14. Basic Principles of Organic Chemistry

Can you recall?

- Which is the essential element in all organic compounds ?
- What is the unique property of carbon that makes organic chemistry a separate branch of chemsitry?
- Which classes of organic compounds are often used in our daily diet ?

14.1 Introduction : Of all the elements, only carbon is able to form an immense array of compounds, ranging from methane having one carbon atom to deoxyribonucleic acid (DNA) with billions of carbon atoms. Crude oil is a complex mixture of compounds called hydrocarbons. The pharmaceutical industry is one of the most important chemical industries that provides us medicines which are organic compounds. We need to study the organic compounds for they are interesting in their own right and their functions are greatly important to life.

Try this

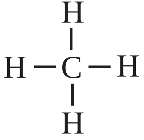
Find out the structures of glucose, vanillin, camphor and paracetamol using internet. Mark the carbon atoms present in them. Assign the hybridization state to each of the carbon and oxygen atom. Identify sigma (σ) and pi (π) bonds in these molecules.

14.2 Structural Representation of organic molecules

Try this

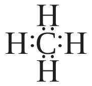
- Draw the structural formula of ethane.
- Draw electron-dot structure of propane.

In the previous standards you learnt how to write structural formulae and electron dot structure of hydrocarbons. Structural formula of a molecule shows all the constituent atoms denoted with their symbols and all covalent bonds therein represented by a dash joining mutually bonded atoms. For example, structural formula of CH_4 is :



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

In the electron dot structures of molecules, the valence electrons of all the atoms are shown as dots around them. Two dots drawn in between two atoms indicate one covalent bond between them. For example, the electron dot structure of methane is as shown here



$$\begin{array}{c} H \\ H:\overset{..}{\underset{..}{C}}:H \\ H \end{array}$$

Electron dot structures are called Lewis structures and the dash formula represents simplified Lewis formula. Chemists have developed some more ways to represent organic molecules fulfilling specific requirements.

14.2.1 Condensed formula :

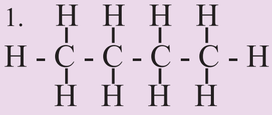
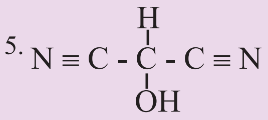
The complete structural formula can be further simplified with hiding of some or all the covalent bonds and indicating the number of identical groups attached to an atom by a subscript. The resulting formula of a compound is known as **condensed formula**. For example : condensed formula of ethane can be written as CH_3 - CH_3 or CH_3CH_3.

14.2.2 Bond line formula or zig-zag formula

In this representation of a molecule symbols of carbon and hydrogen atoms are not written. The lines representing carbon-carbon bonds are drawn in a zig-zag manner and the terminals of the zig-zag line represent methyl groups. The intersection of lines denotes a carbon atom bonded to appropriate number of hydrogen which satisfy the tetravalency of carbon atoms. For example : propane is represented by the zig-zag formula  . However the heteroatoms or hydrogen atoms bonded to heteroatoms are written clearly. For example : The bond line formula of C_2H_5OH is OH.

Try this Complete the Table 14.1

Table 14.1 : Representation of structural formula

Dash formula	Condensed formula A	Condensed formula B	Bond line or zig-zag formula
1.  $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$	$CH_3(CH_2)_2CH_3$	$CH_3-CH_2-CH_2-CH_3$	
2.	....	....	
3.	$CH_3(CH_2)_2CHO$	....	....
4.	$CH_3CH_2CH(CH_3)OH$	....	....
5.  $N\equiv C-\underset{OH}{\overset{H}{C}}-C\equiv N$	....	....	....

14.2.3 Drawing the molecules in three dimensions : Most organic molecules have three dimensional shapes. Four different methods are used to represent three dimensional molecules on plane paper.

I. Wedge formula : The three dimensionl (3-D) view of a molecule can be represented on plane paper by representing the single bonds using solid wedge (◀), dashed wedges (ıııııııı) and normal line (–). A solid wedge is used to represent a bond projecting up from the paper towards the reader. A dashed wedge is used to represent a bond going backward, below the paper away from the reader. Normal lines depict bonds in the plane of the paper. See Fig. 14.1 (for convenience solid and dashed wedge can be replaced by solid/bold and dashed lines.)

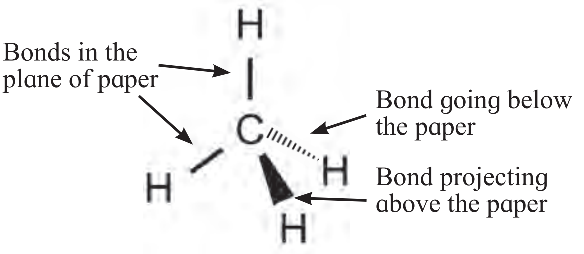


Fig. 14.1 : Wedge formula

II. Fischer projection formula or cross formula : In this representation a three dimensional molecule is projected on plane of paper. A Fischer projection formula can be drawn by visualizing the molecule with its main carbon chain vertical. Each carbon on the vertical chain is represented by a cross. The convention is that the horizontal lines of the cross represent bonds projecting up from the carbon and the vertical lines represent the bonds going below the carbon. Figure 14.2 illustrates the conventions of Fischer projection formula.

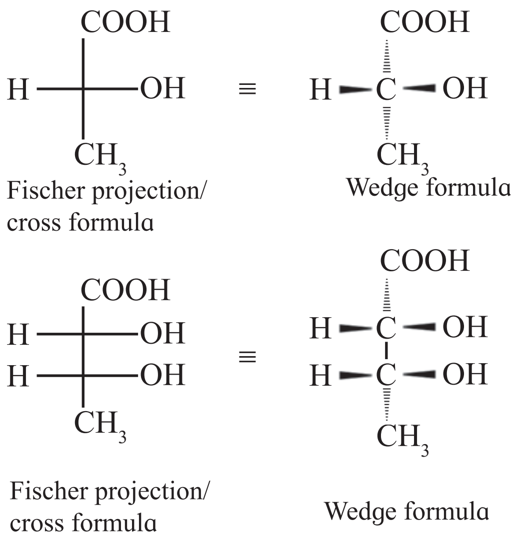


Fig 14.2 : Fischer projection (cross) formula

Fischer projection formula is more commonly used in carbohydrate chemistry

III Newman projection formula : In this method projection of a three dimensional molecule on the plane of the paper is drawn by visualizing the molecule by looking through a

C-C single bond. In such case the C-C is not visible. A convention is followed to represent the front carbon by a point and the rear carbon by a circle around it. The remaining three bonds at each of these two carbons are drawn like spokes of a wheel. Conventionally three bonds at the front carbon are shown to radiate from the centre of the circle (which is the front carbon) and three bonds at the rear carbon are shown to radiate from the circumference of the circle. Figure 14.3 shows two representations of ethane (CH$_3$-CH$_3$) molecule by this method.

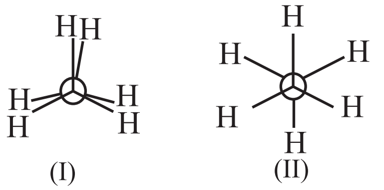


Fig 14.3 : Newman projection formula of ethane

IV. Sawhorse or andiron or perspective formula : In this representation a C-C single bond is represented by a long slanting line. The lower end of the line represents the front carbn and the upper end the rear carbon. The remaining three bonds at the two carbons are shown to radiate from the respective carbons. (As the central C-C bond is drawn rather elongated the bonds radiating from the front and rear carbons do not intermingle.) Figure 14.4 shows two sawhorse (i.e. andiron or pesrpective) formulae for ethane.

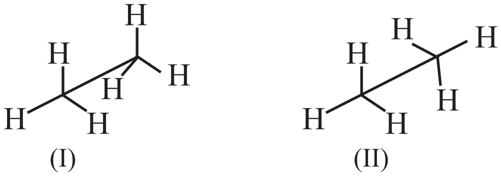


Fig. 14.4 : Sawhorse formula of ethane

Try this

Draw two Newman projection formulae and two sawhorse formulae for the propane molecule.

14.3 Classification of organic compounds :

With so many different molecules to study, it is important to find ways of relating different structures of molecules to their chemical properties. This provides basis for classifying organic compounds. Organic compounds are broadly classified in two ways, on the basis of (i) carbon skeleton and (ii) functional group.

Do you know ?

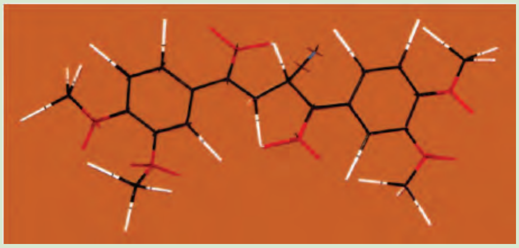
Molecular models (Fig 14.5) are used for an easier visualisation of three dimensional shapes of organic molecules. Three types of molecular models are common.

i. Frame work model : It emphasizes the skeletal pattern of bonds ignoring size of atoms.

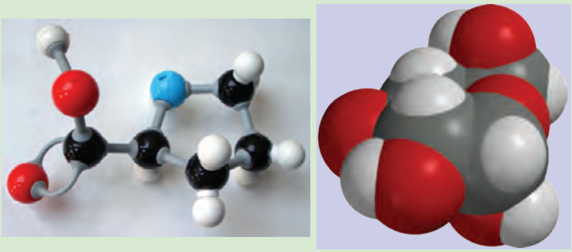
ii. Ball and stick model : In this model a ball represents an atom and stick a bond.

iii. Space filling model : It emphasizes on relative size of each atom. Bonds are not shown. It conveys volume occupied by each atom in the molecule.

Now a days computer graphics can be used for molecular modeling.



(a) Framework model



(b) Ball and stick model (c) Space filling model

Fig. 14.5 Molecular models

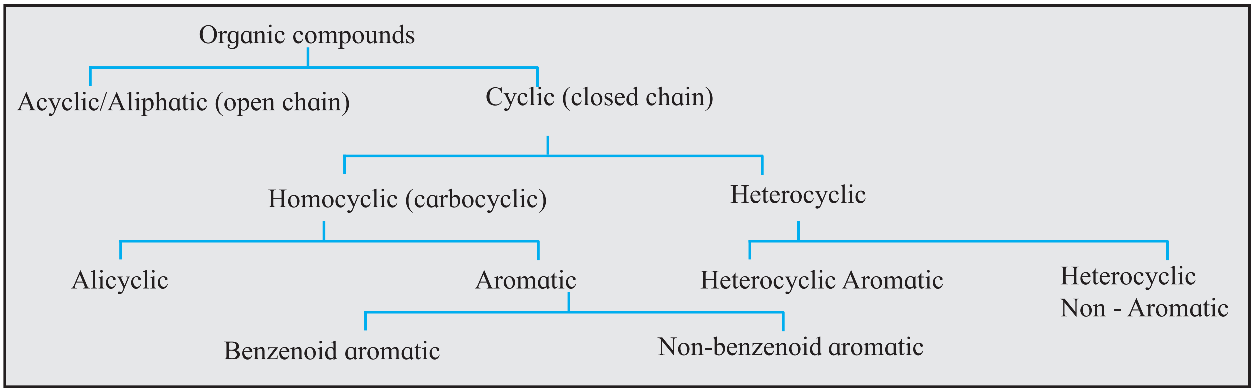


Fig 14.6 : Tree of classification of organic compounds

14.3.1 Classification based on carbon skeleton

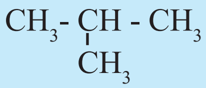
Try this

Construct a model of propane (C_3H_8) molecule. Which atoms are on the surface of the molecule ? Which atoms lie in the core of the molecule ?

The carbon atoms bonded to each other lie in the core of an organic molecule and are described as the carbon skeleton of the molecule. It is the carbon skeleton of a molecule that decides its shape and size. A variety of carbon skeleton are found in different organic compounds and accordingly they are classified into various types as shown in Fig. 14.6

Acyclic or open chain compounds : These are also known as **aliphatic compounds**. Molecules of these compounds have chains of carbon atoms. These may be straight chains formed by carbon atoms bonded to one or two other carbons or branched chains having at least one carbon bonded to three or four other carbons. Table 14.2 shows examples of acyclic compounds.

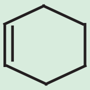
Table 14.2 : Acyclic/Aliphatic compounds

$CH_3-CH_2-CH_3$ propane	$CH_3-CH_2-CH_2-OH$ n - propyl alcohol
straight chain	
 $CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_3$ isobutane Branched chain	

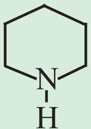
Cyclic compounds : These are compounds in which molecules are formed by joining atoms to form ring like structures.

The compounds in which the ring is made of only carbon atoms are known as **homocyclic** or **carbocyclic** compounds. Carbon is an essential atom in any organic molecule. One or more hydrogen atoms are present in most of the organic molecules. All the other atoms that are found in organic molecules are called **heteroatoms**. The cyclic compounds in which the ring includes one or more heteroatoms (oxygen, nitrogen, sulphur etc.) are known as **heterocyclic** compounds.

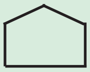
Try this



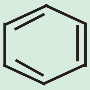
Cyclohexene
(a)



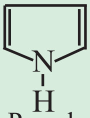
Piperidine
(b)



Cyclopentane
(c)



Benzene
(d)



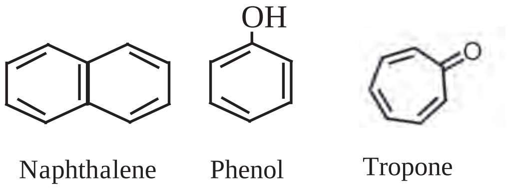
Pyrrole
(e)

i. Observe the compounds (a) to (e)
ii. Identify the compounds those contain a ring of carbon atoms only.
iii. Identify the compounds in which ring contains at least one atom other than carbon.

Alicyclic compounds : These are cyclic compounds exhibiting properties similar to those of aliphatic compounds. For example : Cyclobutane, cyclohexene. See Fig. 14.7.

Aromatic compounds : Aromatic compounds have special stability. Aromatic compounds containing benzene ring are known as benzenoid aromatics while those not containing benzene ring are called non-benzenoid aromatics. For example : benzene, tropone. See Fig. 14.7

(a) Alicyclic compound

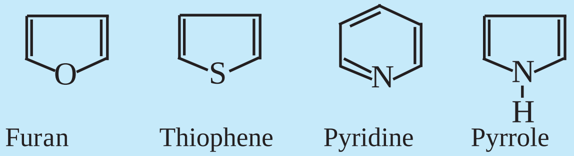


(b) Benzenoid Aromatic compounds **(c) Non benzenoid Aromatic compounds**

Fig. 14.7 : Carbocyclic compounds

Figure 14.8 illustrates some heterocyclic compounds

Heterocyclic aromatic compounds



Heterocyclic non-aromatic compounds

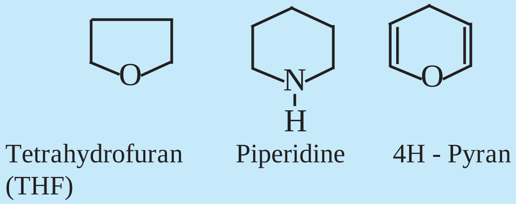


Fig. 14.8 : Heterocyclic compounds

14.3.2 Classification based on functional group :

Can you tell?

Consider the following reaction :

$$2CH_3 - CH_2 - CH_2 - OH + 2Na \longrightarrow 2CH_3 - CH_2 - CH_2 - ONa + H_2$$

Compare the structure of the substrate propanol with that of the product sodium propoxide. Which part of the substrate, the carbon skeleton or the OH group has undergone a change during the reaction ?

A part of an organic molecule which undergoes change as a result of a reaction is called functional group. In the above illustration, OH is the functional group present in propanol. Inspection of structures of various organic compounds tells us that there are a large variety of functional groups present in them. The second method of classification of organic compounds is based on the nature of functional group present. The resulting individual class is called a **family** named after the constituent functional group. For example: family of alcohols, family of halogen derivatives. Table 14.3 shows some common functional groups with their names, bond structures and examples.

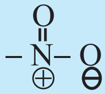
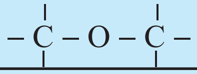
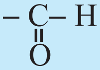
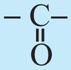
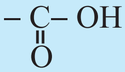
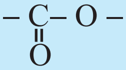
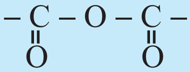
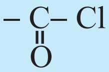
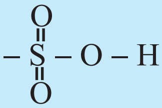
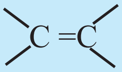
Homologous series : A family of functional group, in turn, comprises different homologous series. A series of compounds of the same family in which each member has the same type of carbon skeleton and functional group, and differs from the next member by a constant difference of one methylene group ($-CH_2-$) in its molecular and structural formula is called as homologous series. An individual member of a homologous series is called **homologue**. All the members, or homologues of such series are represented by the same general formula.

The members of a particular homologous series possess similar chemical properties those very gradually in their physical properties namely, melting point, boiling point, density, solubility, etc. Table 14.4 illustrates this with the help of homologous series of straight chain aldehydes having general formula $C_nH_{2n}O$.

Do you know ?

- **Aliphatic compounds** are named so because of their attraction towards fats.
- **Aromatic compounds** are named so because some of these compounds discovered in early 19th century possessed aroma.

Table 14.3 : Functional groups in organic compounds

Sr. No.	Name of the family/ functional group	structure of the functional group	Example
1.	Halide	$-X$	CH_3Br methyl bromide
2.	Cyanide (or Nitrile)	$-C\equiv N$	CH_3CN methyl cyanide (or acetonitrile)
3.	Isocyanide	$-N^{\oplus}\equiv C^{\ominus}$	CH_3NC methyl isocyanide
4.	Nitro compound/group	 $-\overset{\overset{O}{\parallel}}{\underset{\oplus}{N}}-\underset{\ominus}{O}$	CH_3NO_2 Nitromethane
5.	Alcohol	$-OH$	CH_3OH methyl alcohol
6.	Phenol	$Ar-OH$	C_6H_5OH Phenol
7.	Primary amine	$-NH_2$	CH_3NH_2 methyl amine
8.	Secondary amine	$-NH-$	$CH_3-NH-CH_3$ Dimethyl amine
9.	Tertiary amine	 $-\underset{\mid}{N}-$	$(CH_3)_3N$ Trimethyl amine
10.	Ether	 $-\overset{\mid}{\underset{\mid}{C}}-O-\overset{\mid}{\underset{\mid}{C}}-$	CH_3-O-CH_3 Dimethyl ether
11.	Aldehyde	 $-\underset{\underset{O}{\parallel}}{C}-H$	CH_3CHO Acetaldehyde
12.	Ketone	 $-\underset{\underset{O}{\parallel}}{C}-$	$CH_3-CO-CH_3$ Acetone
13.	Carboxylic acid	 $-\underset{\underset{O}{\parallel}}{C}-OH$	CH_3-COOH Acetic acid
14.	Ester	 $-\underset{\underset{O}{\parallel}}{C}-O-$	$CH_3-COOC_2H_5$ Ethyl acetate
15.	Amide	 $-\underset{\underset{O}{\parallel}}{C}-NH_2$	CH_3-CONH_2 Acetamide
16.	Secondary amide	 $-\underset{\underset{O}{\parallel}}{C}-NH-$	$CH_3-CO-NH-CH_3$ N-methyl acetamide
17.	Tertiary amide	 $-\underset{\underset{O}{\parallel}}{C}-\underset{\mid}{N}-$	$CH_3-CO-N(CH_3)_2$ N, N - dimethyl acetamide
18.	Acid anhydride	 $-\underset{\underset{O}{\parallel}}{C}-O-\underset{\underset{O}{\parallel}}{C}-$	$CH_3-CO-O-CO-CH_3$ Acetic anhydride
19.	Acyl chloride	 $-\underset{\underset{O}{\parallel}}{C}-Cl$	CH_3-COCl Acetyl chloride
20.	Sulphonic acid	 $-\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{S}}-O-H$	$C_6H_5SO_3H$ Benzene sulphonic acid
21.	Alkene/Olfin	 $>C=C<$	$CH_2=CH_2$ Ethylene
22.	Alkyne	$-C\equiv C-$	$CH\equiv CH$ Acetylene
23.	Alkane	No functional group	CH_3 - CH_3 Ethane

Problem 14.1 : Alkanes constitute a homologous series of straight chain saturated hydrocarbons. Write down the structural formulae of the first five homologues of this series. Write their molecular formulae and deduce the general formula of such homologous series.

Solution :

The first five homologues are generated by adding one - CH_2 - at a time, starting with the first homologue CH_4.

$$\underset{\text{1st homologue}}{CH_4} \xrightarrow{\text{add - }CH_2\text{ -}} \underset{\text{2nd homologue}}{CH_3 - CH_3} \xrightarrow{\text{add - }CH_2\text{ -}} \underset{\text{3rd homologue}}{CH_3 - CH_2 - CH_3}$$

$$\xrightarrow{\text{add - }CH_2\text{ -}} \underset{\text{4th homologue}}{CH_3 - CH_2 - CH_2 - CH_3} \xrightarrow{\text{add - }CH_2\text{ -}} \underset{\text{5th homologue}}{CH_3 - CH_2 - CH_2 - CH_2 - CH_3}$$

By counting carbon and hydrogen atoms in the five homologues we get their molecular formulae as CH_4, C_2H_6, C_3H_8, C_4H_{10} and C_5H_{12}. Comparing these molecular formulae, the following general formula is deduced : $C_n H_{2n+2}$.

Problem 14.2 : Write down structural formulae of (a) the third higher and (b) the second lower homologue of CH_3CH_2COOH.

Solution :

a. structural formula of the third higher homologue is obtained by adding three – CH_2 – units to the carbon chain of given structure.

$$CH_3 - CH_2 - COOH \xrightarrow[-\,CH_2\,-\text{ units}]{\text{add three}} \underset{\text{third higher homologue}}{CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - COOH}$$

b. structural formula of the second lower homologue is obtained by removing two – CH_2 – units from the carbon chain of the given structure.

$$CH_3 - CH_2 - COOH \xrightarrow[\substack{\text{two}\\ -\,CH_2\,-\text{ units}}]{\text{remove}} H - COOH$$

Remember

The saturated (sp^3) carbons in a molecule are labelled as primary, secondary, tertiary and quaternary in accordance with the number of other carbons bonded to it by single bonds.

- **Primary carbon** (1^0) is bonded to only one other carbon. For example: both the carbons in ethane CH_3-CH_3.
- **Secondary carbon** (2^0) is bonded to two other carbons. For example: the middle carbon in propane CH_3-CH_2-CH_3
- **Tertiary Carbon** (3^0) is bonded to three other carbons. For example: the middle carbon in isobutane $CH_3CH(CH_3)_2$.
- **Quaternary Carbon** (4^0) in bonded to four other carbons. For example: the middle carbon in neo-pentane $C(CH_3)_4$

14.4 Nomenclature of organic compounds

14.4.1 Common/trivial names

As organic chemistry developed, attempts were made to devise a name for every organic compound. These old names are now reffered to as common / trivial names. Common name of a compound usually has some history behind and usually accepted on account of its long usage. Though a systematic method of nomenclature was developed later, common names are still useful and in many cases can not be avoided, particularly for commonly used commercial organic compounds. Stem names of certain common organic compounds are given in Table 14.5.

Table 14.4 : Homologous series of straight chain aldehydes

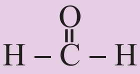
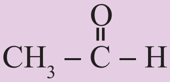
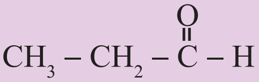
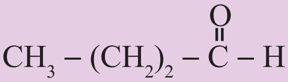
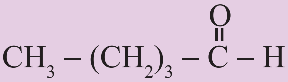
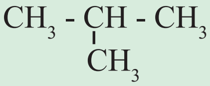
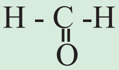
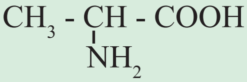
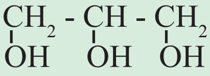
Name	Number of carbons	Molecular formula $C_nH_{2n}O$	Condensed structural formula	Boiling point
Formaldehyde	n = 1	CH_2O	 $H-\overset{O}{\overset{\|}{C}}-H$	- 21^{0}C
Acetaldehyde	n = 2	C_2H_4O	 $CH_3-\overset{O}{\overset{\|}{C}}-H$	21^{0}C
Propionaldehyde	n = 3	C_3H_6O	 $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$	48 ^{0}C
Butyraldehyde	n = 4	C_4H_8O	 $CH_3-(CH_2)_2-\overset{O}{\overset{\|}{C}}-H$	75^{0}C
Valeraldehyde	n = 5	$C_5H_{10}O$	 $CH_3-(CH_2)_3-\overset{O}{\overset{\|}{C}}-H$	103^{0}C

Table 14.5 : Trivial names of some organic compounds

Structural formula	Common Name/ Trivial Name
$CH_3 - CH_2 - CH_2 - CH_3$	n - Butane
 $CH_3 - \underset{\underset{CH_3}{\vert}}{CH} - CH_3$	Isobutane
$C_6H_5NH_2$	Aniline
 $CH_3 - \underset{\underset{OH}{\vert}}{CH} - COOH$	Lactic acid
$CHCl_3$	Chloroform
$CH \equiv CH$	Acetylene
$C_2H_5 - O - C_2H_5$	Diethyl ether
CH_3COOH	Acetic acid
 $H - \underset{\underset{O}{\|}}{C} -H$	Formaldehyde
 $CH_3 - \underset{\underset{NH_2}{\vert}}{CH} - COOH$	Glycine
 $\underset{\underset{OH}{\vert}}{CH_2} - \underset{\underset{OH}{\vert}}{CH} - \underset{\underset{OH}{\vert}}{CH_2}$	Glycerol

14.4.2 IUPAC Nomenclature : With the rapidly growing number of organic compounds with increasingly complicated structures it becomes difficult to name them. Some confusion can be created when the same compound is named differently. In due course of time **International Union of Pure and Applied Chemistry (IUPAC)** was founded (1919) and a systematic method of nomenclature for organic compounds was developed under its banner. This system of nomenclature is accepted and widely used all over the world today. This system gives the unique name to each organic compound.

To arrive at the IUPAC name of an organic compound, its structure is considered to be made of three main parts : parent hydrocarbon, branches and functional groups. The IUPAC names of a compound are obtained by modifying the name of its parent hydrocarbon further incorporating names of the branches and functional groups as prefix and suffix. For doing this, certain rules were formulated by IUPAC. We consider the IUPAC rules for naming saturated and unsaturated hydrocarbons, simple monocyclic hydrocarbons, simple mono and polyfunctional compounds and substituted benzenes in the following.

14.4.3 IUPAC names of straight chain alkanes : The homologous series of straight chain alkanes forms the parent hydrocarbon part of the IUPAC names of aliphatic compounds. The IUPAC name of a straight chain alkane is derived from the number of carbon atoms it contains. Table 14.6 gives the list of the IUPAC names of first twenty straight chain alkanes. It may be noted that the stem names of first four members are accepted as their IUPAC names.

Table 14.6 : IUPAC names of the first twenty alkanes

Number of carbons	Molecular formula	Condensed formula	IUPAC name
1	CH_4	CH_4	Methane
2	C_2H_6	CH_3 - CH_3	Ethane
3	C_3H_8	CH_3 - CH_2- CH_3	Propane
4	C_4H_{10}	CH_3 - $(CH_2)_2$- CH_3	Butane
5	C_5H_{12}	CH_3 - $(CH_2)_3$- CH_3	Pentane
6	C_6H_{14}	CH_3 - $(CH_2)_4$- CH_3	Hexane
7	C_7H_{16}	CH_3 - $(CH_2)_5$- CH_3	Heptane
8	C_8H_{18}	CH_3 - $(CH_2)_6$- CH_3	Octane
9	C_9H_{20}	CH_3 - $(CH_2)_7$- CH_3	Nonane
10	$C_{10}H_{22}$	CH_3 - $(CH_2)_8$- CH_3	Decane
11	$C_{11}H_{24}$	CH_3 - $(CH_2)_9$- CH_3	Undecane
12	$C_{12}H_{26}$	CH_3 - $(CH_2)_{10}$- CH_3	Dodecane
13	$C_{13}H_{28}$	CH_3 - $(CH_2)_{11}$- CH_3	Tridecane
14	$C_{14}H_{30}$	CH_3 - $(CH_2)_{12}$- CH_3	Tetradecane
15	$C_{15}H_{32}$	CH_3 - $(CH_2)_{13}$- CH_3	Pentadecane
16	$C_{16}H_{34}$	CH_3 - $(CH_2)_{14}$- CH_3	Hexadecane
17	$C_{17}H_{36}$	CH_3 - $(CH_2)_{15}$- CH_3	Heptadecane
18	$C_{18}H_{38}$	CH_3 - $(CH_2)_{16}$- CH_3	Octadecane
19	$C_{19}H_{40}$	CH_3 - $(CH_2)_{17}$- CH_3	Nonadecane
20	$C_{20}H_{42}$	CH_3 - $(CH_2)_{18}$- CH_3	Icosane

14.4.4 IUPAC names of branched saturated hydrocarbons

The branches or the side chains in saturated hydrocarbons are alkyl groups or alkyl substituents. Before looking at the IUPAC nomenclature of the branched saturated hydrocarbons, we look at the naming of alkyl groups.

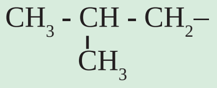
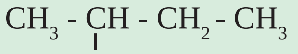
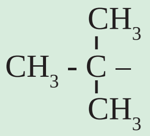
Alkyl groups : An alkyl group may be a straight or branched chain. **A straight chain alkyl group** is generated by removing one hydrogen atom from the terminal carbon of an alkane molecule and is named by replacing 'ane' of the alkane by 'yl'. Some straight chain alkyl groups are listed in Table 14.7.

Table 14.7 : Straight chain alkyl groups

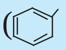
Alkane		Alkyl group		
Molecular formula	IUPAC name	Condensed formula	IUPAC name	Abbridged name
CH_4	methane	- CH_3	methyl	Me
C_2H_6	ethane	- CH_2- CH_3	ethyl	Et
C_3H_8	propane	- $(CH_2)_2$- CH_3	propyl	Pr
C_4H_{10}	butane	- $(CH_2)_3$- CH_3	butyl	Bu
$C_{10}H_{22}$	decane	- $(CH_2)_9$- CH_3	decyl	-

A branched chain alkyl group is obtained by removing a hydrogen atom from any one of the nonterminal carbons of an alkane or any hydrogen atom from a branched alkane. Stem names of branched alkyl groups containing upto four carbons are used in IUPAC names (see Table 14.8)

Table 14.8 : Trivial names of small branched alkyl groups

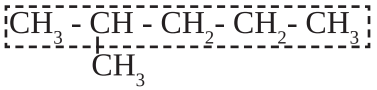
Structural formula	Name
 $CH_3-\underset{\vert}{CH}-CH_3$	Isopropyl
 $CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-$	Isobutyl
 $CH_3-\underset{\vert}{CH}-CH_2-CH_3$	sec-Butyl
 $CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-$	tert-Butyl

Do you know ?

The group C_6H_5- () is named as phenyl group and abbriviated as Ph.

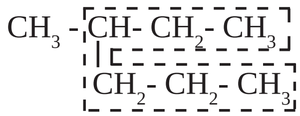
Rules for IUPAC nomenclature of branched saturated hydrocarbons :

1. Select the longest continuous chain of carbon atoms to be called the parent chain. All other carbon atoms not included in this chain constitute side chains or branches or alkyl substitutents. For example :

i. 

$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-CH_2-CH_3$

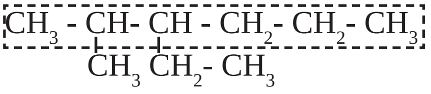
Parent chain has five carbon atoms and - CH_3 group is the alkyl sustituent.

ii. 

$CH_3-\underset{\displaystyle CH_2-CH_2-CH_3}{\underset{\vert}{CH}}-CH_2-CH_3$

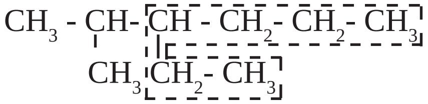
Parent chain has six 'C' atoms and methyl group is the alkyl substituent.

If two chains of equal length are located, the one with maximum number of substituents is selected as the parent chain. For example :

i. 

$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-\underset{\displaystyle CH_2-CH_3}{\underset{\vert}{CH}}-CH_2-CH_2-CH_3$

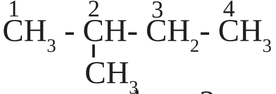
Parent chain hexane with two alkyl substituents (correct parent chain)



$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-\underset{\displaystyle CH_2-CH_3}{\underset{\vert}{CH}}-CH_2-CH_2-CH_3$

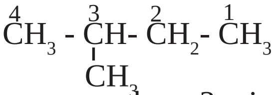
Parent chain hexane with one alkyl substituent (incorrect chain)

2. The parent chain is numbered from one end to the other to locate the position, called locant number of the alkyl substitutent. The **numbering** is done in that direction which will result in lowest possible locant numbers .



$\overset{1}{CH_3}-\overset{2}{\underset{\displaystyle CH_3}{\underset{\vert}{CH}}}-\overset{3}{CH_2}-\overset{4}{CH_3}$

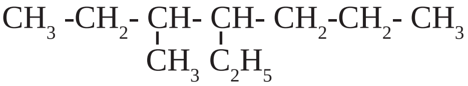
(locant number : 2 ~ proper numbering)



$\overset{4}{CH_3}-\overset{3}{\underset{\displaystyle CH_3}{\underset{\vert}{CH}}}-\overset{2}{CH_2}-\overset{1}{CH_3}$

(locant number : 3 ~ improper numbering)

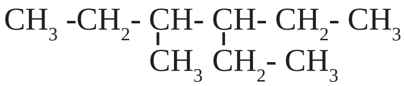
3. Names of the alkyl substituents are added as **prefix** to the name of the parent alkane. Different alkyl substituents are listed in alphabetical order with each substituent name preceded by the appropriate **locant number**. The name of the substituent is separated from the locant number by **a hyphen**.



$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-\underset{\displaystyle C_2H_5}{\underset{\vert}{CH}}-CH_2-CH_2-CH_3$

The name is 4 - ethyl-3-methylheptane and not 3-methyl-4-ethylheptane.

4. When both the numberings give the same set of locants, that numbering is chosen which gives **smaller locant** to the substituent having **alphabetical priority**. Thus the IUPAC name of the following structure is 3-ethyl-4-methylhexane and **not** 3-methyl-4-ethylhexane.

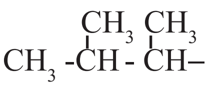


$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-\underset{\displaystyle CH_2-CH_3}{\underset{\vert}{CH}}-CH_2-CH_3$

5. If two or more identical substituents are present the prefix **di** (for 2), **tri** (for 3), tetra (for 4) and so on, are used before the name of the substituent to indicate how many identical substituents are there. The locants of identical substituents are listed together, separated by **commas**.

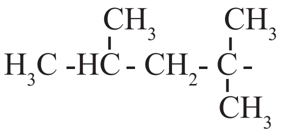
There must be as many numbers in the name as the substituents. A digit and an alphabet is separated by hyphen. The prefixes di, tri, tetra, sec and tert are ignored in alphabetizing the substituent names. Substituent and parent hydrocarbon names are joined into **one word** (note that isopropyl comes before methyl).

6. Branched alkyl group having no accepted trivial name is named with the longest continuous chain begining at the point of attachment as the base name. Carbon atom of this group attached to parent chain is numbered 1. Name of such substituent is enclosed in bracket. For example :



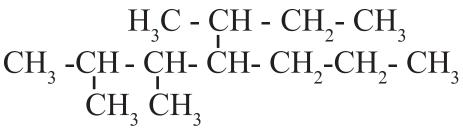
$CH_3-\overset{CH_3}{\overset{|}{C}H}-\overset{CH_3}{\overset{|}{C}H}-$

1, 2 di-methylpropyl



$H_3C-H\overset{CH_3}{\overset{|}{C}}-CH_2-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-$

1, 1, 3- trimethylbutyl



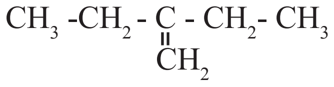
$CH_3-\underset{CH_3}{\underset{|}{C}H}-\underset{CH_3}{\underset{|}{C}H}-\overset{H_3C-CH-CH_2-CH_3}{\overset{|}{C}H}-CH_2-CH_2-CH_3$

2, 3 - dimethyl - 4 - (1methylpropyl)heptane

14.4.5 IUPAC nomenclature of unsaturated hydrocarbons (Alkenes and Alkynes)

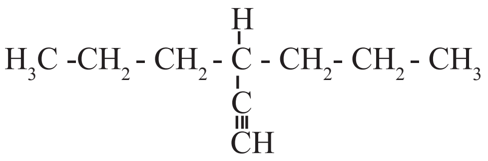
While writing IUPAC names of alkenes and alkynes following rules are to be followed in addition to rules already discussed.

1. The longest continuous **chain must include** carbon-carbon **multiple bond**. Thus the longest continuous chains in I and II contain four and six carbons, respectively.



$CH_3-CH_2-\underset{CH_2}{\underset{\|}{C}}-CH_2-CH_3$

(I)



$H_3C-CH_2-CH_2-\overset{H}{\overset{|}{\underset{\underset{CH}{\underset{|||}{C}}}{\underset{|}{C}}}}-CH_2-CH_2-CH_3$

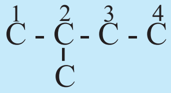
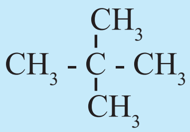
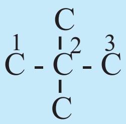
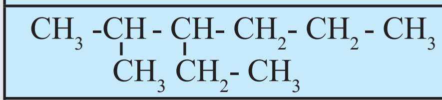
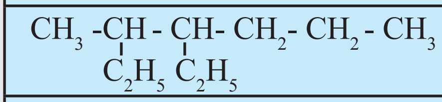
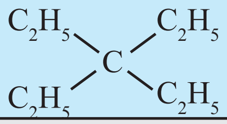
(II)

2. Numbering of this chain must be done such that carbon-carbon **multiple bond** has the **lowest possible locant** number.

Proper numbering	improper numbering
$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H_2$	$\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H=\overset{4}{C}H_2$
$H\overset{1}{C}\equiv\overset{2}{C}-\overset{3}{C}H_2-\overset{4}{C}H_3$	$H\overset{4}{C}\equiv\overset{3}{C}-\overset{2}{C}H_2-\overset{1}{C}H_3$

Problem 14.3 :

Complete the following table

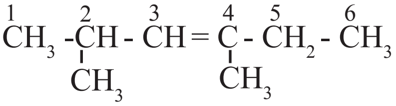
Structural formula	Numbering	Prefix	IUPAC Name
 $CH_3-\underset{CH_3}{\underset{\vert}{C}H}-CH_2-CH_3$	 $\overset{1}{C}-\underset{C}{\underset{\vert}{\overset{2}{C}}}-\overset{3}{C}-\overset{4}{C}$	2 - methyl	2 - methylbutane
 $CH_3-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-CH_3$	 $\overset{1}{C}-\overset{C}{\overset{\vert\,2}{\underset{C}{\underset{\vert}{C}}}}-\overset{3}{C}$	2, 2 - dimethyl	2, 2-dimethylpropane
 $CH_3-\underset{CH_3}{\underset{\vert}{C}H}-\underset{CH_3}{\underset{\vert}{C}H}-\underset{CH_3}{\underset{\vert}{C}H_2}$			
 $CH_3-\underset{CH_3}{\underset{\vert}{C}H}-\underset{CH_2-CH_3}{\underset{\vert}{C}H}-CH_2-CH_2-CH_3$			
 $CH_3-\underset{C_2H_5}{\underset{\vert}{C}H}-\underset{C_2H_5}{\underset{\vert}{C}H}-CH_2-CH_2-CH_3$			
			

3. The ending 'ane' of alkane is replaced by 'ene' for an alkene and '**yne**' for an alkyne.

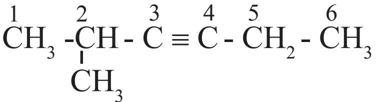
4. Position of carbon atom from which **multiple bond** starts is indicated by smaller locant number of two multiply bonded carbons before the ending 'ene' or 'yne' For example :

$CH_3\text{-}CH_2\text{-}CH=CH_2$	$HC\equiv C\text{-}CH_2\text{-}CH_3$
but-1-ene	but-1-yne

5. If the multiple bond is equidistant from both the ends of a selected chain then carbon atoms are numbered from that end which is nearer to **first branching**. For example :



$\overset{1}{CH_3}\text{-}\underset{CH_3}{\overset{2}{C}H}\text{-}\overset{3}{C}H=\underset{CH_3}{\overset{4}{C}}\text{-}\overset{5}{C}H_2\text{-}\overset{6}{C}H_3$



$\overset{1}{CH_3}\text{-}\underset{CH_3}{\overset{2}{C}H}\text{-}\overset{3}{C}\equiv\overset{4}{C}\text{-}\overset{5}{C}H_2\text{-}\overset{6}{C}H_3$

6. If the parent chain contains two double bonds or two triple bonds, then it is named as **diene** or **diyne**. In all these cases 'a' of 'ane' (alkane) is retained .

$$CH_3\text{ - }CH=CH\text{ - }CH=CH_2$$

penta-1, 3-diene

$$CH_3\text{ - }C\equiv C-CH_2-C\equiv C-H$$

hexa - 1, 4 -diyne

7. If the parent chain contains both double and triple bond, then carbon atoms are numbered from that end where multiple bond is nearer. Such systems are named by putting '**en**' ending first followed by '**yne**'. The number indicating the location of multiple bond is placed before the name.

$$CH_2=CH\text{ - }C\equiv C-CH_3$$

pent-1-en-3-yne

$$H\text{ - }C\equiv C-CH_2-CH=CH_2-CH_3$$

hex-4-en-1-yne

8. If there is **a tie** between a double bond and a triple bond, the double bond gets the lower number.

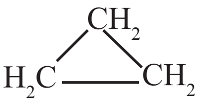
$H\text{ - }C\equiv C-CH_2-CH=CH_2$

pent-1-en-4-yne

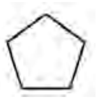
14.4.6 IUPAC Names of simple monocyclic hydrocarbons :

A saturated monocyclic hydrocarbon is named by attaching prefix '**cyclo**' to the name of the corresponding open chain alkane.

For example :



Cyclopropane



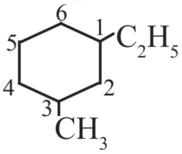
Cyclopentane

An unsaturated monocyclic hydrocarbon is named by substituting '**ene**', '**yne**' etc. for 'ane' in the name of corresponding cycloalkane. For example:

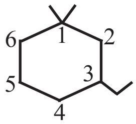
Cyclohexene

Cyclopentene

If side chains are present then the above discussed rules are applied. **Numbering** of the ring carbon is **started from a side chain**. For example :



1 - ethyl - 3 - methylcyclohexane

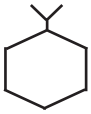


3 - ethyl - 1, 1 - dimethylcyclohexane

If alkyl groups contain greater number of carbon atoms than the ring, the compound is named as derivative of alkane. Ring is treated as substituent. For example :

$CH_3\text{ -}CH_2\text{ - }CH\text{ - }CH_2\text{ - }CH_2\text{ - }CH_3$

3 - cyclopropylhexane



isopropylcyclohexane

14.4.7 IUPAC nomenclature of compounds containing one or more functional groups :

The IUPAC names of compounds containing one or more functional groups include the names of the functional groups as prefix and/ or suffix. Table 14.8 shows how names of functional groups are modified when included as prefix or suffix in the IUPAC name. Some functional groups appear only as prefixes and are shown in Table 14.9. (a and b)

Table 14.9 : Modified names of functional groups as in IUPAC nomenclature

a. Functional groups appearing prefix and suffix

Functional group	Prefix	Suffix
$-COOH$	carboxy	– oic acid
$-COOR$	alkoxycarbonyl	– oate
$-COCl$	chlorocarbonyl	– oyl chloride
$-CONH_2$	carbamoyl	– amide
$-CN$	cyano	– nitrile
$-CHO$	formyl	– al
$-CO-$	oxo	– one
$-OH$	hydroxy	– ol
$-NH_2$	amino	– amine

b. Functional groups appearing only as prefix

Functional group	Prefix
$-NO_2$	nitro
$-X$ ($-F$, $-Cl$, $-Br$, $-I$.)	halo (fluro, chloro, bromo, iodo)
$-OR$ ($-OCH_3$, $-OC_2H_5$, etc)	alkoxy (methoxy, ethoxy, etc.)

Naming monofunctional compounds : When a molecule contains only one functional group, the longest carbon chain containing that functional group is identified as the parent chain and numbered so as to give the smallest locant number to the carbon bearing the functional group. The parent name is modified by applying appropriate suffix. Location of the functional group is indicated where necessary and when it is NOT '1'.

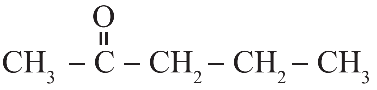
For example :

$CH_3-CH_2-CH_2-COOH$

butanoic acid (No need to mention -1-)

$CH_3-CH_2-C\equiv N$

propanenitrile (No need to mention -1-)



$CH_3-\overset{\overset{\large O}{\|}}{C}-CH_2-CH_2-CH_3$

pentan-2-one (Necessary to mention -2-)

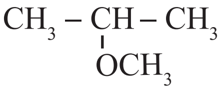
$CH_3-\overset{\overset{\large O}{\|}}{C}-CH_2-CH_3$

butanone (No need to mention -2-)

When the functional group cannot be used as suffix, and can be only the prefix, the molecule is named as parent alkane carrying the functional group as substituent at specified carbon. For example :

$H_3C-CH_2-CH_2-NO_2$

1 - Nitropropane



$CH_3-\underset{\underset{\large OCH_3}{|}}{CH}-CH_3$

2- Methoxypropane

Polyfunctional compounds : The organic compounds possessing two or more functional groups (same or different) in their molecules are called polyfunctional compounds. When there are two or more different functional groups, one of them is selected as the **principal functional group** and the others are considered as substituents. The principal functional group is used as suffix of the IUPAC name while the other substituents are written with appropriate perfixes. The principal functional group is decided on the basis of the following order of priority.

$-COOH > -SO_3H > -COOR > -COCl > -CONH_2 > -CN > -CHO > \rangle C=O > -OH > -NH_2 > \overset{|}{\underset{|}{C}} = \overset{|}{\underset{|}{C}} > -C\equiv C-$

IUPAC Rules for naming mono or polyfunctional compounds

i. The longest carbon **chain containing** or bearing the single or the **principal functional group** is identified as parent chain. Ether is named as alkoxyalkane. While naming it, the larger alkyl group is chosen as parent chain.

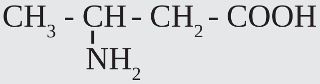
Numbering of parent chain is done so as to give the **lowest** possible **locant** numbers to the carbon atom of this functional group.

ii. The name of the parent hydrocarbon is modified adequately with **appropriate suffix** in accordance with the single/principal **functional group**.

iii. Names of the **other functional groups** (if any) are attached to this modified name as **prefixes**. The locant numbers of all the functional groups are indicated before the corresponding suffix/prefix. The carbon atom in - COOR, - COCl, -$CONH_2$, - CN and - CHO is C - 1 by rule and therefore, is not mentioned in the IUPAC name.

Problem 14.4 : Write IUPAC names for the following structures :

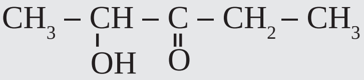
i. 
$CH_3 - \underset{\overset{|}{OH}}{CH} - \underset{\overset{\|}{O}}{C} - CH_2 - CH_3$

ii. 
$CH_3 - \underset{\overset{|}{NH_2}}{CH} - CH_2 - COOH$

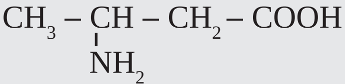
iii. 
$CH_3 - \underset{\overset{|}{OH}}{CH} - CH_2 - OH$

iv. $CH_2 = CH - CH = CH_2$

Solution :

i. 
$CH_3 - \underset{\overset{|}{OH}}{CH} - \underset{\overset{\|}{O}}{C} - CH_2 - CH_3$

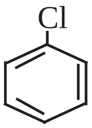
Here the principal functional group, ketone is located at the C-3 on the five carbon chain. The -OH group, the hydroxyl substituent is at C-2. Therefore the IUPAC name is 2-hydroxypentan-3-one.

ii. 
$CH_3 - \underset{\overset{|}{NH_2}}{CH} - CH_2 - COOH$

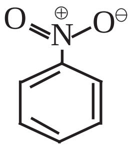
Here the principal functional group is carboxylic acid. The amino substituent is located at C-3 on four carbon chain. Therefore the IUPAC name 3-aminobutanoic acid.

14.4.8 IUPAC nomenclature of substitued benzene

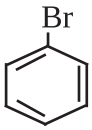
I. Monosubstituted benzene : The IUPAC name of a monosubstituted benzene is obtained by placing the name of substituent as prefix to the parent skeleton which is benzene. For example :



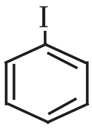
Chlorobenzene



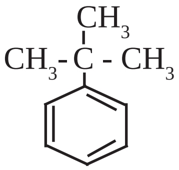
Nitrobenzene



Bromobenzene

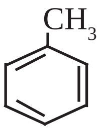


Iodobenzene

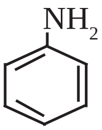


tert- Butylbenzene

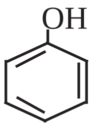
Some monosubstituted benzenes have trivial names which may show no resemblance with the name of the attached substituent group. For example, methylbenzene is known as **toluene**, aminobenzene as aniline, hydroxybenzene as phenol and so on. The common names written in the bracket are also used universally and accepted by IUPAC.



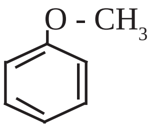
Methylbenzene
(Toluene)



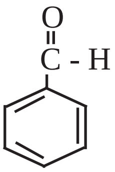
Aminobenzene
(Aniline)



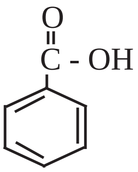
Hydroxybenzene
(Phenol)



Methoxybenzene
(Anisole)



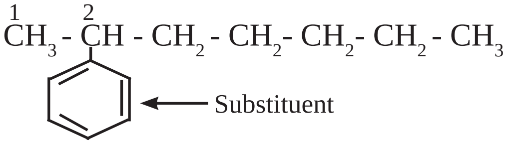
Benzaldehyde



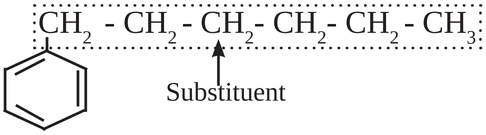
Benzoic acid

If the alkyl substituent is larger than benzene ring (7 or more carbon atoms) the compound is named as phenyl-substituted alkane.

For example :

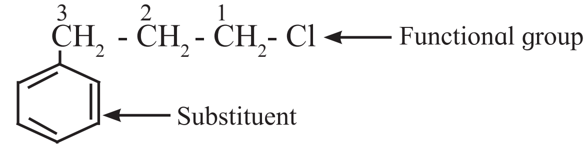


2 - Phenylheptane

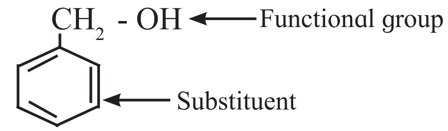


Hexyl benzene

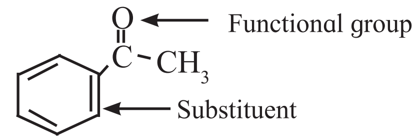
Benzene ring can as well be considered as substituent when it is attached to an alkane with a functional group.



1 - Chloro - 3 - phenylpropane



Phenylmethanol (Benzyl alcohol)

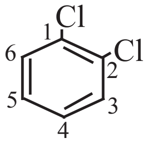


1 - Phenylethanone (Acetophenone)

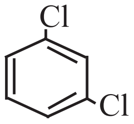
II. Disubstituted benzene derivatives :

Common names of the three possible isomers of disubstitued benzene derivatives are given using one of the prefixes ortho (o-), meta (m-) or para (p-).

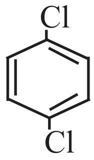
IUPAC system, however, uses numbering instead of prefixes, o-, m-, or p-.



1,2 - dichlorobenzene
(o - Dichlorobenzene)

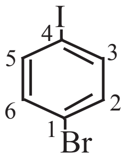


1,3 - dichlorobenzene
(m - Dichlorobenzene)

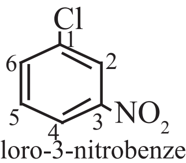


1,4 - dichlorobenzene
(p - Dichlorobenzene)

If two substituents are different, then they enter in alphabetical order.

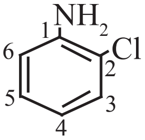


1-bromo-4-iodobenzene
(p - Bromoiodobenzene)

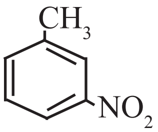


1-chloro-3-nitrobenzene
(m-Chloronitrobenzene)

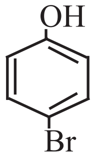
If one of the two groups gives special name to the molecule then the compound is named as derivative of that special compound.



2 - chloroaniline
(o - Chloroaniline)

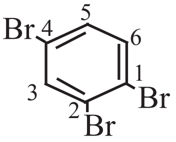


3 - nitrotoluene
(m - Nitrotoluene)

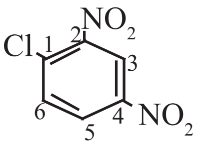


4 - Bromophenol
(p - bromophenol)

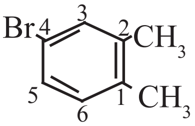
III. Trisubstituted benzene derivatives : If more than two substituents are attached to benzene ring, numbers are used to indicate their relative positions following the alphabetical order and lowest locant rule. In some cases, common name of benzene derivatives is taken as parent compound. For example :



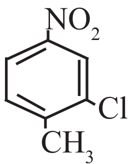
1,2,4-Tribromobenzene



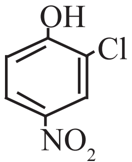
1 - chloro - 2, 4 -dinitrobenzene



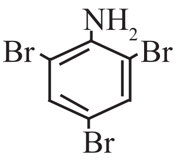
4 - bromo - 1, 2 -dimethylbenzene



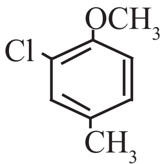
2 - chloro - 1 - methyl - 4 - nitrobenzene



2 - chloro - 4 - nitrophenol



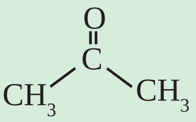
2, 4, 6 - tribromoaniline

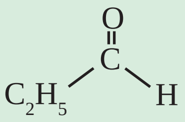


2 - chloro - 4 - methylanisole

14.5 Isomerism

Activity :


i.


ii.

a. Observe the structural formulae (i) and (ii)

b. Find out their molecular formulae

c. What is the difference between them ?

d. What is the relation between the two compounds represented by these structural formulae ?

The phenomenon of existence of two or more compounds possessing the same molecular formula is known as **isomerism**. Such compounds are known as isomers of each other. Two types of isomerism are observed in the organic compounds, namely, **structural isomerism** and **stereoisomerism**. When two or more compounds have the same molecular formula but different structural formulae, it is called structural isomerism. On the other hand, when different compounds have the same structural formula but different relative arrangement of groups / atoms in space, that is, different spatial arrangement of groups / atoms it is called stereoisomerism. In this chapter we are going to look at some details of only structural isomerism.

14.5.1 Structural isomerism

We have seen in the begining of this chapter that the structural formula describes the sequence in which the constituent atoms of a molecule are bonded and the nature of the bonds between them. **When two or more compounds have same molecular formula and different structural formula they are said to be structural isomers of each other. The phenomenon is known as structural isomerism**. Structural isomerism is further classified as **chain isomerism**, **position isomerism**, **functional group isomerism**, **metamerism and tautomerism**. Figure 14.9 shows various types of isomerism.

a. Chain isomerism : When two or more compounds have the same molecular formula but different parent chain or different carbon skeleton, it is refered to as chain isomerism and such isomers are known as chain isomers. For example : Butane ($CH_3 - CH_2 - CH_2 - CH_3$) and 2-methylpropane [$CH_3 - CH(CH)_3 - CH_3$] are chain isomers of each other as they have different carbon skeletons and the same molecular formula C_4H_{10}.

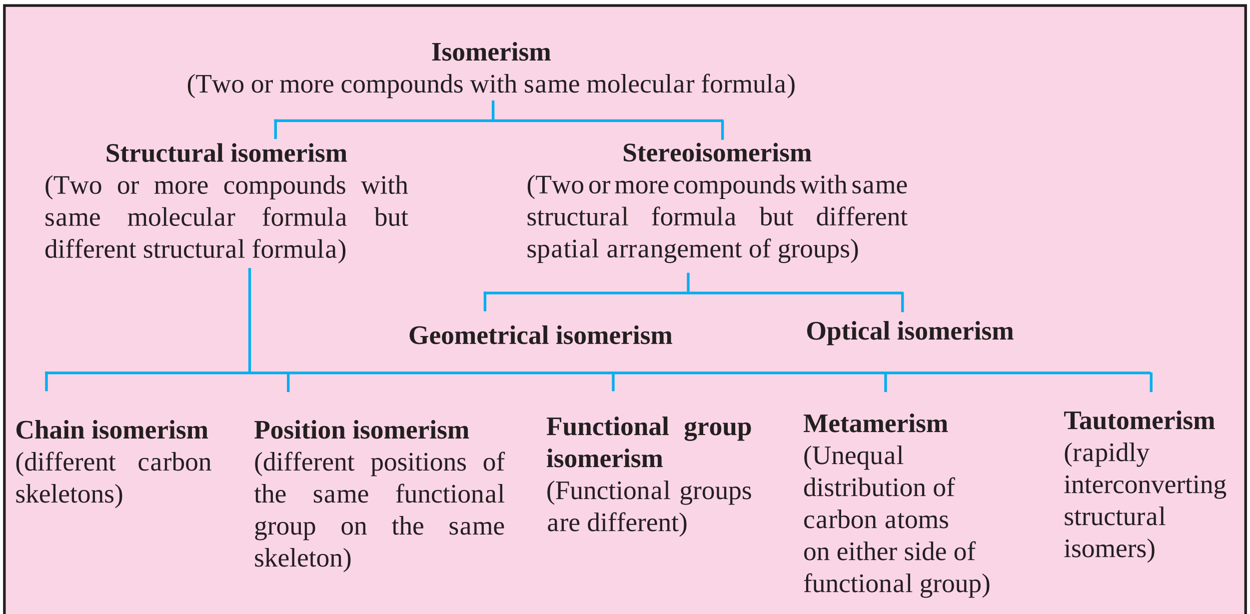


Fig. 14.9 : Types of isomerism

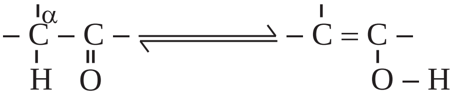
b. Position isomerism : The phenomenon in which different compounds having the same functional groups at different positions on the parent chain is known as position isomerism.

For example : But-2-ene [$CH_3 - CH = CH - CH_3$] and but-1-ene [$CH_2 = CH - CH_2 - CH_3$] are position isomers of each other as they have the same molecular formula C_4H_8 and the same carbon skeleton but the double bonds are located at different positions.

c. Functional group isomerism : The phenomenon in which different compounds with same molecular formula have different functional groups is known as functional group isomerism. For example : Dimethylether ($CH_3 - O - CH_3$) and ethyl alcohol ($CH_3 - CH_2 - OH$) have same molecular formula C_2H_6O but the former has ether (– O –) functional group and the latter has alcohol (– OH) functional group.

d. Metamerism : Different compounds with the same molecular formula and the same functional group, but having unequal distribution of carbon atoms on either side of the functional group is refered to as metamerism and the isomers are known as metamers. For example : Ethoxyethane ($CH_3 - CH_2 - O - CH_2 - CH_3$) and methoxypropane ($CH_3 - O - CH_2 - CH_2 - CH_3$) have the same molecular formula $C_4H_{10}O$ and the same functional group ether but have different distribution of carbon atoms attached to etheral oxygen. These are metamers of each other.

e. Tautomerism : Same compounds exists as mixture of two or more stucturally distinct molecules which are in rapid equilibrium with each other. This phenomenon is referred to as tautomerism. Such interconverting isomers are called tautomers. In nearly all the cases, it is the proton which shifts from one atom to another atom in the molecule to form its tautomer.



Keto form Enol form

For example : **Keto-enol tautomerism** is very common form of tautomerism. It is found in carbonyl compounds. Here a hydrogen atom shifts reversibly from the α - carbon of the keto form to oxygen atom of the enol.

14.6 Theoretical basis of organic reactions :

All the organic molecules primarily contain various types of covalent bonds between the constituents atoms. During an organic reaction, molecules of the reactant undergo change in their structure. A covalent bond at a carbon atom in the reactant is broken and a new covalent bond is formed at it, giving rise to the product. Often this change is brought about by means of another reactant. The reactant that provides carbon to the new bond is called **substrate.** The other reactant which brings about this change is called **reagent**. In case both the reactants provide carbon atoms to a new bond, the reactant considered is called substrate. Apart from the product of interest some other products are formed in a reaction. These are called **byproducts**. For example :

$$\underset{\text{substrate}}{CH_4} + \underset{\text{reagent}}{Cl_2} \xrightarrow{h\nu} \underset{\text{product}}{CH_3Cl} + \underset{\text{byproduct}}{HCl}$$

Covalent bonds are made of valence electrons of the constituent atoms. Redistribution of valence electrons of constituent atoms results in the **bond breaking** or **bond forming** processes along the organic reaction; and which are usually not instantaneous. As a result, the overall organic reaction is punctuated by formation of one or more unstable species called **intermediates**. Overall the organic reaction is often a **multi-step process**.

A sequential account of (i) the electron movement taking place during each step (ii) the bond cleavage and/or bond formation (iii) accompanying changes in energy and shapes of various species and (iv) rate of the overall reaction. The individual steps, constitue the **reaction mechanism**. The knowledge of mechanism of a reaction is useful for **understanding the reactivity** of the concerned organic compounds and, in turn, helpful for **planning synthetic strategies**.

In the following subsection we are going to look at the types of bond cleavage, types of reagents, the factors that influence stability of various species involved and representation of electron movement occuring during organic reactions.

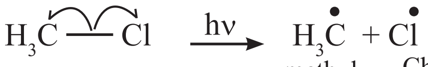
14.6.1 Types of cleavage of covalent bond

A covalent bond can undergo cleavage or fission in two ways (i) **Homolytic cleavage**, (ii) **Heterolytic cleavage**

A covalent bond comprises two electrons (bond pair of electrons) shared between the two bonded atoms. In **homolytic cleavage** of a covalent bond one of the two electrons goes to one of the bonded atoms and the other is bound to the other. Movement of a single electron is represented by a half headed curved arrow or fish hook (⌒). The tail of the curved arrow indicates the place from where the electron is removed while the head of the curved arrow indicates the place where the electron reaches as the result of the movement. Such homolytic cleavage of a covalent bond gives rise to two neutral species carrying one unpaired electron each. A species with single unpaired electron is called **'free radical'** or sometimes just '**radical**'. A free radical is unstable and thereby a reactive species, having a tendency to seek an electron for pairing. A homolytic cleavage, thus, is represented as :

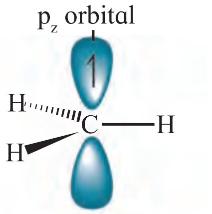
$$A-B \longrightarrow \dot{A} + \dot{B}$$

For example,



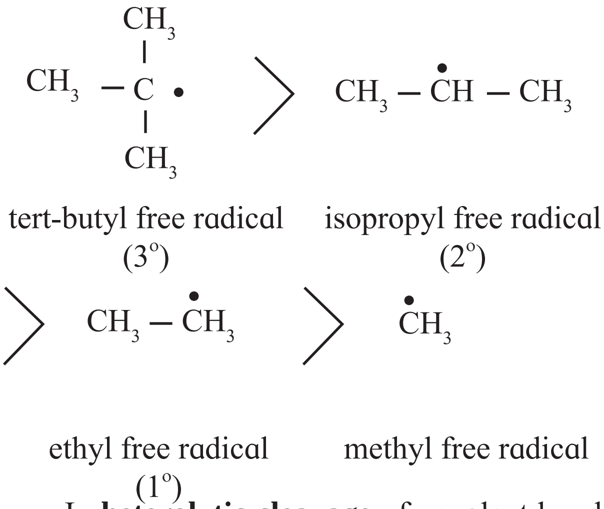
$$H_3C-Cl \xrightarrow{h\nu} H_3\dot{C} + \dot{Cl}$$

Homolytic fission is favoured in the presence of ultravoilet radiation or suitable peroxides or at high temperatures. The organic reactions which proceed by homolytic fission are known as **free radical or non-polar reactions**. Free radicals have only transitory existence. These are formed as reaction intermediate which subsequently react with another radical/molecule to restore stable bonding pair. A carbon free radical is sp^2 hybridized and reveals planar trigonal geometry.



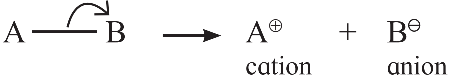
Shape of methyl free radical

Alkyl free radicals are classified as primary (1^0), secondary (2^0) and tertiary (3^0). The observed stability order of alkyl free radicals is :



$$(CH_3)_3\dot{C} > CH_3-\dot{C}H-CH_3 > CH_3-\dot{C}H_2 > \dot{C}H_3$$

In **heterolytic cleavage** of covalent bond both shared electrons go to one of the two bonded atoms. This turns out to be the more electronegative atom of the two. Movement of an electron pair is represented by a curved arrow (⌒). Heterolytic cleavage of a covalent bond gives rise to two **charged species**, one with negative charge and the other with positive charge. The negatively charged (anionic) species has the more electronegative atom which has taken away the shared pair of electron with it. A heterolytic cleavage is represented as :



$$A-B \longrightarrow A^{\oplus} + B^{\ominus}$$

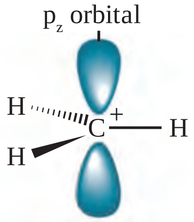
(B is more electronegative than A)

$$H_3C - Br \longrightarrow \underset{\text{methyl carbocation}}{H_3C^{\oplus}} + \underset{\text{bromide}}{Br^{\ominus}}$$

(Br is more electronegative than C)

Heterolysis is favoured in polar solvents. In methyl bromide, bromine is more electronegative. Thus heterolysis of methyl bromide results in formation of methyl carbocation and bromide anion.

A carbon atom having sextet of electrons and a positive charge is known as **carbocation** (earlier called carbonium ion). Carbocations are highly unstable and reactive species formed as intermediates in many organic reactions.



Shape of methyl carbocation

The central carbon atom of a carbocation is sp^2 hybrid state and has trigonal planar geometry. The p_z atomic orbital is vacant and is perpendicular to the plane containing the three sigma bonds at the carbon.

Carbocations are classified as primary (1^0), secondary (2^0) and tertiary (3^0). The observed stability of alkyl carbocations follows the order :

$$\underset{\text{t-butyl carbocation}}{(CH_3)_3\overset{\oplus}{C}} > \underset{\text{iso-propyl carbocation}}{CH_3 - \overset{\oplus}{C}H - CH_3} > \underset{\text{ethyl carbocation}}{CH_3 - \overset{\oplus}{C}H_2} > \underset{\text{methyl carbocation}}{\overset{\oplus}{C}H_3}$$

Heterolytic bond fission generates a species called **carbanion** in which carbon gets the shared pair of electrons. This happens when a carbon atom is bonded to the electropositive atom.

$$H_3C - Z \xrightarrow{\text{Heterolysis}} H_3C^{\ominus} + Z^{\oplus}$$

(Z is more electropositive than C)

The central carbon atom of a carbanion has completed octet of electrons and a negative charge. The carbanion is unstable and reactive which is formed as the reaction intermediate. Heterolytic fission is favoured in the polar solvents. The organic reactions proceed via heterolytic fission known as **heteropolar / polar / ionic reactions**. Most organic reactions taking place in solutions follow ionic mechanism.

Can you tell?

Some bond fissions are described in the following table. For each of them, show the movement of electron/s using curved arrow notation. Classify them as homolysis or heterolysis and idetify the intermediate species produced as carbacation, carbonion or free radical.

Bond fission	Types of cleavage	Intermediate
$CH_3 - Cu \longrightarrow CH_3^{\ominus} + Cu^{\oplus}$	heterolysis	carbanion
$C_6H_5 - \ddot{O} - \ddot{O} - C_6H_5 \longrightarrow 2C_6H_5\ddot{O}\cdot$	....	....
$CH_3 - \overset{O}{\overset{\Vert}{C}} - CH_2 - H + \overset{\ominus}{O}H \longrightarrow CH_3 - \overset{O}{\overset{\Vert}{C}} - \overset{\ominus}{C}H_2 + H_2O$	....	....
$CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - Br \longrightarrow \underset{CH_3 \quad CH_3}{\overset{CH_3}{C^{\oplus}}} + Br^{\ominus}$	....	....
$CH_3 - CN \longrightarrow \overset{\oplus}{C}H_3 + \overset{\ominus}{C}N$	....	....

14.6.2 Types of reagent

Can you recall?

1. What is meant by 'reagent' ?
2. Identify the 'reagent', 'substrate', 'product' and 'byproduct' in the following reaction.

$CH_3\,COCl + NH_3 \longrightarrow CH_3\,CONH_2 + HCl$

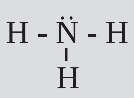
The **polar organic reactions** are brought about by two types of reagents. Depending upon their ability to accept or donate electrons from or to the substrate, reagents are classified as (i) Electrophiles ($E^{\oplus}$) (ii) Nucleophiles (Nu:)

Electrophiles (meaning electron loving spicies) accept electrons from the substrate. Thus electrophiles are electron seeking species. This is because they themselves are electron deficient. For example ; a positively charged ion such as $Br,\ ^{\oplus}CH_3$ or a neutral species having a vacant orbitals such as $AlCl_3$.

Nucleophiles (nucleus seeking species) give away electrons to the substrate. This is because nucleophiles are electron rich species. For example : negatively charged species such as $OH^{\ominus}$ or neutral species such as $H_2\ddot{O}$, having lone pair of electrons.

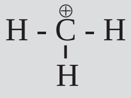
Problem 14.5 : Identify the nucleophile and electrophile from NH_3 and $CH_3^{\oplus}$. Also indicate the nucleophilic and electrophilic centres in them. Justify.

Solution : The structural formulae of two reagents showing all the valence electrons are :



$\mathrm{H-\ddot{N}-H}$ with H below N

and



$\mathrm{H-\overset{\oplus}{C}-H}$ with H below C

Thus NH_3 contains N with a lone pair of electrons which can be given away to another species. Therefore NH_3 is a nucleophile and 'N' in it is the nucleophilic centre. The $CH_3^{\oplus}$ is a positively charged electron deficient species having a vacant orbital on the carbon. It is an electrophile. The 'C' in it is the electrophilic centre.

A polyatomic electrophile has an electron deficient atom in it called the **electrophilic centre**, while a polyatomic nucleophile has an electron rich atom in it is called the **nucleophilic centre**. For example : the electrophilic centre of the electrophile $AlCl_3$ is Al which has only 6 valence electrons. The nucleophilic centre of the nucleophile H_2O is 'O' which has two lone pairs of electrons.

A nucleophile attacks the electrophilic centre in the substrate and brings about a nucleophilic reaction. On the other hand an electrophile attacks a nucleophilic centre in the substrate and brings about an electrophilic reaction. This principle is illustrated in the following simple reaction though, it is not an organic reaction.

$$\ddot{N}H_3 + BF_3 \longrightarrow H_3\overset{\oplus}{N}-\overset{\ominus}{B}F_3$$

Here the nucleophilic centre $\ddot{N}$ in the nucleophile NH_3 attacks the electrophilic centre 'B' in the electrophile BF_3 and gives the product.

14.6.3 Electronic effects in organic reaction

We noted earlier that in polar organic reactions the nucleophilic centre in a nucleophile attacks the electrophilic centre in the substrate whereas the electrophilic centre in an electrophile attacks the nucleophilic centre in the substrate. **How electrophilic or nucleophilic centre generated in a neutral substrate ?** This happens because of displacement of valence electrons within some organic molecules, which results in their polarization. **The displacement of valence electrons resulting in polarization of an organic molecule is called electronic effect.** The electronic effect that occurs in the **ground state** is **permanent** effect. This takes place due to influence of certain atom or substituent or certain structural feature present in the molecule. **Inductive effect** and **resonance effect** are two examples of permanent electronic effect.

On the other hand the electron displacement effect occuring in a substrate due to approach of the attacking reagent is a **temporary effect**. This type of electronic effect is called **electromeric effect or polarisability effect**. We consider various types of electronic effects in the following sections.

14.6.4 Inductive effect

Can you recall?

- How is covalent bond formed between two atoms ?
- Consider two covalently bonded atoms Q and R where R is more electronegative than Q. Will these atoms share the electron pair equally between them ?
- Represent the above polar covalent bond between Q and R using fractional charges $\delta^{\oplus}$ and $\delta^{\ominus}$.

We learnt earlier that covalent bond between two atoms differing in their electronegativity is polar covalent bond. For example : the covalent bond between carbon and more electronegative chlorine is a polar covalent bond. **When an organic molecule has a polar covalent bond in its structure, polarity is induced in adjacent carbon-carbon single bonds too. This is called inductive effect.** Consider, for example, the chloroethane molecule :

$$\overset{2}{C}H_3 - \overset{1}{C}H_2 - Cl$$

In this molecule a positive polarity is developed on C^2 by inductive effect of the Cl atom bonded to C^1. Normally the C^2 - C^1 bond would not be expected to be polar as it is a covalent bond between two atoms of the same element carbon. Yet this bond aquires some polarity, because of the presence of chlorine atom in the molecule. Chlorine being more electronegative than carbon, the C^1 - Cl bond is a polar covalent bond with partial negative charge on Cl and equal amount of partial positive charge on C^1. As the C^1 is further bonded to C^2, the positive polarity of C^1 pulls the shared pair of electrons of the C^2 - C^1 bond more towards itself. As a result a part of partial positive charge produced on C^1 is transfered to C^2. This results in developing a still smaller positive charge on C^2. In other words, the electron density gets displaced towards the chlorine atom not only along the C^1 - Cl bond, but also along the C^2 - C^1 bond due to the inductive effect of Cl. This is represented as :

$$\overset{2}{C}H_3 \rightarrow \overset{1}{C}H_2 \rightarrow Cl$$

The **arrow head** put **in the centre of the bond** is used to **represent the inductive effect**. The direction of the arrow head indicates the direction of the permanent electron displacement taken place along the sigma bond in the ground state.

Inductive effect of an influencing group is transfered to subsequent carbon atoms along the chain of C - C bonds, as it decreases rapidly as the number of intervening C - C bonds increases and becomes negligibly small beyond three bonds. This can be represented as

$$CH_3 - \overset{\delta_3\oplus}{CH_2} \rightarrow \overset{\delta_2\oplus}{CH_2} \rightarrow \overset{\delta_1\oplus}{CH_2} \rightarrow \overset{\delta\ominus}{Cl}$$

Where $\delta_3\oplus < \delta_2\oplus < \delta_1\oplus$

The direction of the inductive effect of a bonded group depends upon whether electron density of the bond is withdrawn from the bonded carbon or donated by the bonded carbon. According to this ability the groups substituents are classified as either **electron withdrawing** (accepting) or **electron donating** (releasing) groups with respect to hydrogen.

In the above example, electron displacement takes place towards chlorine. This means that Cl withdraws electron density from the carbon chain and is electron withdrawing. Chlorine is said to exert an **electron withdrawing inductive effect or negative inductive effect (-I effect)** on the carbon chain. Some other groups having - I effect are - NO_2 (nitro), - CN (cyano), - COOH (carboxy), - COOR (ester), - OAr (aryloxy).

On the other hand alkyl groups ($-CH_3$, $-CH_2-CH_3$) are considered as groups exerting **electron releasing inductive effect (+I effect) on the carbon chain**.

Problem 14.6 : Consider the following molecules and answer the questions, $CH_3- CH_2- CH_2- Cl$, $CH_3- CH_2- CH_2- Br$, $CH_3- CH_2- CH_2- I$.

(i) What type of inductive effect is expected to operate in these molecules ?

(ii) Identify the molecules from these three, having the strongest and the weakest inductive effect.

Solution : (i) The groups responsible for inductive effect in these molecules are -Cl, -Br and -I, respectively. All these are halogen atoms which are more electronegative than carbon and therefore all of them exert - I effect, that is, electron withdrawing inductive effect.

(ii) The - I effect of halogens is due to their electronegativity. A decreasing order of electronegativity in these halogens follows Cl > Br > I. Therefore the strongest -I effect is expected in $CH_3 - CH_2 - CH_2 - Cl$, while the weakest -I effect is expected for $CH_3- CH_2- CH_2- I$.

Problem 14.7 : Which of the $CH_3 - CHCl_2$ and CH_3CH_2Cl is expected to have stronger -I effect ?

Solution : The group exerting -I effect in CH_3CH_2Cl is one - Cl while in $CH_3 - CHCl_2$ there are two - Cl atoms. Therefore $CH_3 - CHCl_2$ is expected to have strong -I effect.

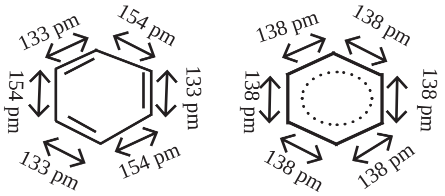
14.6.5 Resonance structures

Try this

1. Draw a bond line structure of benzene (C_6H_6)
2. How many C - C and C = C bonds are there in this structure ?
3. Write down the expected values of the bond lengths of the carbon carbon bonds in benzene (refer to Table 5.7).

The cyclic structure of benzene incorporating three alternating C-C single bonds and C=C double bonds implies two distinct bond length of 154 pm and 133 pm respectively (refer to Table 5.2 and see Fig. 14.10). Experimental measurements show that benezene has a regular hexagonal shape and all the six carbon bonds, have the same bond length of 138 pm which is intermediate between C-C single bond and C=C double bond. This means that all the six carbon carbon bonds in benzene are equivalent, unlike what appears from the single Lewis structure.

Benzene



Expectation (two different bondlengths)

Observation (all bond lengths equal)

Fig 14.10 Structure of Benzene

Can you recall?

- Write down two Lewis structures for ozone. (Refer to chapter 5)
- How are these two Lewis structures related to each other ?
- What are these two Lewis strucutres called ?

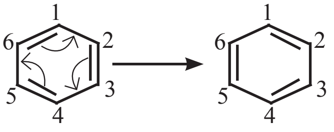
When Lewis structure of a compound has two or more multiple bonds alternating with single bonds, it is called **a conjugated system of π bonds**. In such a system or in species having an atom carrying p orbital attached to a multiple bond, **resonance theory** is applicable.

We understand the following points from the resonance theory :

(i) The π electrons in conjugated system of π bonds are not localized to a particular π bond.

(ii) For a compound having a conjugated system of π bonds (or similar other systems) two or more Lewis structures are written by showing movement of π electrons (that is delocalization of π electrons) using curved arrows.

The Lewis structures so generated are linked by **double headed arrow** and are called **resonance strucutres** or **contributing structures** or **cononical structures** of the species. Thus, two resonance structures can be drawn for benzene by delocalizing or shifting the π electrons :



I II

(iii) The positions of the carbon atoms in the conjugated system of π bonds remain unchanged, but the positions of π electrons are different in different resonance structures. For example, in the resonance structure I of benzene there is a single bond between C^1 and C^2 while in the resonance structure II there is a double bond between C^1 and C^2.

(iv) Any resonance structure is hypothetical and does not by itself represent any real molecule and can explain all the properties of the compound. The real molecule has, however, character of all the resonance structures those can be written. The real or actual molecule is said to be the **resonance hybrid** of all the resonance structures. For example an actual benezene molecule is the resonance hybrid of structures I and II and exhibit character of both these structures. Its approximate representation can be shown as a dotted circle inscribed in a regular hexagon. Thus each carbon carbon bond in benzene has single as well as double bond character and the ring has a regular hexagonal shape.

Resonance hybrid of
structures I and II

(v) Hypothetical energy of an individual resonance structure can be calculated using bond energy values. The energy of actual molecule is, however, lower than that of any one of the resonance structures. In other words, **resonance hybrid is more stable** than any of the resonance structures. The difference in the actual energy and the lowest calculated energy of a resonance structure is called **resonance stabilization energy** or just **resonance energy**. Thus, resonance leads to stabilization of the actual molecule.

Problem 14.8 : Identify the species that contains a conjugated system of π bonds. Explain your answer.

$CH_2 = CH - CH_2 - CH = CH_2$

I

$CH_2 = CH - CH = CH - CH_3$

II

Solution : I Does not contain conjugated system of π bonds, as the two C = C double bonds are separated by two C - C single bonds.

II Contains a conjugated system of π bonds, as the two C = C double bonds are saparated by only one C - C single bond.

Rules to be followed for writing resonance structure :

(i) Resonance structures can be written only when all the atoms involved in the π conjugated system lie in the same place.

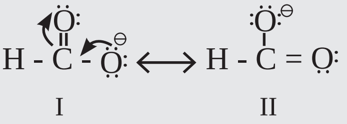
(ii) All the resonance structures must have the same number of unpaired electrons.

(iii) Resonance structures contribute to the resonance hybrid in accordance to their energy or stability. More stable (having low energy) resonance structures contribute to largely and thus are important.

Thus, between the compared resonance structures, that resonance structure is more stable and therefore important which has (a) more number of covalent bonds, (b) more number of atoms with complete octet or duplet, (c) less separation, if any, of opposite charges, (d) negative charge, if any, on more electronegative atom and positive charge, if any, on more electropositive atom and (e) more dispersal of charge.

Problem 14.9 : Write resonance structures of H - COO$^{\ominus}$ and comment on their relative stability.

Solution : First the detailed bond structure of H - COO$^{\ominus}$ showing all the valence electron is drawn and then other resonance strucutres are generated using curved arrow to show movement of π-electrons. Two resonance structures are written for H - COO$^{\ominus}$.



Both the resonance structures I and II are equivalent to each other, and therefore, are equally stable.

Problem 14.10 : Identify the species which has resonance stabilization. Justify your answer.

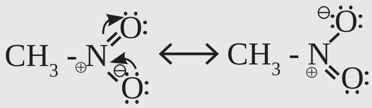
(i) $CH_3 - \ddot{O} - H$ (ii) $CH_3 - NO_2$

(iii) buta - 1, 3 - diene

Solution :

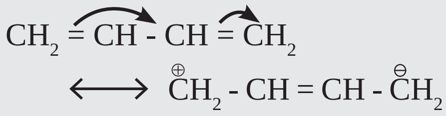
(i) The bond structure shows that there is no π bond. Therefore no resonance and no resonance stabilization.

(ii)



N= O double bond is attached to 'O' which carries lone pair of electrons in a p orbital. Therefore resonance strucutres can be written and species is resonance stabilized.

(iii)

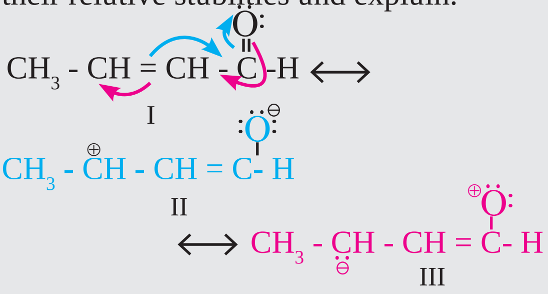


The Lewis structure shows two C=C double bonds alternating with a C-C single bond. Therefore resonance structures can be written as shown, and the species is resonance stabilized.

Remember

When all the resonance structures of a species are equivalent to each other, the species is highly resonance stabilized. For example, R - COO$^{\ominus}$, $CO_3^{2\ominus}$

Problem 14.11 : Write three resonance structures for CH_3-CH = CH-CHO. Indicate their relative stabilties and explain.



Stabilty order : I > II > III

I : Contains more number of covalent bonds, each carbon atom and oxygen atom has complete octet, and involves no separation of opposite charges. Therefore the most stable resonance structure.

II : Contains one covalent bond less than in I, one carbon ($C^{\oplus}$) has only 6 valence electrons, involves separation of opposite charges; the resonance structure II has -ve charge on more electronegative 'O' and +ve charge on more electroposoitve 'C'. It has intermediate stability.

III : Contains one covalent bond less than in I, oxygen has only 6 valence electrons, involves separation of opposite charge , has -ve charge on the more electropositive 'C' and +ve charge on more electronegative 'O'. All these factors are unfavourable for stability. Therefore it is the least stable.

14.6.6 Resonance Effect : The existence of resonance often results in developing polarity in a molecule. **The polarity produced in the molecule by the interaction between conjugated π bonds (or that between π bond and p orbital on attached atom) is called the resonance effect** or **mesomeric effect**. The effect is transmitted through a chain of conjugated π bonds. There are two types of resonance effects (or mesomeric effect) designated as positive resonance effect (+R or +M) and negative resonance effect (-R or -M).

Positive resonance effect or electron donating / releasing resonance effect (+ R effect) : If the substituent group has a lone pair of electrons to donate to the attached π bond or cojugated system of π bonds, the effect is called +R effect. Group such as - OH, - OR, - $O^{\ominus}$, - NHR, - halogen, etc. having lone pair of electrons show +R effect. The +R effect increases electron density at certain positions in a molecule. Figure 14.11 shows how the +R effect in aniline increases the electron density at ortho and para positions.

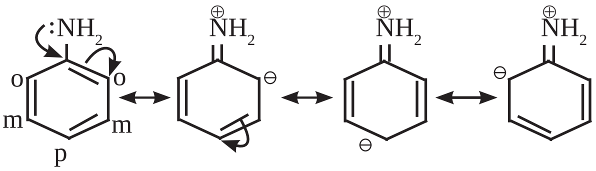


Fig. 14.11 : +R effect in aniline

Negative resonace effect or electron withdrawing resonance effect (-R effect) :

If the substituent group has a tendency to withdraw electrons from the attached π bond or conjugated system of π bonds towards itself, the effect is called -R effect. Group such as -COOH, -CHO, -CO-, -CN, -NO_2, - COOR, etc. show -R effect. The -R effect results in developing a positive polarity at certain positions in a molecule. Figure 14.12 shows how -R effect in nitrobenzene develops positive polarity at the ortho and para positions.

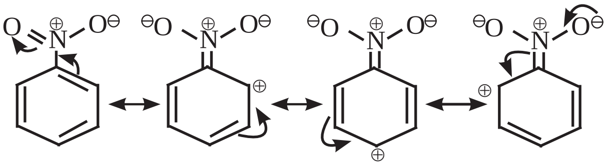
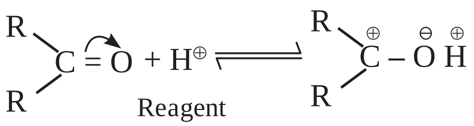


Fig. 14.12 : -R effect in aniline

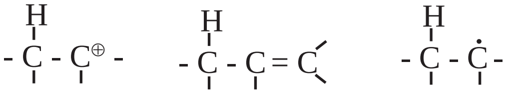
14.6.7 Electromeric effect : This is a temporary electronic effect exhibited by multiple-bonded groups in the excited state in the presence of a reagent. When a reagent approaches a multiple bond, the electron pair gets completely shifted to one of the multiply bonded atoms, giving a charged separated structure. For example :



This effect is temporary and disappears when the reagent is removed from the reacting system.

14.6.8 Hyperconjugation :

Hyperconjugation is **a permanent electronic effect** explains stability of a carbocation, free radical or alkene. It is delocalization of σ (sigma) electrons of a C - H bond of an alkyl group directly attached to a carbon atom which is part of an unsaturated system or has an empty p- orbital or a p - orbital with an unpaired electron (see Fig. 14.13).



(I) (II) (III)

Fig. 14.13 Species stabilized by hyperconjugation

Let us consider ethyl cation ($CH_3\overset{\oplus}{C}H_2$). Here the positively charged carbon atom with an empty p -orbital has an adjacent methyl group, that is an α - (alpha) methyl group. One of the C-H bonds of this α methyl group is in allignment with the empty p-orbital. The σ electrons of this C-H bond or delocalized into the empty p -orbital and thereby stabilize the cation (see Fig. 14.14).

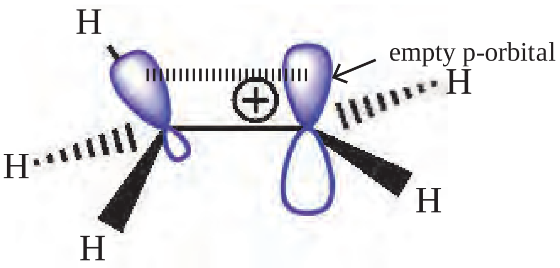
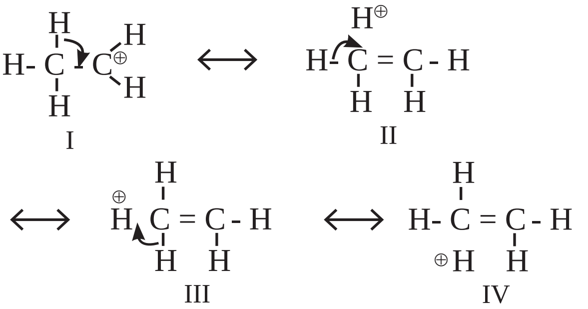
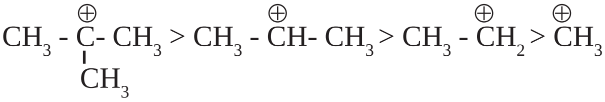


Fig. 14.14 Hyperconjugation in ethyl carbocation

Hyperconjugation is, thus a σ-π conjugation.

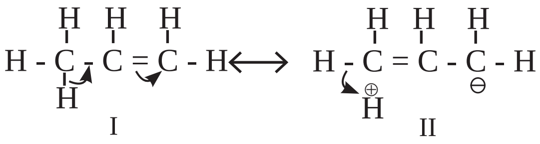


The contributing structures II, III and IV involving delocalization of σ electrons of C-H bond shows no covalent bond between carbon and one of the α-hydrogens. Hyperconjugation is, therefore, called **'no bond resonance'**. More the number of such α–hydrogens (that is, hydrogen on the α- carbon), more are the no bond resonance structures and more is the stability. The relative stability of carbocations, therefore decreases in the order :



$$CH_3-\overset{\oplus}{\underset{CH_3}{C}}-CH_3 > CH_3-\overset{\oplus}{C}H-CH_3 > CH_3-\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3$$

Let us now look at propene which has a methyl group attached to C = C. Delocalization of electrons by hyperconjugation in propene can be depicted as shown.



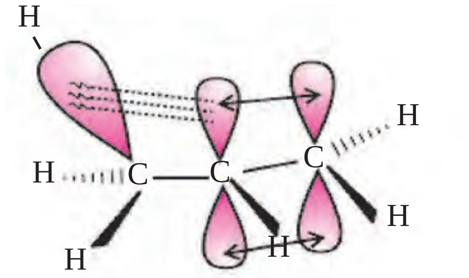


Fig. 14.15 : shows the orbital diagram of hyperconjugation in propene

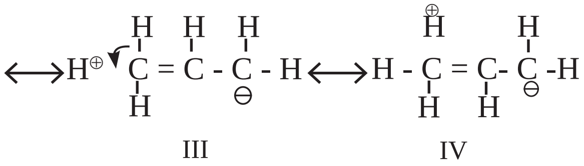


Figure 14.15 shows the orbital diagram of hyperconjugation in propene.

The effect of hyperconjugation is usually stronger than inductive effect.

Internet my friend

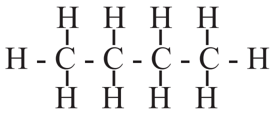
1. Basic principles of organic chemistry https://authors.library.caltech.edu/25034
2. Collect information about Isomerism

Exercises

1. Answer the following :

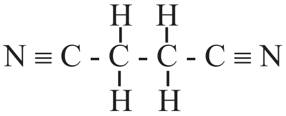
A. Write condensed formulae and bond line formulae for the following structures.

a.



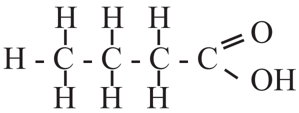
$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$$

b.



$$N\equiv C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-C\equiv N$$

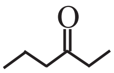
c.



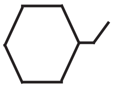
$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-C{\genfrac{}{}{0pt}{}{=O}{\diagdown OH}}$$

B. Write dash formulae for the following bond line formulae.

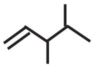
a.



b.



c.



d.

C. Write bond line formulae and condensed formulae for the following compounds

a. 3-methyloctane   b. hept-2-ene

c. 2, 2, 4, 4- tetramethylpentane

d. octa-1,4-diene   e. methoxyethane

D. Write the structural formulae for the following names and also write correct IUPAC names for them.

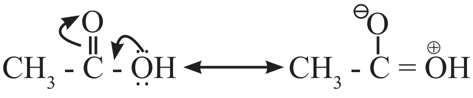
a. 5-ethyl-3-methylheptane

b. 2,4,5-trimethylthexane

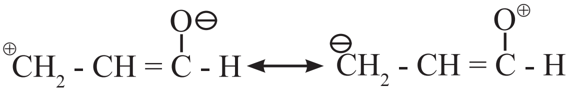
c. 2,2,3-trimethylpentan-4-01

E. Identify more favourable resonance structure from the following. Justify.

a.

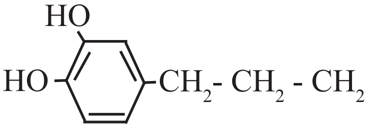


b.

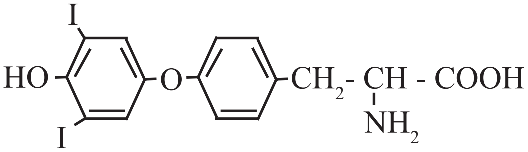


F. Find out all the functional groups present in the following polyfunctional compounds.

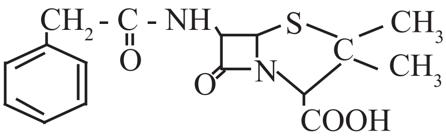
a. Dopamine a neurotransmitter that is deficient in Parkinson's disease.



b. Thyroxine the principal thyroid hormone.

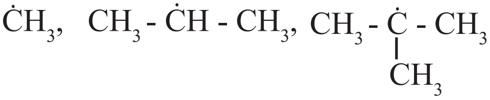


c. Penicillin G a naturally occuring antibiotic



G. Find out the most stable species from the following. Justify.

a.



$$\dot{C}H_3,\ CH_3-\dot{C}H-CH_3,\ CH_3-\underset{CH_3}{\underset{|}{\dot{C}}}-CH_3$$

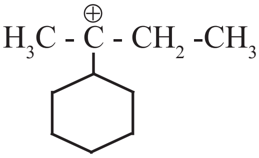
b. $\overset{\ominus}{C}H_3,\ \overset{\ominus}{C}H_2Br,\ \overset{\ominus}{C}Br_3$

c. $\overset{\oplus}{C}H_3,\ \overset{\oplus}{C}H_2Cl,\ \overset{\oplus}{C}Cl_3$

H. Identify the α - carbons in the following species and give the total number of α-hydrogen in each.

a. $CH_3-CH_2-\overset{\oplus}{C}H-CH_2-CH_3$

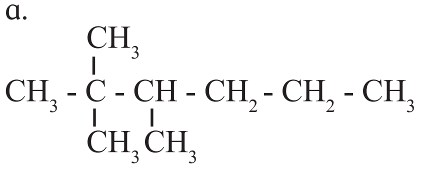
b.



c. $CH_2=CH-CH_2-CH_3$

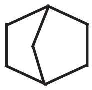
I. Identify primary, secondary, tertiary and quaternary carbon in the following compounds.

a.



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

b.



2. Match the pairs

Column 'A'	Column 'B'
i. Inductive effect	a. delocalisation of π electrons
ii. Hyperconjugation	b. displacement of π electrons
iii. Resonance effect	c. delocalisation of σ electrons
	d. displacement of σ electrons

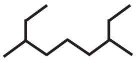
3. What is meant by homologous series ? Write the first four members of homologous series that begins with

A. CH_3CHO B. $H-C\equiv C-H$

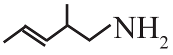
Also write down their general molecular formula.

4. Write IUPAC names of the following

A.

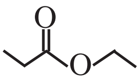


B.

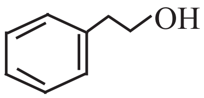


C.

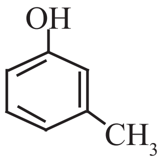
D.



E.



F.



5 Find out the type of isomerism exhibited by the following pairs.

A. $CH_3-CH_2-NH-CH_2-CH_3$
and $CH_3-NH-CH_2-CH_2-CH_3$

B.

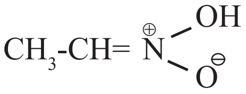
$$CH_3-\underset{OH}{CH}-CH_2-CH_3$$

and

$CH_3-CH_2-O-CH_2-CH_3$

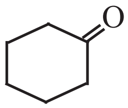
C.

and

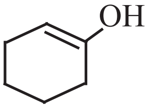


$$CH_3-CH_2-\overset{\oplus}{N}\begin{matrix}=O\\ -O^{\ominus}\end{matrix} \text{ and } CH_3-CH=\overset{\oplus}{N}\begin{matrix}-OH\\ -O^{\ominus}\end{matrix}$$

D.



and



6. Draw resonance srtuctures of the following :

A. Phenol B. Benzaldehyde

C. Buta-1,3-diene D. Acetate ion

7. Distinguish :

A. Inductive effect and resonance effect

B. Electrophile and nucleophile

C. Carbocation and carbanion

D. Homolysis and heterolysis

8. Write true or false. Correct the false stament

A. Homolytic fission involves unsymmetrical breaking of a covalent bond.

B. Heterolytic fission results in the formation of free radicals.

C. Free radicals are negatively charged species

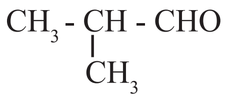
D. Aniline is heterocyclic compound.

9. Phytane is naturally occuring alkane produced by the alga spirogyra and is a constituent of petroleum. The IUPAC name for phytane is 2,6,10,14-tetramethylhexadecane. Write zig-zag formula for phytane. How many primary, secondary, tertiary and quaternary carbons are present in this molecule.

10. Observe the following structures and answer the questions given below.

(i) $CH_3-CH_2-CH_2-CHO$

(ii)



$$CH_3-\underset{CH_3}{CH}-CHO$$

a. What is the relation between (i) and (ii) ?

b. Write IUPAC name of (ii).

c. Draw the functional group isomer of (i).

11. Observe the following and answer the questions given below

$CH_3 - CH_3 \xrightarrow{\text{U. V. light}} \dot{C}H_3 + \dot{C}H_3$

a. Name the reactive intermediae produced

b. Indicate the movement of electrons by suitable arrow to produce this intermediate

c. Comment on stability of this intermediate produced.

12. An electronic displacement in a covalent bond is represented by following noation.

$\overset{\delta\oplus}{CH_3} \rightarrow \overset{\delta\oplus}{CH_2} \rightarrow \overset{\delta\ominus}{Cl}$

A. Identify the effect

B. Is the displacement of electrons in a covalent bond temporary or permanent.

13. Draw all the no-bond resonance structures of isopropyl carbocation.

14. A covalent bond in tert-butylbromide breaks in a suitable polat solvent to give ions.

A. Name the anion produced by this breaking of a covalent bond.

B. Indicate the type of bond breaking in this case

C. Comment on geometry of the cation formed by such bond cleavage.

15. Choose correct options

A. Which of the following statements are true with respect to electronic displacement in covalent bond ?

a. Inductive effect operates through π bond

b. Resonance effect operates through σ bond

c. Inductive effect operates through σ bond

d. Resonance effect operates through π bond

i. a. and b   ii. a and c

iii. c and d   iv. b and c

B. Hyperconjugation involves overlap of ..... orbitals

a. σ − σ   b. σ −p

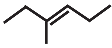
c. p − p   d. π − π

C. Which type of isomerism is possible in $CH_3CHCHCH_3$?

a. Position   b. Chain

c. Geometrical   d. Tautomerism

D. The correct IUPAC name of the compound


is .....

a. hept-3-ene

b. 2-ethylpent-2-ene

c. hex-3-ene

d. 3-methylhex-3-ene

E. The geometry of a carbocation is ......

a. linear   b. planar

c. tetrahedral   d. octahedral

F. The homologous series of alcohols has general molecular formula ....

a. $C_nH_{2n+1}OH$ b. $C_nH_{2n+2}OH$

c. $C_nH_{2n-2}OH$ c. $C_nH_{2n}OH$

G. The delocaalization of electrons due to overlap between p-orbital and sigma bond is called

a. Inductive effect

b. Electronic effect

c. Hyperconjugation

d. Resonance

Activity :

Construct models of different types of organic compounds. Explain each compound in class.