24

General Organic Chemistry

Organic Chemistry

The hydrides of carbon (hydrocarbons) and their derivatives are called **organic compounds.** The branch of chemistry which deals with these compounds is called **organic chemistry**.

Berzelius (1808) defined organic chemistry as the chemistry of substances found in living matter and gave the vital force theory. Synthesis of urea, the first organic compound synthesised in laboratory, by Wohler, gave death blow to the vital force theory.

$$(NH_4)_2SO_4 + 2KCNO \xrightarrow[-\,K_2SO_4]{} 2NH_4CNO \xrightarrow{\Delta} \underset{\text{urea}}{NH_2CONH_2}$$

Acetic acid is the first organic compound synthesised from its elements.

Reasons for Large Number of Organic Compounds

(a) **Catenation** It is the tendency of self combination and is maximum in carbon. A carbon atom can combine with other carbon atoms by single, double or triple bonds. Thus, it forms more compounds than the others.

(b) **Tetravalency and small size** Carbon being tetravalent, is capable of bonding with four other C-atoms or some other monovalent atoms. Carbon can form compound with oxygen, hydrogen, chlorine, sulphur, nitrogen and phosphorus. These compounds have specific properties depending upon the nature of the element or group attached with the carbon.

Furthermore, these compounds are exceptionally stable because of the small size of carbon.

General Characteristics of Organic Compounds

1. These are the compounds of carbon with H, O, N, S, P, F, Cl, Br and I.

2. These are generally found in living organisms.
   e.g. carbohydrates, proteins etc.
3. These may be gases, liquids or solids.
4. Being covalent in nature, these have low boiling point and melting point and soluble in organic solvents.
5. These are generally volatile and inflammable.
6. They do not conduct electricity because of the absence of free ions.
7. They posses distinct colour and odour.

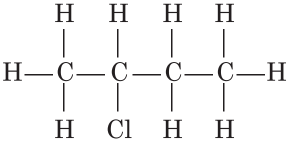
Representation of Different Formula

An organic compounds can be represented by the following ways :

1. **Complete formula**

In it, all the bonds present between any two atoms are shown clearly.

e.g.



$$\begin{array}{ccccccccc} & & H & & H & & H & & H & \\ & & | & & | & & | & & | & \\ H & — & C & — & C & — & C & — & C & — & H \\ & & | & & | & & | & & | & \\ & & H & & Cl & & H & & H & \end{array}$$

2. **Condensed Formula**

In it, all the bonds are not shown clearly.

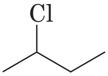
e.g.

$$\begin{array}{l} CH_3\,\underset{\displaystyle Cl}{\underset{|}{CH}}\,CH_2CH_3 \end{array}$$

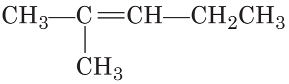
or $CH_3CH(Cl)CH_2CH_3$

3. **Bond Line Formula**

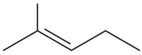
In it, every fold and free terminal represents a carbon and lines represent the bonds. e.g.



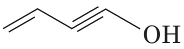
In such formulae, it is assumed that required number of H-atoms are present, **wherever**, they are necessary (to satisfy tetravalency of carbon), e.g.



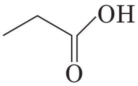
$$CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}=CH—CH_2CH_3 \equiv$$



$CH_2=CH—C\equiv C— OH \equiv$

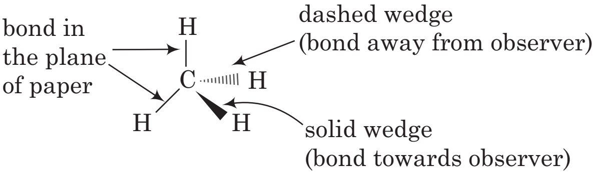


$CH_3—CH_2—COOH \equiv$



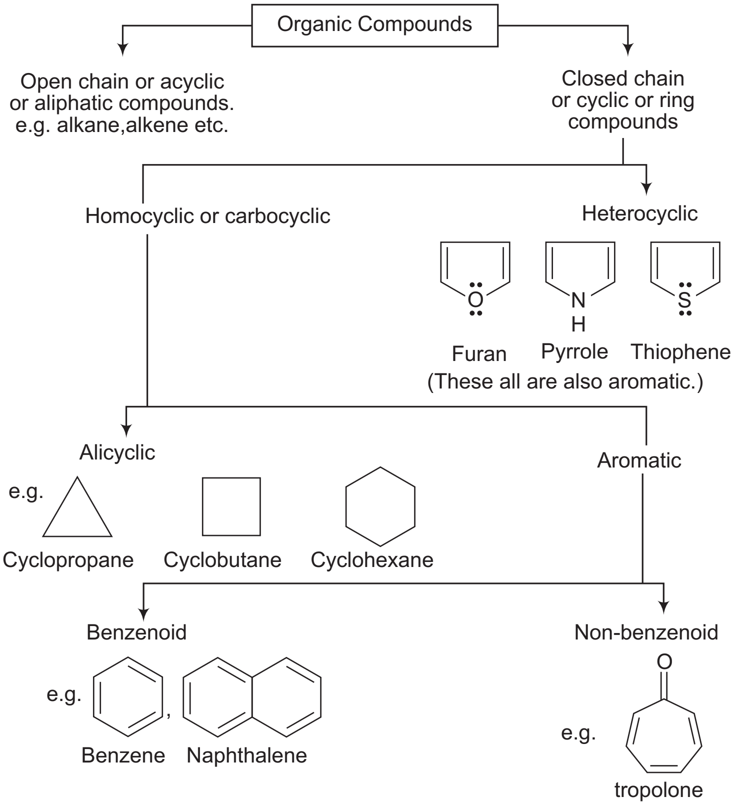
Three-dimensional Representation of Organic Molecule

The three-dimensional (3-D) structure of organic molecule can be represented on paper by using certain convention, e.g. by using solid (◀) and dashed (┈)wedge formula, the 3-D image of a molecule from a two-dimensional picture can be perceived. 3-D representation of methane molecule on paper has been shown below :



wedge-and-dash representation of CH_4.

Classification of Organic Compounds



Classification of Carbon Atoms

1. On the Basis of Number of C Attached

(i) **Primary carbon atom** When carbon atom is attached with one other carbon atom only, it is called primary or 1° carbon atom.

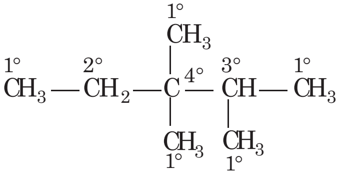
(ii) **Secondary carbon atom** When carbon atom is attached with two other carbon atoms, it is called secondary or 2°carbon atom.

(iii) **Tertiary carbon atom** When carbon atom is attached with three other carbon atoms, it is called tertiary or 3° carbon atom.

(iv) **Quaternary carbon atom** When carbon atom is attached with four other carbon atoms, it is called quaternary or 4° carbon atom.

Reactivity order of carbon atoms is as follows 3° > 2° > 1°.

e.g.



$$\overset{1^\circ}{CH_3}-\overset{2^\circ}{CH_2}-\underset{\underset{1^\circ}{CH_3}}{\overset{\overset{1^\circ}{CH_3}}{\underset{|}{\overset{|}{C}}}}\overset{4^\circ}{-}\underset{\underset{1^\circ}{CH_3}}{\underset{|}{\overset{3^\circ}{CH}}}-\overset{1^\circ}{CH_3}$$

On the Basis of Position of Functional Group

(i) **α-carbon** Carbon which is directly attached to the functional group.

(ii) **β-carbon** Carbon which is directly attached to the α-carbon.

Classification of Hydrogen Atoms

1°-hydrogen (primary) attached to 1°-carbon.

2°-hydrogen (secondary) attached to 2°-carbon.

3°-hydrogen (tertiary) attached to 3°-carbon.

α-hydrogen(s) Hydrogens which are attached to α-carbon atom.

β-hydrogen(s) Hydrogens which are attached to β-carbon atom.

e.g.

$$\overset{\beta}{CH_3}-\overset{\alpha}{CH_2}-Cl,$$

$$\overset{\beta}{CH_3}-\overset{\alpha}{CH_2}-COOH$$

$$\overset{\beta}{CH_3}-\overset{\alpha}{CH_2}-CHO$$

Functional Group

The atom, e.g. —Cl, —Br etc., or group of atoms e.g. —COOH, —CHO, which is responsible for the chemical properties of the molecule, is called functional group.

Double and triple bonds are also functional groups.

$$R\text{—OH}$$

R is called alkyl group, it contains only single bond; alkenyl group contains double bond and alkynyl group contains triple bond.

Homologous Series

The series in which the molecular formula of adjacent members differ by a —CH_2 unit, is called **homologous series** and the individual members are called **homologues**. e.g. The homologous series of alkene group is

$$\left.\begin{matrix} C_2H_4 \\ C_3H_6 \\ C_4H_8 \\ C_5H_{10} \end{matrix}\right\} \text{difference of —}CH_2\text{ unit or 14 unit mass}$$

The general characteristics of this series are :

1. All the homologues contain same functional group. That's why their chemical properties are almost similar.
2. All the members of a series have same general formula, e.g.

Series	General formula
Alkanes	C_nH_{2n+2}
Alkenes	C_nH_{2n}
Alkynes	C_nH_{2n-2}
Alcohol and ether	$C_nH_{2n+2}O$
Aldehyde and ketone	$C_nH_{2n}O$
Acid and ester	$C_nH_{2n}O_2$

3. All the members can be prepared by almost similar methods.
4. With increase in the molecular weight of a series, the physical properties varies gradually.

Nomenclature of Organic Compounds

Trivial System

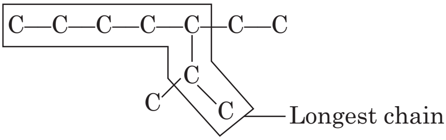
It is the oldest system in which names are derived from source or some property. These are mainly derived from Latin or Greek names. e.g. acetic acid (acetum = vinegar), oxalic acid (oxalus), malic acid (pyrus malus), citric acid (citrum), formic acid (obtained from red ant (formicus)].

IUPAC System

The IUPAC (International Union of Pure and Applied Chemistry) system, given in 1957, is superior and widely used. IUPAC amends these rules from time to time. Here, we are following the 1993 recommendations of IUPAC nomenclature. Following rules are used to write the IUPAC name of an organic compound.

Rule I

Longest chain rule The chain containing the principal functional group, secondary functional group and multiple bonds as many as possible is the longest possible chain. In the absence of functional group, secondary group and multiple bonds, the chain containing the maximum number of C-atoms will be the longest possible chain. e.g.



Choose the word root from the table given below for the longest possible chain.

Word Root for Carbon Chain

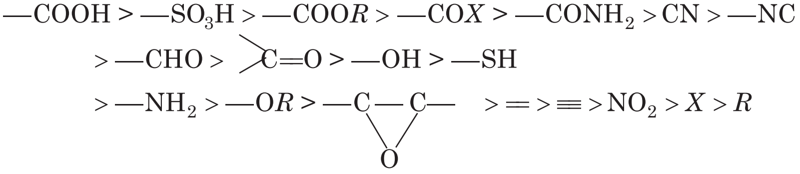
Chain length	Word root	Chain length	Word root
C_1	Meth-	C_7	Hept
C_2	Eth-	C_8	Oct
C_3	Prop-	C_9	Non
C_4	But-	C_{10}	Dec
C_5	Pent	C_{11}	Undec
C_6	Hex-	C_{12}	Dodec

Rule 2

Lowest number rule Numbering is done in such a way so that

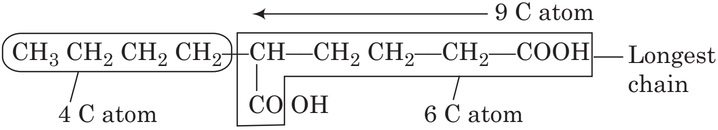
1. branching if present gets the lowest number.
2. the sum of numbers of side chain is lowest.
3. principal functional group gets the lowest number.

Select the principal functional group from the preference series :



$$-COOH > -SO_3H > -COOR > -COX > -CONH_2 > CN > -NC > -CHO > \rangle C=O > -OH > -SH > -NH_2 > -OR > -\underset{\underset{O}{\diagdown\,\diagup}}{C-C}- > \,=\, > \,\equiv\, > NO_2 > X > R$$

Functional group other than the principal functional group are called substituents.



Rule 3.

Naming the prefixes and suffixes Prefix represents the substituent and suffix is used for principal functional group.

Primary prefixes are cyclo, bicyclo, di, tri, tetra, tries, tetrakis etc.

Primary suffix are ene, ane, or yne used for double, single and triple bonds respectively.

Substituent	Prefix	Substituent	Prefix
—F	Fluoro	—N=N—	diazo
—Cl	Chloro	—N=O	nitroso
—Br	Bromo	$-NO_2$	nitro

Secondary suffixes are tabulated below :

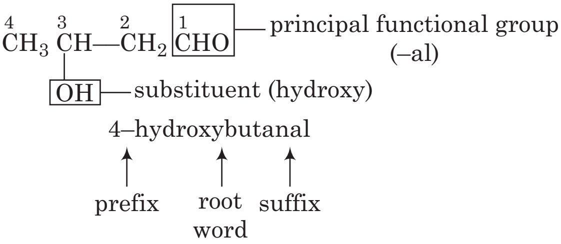
S. No.	Class	Formula	Prefix	Suffix
1.	Acid halides	$-\overset{\overset{O}{\|}}{C}-X$	halocarbonyl	—oyl halide —carbonyl halide
2.	Alcohols	—OH	hydroxy	—ol
3.	Aldehydes	—CHO	formyl	—al —carbaldehyde
4.	Ketones	$\rangle C=O$	oxo	—one

S. No.	Class	Formula	Prefix	Suffix
5.	Amides	—$CONH_2$	carbamoyl	—amide
6.	Amine	—NH_2	amino	—amine
7.	Carboxylic acid	—COOH	carboxy	—carboxylic acid
8.	Ester	—$COOR$	oxy carbonyl	—alkyl alkanoate
9.	Nitriles	—CN	cyano	—nitrile
10.	Sulphonic acid	—SO_2—OH	sulpho	—sulphonic acid

Hence, according to the rules, given above, the IUPAC name of a compound can be written as

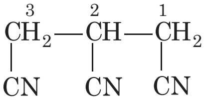
Prefixes + root word + suffixes primary prefix + secondary prefix
+ root word + primary suffix + secondary suffix

e.g.



$$\overset{4}{CH_3}\,\underset{\boxed{OH}}{\overset{3}{CH}}—\overset{2}{CH_2}\,\boxed{\overset{1}{CHO}}$$

If more than two similar functional groups are present, all the groups are considered as substituent, e.g.

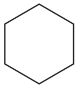


$$\underset{CN}{\overset{3}{CH_2}}—\underset{CN}{\overset{2}{CH}}—\underset{CN}{\overset{1}{CH_2}}$$

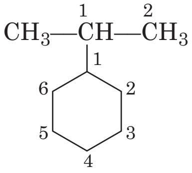
propane-1, 2, 3-cyanide

Naming Alicyclic Compounds

For alicyclic compounds, prefix cyclo is used e.g.

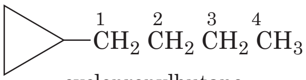


cyclohexane



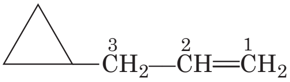
1-(1-methylethyl)
cyclohexane

If the alkyl chain contains a greater number of C-atoms than the ring, the ring is designated as substituent, e.g.



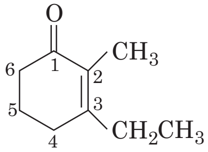
cyclopropylbutane

If side chain contains a multiple bond or a functional group, the ring is treated as a substituent e.g.



3-cyclo propylprop-1-ene

Other examples are :

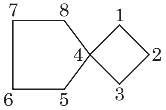


3-ethyl-2-methylcyclohex-2-en-1-one

Naming Spiro Compounds

Prefix 'spiro' is used for the compounds in which one carbon is common between two rings :

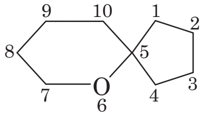
Here, smaller ring is numbered first, e.g.



spiro [3.4] octane

↑

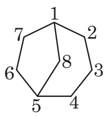
number of atoms in ring
in ascending order



6-oxaspiro [4.5] decane

Naming Bicyclo Compounds

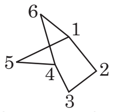
Prefix 'bicyclo' is used for such compounds, e.g.



bicyclo [3.2.1] octane

↑

number of atoms in each ring
in descending order



bicyclo [2.1.1] hexane

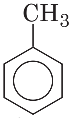
In bicyclo compounds, numbering is done first in larger ring, then in smaller ring.

Naming Aromatic Compounds

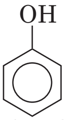
IUPAC accepted their common trivial names, e.g.

benzene

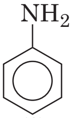
chlorobenzene



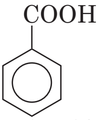
toluene



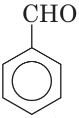
phenol



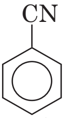
aniline



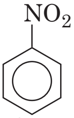
benzoic acid



benzaldehyde

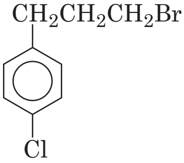


benzonitrile



nitrobenzene

1,4-dichlorobenzene



1-bromo-3-(4-chlorophenyl) propane

Isomerism

The compound having same molecular formula but differ in properties are known as isomers and the phenomenon is known as isomerism.

There are two main types of isomerism i.e.

1. Structural Isomerism

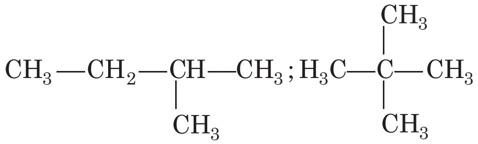
In this type of isomerism, compounds have same molecular formula but different structures.

It can further be of following types :

(i) Chain Isomerism

It arises when two or more compounds have similar molecular formula but different carbon skeletons, e.g. for C_5H_{12}. we have

$$\underset{n-\text{pentane}}{CH_3—CH_2—CH_2—CH_2—CH_3}$$



$$\mathrm{CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_3\,;\; H_3C-\overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{C}}}-CH_3}$$

iso– pentane *neo*– pentane

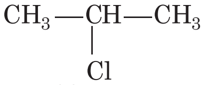
(ii) **Position Isomerism**

When two or more compounds have same molecular formula but different position of functional groups or substituents, they are called positional isomers and the phenomenon is called position isomerism.

e.g. C_3H_7Cl

$CH_3-CH_2-CH_2-Cl$,

1–chloropropane



$$\mathrm{CH_3-\underset{\underset{\displaystyle Cl}{|}}{C}H-CH_3}$$

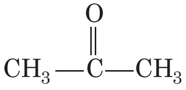
2–chloropropane

(iii) **Functional Isomerism**

It arises when two or more compounds have the same molecular formula but different functional group. e.g. C_3H_6O represents an aldehyde and a ketone as

CH_3-CH_2-CHO,

Propanal



$$\mathrm{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}$$

Propanone

- C_2H_6O represents an alcohol and an ether.

$$\mathrm{CH_3-CH_2-\ddot{\underset{\cdot\cdot}{O}}H,\; CH_3-\ddot{\underset{\cdot\cdot}{O}}-CH_3}\text{ etc.}$$

ethanol dimethyl ether

(iv) **Metamerism**

It arises due to different alkyl groups on either side of the same functional group in a molecule, *e.g.,*

$$\mathrm{CH_3-\ddot{\underset{\cdot\cdot}{O}}-C_3H_7,\; C_2H_5-\ddot{\underset{\cdot\cdot}{O}}-C_2H_5}$$

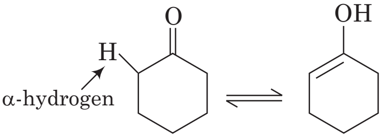
1-methoxypropane diethyl ether

(v) **Tautomerism**

It is a special type of functional isomerism which arises in carbonyl compounds containing α-H atom. e.g.

$$\mathrm{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H \rightleftharpoons CH_2{=}\overset{\overset{\displaystyle OH}{|}}{C}-H}$$

keto form (acetaldehyde) enol form



cyclohexanone (keto form) enol form

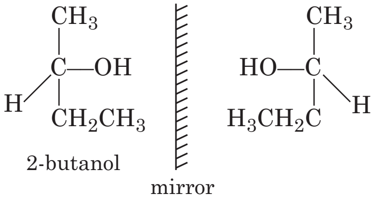
2. Stereoisomerism

The compounds having same molecular formula but different spatial arrangement of atoms or groups are called **stereoisomers** and the phenomenon is called **stereoisomerism**.

Stereoisomerism is of two types : optical isomerism and geometrical isomerism.

(i) Optical Isomerism

Compounds having similar physical and chemical properties but differ only in behaviour towards plane polarised light are called enantiomers or optical isomers and the phenomenon is known as optical isomerism. e.g.



2-butanol

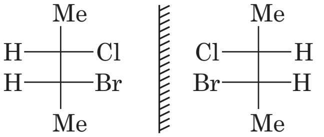
The isomer which rotate the plane of polarised light towards right (clockwise) is known as **dextrorotatory** or ***d*-form** while that which rotates towards left (anticlockwise) is known as **laevorotatory** or ***l*-form**.

Generally asymmetric or chiral compounds show optical isomerism. Chiral compounds are those which contain chiral centre i.e. chiral carbon, the carbon all the four valencies of which are satisfied by four different groups. Allenes, spiranes and biphenyl compounds, although have absence of chiral centre, but are asymmetric. That's why they are also optically active.

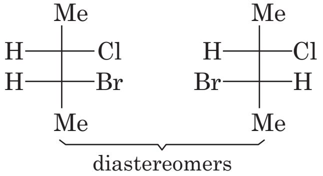
Number of optical active isomers $= 2^n$ (where, $n =$ chiral carbon). If two end are similar number of optical active isomers $= 2^{n-1}$ (if $n =$ even) and *meso* form $= 2^{\frac{n-1}{2}}$. If $n =$ odd, number of optical active isomers $= 2^{n-1} - 2^{(n-1)/2}$.

Terms Related to Optical Isomerism

(a) **Enantiomers** The non-superimposable mirror images are called **enantiomers**. e.g.



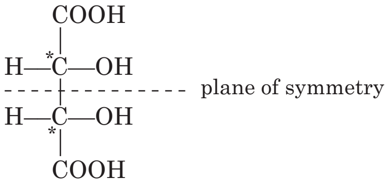
(b) **Diastereomers** The isomers which are non-superimposable and not related to each other as mirror image, are called **diastereomers**.



They have different physical and chemical properties.

(c) ***Meso* form** The compound in which half part of a molecule is the mirror image of other half, is called *meso* form. Generally, a *meso* compound have two or more chiral centres and a plane of symmetry.

It is optically inactive due to internal compensation, thus, it is not possible to convert it into *d* and *l*-form e.g.



meso compound

(d) **Racemic mixture** It is a mixture of enantiomers in 1 : 1. It is optically inactive due to external compensation.

> Separation of a racemic mixture into *d* and *l* form is called **resolution**. It can be done by mechanical method, biochemical method and chemical method.

(e) **Atropisomers** These are the isomers that can be interconvertable by rotation about single bond but for which the rotation barrier is large enough that they can be separated and do not convert readily at room temperature.

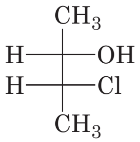
(f) **Specific rotation** It is given by the expression

$$[\alpha] = \frac{\alpha}{l \times d} = \frac{\text{observed rotation (degree)}}{\text{length} \times \text{density}}$$

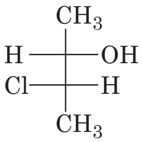
Nomenclature of Enantiomers

(i) ***D-L* configuration** The optical isomer in which H is present towards left hand side and the other group towards right hand side, is *D*-form while in which, H is present towards right and the other group occupy the left position, is *L*-form. This system is applicable mainly for compounds containing one chiral atom.

(ii) **Threo-erythro system** When the same groups are present at the same side of the carbon chain, the form is called erythro form. When the same groups are present on the opposite side of the carbon chain, the form is called threo form. e.g.



erythro form



threo form

(iii) ***R-S* system** This system was proposed by Cahn, Ingold and Prelog. In this system, configuration *R* is given to the isomer in which sequence of groups is clockwise and *S* is given to the isomer in which sequence of groups is anticlockwise.

Priority sequence is decided by following rules :

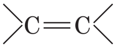
1. Priority is given to the atom having high atomic number, e.g. in Cl, Br and F, the priority order is Br > Cl > F.
2. In case of group of atoms, priority is decided by the atomic number of first atom. e.g. in —COOH, —OH and —NH_2 priority order is

$$\text{—OH} > \text{—NH}_2 > \text{—COOH}$$

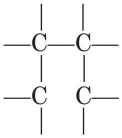
3. If the first atom of the group of atoms is same, the priority is decided by second atom of the group, e.g. among —COOH, —CH_2OH and—CHO, priority order is

$$\text{—COOH} > \text{—CHO} > \text{—CH}_2\text{OH}$$

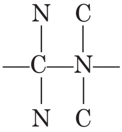
4. When a multiple bond is present in a group, the atom at the end of the multiple bond is like as if it is equal to equivalent number of single bond, e.g.



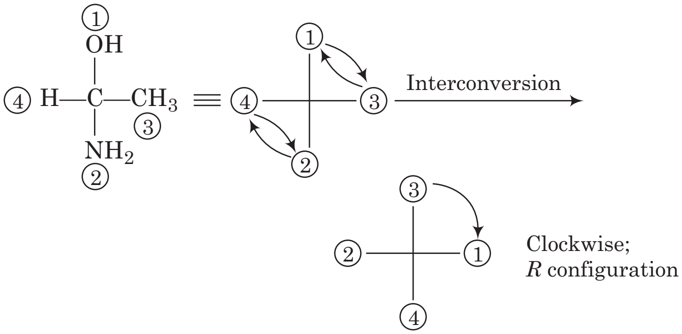
is equivalent to



Similarly, $-C\equiv N$ is equivalent to

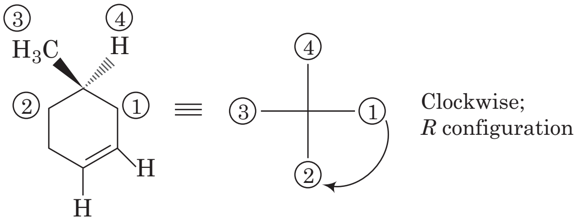


e.g.



Clockwise; *R* configuration

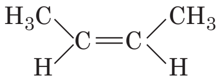
Priority order OH > NH_2 > CH_3 > H



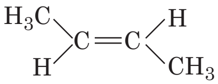
Clockwise; *R* configuration

(ii) Geometrical Isomerism

The isomers having same molecular formula but different spatial arrangement of atoms about the double bond are known as geometrical isomers and this phenomenon is called geometrical isomerism, e.g.



cis-2-butene



trans-2-butene

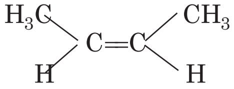
For exhibiting geometrical isomerism, the essential conditions are :

1. The compound must contain at least one double bond.
2. The groups present at the double bonded carbon atoms, must be different. However, one similar group should be present at the adjacent double bonded carbon atoms.

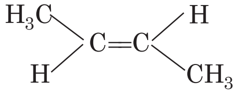
   Number of geometrical isomers (if two ends are not similar = 2^n where, n = number of double bonds).

Types of Geometrical Isomers

(a) ***Cis-trans* isomers** In *cis*-isomer, similar groups are present on the same side of the double bond and in *trans*-isomer, similar groups are present on the opposite side of the double bond. e.g.

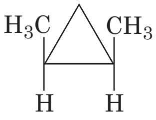


cis–form

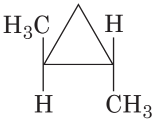


trans–form

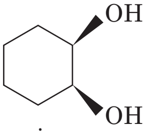
Cycloalkanes also exhibit *cis-trans* isomerism.



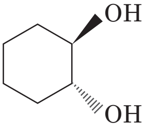
cis-form



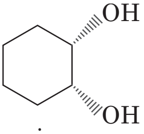
trans-form



cis

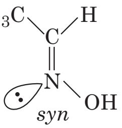


trans

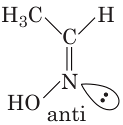


cis

(b) ***Syn-anti* isomers** compounds containing C=N bond (as in aldoxime), N=N bond (as in H_2N_2O) exhibit this type of isomerism. e.g.

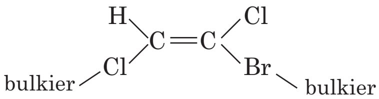


syn



anti

(c) ***E-Z* isomers** In *E*-isomer, bulkier (heavier) groups are present on the opposite side of the double bond and in *Z*-isomer, heavier groups are present on the same side of the double bond. *E* is *entgegen* means opposite and *Z* is *Zusammen* means together, e.g.



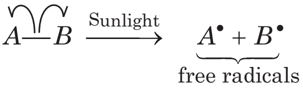
Z isomer

Z-3-hexene

Fission of a Covalent Bond

1. Homolytic Fission

In this, one of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms. The neutral chemical species thus formed, is called free radical. Generally, homolytic fission takes place in non-polar, covalent molecules in the presence of sunlight or high temperature.



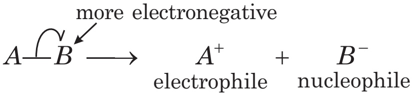
$$A-B \xrightarrow{\text{Sunlight}} \underbrace{A^\bullet + B^\bullet}_{\text{free radicals}}$$

e.g. $$Cl_2 \xrightarrow{\text{Sunlight}} 2Cl^\bullet$$

Free radicals are highly reactive, neutral and electron deficient species.

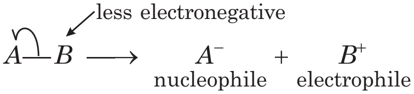
2. Heterolytic Fission

In this, the bond breaks in such a fashion that the shared pair of electrons goes with one of the fragments.



$$A-\overset{\text{more electronegative}}{B} \longrightarrow \underset{\text{electrophile}}{A^+} + \underset{\text{nucleophile}}{B^-}$$

or



$$A-\overset{\text{less electronegative}}{B} \longrightarrow \underset{\text{nucleophile}}{A^-} + \underset{\text{electrophile}}{B^+}$$

Carbon bearing a positive charge is called **carbocation** and carbon bearing negative charge is called **carbanion**.

> Heterolytic fission generally takes place in polar covalent molecules but in non-polar molecules, it takes place in the presence of catalyst like $AlCl_3$ (anhy.), $FeCl_3$(anhy.) etc.

Attacking Reagents

These are of two types :

1. Electrophiles or Electrophilic Reagents

These are electron deficient species i.e. behave as Lewis acids. The following species behave as electrophiles :

(i) All non-metal cations and metal cations which have vacant *d*-orbitals. e.g. Cl^+, NO_2^+, CH_3CO^+ etc.

(ii) Lewis acids (incomplete octet), e.g. BF_3, $ZnCl_2$ (anhydrous), $FeCl_3$ (anhydrous), $AlCl_3$ (anhydrous), $:CH_2$ etc.

(iii) Non-metal (acidic) oxides e.g. CO_2, SO_2 etc.

2. **Nucleophiles or Nucleophilic Reagents**

These are electron rich species i.e. behave as Lewis bases.

These attack at electron deficient area.

The following species behave as nucleophiles :

(i) All anions e.g. Cl^-, NH_2^-, OH^- etc.

(ii) Lewis bases e.g. $:NH_3, H_2O, R—\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}—R, R—\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}H$ etc.

(iii) Benzene, alkenes etc.

Nucleophilicity order is

$$H^- > CH_3^- > NH_2^- > RO^- > OH^-$$

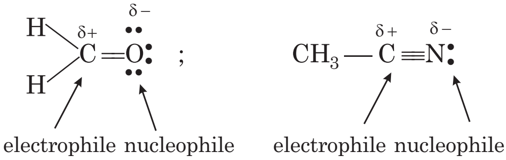
In case of same nucleophilic site, nucleophilicity parallels basicity i.e. as the basicity increases, nucleophilicity also increases.

> If nucleophilic sites (or attacking atoms) are different nucleophilicity varies inversely with electronegativity.

3. **Ambiphiles**

These species behave like both electrophiles as well as nucleophiles.

Organic compounds containing a multiple bond between carbon and a more electronegative atom can act as ambiphiles. e.g.



Reaction Intermediates

These are formed as a intermediate during the course of a reaction. These are short lived and highly reactive.

Free radicals, carbocations, carbanions, carbenes and nitrenes are important reactions intermediates.

1. **Free Radicals**

These are the product of homolysis and contain an odd electron. These are highly reactive planar species with sp^2-hybridisation.

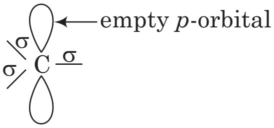
Their order of stability is

$$(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > C_6H_5\dot{C}H_2$$
$$> CH_2{=}CH{-}\dot{C}H_2 > 3^\circ > 2^\circ > 1^\circ > CH_2{=}\dot{C}H$$

2. **Carbocations**

These are the product of heterolysis and contain a carbon bearing positive charge. These are electron deficient species. Carbocations contain six electrons in the valence shell.

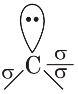
These are also planar chemical species, i.e. sp^2-hybridised with an empty p-orbital.



The stability order of carbocations is :

$$(C_6H_5)_3C^+ > (C_6H_5)_2\overset{+}{C}H > (CH_3)_3\overset{+}{C} > C_6H_5\overset{+}{C}H_2 > 2^\circ$$
$$> CH_2{=}CH{-}\overset{+}{C}H_2 > 1^\circ > \overset{+}{C}_6H_5 > CH_2{=}\overset{+}{C}H$$

3. **Carbanions**



These are also the product of heterolysis and contain a carbon bearing negative charge and 8 electrons in its valence shell.

These have pyramidal shape with sp^3-hybridised carbon (having one lone pair)

The order of stability of carbanions is

$$(C_6H_5)_3C^- > (C_6H_5)_2\bar{C}H > C_6H_5\bar{C}H_2 > CH_2{=}CH{-}\bar{C}H_2$$
$$> \bar{C}H_3 > 1^\circ > 2^\circ > 3^\circ \text{ carbanions}$$

4. **Carbenes**

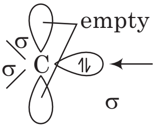
These are divalent carbon species having two non-bonding electrons along with two bond pairs.

These are obtained by photolysis or pyrolysis, e.g.

$$\underset{\text{ketene}}{CH_2{=}C{=}O} \xrightarrow[\text{or }\Delta]{h\nu} {:}CH_2 + {:}C{=}O$$

These being electron deficient behave as Lewis acids. These are of two types :

(i) **Singlet carbene** In it, the C-atom is sp^2-hybridised. The unhybridised orbitals contain no electrons and a hybridised orbital contains two electrons :



sp^2-hybridised with 2 unbonded electrons

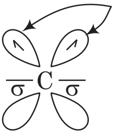
Singlet carbene has bent structure and is less stable than triplet carbene.

The order of stability of singlet carbenes is

$$\ddot{C}H_2 > \ddot{C}F_2 > \ddot{C}Cl_2 > \ddot{C}Br_2$$

(ii) **Triplet carbene** In it, the central C-atom is *sp*-hybridised. The unhybridised orbitals contain 1 electron each.

unhybridised orbitals with 1 electron



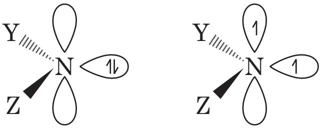
Triplet carbene has linear geometry.

5. **Nitrene**

These are neutral monovalent nitrogen species in which N atom has two unshared pair of electrons with a mono valent atom or group attached.

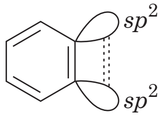
These are obtained by thermolysis of azides and as reactive as carbenes.

These are of two types : singlet nitrene and triplet nitrene



Singlet Nitrene Triplet Nitrene

6. **Arynes**



It contains a formal carbon-carbon triple bond in aromatic molecule.

The additional bond is formed between two neighbouring C-atoms by sideways overlapping of two sp^2-orbitals. The new bond lies along with side of the ring and has little interaction with the π electron cloud lying above and below the ring. The sideways overlapping is weak and thus, makes the benzene more reactive.

Inductive Effect

It is just like shifting of shared pair of electrons in polar covalent molecules. If shared pair is more shifted towards the more electronegative atom, the less electronegative atom acquires slight positive charge and more electronegative atom acquires partial negative charge, e.g.

$$\overset{+\delta}{CH_3} \rightarrow\!\!- \overset{-\delta}{Cl}$$

It is a permanent effect and propagates through carbon chain. Atoms or groups having greater electron affinity than hydrogen, are said to have electron attracting or negative inductive effect ($-I$) while that having, smaller electron affinity than hydrogen are said to have electron releasing or positive inductive effect ($+I$). e.g.

$$\overset{+\delta\delta}{CH_3} \rightarrow\!\!- \overset{+\delta}{CH_2} \rightarrow\!\!- \overset{-\delta}{Cl}$$

$$\overset{+\delta\delta\delta}{CH_3} \rightarrow\!\!- \overset{+\delta\delta}{CH_2} \rightarrow\!\!- \overset{+\delta}{CH_2} \rightarrow\!\!- \overset{-\delta}{Cl}$$

1°alkyl halide

Here, Cl has $-I$ effect and alkyl group has $+I$ effect.

Order of groups producing $-I$ effect is

$$R_3\overset{+}{N} > NO_2 > CN > SO_3H > CHO > CO > COOH > F >$$
$$Cl > Br > I > OH > OR > NH_2 > C_6H_5 > H$$

Order of groups producing $+I$ effect is

$$O^- > —COO^- > 3° \text{ alkyl group } > 2° \text{ alkyl group}$$
$$> 1° \text{ alkyl group} > CH_3 > H$$

Applications of Inductive Effect

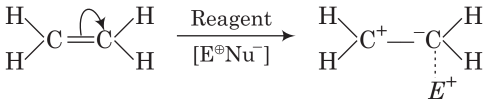
1. Presence of groups showing $+I$ effect increases the stability of carbocation while presence of groups showing $-I$ effect decreases their stability.

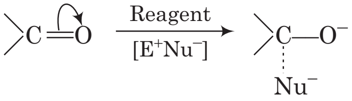
2. Strength of acid increases with the attachment of group showing – *I* effect and decreases with the attachment of group showing + *I* effect.
3. Presence of + *I* effect showing groups increases the basic strength of amines.
4. Reactivity of carbonyl compound is increased by – *I* effect showing groups.
5. Reactivity of alkyl halides towards S_N1 is increased by + *I* showing groups.

Electromeric Effect

It is defined as the polarity produced in a multiple bonded compound as a reagent approaches it. In the presence of attacking reagent, the two π electrons are completely transferred to any of the one atom. This effect is temporary.

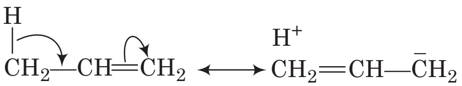
This may be of + *E* type (when displacement of electron pair is away from the atom or group) or of – *E* type (when the displacement is towards the atom or group). e.g.





Hyperconjugation

It involves delocalisation of σ electron of a C—H bond of an alkyl group attached directly to an atom of unsaturated system or to an atom with an unshared *p*-orbital.

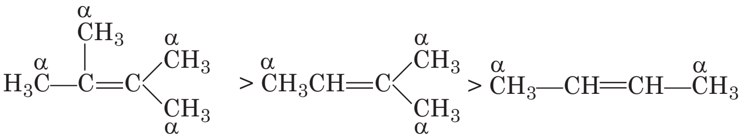


$$\overset{\mathrm{H}}{\mathrm{CH_2}}-\mathrm{CH}=\mathrm{CH_2} \longleftrightarrow \overset{\mathrm{H^+}}{\mathrm{CH_2}}=\mathrm{CH}-\bar{\mathrm{C}}\mathrm{H_2}$$

This effect is also called **no bond resonance or Baker Nathan effect**.

Applications of Hyperconjugation

(i) **Stability of alkenes** More the number of α-hydrogen atoms, more stable is the alkene.



$$H_3\overset{\alpha}{C}—\overset{\overset{\alpha}{CH_3}}{C}=C(\overset{\alpha}{CH_3})_2 > \overset{\alpha}{C}H_3CH=C(\overset{\alpha}{CH_3})_2 > \overset{\alpha}{C}H_3—CH=CH—\overset{\alpha}{C}H_3$$

(ii) **Stability of carbocation** Greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the stability.

$$(CH_3)_3C^+ > (CH_3)_2\overset{+}{C}H > CH_3—\overset{+}{C}H_2 > \overset{+}{C}H_3$$

Resonance Effect

When all the properties of a molecule cannot be shown by a single structure and two or more structures are required to show all the properties of that molecule, then the structures are called **resonating structures** or **canonical forms** and the molecule is referred as resonance hybrid. This phenomenon is called resonance.

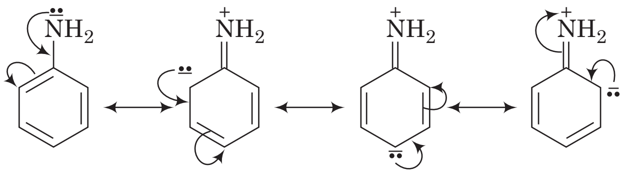
In resonance,

1. The arrangement of atoms must be identical in all the formulae.
2. The energy content of all the canonical forms must be nearly same.
3. Each canonical form must have the same number of unpaired electrons.

It involves delocalisation of π electrons. This effect may be of + *R* type or – *R* type.

Positive Resonance Effect (+R)

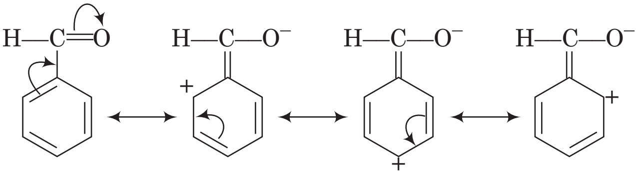
Electron donating groups with respect to conjugate system show +*R* effect. Central atom of functional groups should be more electronegative than the surrounding atoms or groups to show + *R* effect. e.g. halogens, —OH, —O*R*, —OCO*R*, —NH_2,—NHCO*R* etc.



Electron donating groups producing, + *R* effect are *ortho* and *para* directing. They activate the benzene ring towards the electrophilic substitution reactions except halogens. Halogens slightly deactivate the benzene ring towards the electrophilic substitution reaction. More the E.D.G, more is the basic nature.

Negative Resonance Effect (–R)

Electron withdrawing groups with respect to conjugate system show $-R$ effect. Central atom of functional groups should be less electronegative than surrounding atoms or groups to show $-R$ effect. e.g. halogens, — COOH, — COOR, — CHO,— CN,—NO_2 etc.



Electron withdrawing group (E.W.G.) producing $-R$ effect are *meta* directing. They deactivate the benzene ring towards the electrophilic substitution reaction. More the E.W.G, more is the acidic nature.

Stability of Canonical Forms

It can be judged by the following rules :

1. Non-polar structure is more stable than the polar structure.
2. Among polar structures, structure with maximum number of covalent bonds is most stable.
3. The structure with maximum charge separation is more stable.
4. Structure with positive charge on more electropositive element and negative charge on more electronegative element is more stable.

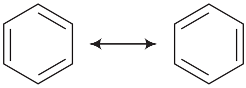
Resonance Energy

Number of π bonds $\propto$ contributing structures $\propto$ resonance energy $\propto$ stability.

In benzene, resonance energy is 36 kcal/mol.

Relation Between Resonance and Bond order

$$\text{Bond order} = \frac{\text{Total number of bonds betwen two atoms}}{\text{Total number of resonating structures}}$$

e.g.  $\text{BO} = \frac{2+1}{2} = 1.5$

Types of Organic Reactions

Reactions are of following types :

1. Addition Reactions

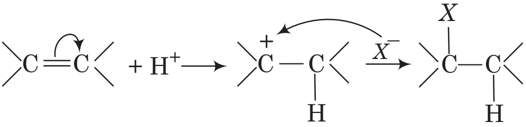
These reactions are given by unsaturated compounds or compounds containing multiple bonds.

In these reactions, the reagent adds to the substrate molecule.

These are of two types (depending upon the nature of attacking species) :

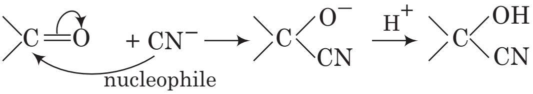
(i) **Electrophilic addition reactions** In these reactions, H^+ (or electrophile) is added to the substrate in the rate determining step.

These reactions are given by alkenes and alkynes. e.g.



(ii) **Nucleophilic addition reactions** In these reactions, nucleophile is added to the substrate in the rate determining step.

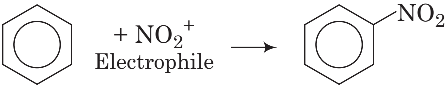
These reactions are given by carbonyl compounds. e.g.



2. Substitution Reactions

In these reactions, one atom or group of atoms, called the leaving group, is substituted by a nucleophile or an electrophile. On this basis these reactions are of two types :

(i) **Electrophilic substitution reactions** When leaving group is replaced by an electrophile, the reaction is called electrophilic substitution reaction.



(ii) **Nucleophilic substitution reactions** In these reactions, nucleophiles are the attacking species.

These are of two types :

(a) S_N1 **(Nucleophilic substitution unimolecular)** reaction is a two step process, e.g.

$$R\text{—}X \longrightarrow R^+ + X^-$$

$$R^+ + \underset{\text{nucleophile}}{OH^-} \longrightarrow ROH$$

For such reaction, rate $= k\,[R - X]$

The reactivity of alkyl halides towards S_N1 reaction is $3° > 2° > 1°$ alkyl halide.

(b) S_N2 **(Nucleophilic substitution bimolecular)** reaction is a single step process e.g.

$$\underset{\text{nucleophile}}{OH^-} + R\text{—X} \longrightarrow H\overset{\delta-}{O}\ldots R\ldots\overset{\delta-}{X} \longrightarrow R\text{—OH} + X^-$$

For such reactions, rate $= k\,[RX]\,[OH^-]$

These reactions involve inversion of configuration.

For such reactions the order of reactivity of alkyl halide is

$$1° > 2° > 3°$$

3. **Elimination Reactions**

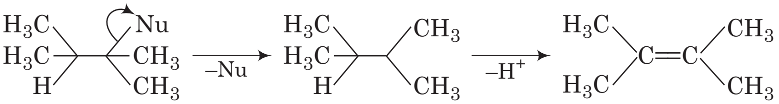
In these reactions, two groups from the same or adjacent atoms are lost and electron deficient or unsaturated compound is formed.

These can be of two types :

(i) **α-elimination** In it, both the groups are eliminated from the same carbon atom. Such reactions are rare. e.g.

$$CHCl_3 \longrightarrow :\overset{-}{C}Cl_3 \longrightarrow \underset{\text{carbene}}{:CCl_2}$$

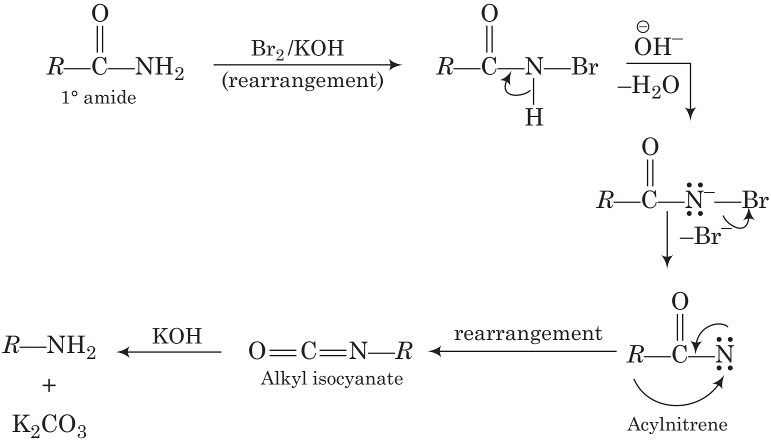
(ii) **β-elimination** Here, the groups are eliminated from the adjacent carbon atoms. These can further be E_1 or E_2 reactions .e.g.



4. **Rearrangement Reactions**

Reactions involving the migration of an atom or a group from one atom to another within the same molecule are called rearrangement reactions.

e.g. Hofmann bromamide reaction involving the conversion of 1° amides to 1° amines on treatment with Br_2 in the presence of KOH.



This reaction involves the migration of alkyl group, *R* from C to N to form alkyl isocyanate.