non-luminous zone of the Bunsen flame. A *bluish green coloured* flame indicates the presence of halogen.

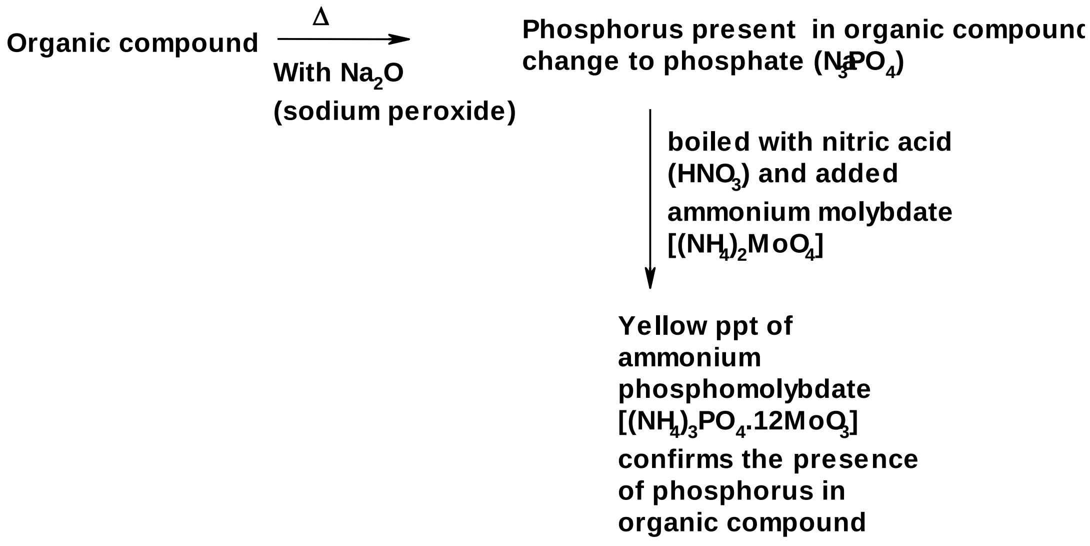
Test for Phosphorus

Organic compound containing phosphrous is fused with sodium peroxide. The phosphorus of the compound is oxidised to phosphate. The fused mass is extracted with water and filtered. The filtrate containing sodium phosphate is boiled with nitric acid and then treated with ammonium molybdate. A yellow solution or precipitate indicates the presence of phosphorus.

$$Na + P + O \rightarrow Na_3PO_4$$

$$Na_3PO_4 + 3HNO_3 \rightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + \underset{\text{ammonium molyblate}}{12(NH_4)_2MoO_4} + 2HNO_3 \rightarrow \underset{\text{ammonium phosphomolybdate}}{(NH_4)_3PO_4 12MoO_3} + 21NH_4NO_3 + 12H_2O$$



Yellow ppt of ammonium phosphomolybdate [$(NH_4)_3PO_4.12MoO_3$] confirms the presence of phosphorus in organic compound

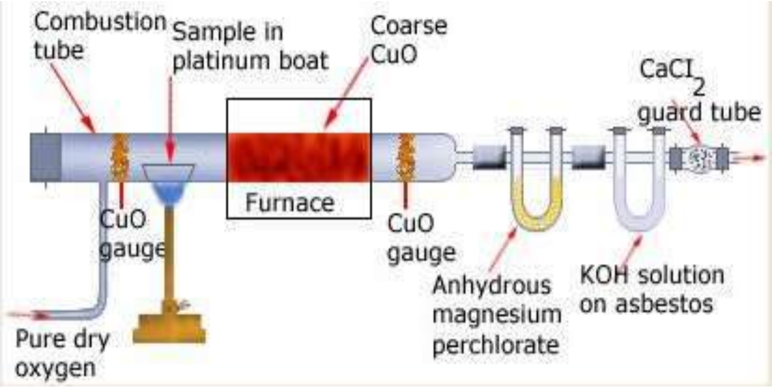
(3) Quantitative analysis The quantitative analysis deals with the determination of percentage of various elements. The following methods are employed for the determination of percentage composition of elements present in the organic compounds.

Estimation of carbon and hydrogen by Liebig's combustion method

Principle: A known mass of organic compound is oxidized with cupric oxide in CO_2 free atmosphere. C gets oxidized to CO_2, H to H_2O. Water formed is absorbed in weighed anhydrous $CaCl_2$ U bulbs and carbon dioxide absorbed in weighed KOH bulbs. Increase in mass of $CaCl_2$ and KOH bulbs are determined. Difference in mass corresponds to the mass of H_2O and CO_2 respectively.

Knowing the increase in mass, the percentage of C and H in the organic compound can be calculated.

$$C_xH_y + \left(x+\frac{y}{4}\right)O_2 \xrightarrow{\Delta} xCO_2 + \frac{y}{2}H_2O$$



Calculations

- Let the mass of organic compound taken = m g
- Mass of water formed = m_1 g

  (increase in $CaCl_2$ U-tube)
- Mass of carbon dioxide formed = m_2 g

  (increase in potash tubes)

(a) Percentage of Carbon

We know that 1 mole of carbondioxide (44 g) contains 1 gram atom of carbon (12g).

44 g of CO_2 contain C = 12g

m_2 g of CO_2 contains C = $\frac{12}{44} \times m_2$ g

Hence Percentage of carbon = $\frac{12m_2}{44\times m} \times 100$

(b) Percentage of Hydrogen

We know that one mole of water (18g) contains 2gram atom of hydrogen (2g)

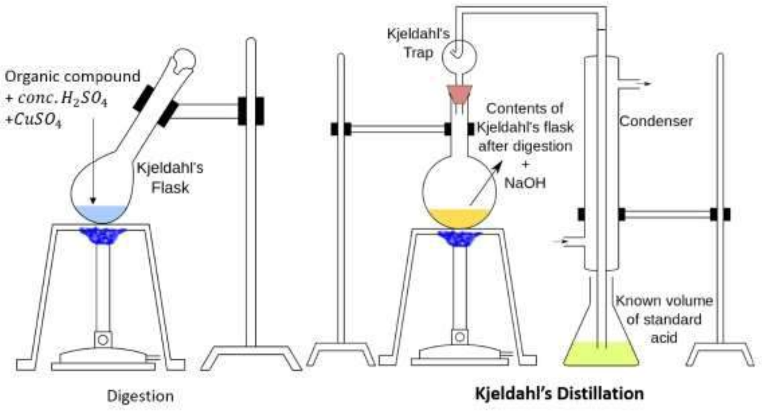
$H_2O = 2H$

18g of H_2O contain H = 2g

m_1 g of H_2O contains H = $\frac{2}{18} \times m_1$ g

Percentage of hydrogen = $\frac{2m_1}{18\times m} \times 100$

Estimation of nitrogen by Kjeldahl's method



Principle: Kjeldahl's method is based on the quantitative conversion of nitrogen of the organic compound to ammonium sulphate by sulphuric acid. The reaction product is treated with an alkali and the ammonia released is determined. From this the amount of nitrogen in the organic compound is calculated.

$$\underset{organiccompound}{[C,H,N,S]} \xrightarrow[heat]{conc.H_2SO_4} CO_2 + H_2O + SO_2 + (NH_4)_2SO_4$$

$$(NH_4)_2SO_4 + 2NaOH \xrightarrow{heat} Na_2SO_4 + 2H_2O + 2NH_3$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

This method is simple, convenient and largely used for the estimation of nitrogen in food stuffs, drugs, fertilizers and many other organic compounds. However, this method cannot be employed for the estimation of nitrogen in following types of organic compounds.

- Organic compound containing nitrogen in aromatic ring such as pyridine, quinoline, etc.,
- Organic compounds containing nitro ($-NO_2$) and diazo ($- N = N -$) groups.

Calculations

Let the mass of organic compound = w g

Volume of standard acid taken = V cm^3

Normality of acid = N_1

Let vol. of standard alkali used for neutralisation of unused acid = V_2 cm^3

Normality of standard alkali = N_2

$$\underbrace{N_1V_1}_{alkali} = \underbrace{N_2V_2}_{acid}$$

Let this volume of v cm^3

Vol. of acid used for neutralisation of ammonia = (V – v) cm^3 of N_1 normality

Ammonia liberated = (V – v) cm^3 of N_1 solution

Now, 1000 cm^3 of 1N NH_3 solution contains nitrogen = 14 g

(V – v) cm^3 of N_1 NH_3 solution contains

nitrogen = $\frac{14(V-v)xN_1}{1000}$ g

Percentage of nitrogen = $\frac{\text{Mass of nitrogen}}{\text{Mass of organic compound}}$ × 100

$$= \frac{14(V-v)xN_1}{1000} \times \frac{100}{w} = \frac{1.4(V-v)xN_1}{w}$$

Percentage of nitrogen in the compoun $= \frac{\text{volume of the acid (cm}^3) \times \text{ normality of the acid} \times 1.4}{\text{mass of organic compound in g}}$

Estimation of Nitrogen by Duma's method

Principle: The organic compound containing nitrogen when heated with excess of copper oxide in the atmosphere of carbon dioxide, yields nitrogen in addition to carbon dioxide and water.

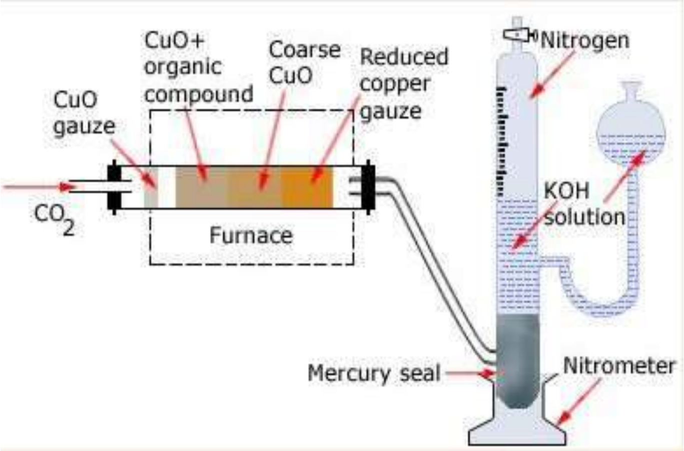
$$C + 2H + 3CuO \rightarrow CO_2 + H_2O + 3Cu$$

$$2N + 2CuO \rightarrow N_2 + \text{oxide of nitrogen}$$

or

$$\underset{Organiccompound}{[C_xH_yN_z]} + \left(2x + \frac{y}{2}\right) CuO \rightarrow \left(2x + \frac{y}{2}\right) Cu + xCO_2 + \frac{y}{2} H_2O + \frac{z}{2} N_2$$

Traces of nitrogen oxides formed during combustion of organic compound are reduced to nitrogen by passing the gaseous mixture over a heated copper gauze. The percentage of nitrogen present in a given organic compound is calculated from the volume of nitrogen collected over potassium hydroxide solution from a known mass of organic compound.



Calculations

Let the mass of organic compound = wg

The volume of nitrogen collected = Vcm^3

Atmospheric pressure from barometer) = P mm of Hg

Room temperature = t^{0}C

Aqueous tension at t^{0}C = a mm of Hg

Pressure of dry nitrogen = (P – a) mm of Hg

Let us first convert the volume of nitrogen to volume at S.T.P.

Experimental conditions	**S.T.P. conditions**
$P_1 = (P - a)$mmHg	$P_2 = 760$ mm
$T_1 = (273 + t)$K	$T_2 = 273$
$V_1 = V$ cm^3	$V_2 = ?$

Applying gas equation $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$V_2 = \frac{P_1V_1T_2}{P_2T_1} = \frac{(P-a)xVx273}{760(273+t)}$ = x cm^3 (say)

Now 22400 cm^3 of N_2 at S.T.P. weight = 28 g

x cm^3 of N_2 at S.T.P. will weigh = $\times \frac{28}{22400}$ xg

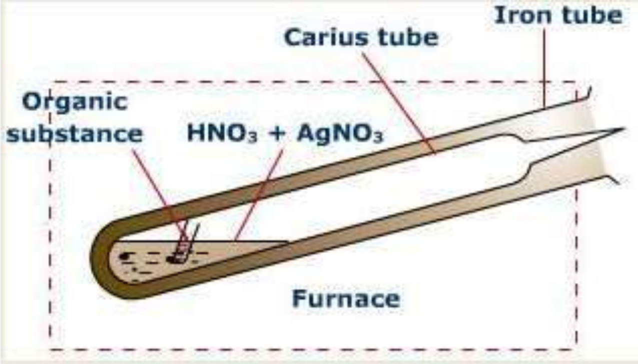
Percentage of nitrogen = $\frac{Massofnitrogen}{Massoforganiccompound}$x 100 = $\frac{28xx100}{22400xw}$

% of N = $\frac{28}{22400} \times \frac{V}{W} \times 100$

Where, V= volume of N_2in nitrometer (in ml) at NTP,

W= Weight of substance taken; % of $N = \frac{1.4 \times N \times V}{W}$

Estimation of Halogen by Carius method



Principle: A known mass of an organic compound is heated with fuming nitric acid and a few crystals of silver nitrate in a sealed tube called Carius tube. The Carbon, hydrogen or sulphur present in the compound will be oxidised to CO_2, H_2O and H_2SO_4 respectively. Halogen is precipitated to give silver halide.

$$\underset{\text{Organic compound}}{[C\ H\ X]} + [O] \xrightarrow[\text{heat}]{\text{fuming HNO}_3} CO_2 + H_2O + HX$$

$$HX + AgNO_3 \rightarrow \underset{\text{Precipitate}}{AgX} + HNO_3$$

- This method does not give satisfactory results in the estimation of iodine as AgI is slightly soluble in nitric acid and iodide may oxidise to iodine to some extent.
- The results of this method is not very accurate in case of polyhalogenated aromatic compounds
- Estimation of fluorine can not be carried out as AgF is soluble in water.

Calculations:

Let the mass of organic compound be w g

Mass of silver halide formed = a g

Now, AgX = X

108 + X parts by weight of silver halide contains X parts by weight of halogen (X is its atomic mass)

(108 + X) g of silver halide give halogen = X

a g of silver halide will give halogen = $\frac{X}{(108+X)}$ × ag

$$\text{Percentage of halogen} = \frac{\text{atomic mass of X}}{\text{molecular mass of AgX}} \times \frac{\text{mass of silver halide in grams}}{\text{mass of organic compound in grams}} \times 100 = \frac{\text{Xxa}}{(108+\text{X})} \times \frac{100}{\text{w}}$$

Here X is the atomic mass of halogen, e.g. Cl = 35.5 , Br = 80 (79.9 exact), I = 127 (126.9 exact)

$$\text{Percentage of chlorine} = \frac{35.5}{(108+35.5)} \times \frac{\text{mass of silver chloride in grams}}{\text{mass of organic compound in grams}} \times 100$$

$$\text{Percentage of bromine} = \frac{80.0}{(108+80)} \times \frac{\text{mass of silver bromide in grams}}{\text{mass of organic compound in grams}} \times 100$$

$$\text{Percentage of iodine} = \frac{127}{(108+127)} \times \frac{\text{mass of silver iodide in grams}}{\text{mass of organic compound in grams}} \times 100$$

Estimation of sulphur by Carius method

Principle: An organic compound is digested with fuming nitric acid in a sealed tube. The sulphur present in the compound is quantitatively oxidised into sulphuric acid. Sulphuric acid so formed is precipitated as barium sulphate by adding excess of barium chloride.

The main reactions are : $S + H_2O + 3O \xrightarrow{HNO_3} H_2SO_4$

$$H_2SO_4 + BaCl_2 \longrightarrow \underset{\text{ppt.}}{BaSO_4}$$

Calculations :

Let the mass of organic compound = w g

Mass of BaSO4 formed = ag

BaSO4 □□137 + 32 + 64 = 32 = 233

233 g of BaSO4 contain sulphur = 32 g

ag of BaSO4 will contain sulphur = $\frac{32\text{xa}}{233}$ g

Percentage of sulphur = $\frac{\text{Mass ofsulphur}}{\text{Massoforganiccompound}} \times 100 = \frac{32a}{233} \times \frac{100}{w}$

$$\text{Percentage of sulphur} = \frac{32}{233} \times \frac{\text{mass of barium sulphate in grams}}{\text{mass of organic compounds in grams}} \times 100$$

Estimation of phosphrous by Carius method

Principle: The phosphorus present in the organic compound is oxidised to orthophosphoric acid by heating with fuming nitric acid. The phosphoric acid so obtained is precipitated as $MgNH_4PO_4$ which on ignition is converted into $Mg_2P_2O_7$.

$$\underset{\text{Organic compound}}{[C, H, P]} + [O] \xrightarrow[\text{nitric acid}]{\text{fuming}} H_3PO_4 + H_2O + CO_2$$

$$H_3PO_4 + \underset{\text{magnesia mixture}}{[NH_4Cl + NH_4OH + MgCl_2]} \rightarrow \underset{\text{white precipitate}}{MgNH_4PO_4}$$

$$2MgNH_4PO_4 \xrightarrow{\text{ignite}} \underset{\text{magnesium pyrophoshate}}{Mg_2P_2O_7} + H_2O + 2NH_3$$

$$\text{Percentage of phosphorus} = \frac{62}{222} \times \frac{\text{mass of } Mg_2P_2O_7 \text{ in grams}}{\text{mass of organic compound in grams}} \times 100$$

Estimation of oxygen

There is no direct method for the estimation of oxygen present in the organic compound. The percentage of oxygen in the compound is generally estimated by difference.

Percentage of oxygen = 100 – [sum of percentage of all other elements present in it]

The percentage of oxygen in an organic compound is usually found by difference between the total percentage composition (100) and the sum of the percentages of all other elements. However, oxygen can also be estimated directly as follows:

A definite mass of an organic compound is decomposed by heating in a stream of nitrogen gas. The mixture of gaseous products containing oxygen is passed over red-hot coke when all the oxygen is converted to carbon monoxide. This mixture is passed through warm Iodine pentoxide (I_2O_5) when carbon monoxide is oxidised to carbon dioxide producing iodine.

Compound $\xrightarrow{\text{heat}}$ O_2 + other gaseous products

$2C + O_2 \xrightarrow{1373\ K} 2CO] \times 5$ … (A)

$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2] \times 2$ … (B)

On making the amount of CO produced in equation (A) equal to the amount of CO used in equation (B) by multiplying the equations (A) and (B) by 5 and 2 respectively; we find that each mole of oxygen liberated from the compound will produce two moles of carbon dioxide.

Thus 88 g carbon dioxide is obtained if 32 g oxygen is liberated.

Let the mass of organic compound taken be mg

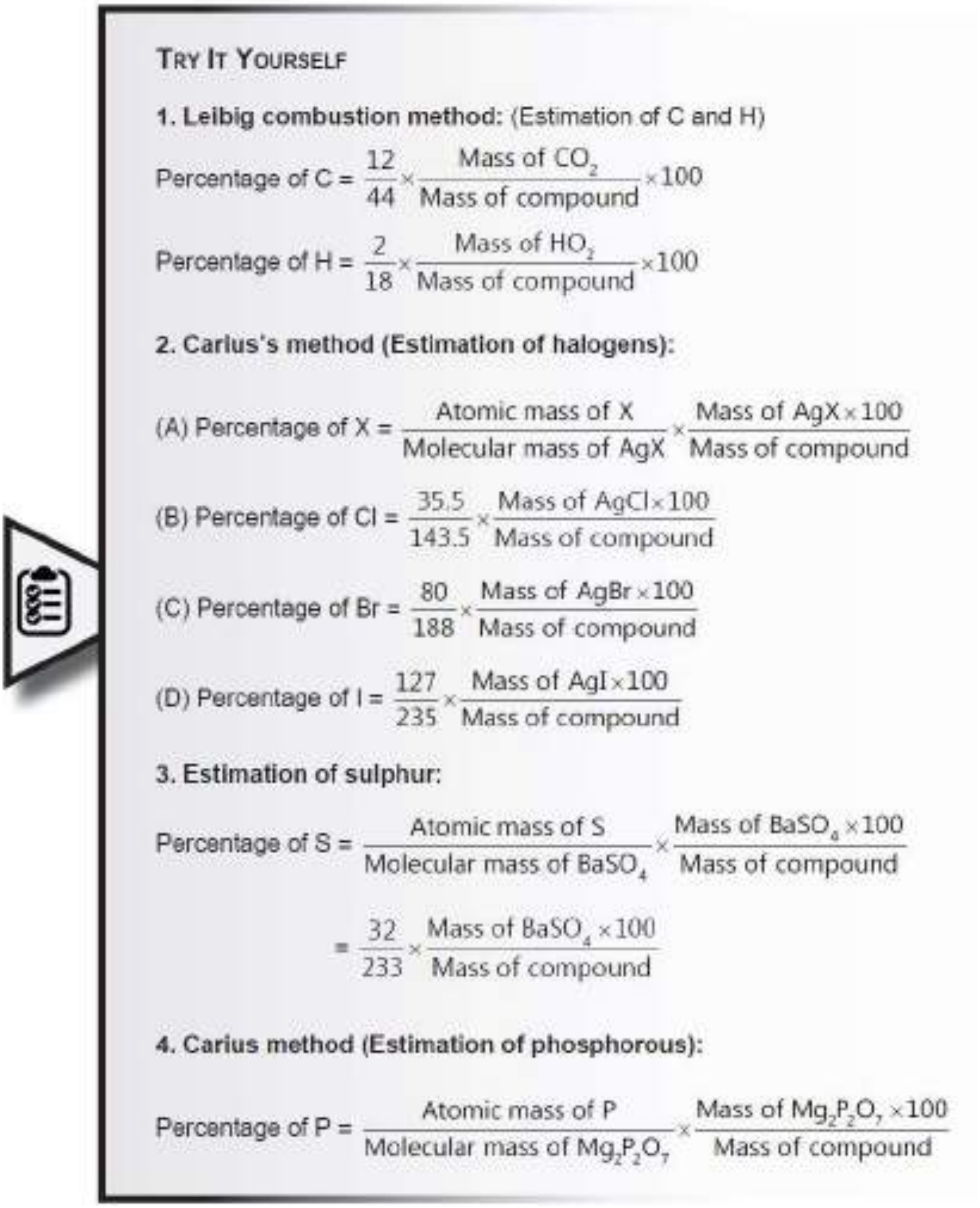
Mass of carbon dioxide produced be m_1g

$\therefore$ m_1g carbon dioxide is obtained from $\frac{32 \times m_1}{88}$ g O_2

$\therefore$ Percentage of oxygen = $\frac{32 \times m_1 \times 100}{88 \times m}\%$

The percentage of oxygen can be derived from the amount of iodine produced also.

Presently, the estimation of elements in an organic compound is carried out by using microquantities of substances and automatic experimental techniques. The elements, carbon, hydrogen and nitrogen present in a compound are determined by an apparatus known as CHN elemental analyser. The analyser requires only a very small amount of the substance (1-3 mg) and displays the values on a screen within a short time. A detailed discussion of such methods is beyond the scope of this book.



TRY IT YOURSELF

1. Leibig combustion method: (Estimation of C and H)

$$\text{Percentage of C} = \frac{12}{44} \times \frac{\text{Mass of } CO_2}{\text{Mass of compound}} \times 100$$

$$\text{Percentage of H} = \frac{2}{18} \times \frac{\text{Mass of } HO_2}{\text{Mass of compound}} \times 100$$

2. Carius's method (Estimation of halogens):

$$\text{(A) Percentage of X} = \frac{\text{Atomic mass of X}}{\text{Molecular mass of AgX}} \times \frac{\text{Mass of AgX} \times 100}{\text{Mass of compound}}$$

$$\text{(B) Percentage of Cl} = \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl} \times 100}{\text{Mass of compound}}$$

$$\text{(C) Percentage of Br} = \frac{80}{188} \times \frac{\text{Mass of AgBr} \times 100}{\text{Mass of compound}}$$

$$\text{(D) Percentage of I} = \frac{127}{235} \times \frac{\text{Mass of AgI} \times 100}{\text{Mass of compound}}$$

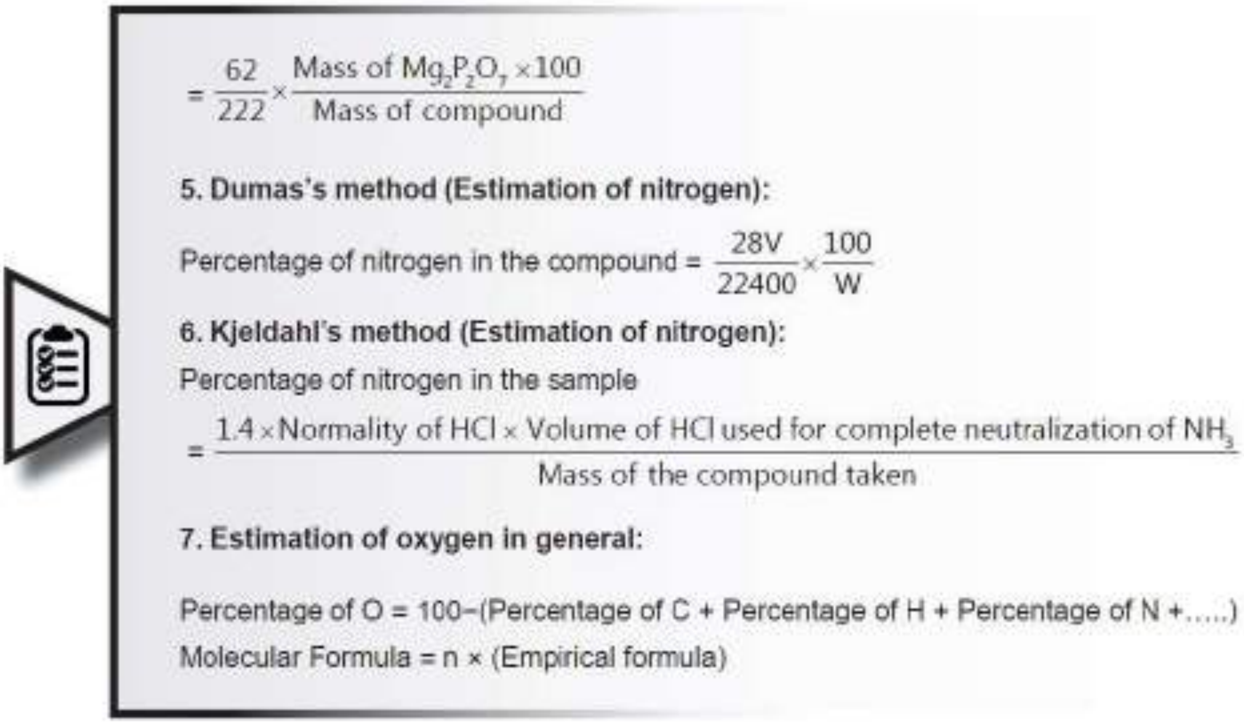
3. Estimation of sulphur:

$$\text{Percentage of S} = \frac{\text{Atomic mass of S}}{\text{Molecular mass of } BaSO_4} \times \frac{\text{Mass of } BaSO_4 \times 100}{\text{Mass of compound}}$$

$$= \frac{32}{233} \times \frac{\text{Mass of } BaSO_4 \times 100}{\text{Mass of compound}}$$

4. Carius method (Estimation of phosphorous):

$$\text{Percentage of P} = \frac{\text{Atomic mass of P}}{\text{Molecular mass of } Mg_2P_2O_7} \times \frac{\text{Mass of } Mg_2P_2O_7 \times 100}{\text{Mass of compound}}$$



$$= \frac{62}{222} \times \frac{\text{Mass of } Mg_2P_2O_7 \times 100}{\text{Mass of compound}}$$

5. Dumas's method (Estimation of nitrogen):

Percentage of nitrogen in the compound = $\frac{28V}{22400} \times \frac{100}{W}$

6. Kjeldahl's method (Estimation of nitrogen):

Percentage of nitrogen in the sample

$$= \frac{1.4 \times \text{Normality of HCl} \times \text{Volume of HCl used for complete neutralization of } NH_3}{\text{Mass of the compound taken}}$$

7. Estimation of oxygen in general:

Percentage of O = 100−(Percentage of C + Percentage of H + Percentage of N +.....)

Molecular Formula = n × (Empirical formula)


HOW TO FOCUS ON STUDIES DURING EXAMS
Turn Off The Phone
Find a Comfortable Place
Make a List
X M H
Learn then
Shut Off Everything
Time Yourself
Clear Your Desk
Award Yourself
Frame a Picture Of Your Goal
?