General Organic Chemistry

Carbon is an essential element of organic compounds, it has four electrons in its outer most shell.

According to the ground state electronic configuration of carbon, it is divalent. Tetravalency of carbon can be explained by promoting one of the $2s^2$ - electrons to the unoccupied $2p_{z^1}$ atomic orbital.

The four valencies of carbon atom are similar and they are symmetrically arranged around the carbon atom. According to **Le Bell and Van't Hoff** the four valencies of carbon do not lie in one plane. They are directed towards the corners of a regular tetrahedron with carbon atom at the centre and the angle between any two valencies is $109.28'$.

Hybridisation in Organic Compounds

(1) The process of mixing atomic orbitals to form a set of new equivalent orbitals is termed as *hybridisation*. There are *three types* of hybridisation,

(i) sp^3 *hybridisation* (involved in saturated organic compounds containing only single covalent bonds),

(ii) sp^2 *hybridisation* (involved in organic compounds having carbon atoms linked by double bonds) and

(iii) sp *hybridisation* (involved in organic compounds having carbon atoms linked by a triple bonds).

Table : 23.1

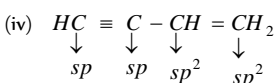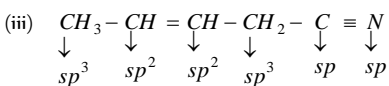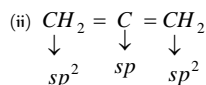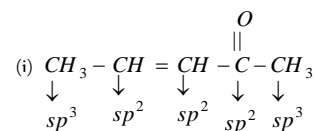| Type of hybridisation	sp^3	sp^2	sp
Number of orbitals used	1s and 3p	1s and 2p	1s and 1p
Number of unused p-orbitals	Nil	One	Two
Bond	Four -σ	Three -σ One -π	Two -σ Two -π
Bond angle	109.5°	120°	180°
Geometry	Tetrahedral	Trigonal planar	Linear
% s-character	25 or 1/4	33.33 or 1/3	50 or 1/2

(2) **Determination of hybridisation at different carbon atoms :** It can be done by two methods,

(i) *First method* : In this method hybridisation can be know by the number of $\pi -$ bonds present on that particular atom.

Number of π– bond/s	0	1	2

Type of hybridisation	sp	sp	sp

Examples :

(i)
$$CH_3 - CH = CH - \overset{\overset{O}{||}}{C} - CH_3$$
$$\downarrow \quad \downarrow \quad \downarrow \quad \downarrow \quad \downarrow$$
$$sp^3 \quad sp^2 \quad sp^2 \quad sp^2 \quad sp^3$$

(ii)
$$CH_2 = C = CH_2$$
$$\downarrow \quad \downarrow \quad \downarrow$$
$$sp^2 \quad sp \quad sp^2$$

(iii)
$$CH_3 - CH = CH - CH_2 - C \equiv N$$
$$\downarrow \quad \downarrow \quad \downarrow \quad \downarrow \quad \downarrow \quad \downarrow$$
$$sp^3 \quad sp^2 \quad sp^2 \quad sp^3 \quad sp \quad sp$$

(iv)
$$HC \equiv C - CH = CH_2$$
$$\downarrow \quad \downarrow \quad \downarrow \quad \downarrow$$
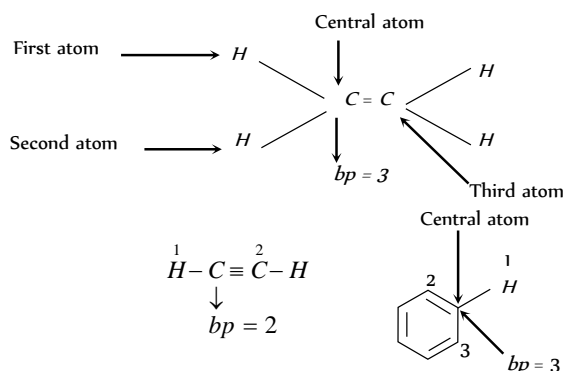$$sp \quad sp \quad sp^2 \quad sp^2$$

❑ In diamond carbon is sp hybridised and in graphite carbon is sp^2 hybridised.

(ii) *Second method* : (Electron pair method)

$ep = bp + lp$; where ep = electron pair present in hybrid orbitals , bp = bond pair present in hybrid orbitals

Number of bp = Number of atoms attached to the central atom of the species

$$\overset{1}{H} - C \equiv \overset{2}{C} - H$$
$$\downarrow$$
$$bp = 2$$

Number of lp's can be determined as follows,

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

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

Number of electron pairs (ep) tells us the type of hybridisation as follows,

ep	2	3	4	5	6
Type of hybridisation	sp	sp^2	sp^3	sp^3d	sp^3d^2

Example :

(i) $\overset{\oplus}{CH_2 = CH}$

$bp = 2$
$lp = 0$
$ep = 2, sp$

(ii) $\overset{\ominus}{CH_2 = CH}$

$bp = 2$
$lp = 1$
$ep = 3, sp^2$

(iii) $CH_2 = \overset{\bullet}{C} - CH_3$
       |
      CH_3

$bp = 3$
$lp = 0$
$ep = 3, sp^2$

(iv) $CH \equiv \overset{\ominus}{C}$

$bp = 1$
$lp = 1$
$ep = 2, sp$

(v) $CH_3 - \overset{\ominus}{CH} - CH_3$

$bp = 3$
$lp = 1$
$ep = 4, sp^3$
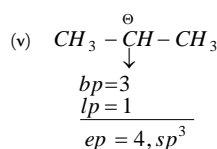
(3) Applications of hybridisation

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

$$sp^3 > sp^2 > sp$$

(ii) *Electronegativity of different orbitals*

(a) Electronegativity of s-orbital is maximum.

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

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

s-character in decreasing order and electronegativity in decreasing order

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

$CH_3 - \overset{\oplus}{CH_2}$ → sp^2 → Electropositive carbon

$CH_2 = \overset{\oplus}{CH}$ → sp → Electronegative carbon having positive charge
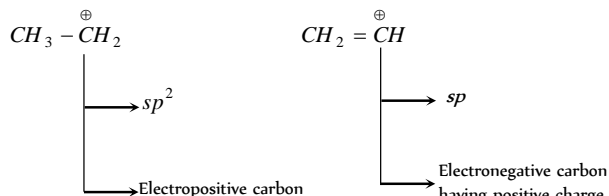
(c) Electronegativities of different hybrid and unhybrid orbitals in decreasing order is as follows

$$s > sp > sp^2 > sp^3 > p$$

% s - character and electronegativity in decreasing order.

(iii) *Bond length variation in hydrocarbons*

% of s orbital character

$$\propto \frac{1}{C - C \text{ bond length}} \propto \frac{1}{C - H \text{ bond length}}$$

Table : 23.2

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

(iv) *Bond strength in hydrocarbons* : The shorter is the bond length, the greater is the compression between atomic nuclei and hence greater is the strength of that bond.
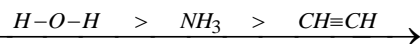
Table : 23.3

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

(v) *Acidity of hydrocarbons*

(a) Hydrogen present on electronegative carbon is acidic in nature.

(b) Acidity of hydrogen is directly proportional to the electronegativity of the atom on which hydrogen is present.

Thus

$$H-O-H \quad > \quad NH_3 \quad > \quad CH \equiv CH$$

Electronegativity of the atoms
Acidity of compounds in decreasing order

(c) Acidity of hydrocarbon $\propto$ % of s-character

	$CH \equiv CH$	$CH_2 = CH_2$	$CH_3 - CH_3$
% s-character	50	33.33	25
pKa	25	44	50

s- character and acidity in decreasing order

Acidity $\propto Ka$ and Acidity $\propto \dfrac{1}{pKa}$ ($pKa = -\log Ka$)

Order of acidic nature of alkynes is,

$$HC \equiv CH > HC \equiv C - CH_3$$

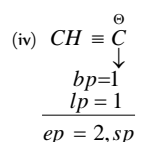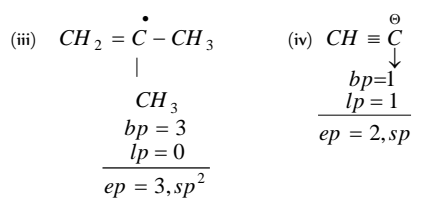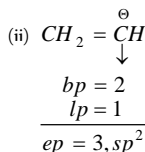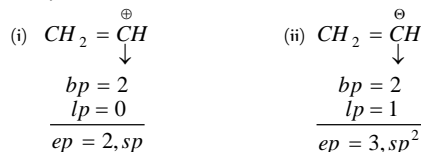The relative acidic character follows the order;

$$H_2O > ROH > HC \equiv CH > NH_3 > CH_2 = CH_2 > CH_3 - CH_3$$

Obviously, the basic character of their conjugate bases follows the reverse order, *i.e.,*

$$CH_3CH_2^{\ominus} > CH_2 = CH^{\ominus} > NH_2^{\ominus} > HC \equiv C^{\ominus} > RO^{\ominus} > HO^{\ominus}$$

Steric effect

On account of the presence of bulkier groups at the reaction centre, they cause mechanical interference and with the result the attacking reagent finds it difficult to reach the reaction site and thus slows down the reaction. This phenomenon is called **steric hinderance or steric effect**.

(1) Tertiary alkyl halides having bulky groups form tertiary carbocation readily when hydrolysed because of the presence of the three bulky groups on the carbon having halogen.
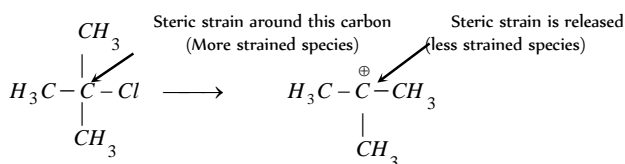

(2) Primary alkyl halide having quaternary β-carbon does not form transition state because of the steric strain around α-carbon by the β-carbon. To release the strain it converts into carbocation.
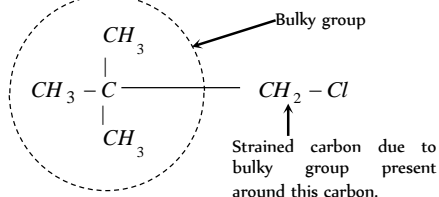
(3) Steric strain inhibits the resonance. This phenomenon is known as **steric inhibitions of resonance**.
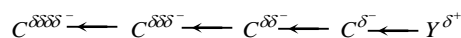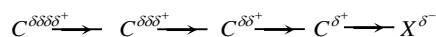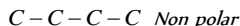
Electronic displacement in covalent bonds

It is observed that most of the attacking reagents always possess either a positive or a negative charge, therefore for a reaction to take place on the covalent bond the latter must possess oppositely charged centres. This is made possible by displacement (partial or complete) of the bonding electrons. The electronic displacement in turn may be due to certain effects, some of which are **permanent** and others are **temporary**. The former effects are permanently operating in the molecule and are known as **polarisation effects**, while the latter are brought into play by the attacking reagent and as soon as the attacking reagent is removed, the electronic displacement disappears; such effects are known as the **polarisability effects**.
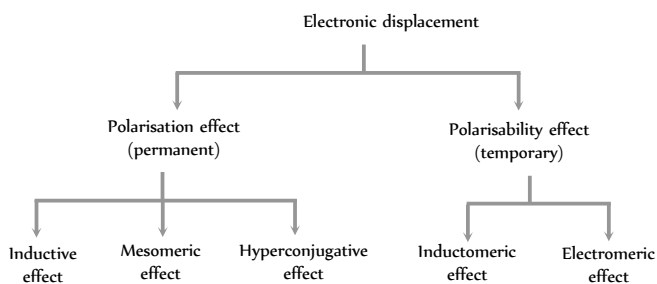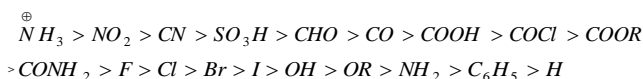

Inductive effect or Transmission effect

(1) When an electron withdrawing (X) or electron-releasing (Y) group is attached to a carbon chain, polarity is induced on the carbon atom and on the substituent attached to it. This permanent polarity is due to displacement of shared electron of a covalent bond towards a more electronegative atom. This is called *inductive effect or simply as I – effect.*

$$C - C - C - C \quad \text{Non polar}$$

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

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

(2) Carbon-hydrogen bond is taken as a standard of inductive effect. Zero effect is assumed for this bond. Atoms or groups which have a greater electron withdrawing capacity than hydrogen are said to have–I effect whereas atoms or groups which have a greater electron releasing power are said to have +I effect.

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

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

$$ter. \text{ alkyl} > sec. \text{ alkyl} > pri. \text{ alkyl} > CH_3 > H$$
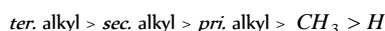
+ I power in decreasing order with respect to the reference H

+ I power $\propto$ number of carbon in the same type of alkyl groups

$$CH_3 - CH_2 - CH_2 - CH_2 - > CH_3 - CH_2 - CH_2 - >$$
$$CH_3 - CH_2 -$$
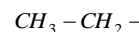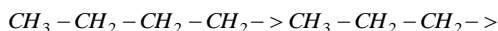
+ I power in decreasing order in same type of alkyl groups

(3) **Applications of Inductive effect**

(i) *Magnitude of positive and negative charges* : Magnitude of +*ve* charge on cations and magnitude of –*ve* charge on anions can be compared by + I or – I groups present in it.

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

power of the group.

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

power of the group.

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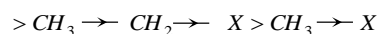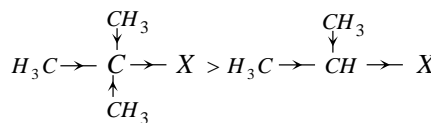
Tertiary > Secondary > Primary > Methyl

(iii) **Relative strength of the acids** :

(a) Any group or atom showing +*I* effect decreases the acid strength as it increases the negative charge on the carboxylate ion which holds the hydrogen firmly. Alkyl groups have + I effect.

Thus, acidic nature is,

$$HCOOH > CH_3COOH > C_2H_5COOH > C_3H_7COOH > C_4H_9COOH$$

+*I* effect increases, so acid strength decreases
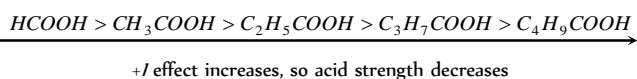
Formic acid, having no alkyl group, is the most acidic among these acids.

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

Thus, acidic nature is,

$$CCl_3COOH > CHCl_2COOH > CH_2ClCOOH > CH_3COOH$$
Trichloro   Dichloro   Monochloro   Aceticacid
aceticacid   aceticacid   aceticacid

(– Inductive effect increases, so acid strength increases)

(c) Strength of aliphatic carboxylic acids and benzoic acid

$$R \longrightarrow COOH \qquad C_6H_5 \longleftarrow COOH$$
$$\uparrow \qquad\qquad\qquad \uparrow$$
$$+I\,group \qquad\qquad -I\,group$$

Hence benzoic acid is stronger acid than aliphatic carboxylic acids but exception is formic acid. Thus,

$$HCOOH \quad > \quad C_6H_5COOH \quad > \quad RCOOH$$

Acid strength in decreasing order

❑ Decreasing order of acids :

$$NO_2CH_2COOH > FCH_2COOH > ClCH_2COOH > BrCH_2COOH .$$

$$F_3C-COOH > Cl_3C-COOH > Br_3C-COOH > I_3C-COOH .$$

$$CH_3OH > CH_3CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$$
Methyl   Ethyl   Iso−propyl   Tert−butyl
alcohol   Alcohol   alcohol   alcohol

As compared to water, phenol is more acidic (−*I* effect) but methyl alcohol is less acidic (+*I* effect).
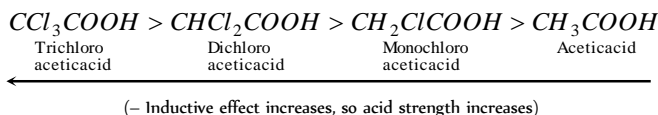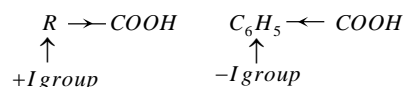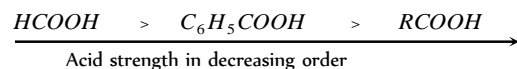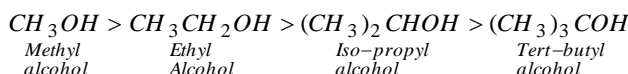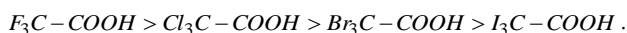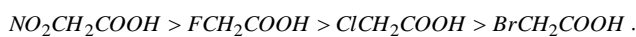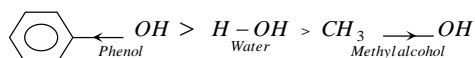
$$\text{Phenol}\longleftarrow OH > H-OH > CH_3\longrightarrow OH$$
         Phenol   Water   Methylalcohol

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

The difference in base strength in various amines can be explained on the basis of inductive effect. The +*I* effect increases the electron density while −*I* effect decreases it. The amines are stronger bases than NH_3 as the alkyl groups increase electron density on nitrogen due to + *I* effect while $ClNH_2$ is less basic due to −*I* effect. "So more is the tendency to donate electron pair for coordination with proton, the more is basic nature, *i.e.,* more is the negative charge on nitrogen atom (due to +*I* effect of alkyl group), the more is basic nature".

Thus, the basic nature decreases in the order;

$$(C_2H_5)_2NH > CH_3CH_2NH_2 > CH_3NH_2 > NH_3 > ClNH_2$$
Diethyl   Ethyl   Methyl   Ammonia   Chloro
amine   amine   amine   amine
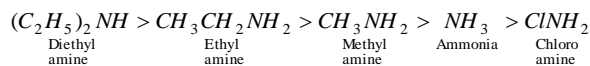
The order of basicity is as given below;

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

❑ The relative basic character of amines is not in total accordance with inductive effect $(t > s > p)$ but it is in the following order: Secondary > Primary > Tertiary. The reason is the steric hindrance existing in the *t*-amines.

❑ In gas phase or in aqueous solvents such as chlorobenzene etc, the solvation effect, *i.e.,* the stabilization of the conjugate acid due to *H* - bonding are absent and hence in these media the basicity of amines depends only on the +*I* effect of the alkyl group thus the basicity of amines follows the order : $3^o > 2^o > 1^o > NH_3$.

(vii) *Basicity of alcohols* : The decreasing order of base strength in alcohols is due to +*I* effect of alkyl groups.

$$(CH_3)_3COH > (CH_3)_2CHOH > CH_3CH_2OH > CH_3OH$$
       (3°) (2°) (1°)
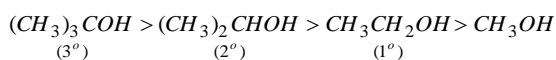
(viii) *Stability of carbonium ion :*+*I* effect tends to decrease the (+*ve*) charge and −*I* effect tends to increases the +*ve* charge on carbocation.

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

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

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

Resonance effect or mesomeric effect

(I) The effect in which π electrons are transferred from a multiple bond to an atom, or from a multiple bond to a single covalent bond or lone pair (*s*) of electrons from an atom to the adjacent single covalent bond is called *mesomeric effect* or simply as *M-effect*. In case of the compound with conjugated system of double bonds, the mesomeric effect is transmitted through whole of the conjugated system and thus the effect may better be known as **conjugative effect**.

(2) Groups which have the capacity to increase the electron density of the rest of the molecule are said to have $+M$ effect. Such groups possess lone pairs of electrons. Groups which decrease the electron density of the rest of the molecule by withdrawing electron pairs are said to have $-M$ effect, e.g.,

(a) The groups which donate electrons to the double bond or to a conjugated system are said to have $+M$ *effect or* $+R$ *effect.*

$+M$ *effect groups* :

$$-Cl, -Br, -I, -\overset{..}{N}H_2, -NR_2, -OH, -OR, -SH, -OCH_3, -\overset{..}{S}\underset{..}{R}$$
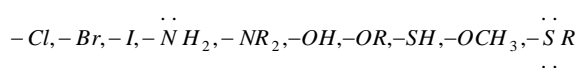
(b) The groups which withdraw electrons from the double bond or from a conjugated system towards itself due to resonance are said to have $-M$ effect or $-R$ effect.

$-M$ effect groups :

$$-NO_2, -C \equiv N, -\overset{\overset{O}{\|}}{C}-, -CHO, -COOH, -SO_3H$$
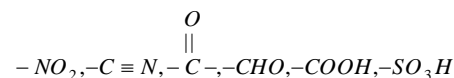
(3) The inductive and mesomeric effects, when present together, may act in the same direction or oppose each other. The mesomeric effect is more powerful than the former. For example, in vinyl chloride due to $-I$ effect the chlorine atom should develop a negative charge but on account of mesomeric effect it has positive charge.

$$: \overset{..}{\underset{..}{Cl}} \leftarrow CH = CH_2 \longleftrightarrow : \overset{\oplus}{Cl} = CH - \overset{\overset{..}{-}}{CH_2}$$
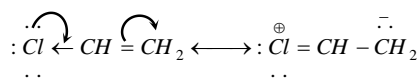
Application of mesomeric effect : It explains,

(1) Low reactivity of aryl and vinyl halides,

(2) The acidic nature of carboxylic acids,

(3) Basic character comparison of ethylamine and aniline,

(4) The stability of some free radicals, carbocations and carbanions.

Difference between Resonance and Mesomerism : Although both resonance and mesomerism represent the same phenomenon, they differ in the following respect : Resonance involves all types of electron displacements while mesomerism is noticeable only in those cases where a multiple bond is in conjugation with a multiple bond or lone pair of electron.

Example :

(i) $\quad H_2\overset{..}{C} = CH - CH = CH_2 \longleftrightarrow H_2\overset{..}{\overset{..}{C}} - CH = CH - \overset{\oplus}{C}H_2$

(ii) $\quad R - \overset{\overset{..}{\overset{\|}{O}}}{C} - \overset{..}{\underset{..}{O}} - H \longleftrightarrow R - \overset{\overset{:\overset{..}{O}:\ominus}{\|}}{C} = \overset{\oplus}{\underset{..}{O}} - H$

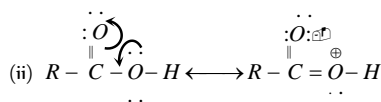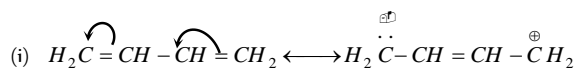Both (i) and (ii) are the examples of mesomerism and resonance effect. Let us consider the following example $H \quad \overset{..}{\underset{..}{Cl}} : \longleftrightarrow \overset{\oplus}{H} \overset{\ominus}{Cl}$. Such an electron displacement is the example of resonance only (not the mesomerism).

Hyperconjugative effect

(1) When a $H - C$ bond is attached to an unsaturated system such as double bond or a benzene ring, the sigma (σ) electrons of the $H - C$ bond interact or enter into conjugation with the unsaturated system. *The interactions between the electrons of π systems (multiple bonds) and the adjacent σ bonds (single $H - C$ bonds) of the substituent groups in organic compounds is called* **hyperconjugation**. The concept of hyperconjugation was developed by Baker and Nathan and is also known as *Baker and Nathan effect*.

In fact hyperconjugation effect is similar to resonance effect. Since there is no bond between the α -carbon atom and one of the hydrogen atoms, the hyperconjugation is also called *no-bond resonance*.

(2) **Structural requirements for hyperconjugation**

(i) Compound should have at least one sp^2 -hybrid carbon of either alkene alkyl carbocation or alkyl free radical.

(ii) α -carbon with respect to sp^2 hybrid carbon should have at least one hydrogen.

If both these conditions are fulfilled then hyperconjugation will take place in the molecule.

(iii) Hyperconjugation is of three types

(iv) Resonating structures due to hyperconjugation may be written involving "*no bond*" between the alpha carbon and hydrogen atoms.

$$H - \overset{\overset{H}{|}}{\underset{\overset{|}{H}}{C}} - CH = CH_2 \longleftrightarrow H - \overset{\overset{\overset{\oplus}{H}}{|}}{\underset{\overset{|}{H}}{C}} = CH - \overset{\ominus}{C}H_2 \longleftrightarrow$$

$$\overset{\oplus}{H}\overset{\overset{H}{|}}{\underset{\overset{|}{H}}{C}} = CH - \overset{\ominus}{C}H_2 \longleftrightarrow H - \overset{\overset{H}{|}}{\underset{\overset{|}{\underset{\oplus}{H}}}{C}} = CH - \overset{\ominus}{C}H_2$$
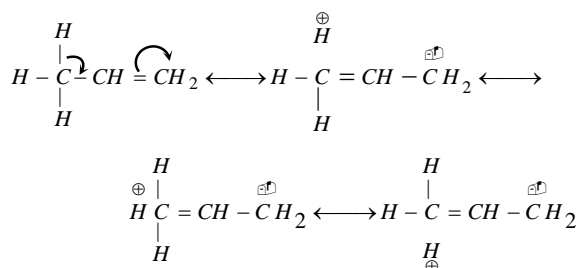
(v) Number of resonating structures due to the hyperconjugation = Number of α -hydrogens + 1.

Applications of hyperconjugation

(1) **Stability of alkenes :** Hyperconjugation explains the stability of certain alkenes over other alkenes.

Stability of alkenes $\propto$ Number of alpha hydrogens $\propto$ Number of resonating structures

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

Stability in decreasing order $\longrightarrow$
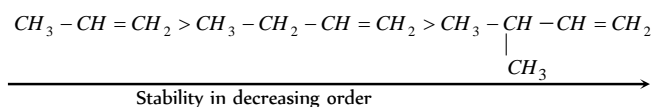
(2) **Carbon-carbon double bond length in alkenes :** As we know that the more is the number of resonating structures, the more will be single bond character in carbon-carbon double bond.

(3) **Stability of alkyl carbocations :** Stability of alkyl carbocations $\propto$ number of resonating structures $\propto$ number of alpha hydrogens.

(4) **Stability of alkyl free radicals :** Stability of alkyl free radicals can be explained by hyperconjugation. Stability depends on the number of resonating structures.

(5) **Electron releasing (or donating) power of R in alkyl benzene :** $CH_3 -$ (or alkyl group) is $+R$ group, ortho-para directing group and activating group for electrophilic aromatic substitution reaction because of the hyperconjugation.

The electron donating power of alkyl group will depends on the number of resonating structures, this depends on the number of hydrogens present on α-carbon. The electron releasing power of some groups are as follows,

$$CH_3 - \ > \ CH_3 - CH_2 - \ > \ \overset{CH_3}{\underset{CH_3}{>}}CH - \ > \ CH_3 - \overset{\overset{CH_3}{|}}{\underset{\overset{|}{CH_3}}{C}} -$$
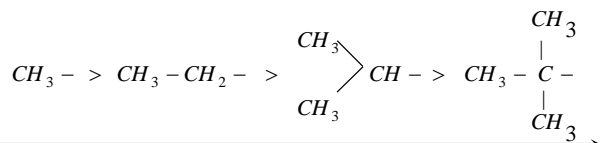
Increasing inductive effect $\longrightarrow$

Electron donating power in decreasing order due to the hyperconjugation.

(6) **Heat of hydrogenation :** Hyperconjugation decreases the heat of hydrogenation.

(7) **Dipole moment :** Since hyperconjugation causes the development of charges, it also affects the dipole moment in the molecule.

The increase in dipole moment, when hydrogen of formaldehyde ($\mu = 2.27D$) is replaced by methyl group, *i.e.*, acetaldehyde ($\mu = 2.72D$) can be referred to hyperconjugation, which leads to development of charges.

$$H - \underset{\substack{| \\ }}{C} = O \ , \ H - \underset{\substack{| \\ H \\ (\mu=2.72D)}}{\overset{\substack{H \\ |}}{C}} - CH = O \longleftrightarrow H - \underset{\substack{| \\ H}}{\overset{H^+}{C}} = CH - \overset{-}{O}$$
$$(\mu=2.27D)$$

(8) **Orienting influence of alkyl group in** o, p **-positions and of** $-CCl_3$ **group in** m **-position :** Ortho-para directing property of methyl group in toluene is partly due to $+I$ effect and partly due to hyperconjugation.

Reverse Hyperconjugation : The phenomenon of hyperconjugation is also observed in the system given below,

$$-\underset{\substack{| \\ }}{\overset{\substack{X \\ |}}{C}} - C = C \ ; \text{ where } X = \text{ halogen}$$

In such system the effect operates in the reverse direction. Hence the hyperconjugation in such system is known as reverse hyperconjugation.

$$Cl - \underset{\substack{| \\ Cl}}{\overset{\substack{Cl \\ |}}{C}} - CH = CH_2 \longleftrightarrow \underset{\substack{| \\ Cl}}{\overset{\substack{Cl \\ |}}{C}} = CH - CH_2^{\oplus} \longleftrightarrow$$

$$\overset{\ominus}{Cl} \quad \underset{\substack{| \\ Cl}}{\overset{\substack{Cl \\ |}}{C}} = CH - CH_2^{\oplus} \longleftrightarrow Cl - \underset{\substack{| \\ \overset{\ominus}{Cl}}}{\overset{\substack{Cl \\ |}}{C}} = CH - CH_2^{\oplus}$$

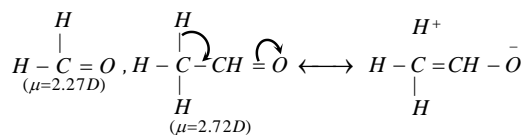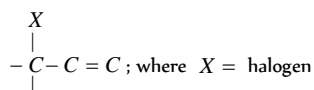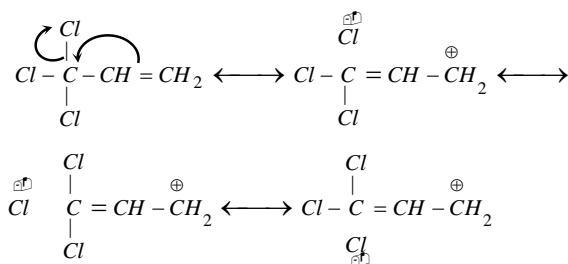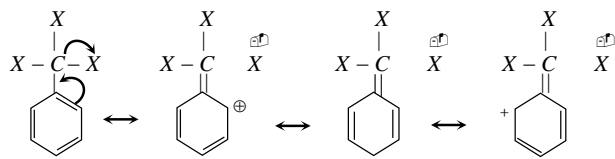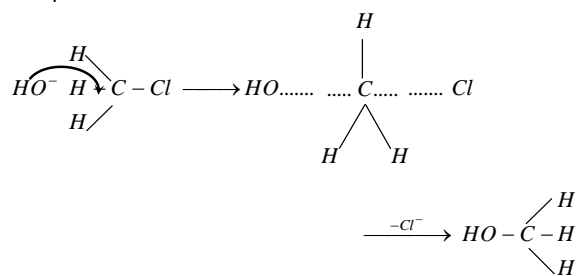The *meta* directing influence and the deactivating effect of CX_3 group in electrophilic aromatic substitution reaction can be explained by this effect.

$$X - \overset{\substack{X \\ |}}{\underset{\substack{| \\ X}}{C}} \leftrightarrow X - \overset{\substack{X \\ |}}{C} \ \overset{\ominus}{X} \leftrightarrow X - \overset{\substack{X \\ |}}{C} \ \overset{\ominus}{X} \leftrightarrow X - \overset{\substack{X \\ |}}{C} \ \overset{\ominus}{X}$$

Inductomeric effect

Inductomeric effect is the temporary effect which enhances the inductive effect and it accounts only in the presence of an attacking reagent.

Example,

$$HO^- \ H \underset{\substack{H}}{\overset{\substack{H}}{C}} - Cl \longrightarrow HO....... \ ..... \ C..... \ .... \ Cl$$

$$\xrightarrow{-Cl^-} HO - \underset{\substack{\diagdown H}}{\overset{\diagup H}{C}} - H$$

In methyl chloride the $-I$ effect of Cl group is further increased temporarily by the approach of hydroxyl ion.

Electromeric effect

(1) The phenomenon of movement of electrons from one atom to another in multibonded atoms at the demand of attacking reagent is called electromeric effect. It is denoted as E-effect and represented by a curved arrow (   ) showing the shifting of electron pair.

$$A = B \xrightarrow[\text{Reagent}]{E} \overset{\oplus}{A} - \overset{\cdot\cdot}{B} :$$
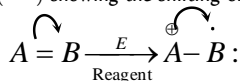
(2) (i)When the transfer of electrons take place towards the attacking reagent, the effect is called $+E$ effect. The addition of acids to alkenes.

$$\underset{\diagup}{\overset{\diagdown}{C}} = \underset{\diagdown}{\overset{\diagup}{C}} + H^{\oplus} \longrightarrow \underset{\diagup}{\overset{\diagdown}{C^+}} - \underset{\substack{| \\ H}}{\overset{\diagup}{C}}$$

$$CH_3 \longrightarrow \underset{\text{Propene}}{CH} = CH_2 + H^+ \to CH_3 - \overset{\oplus}{C}H - CH_3$$
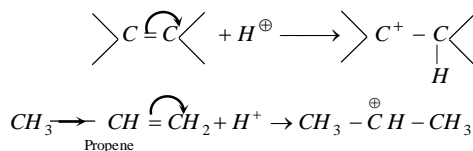
Since, $-CH_3$ group is electron donating, the electrons are transferred in the direction shown.

The attacking reagent is attached to that atom on which electrons have been transferred.

(ii) When the transfer of electrons takes place away from the attacking reagent, the effect is called $-E$ effect. Example, The addition of cyanide ion to carbonyl compounds.

$$\underset{\diagup}{\overset{\diagdown}{C}} = O + CN^{\ominus} \longrightarrow \underset{\diagup}{\overset{\diagdown}{\underset{\substack{| \\ CN}}{C}}} - O^{\ominus}$$
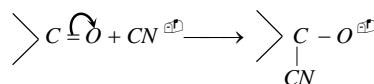
The attacking reagent is not attached to that atom on which electrons have been transferred.

(3) **Direction of the shift of electron pair :** The direction of the shift of electron pair can be decided on the basis of following points.

(i) When the groups linked to a multiple bond are similar, the shift can occur in either direction.

(ii) When the dissimilar groups are linked on the two ends of the double bond, the shift is decided by the direction of inductive effect.

In the case of carbonyl group, the shift is always towards oxygen, *i.e.*, more electronegative atom.

$$\underset{\diagup}{\overset{\diagdown}{C}} = O \longrightarrow \underset{\diagup}{\overset{\diagdown}{C}} - \overset{\oplus \quad \ominus}{O} :$$
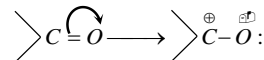
In cases where inductive effect and electromeric effect simultaneously operate, usually electrometric effect predominates.

Cleavage (fission or breaking) of covalent bonds

Breaking of covalent bond of the compound is known as **bond fission**. A bond can be broken by two ways,

(1) **Homolytic bond fission or Homolysis**

(i) In homolysis, the covalent bond is broken in such a way that each resulting species gets its own electron. This leads to the formation of odd electron species known as **free radical**.

$$A \overset{\cdot\cdot}{:} B \longrightarrow \overset{\cdot}{A} + \overset{\cdot}{B}$$
$$\text{Free radical}$$
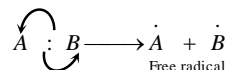
(ii) The factor which favours homolysis is that the difference in electronegativity between A and B is less or zero.

(iii) Homolysis takes place in gaseous phase or in the presence of non polar solvents (CCl_4, CS_2), peroxide, UV light, heat $(\geq 500^o C)$, electricity and free radical.

(iv) Mechanism of the reaction in which homolysis takes place is known as homolytic mechanism or free radical mechanism.

(2) **Heterolytic bond fission or heterolysis**

(i) In heterolysis, the covalent bond is broken in such a way that one species (*i.e.,* less electronegative) is deprived of its own electron, while the other species gains both the electrons.

$$A : B \longrightarrow \underset{\text{carbanion}}{\overset{\ominus}{A :}} + \underset{\text{carbocation}}{\overset{\oplus}{B}}$$
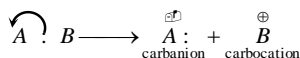
Thus formation of opposite charged species takes place. In case of organic compounds, if positive charge is present on the carbon then cation is termed as **carbocation**. If negative charge is present on the carbon then anion is termed as **carbanion**.

(ii) The factor which favours heterolysis is greater difference of electronegativities between A and B.

(iii) Mechanism of the reaction in which heterolysis takes place is known as heterolytic mechanism or ionic mechanism.

(iv) The energy required for heterolysis is always greater than that for homolysis due to electrostatic forces of attraction between ions.

Reaction Intermediates

Short lived fragments called reaction intermediates result from homolytic and heterolytic bond fission. The important reaction intermediates are free radicals, carbocations, carbanions, carbenes, benzyne and nitrenes.

Table : 23.4

| Characteristic	Free radical	Carbocation	Carbanion	Carbene
Nature	Neutral having odd electron	Positive charge on C	Negative charge on C	Neutral, divalent with 2 unshared electrons
Hybridisation	sp^2	sp^2	sp^3 (non-conjugated) sp^2 (Conjugated)	(i) sp^2 (singlet) (ii) sp (triplet)
Structure	Planar	Planar	Pyramidal/Planar	(i) Planar (singlet) (ii) Linear (triplet)
Magnetism	Paramagnetic	Diamagnetic	Diamagnetic	(i) Diamagnetic (ii) Paramagnetic
Stability order	$Ph_3\overset{.}{C} > Ph_2\overset{.}{C}H > Ph\overset{.}{C}H_2 >$ $CH_2 = CH - \overset{.}{C}H_2 > 3^o > 2^o >$ $1^o > \overset{.}{C}H_2 > CH_2 = \overset{.}{C}H$	$Ph_3\overset{+}{C} > Ph_2\overset{+}{C}H > Ph\overset{+}{C}H_2 >$ $CH_2 = CH - \overset{+}{C}H_2 >$ $3^o > 2^o > 1^o > \overset{+}{C}H_3$	$Ph_3\overset{\ominus}{C} > Ph_2\overset{\ominus}{C}H >$ $Ph\overset{\ominus}{C}H_2 > Allyl$ $\overset{\ominus}{C}H_2 > 1^o > 2^o > 3^o$	Triplet > singlet

Benzyne

(1) 1, 2-Didehydrobenzene, C_6H_4 and its derivatives are called benzyne or arynes and the simplest member is benzyne.

(2) It is neutral reaction intermediate derived from benzene ring by removing two substituents, of *ortho* positions, one in the form of electrophile and other in the from of nucleophile leaving behind two electrons to be distributed between two orbitals.

Abnormal π bond

Two sp-orbitals ouside the ring
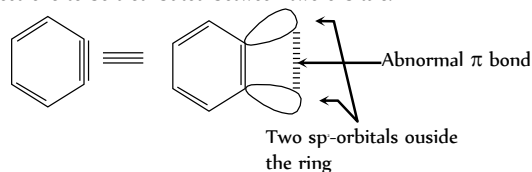
(3) Benzyne intermediate is aromatic in character.

(4) When halobenzene is heated with sodamide formation of benzyne takes place.
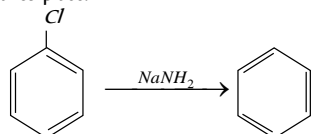
(5) (i) It behaves as dienophile and gives Diels-Alder reaction with diene.

(ii) It reacts with strong nucleophile like $\overset{\ominus}{N}H_2$
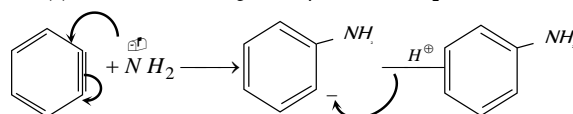
Nitrenes (R – $\overset{..}{N}$:)

(1) The nitrogen analogous of carbenes are called nitrenes.

(2) There is possibility of two spin states for nitrenes depending on whether the two non-bonding electrons (the normal nitrogen lone pair remains paired) have their spins paired or parallel.

These two are lone pair of electrons
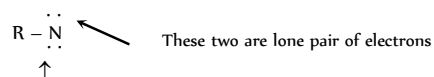
These two may be paired or unpaired

(3) In general nitrenes obey Hunds rule and the ground state triplet with two degenerate sp -orbitals containing a single electron each.

sp-Triplet nitrene
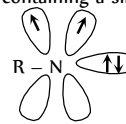
(4) Nitrenes can be generated, in situ, by the following methods,

(i) **By action of Br_2 in presence of a base on a 1° amide** (Hofmann-bromamide reaction),

$$R-\overset{\overset{O}{\parallel}}{C}-NH_2 \xrightarrow{Br_2/NaOH} \left[R-\overset{\overset{O}{\parallel}}{C}-NHBr \xrightarrow[-H_2O]{OH^-} R-\overset{\overset{O}{\parallel}}{C}-\ddot{N}\overset{\curvearrowright}{\underset{\cdot\cdot}{}}Br \right.$$
$$\underset{1^o \text{ Amide}}{}$$

$$\xrightarrow[-Br^-]{} \textcircled{R}-\overset{\overset{O}{\parallel}}{C}-\ddot{N}\overset{\cdot\cdot}{} \xrightarrow{\text{Rearrangement}} \left. O=C=N-R \right]$$
$$\underset{\text{Isocyanate}}{}$$

$$\xrightarrow[\text{(Hydrolysis)}]{KOH} \underset{1^o \text{ Amine}}{R-NH_2} + K_2CO_3$$

(ii) **By decomposition of azides in presence of heat or light.**

$$R-\overset{\cdot\cdot}{N}=\overset{+}{N}=\overset{\cdot\cdot}{N}:^- \xrightarrow{\Delta \, or \, h\nu} \underset{\text{Alkylnitrene}}{R-\overset{\cdot\cdot}{N}:} + N\equiv N$$
$$\underset{\text{Alkylazide}}{}$$

(iii) Unsubstituted nitrene $(H-\overset{\cdot\cdot}{N}:)$ can be obtained by photolysis of (or by passing electric discharge through) NH_3, N_2H_4 or N_3H.

Attacking reagents

The fission of the substrate molecule to create centres of high or low electron density is influenced by attacking reagents. Most of the attacking reagents can be classified into two main groups.

Electrophiles or electrophilic reagents and Nucleophiles or nucleophilic reagents.

(1) **Electrophiles :** Electron deficient species or electron acceptor is an electrophile.

It can be classified into two categories :

(i) *Charged electrophiles* : Positively charged species in which central atom has incomplete octet is called charged electrophile.

$$H^\oplus, X^\oplus, R^\oplus, \overset{\oplus}{N}\overset{\displaystyle O \, \oplus}{\underset{\displaystyle O \, \cdot\cdot}{\diagdown}}, \overset{\oplus}{N}=O, \overset{\oplus}{S}O_3H$$

All cations are charged electrophiles except cations of IA, IIA group elements, Al^{+++} and $\overset{\oplus}{NH_4}$

(ii) *Neutral electrophiles* : It can be classified into three categories,

(a) Neutral covalent compound in which central atom has incomplete octet is neutral electrophile,

$$BeCl_2, BH_3, ZnCl_2, AlX_3, FeX_3, \overset{\cdot}{C}H_3, \overset{\cdot\cdot}{C}H_2, \overset{\cdot\cdot}{C}X_2$$

(b) Neutral covalent compound in which central atom has complete or expended octet and central atom has unfilled $-d$-sub-shell is neutral electrophile,

$$SnCl_4, SiCl_4, PCl_5, SF_6, IF_7$$

(c) Neutral covalent compound in which central atom is bonded only with two or more than two electronegative atoms is called neutral electrophile.

$$BeCl_2, BX_3, AlX_3, FeX_3, SnCl_4, PCl_3 ;$$

$$PCl_5, NF_3, \overset{\cdot\cdot}{C}X_2, CO_2, SO_3, CS_2,$$

Cl_2, Br_2 and I_2 also behave as neutral electrophiles.

Electrophiles are Lewis acids.
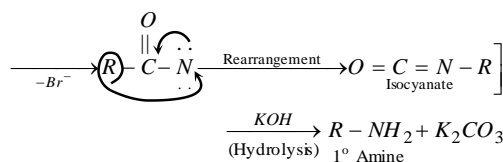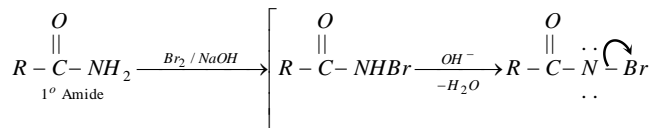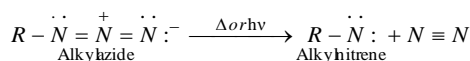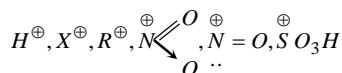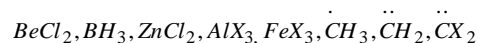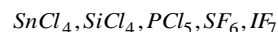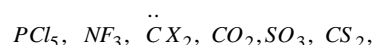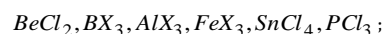
(2) **Nucleophiles :** Electron rich species or electron donors are called nucleophiles. Nucleophiles can be classified into three categories :

(i) *Charged nucleophiles* : Negatively charged species are called charged nucleophiles.

$$\overset{\ominus}{H}, \overset{\ominus}{O}H, R-\overset{\ominus}{O}, \overset{\ominus}{C}H_3, \overset{\ominus}{X}, \overset{\ominus}{S}H, R-\overset{\ominus}{S}$$
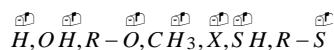
(ii) *Neutral nucleophiles* : It can be classified into two categories :

(a) Neutral covalent compound, in which central atom has complete octet, has at least one lone pair of electrons and all atoms present on central atom should not be electronegative, is neutral nucleophile.

$$\overset{\cdot\cdot}{N}H_3, R-\overset{\cdot\cdot}{N}H_2, R_2\overset{\cdot\cdot}{N}H, R_3\overset{\cdot\cdot}{N}, \overset{\cdot\cdot}{N}H_2-\overset{\cdot\cdot}{N}H_2 \text{ (Nitrogen nucleophile)}$$

$$H-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-H, R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-H, R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-R \quad \text{(Oxygen nucleophiles)}$$

$$H-\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}-H, R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}-H, R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}-R \quad \text{(Sulphur nucleophiles)}$$

$$\overset{\cdot\cdot}{P}H_3, R\overset{\cdot\cdot}{P}H_2, R_2\overset{\cdot\cdot}{P}H, R_3\overset{\cdot\cdot}{P} \quad \text{(Phosphorus nucleophiles)}$$
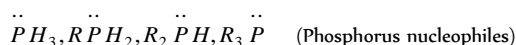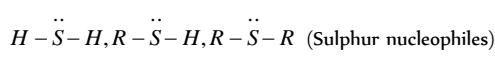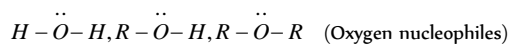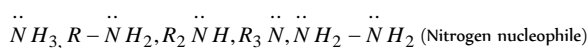
(b) Organic compound containing carbon, carbon multiple bond/bonds behaves as nucleophile.

Alkenes, Alkynes, Benzene,

$$CH_2=CH-CH=CH_2, CH_2=CH-C\equiv CH$$
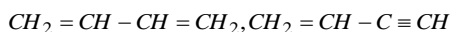
(iii) *Ambident nucleophiles* : Species having two nucleophilic centres out of which, one is neutral (complete octet and has at least one lone pair of electrons) and the other is charged (negative charge) behaves as ambident nucleophile

$$\overset{\ominus}{C}\equiv N, \overset{\cdot\cdot}{O}-\overset{\ominus}{N}=O, \overset{\ominus}{O}-\overset{\overset{\displaystyle O}{\uparrow}}{\underset{\downarrow}{S}}-OH$$
$$\underset{\displaystyle O}{}$$
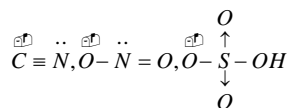
❑ Organometallic compounds are nucleophiles.

❑ Nucleophiles are Lewis bases.

Organic compounds which behave as an electrophile as well as a nucleophile : Organic compound in which carbon is bonded with electronegative atom (*O, N, S*) by multiple bond/bonds behaves as electrophile as well as nucleophile :

$$R-\overset{\overset{O}{\parallel}}{C}-H, R-\overset{\overset{O}{\parallel}}{C}-R, R-\overset{\overset{O}{\parallel}}{C}-OH, R-\overset{\overset{O}{\parallel}}{C}-Cl,$$

$$R-\overset{\overset{O}{\parallel}}{C}-OR, R-\overset{\overset{O}{\parallel}}{C}-NH_2, R-C\equiv N, R-\overset{\oplus}{N}\equiv\overset{\ominus}{C}$$
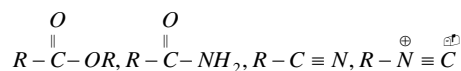
❑ During the course of chemical reaction electrophile reacts with nucleophile.

❑ Strong Lewis acid is stronger electrophile $\overset{\oplus}{CO_2} < \overset{\oplus}{NO_2} < SO_3H$. Stronger is an acid, weaker is its conjugated base or weaker is the nucleophile.

Examples : $HF > H_2O > NH_3 > CH_4$
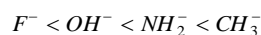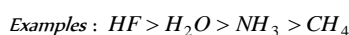
$$\underrightarrow{F^- < OH^- < NH_2^- < CH_3^-}$$
Increasing order of nucleophilicity.

Types of organic reactions

It is convenient to classify the numerous reactions of the various classes of organic compound into four types,

- Substitution reactions,
- Addition reaction,
- Elimination reactions,
- Rearrangement reactions,

Substitution reactions

Replacement of an atom or group of the substrate by any other atom or group is known as substitution reactions.

Examples :

Leaving group → ← Substituting or attacking group

$$CH_3 - CH_2 - Br + NaOH \longrightarrow CH_3 - CH_2OH + NaBr$$
Ethylbromide   *Ethylalcohol*

(Bromine atom is replaced by hydroxyl group)

Types of substitution reactions : On the basis of the nature of attacking species substitution reactions are classified into following three categories,

(1) Nucleophilic substitution reactions

(2) Electrophilic substitution reactions

(3) Free radical substitution reactions

(1) Nucleophilic substitution reactions

(i) Many substitution reactions, especially at the saturated carbon atom in aliphatic compounds such as alkyl halides, are brought about by nucleophilic reagents or nucleophiles.

$$R - X + OH^{\ominus} \longrightarrow R - OH + X^{\ominus}$$
Substrate   *Nucleophile*   *Leaving group*
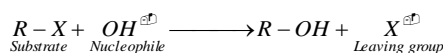
Such substitution reactions are called nucleophilic substitution reactions, *i.e.,* S_N reactions (S stands for substitution and N for nucleophile).

(ii) The weaker the basicity of a group of the substrate, the better is its leaving ability.

$$\text{Leaving power of the group} \propto \frac{1}{\text{Basicity of the group}}$$

Example : $\dfrac{HI > HBr > HCl > HF}{\text{Decreasing acidity}} \longrightarrow$

$$\dfrac{I^{\ominus} \quad Br^{\ominus} \quad Cl^{\ominus} \quad F^{\ominus}}{\text{Increasing basicity}} \longrightarrow$$
$$\Downarrow$$
$$\text{Decreasing leaving ability}$$
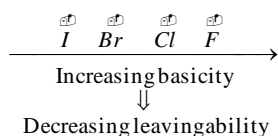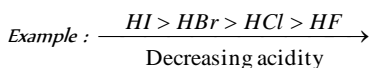
(iii) The leaving power of some nucleophilic groups are given below in decreasing order,

$$CF_3 - \overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}} - O^{\ominus} > Br \bigcirc \overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}} - O^{\ominus} > CH_3 \bigcirc \overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}} - O^{\ominus} >$$

$$C_6H_5 - \overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}} - O^{\ominus} > CH_3 - \overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}} - O^{\ominus}$$

$$> I^{\ominus} > Br^{\ominus} > CF_3 - \overset{O}{\overset{\|}{C}} - O^{\ominus} > HO^{\ominus} > Cl^{\ominus} > F^{\ominus} > CH_3 - \overset{O}{\overset{\|}{C}} - O^{\ominus}$$
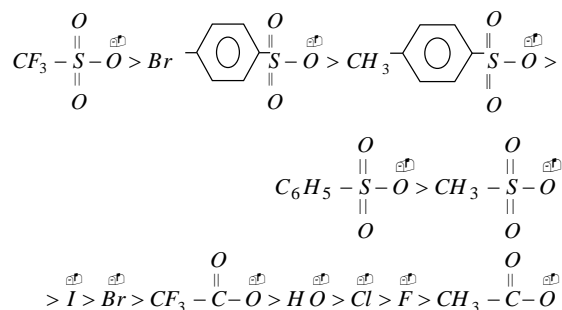
(iv) In these reactions leaving group of the substrate is replaced by another nucleophile. If reagent is neutral then leaving group is replaced by negative part of the reagent. Negative part of the reagent is always nucleophilic in character.

$$R - L \xrightarrow[E-Nu]{+\delta \ -\delta} R - Nu + L^{\ominus}; \quad R - L + \overset{\ominus}{Nu} \longrightarrow R - Nu + L^{\ominus}$$
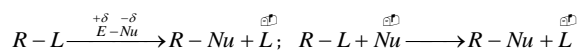
(v) In S_N reactions basicity of leaving group should be less than the basicity of incoming nucleophilic group. Thus strongly basic nucleophilic group replaces weakly basic nucleophilic group of the substrate.

Example : $R - Cl \xrightarrow[(NaOH)]{OH^{\ominus}} R - OH + Cl^{\ominus}$ .....(A)
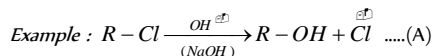
Basicity of $OH^{\ominus}$ is more than $Cl^{\ominus}$ hence $OH^{\ominus}$ replaces $Cl^{\ominus}$ as $Cl^{\ominus}$.

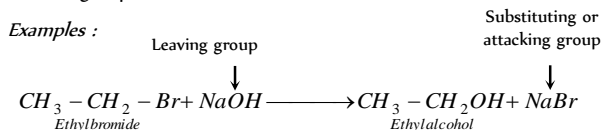$$R - OH \xrightarrow[(HCl)]{\overset{\ominus}{Cl}} R - Cl + \overset{\ominus}{OH} \quad ......(B)$$
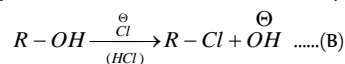
Basicity of $\overset{\ominus}{Cl}$ is less than $OH^{\ominus}$, hence $\overset{\ominus}{Cl}$ will not replace OH as $OH^{\ominus}$ hence reaction (B) will not occur.

(vi) Unlike aliphatic compounds having nucleophilic group as leaving group, aromatic compounds having same group bonded directly with aromatic ring do not undergo nucleophilic substitution reaction under ordinary conditions.

The reason for this unusual reactivity is the presence of lone pair of electron or π bond on the key atom of the functional group. Another factor for the low reactivity is nucleophilic character of aromatic ring.

(vii) The S_N reactions are divided into two classes, S_{N^2} and S_{N^1} reactions.

Table : 23.5 *Distinction between S_2 and S_1 reactions*

Factors	S_2 Reactions	S_1 Reactions
Number of steps	**One:** $\quad R : L + : \overset{\Theta}{Nu} \to R : Nu + : \overset{\Theta}{L}$	**Two:** (i) $R : L \xrightarrow{Slow} R^+ + : L^{\ominus}$ (ii) $R^+ + : Nu^- \xrightarrow{Fast} R : Nu$
Reaction rate and order	**Second order:** Rate $\propto$ [Substrate] [Nucleophile] or Rate $= K_2[RL][:Nu^{\ominus}]$	**First order:** Rate $\propto$ [Substrate] or Rate $= K_1[RL]$
Molecularity	Bimolecular	Unimolecular
TS of slow step	$: \overset{\delta^-}{Nu} - - - C - - - \overset{\delta^-}{: L}$	$: Nu - - - \overset{\delta^+}{C} - - - \overset{\delta^-}{L} - - - Nu :$
Reacting nucleophile	The nucleophile attacks the carbon of the substrate exclusively from the back side.	The nucleophile can attack the carbon of the substrate both from the back and front sides although the back side attack

		predominates.
Stereochemistry	Complete inversion of configuration takes place.	Inversion and retention takes place.
Reactivity order of alkyl halides	Methyl>1°>2°>3°halides. $(I > Br > Cl > F)$	3°>2°>1° > methyl halides. $(I > Br > Cl > F)$
Rearrangement	No rearranged product is formed (except for allylic).	Rearranged products can be formed.
Nature of nucleophiles	Favoured by strong and high concentration of nucleophiles.	Favoured by mild and low concentration of nucleophiles.
Polarity	Favoured by solvents of low polarity.	Favoured by solvents of high polarity.
Reaction rate determining factor	By steric hindrance.	By electronic factor (stability of $\overset{\oplus}{R}$).
Catalysis	Not catalysed by any catalyst (phase transfer).	Catalysed by Lewis and Bronsted acids, *e.g.,* $\overset{\oplus}{Ag}, AlCl_3, ZnCl_2$ and strong HA.

(2) **Electrophilic substitutions reactions :** Electrophilic substitution involves the attack by an electrophile. It is represented as S_E (S stands for substitution and E stands for elctrophile). If the order of reaction is 1, it is written as S_{E^1} (unimolecular) and if the order is 2, it is S_{E^2} (Bimolecular).

S_1 Reaction mechanism : Electrophilic substitution in aliphatic compounds are very rare; some of the important examples are:

(i) Replacement of the metal atom in an organometallic compound by hydrogen :

$$R - M + \overset{\oplus}{H} \rightarrow R - H + \overset{\oplus}{M}$$

e.g., $CH_3 - CH_2 - MgBr \xrightarrow{-MgBr} CH_3 - \overset{\Theta}{CH_2} \xrightarrow{\overset{\oplus}{H}} CH_3 - CH_3$

$CH_3 - CH_2 - MgBr + H - Br \rightarrow CH_3 - \overset{\Theta}{CH_2} \xrightarrow{\overset{\oplus}{H}} CH_3 - CH_3 + MgBr_2$

$CH_3 - CH_2 Na + C_6H_6 \rightarrow CH_3 - CH_3 + C_6H_5 Na$
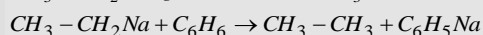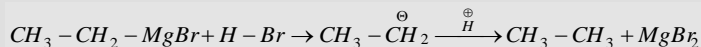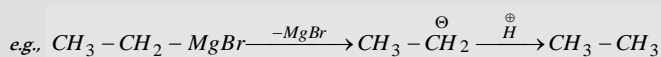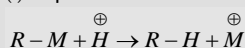
(ii) Decarboxylation of silver salt of carboxylic acid by means of bromine:

$$R_3 C - \underset{\underset{O}{\|}}{C} - OAg + Br - Br \rightarrow R_3C - \underset{\underset{O}{\|}}{C} - \overset{\Theta}{O} + \overset{\delta^+}{Br} - \overset{\delta^-}{Br} + \overset{\oplus}{Ag}$$

$$\rightarrow R_3C - Br + CO_2 + AgBr$$
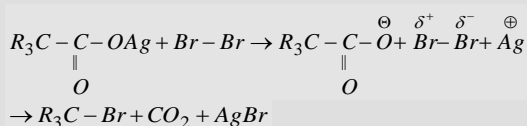
(iii) Isotopic exchange of hydrogen for deuterium or tritium:

$$R - H + \overset{\oplus}{D} \rightleftharpoons R - D + \overset{\oplus}{H}$$

$$R - H + \overset{\oplus}{T} \rightleftharpoons R - T + \overset{\oplus}{H}$$
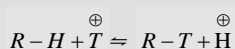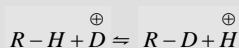
S_2 Reaction mechanism : Electrophilic substitution is very common in benzene nucleus (aromatic compounds) in which π-electrons are highly delocalized and an electrophile can attack this region of high electron density.

In all electrophilic aromatic substitution reactions, it involves:

Step 1. The formation of an electrophile, $\overset{\oplus}{E}$, *i.e.,*

In halogenation; $Cl - Cl + FeCl_3 \rightarrow \overset{\oplus}{Cl} + \overset{\Theta}{Fe Cl_4}$

In nitration; $HNO_3 + 2H_2SO_4 \rightarrow \overset{\oplus}{NO_2} + 2\overset{\Theta}{HSO_4} + \overset{\oplus}{H_3O}$

In sulphonation; $2H_2SO_4 \rightarrow SO_3 + \overset{\Theta}{HSO_4} + \overset{\oplus}{H_3O}$

In Friedel-crafts reaction; $R - Cl + AlCl_3 \rightarrow \overset{\oplus}{R} + \overset{\Theta}{AlCl_4}$

$RCOCl + AlCl_3 \rightarrow \overset{\oplus}{RCO} + \overset{\Theta}{AlCl_4}$
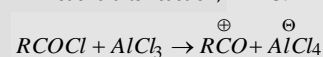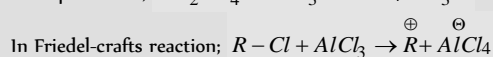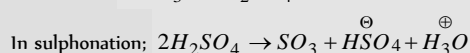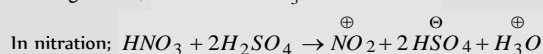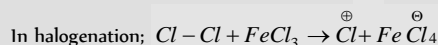
Step 2. The electrophile attacks the aromatic ring to form carbonium ion (or arenium ion) which is stabilized by resonance.
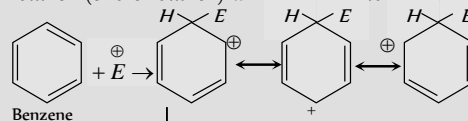
Benzene

Step 3. Carbonium ion loses the proton to form substitution product.
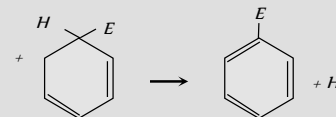
The bromination of benzene in the presence of $FeBr_3$ is a example of electrophilic substitution reaction.

Similarly, Nitration, sulphonation and Friedel-Crafts reaction.....etc., in benzene nucleus are the other examples of electrophilic substitution reactions.

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(3) **Free radical substitution reactions :** Free radical substitution reactions involves the attack by a free radical. These reactions occurs by free radical mechanism which involves Initiation, Propagation and Termination steps. *Examples,*

(i) *Chlorination of methane :* The chlorination of methane in the presence of ultraviolet light is an examples of free radical substitution.

$$\underset{Methane}{CH_4} + Cl_2 \xrightarrow[light]{UV} \underset{Methylchloride}{CH_3Cl} + HCl$$
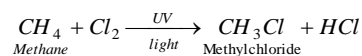
(ii) *Arylation of aromatic compounds* (Gomberg reaction) **:** The reaction of benzene diazonium halide with benzene gives diphenyl by a free radical substitution reaction.

$$C_6H_5 - H + \underset{\text{Benzenediazoniumhalide}}{C_6H_5N_2X} \xrightarrow{\text{Alkali}} \underset{\text{Diphenyl}}{C_6H_5 - C_6H_5} + N_2 + HX$$
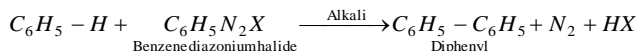
(iii) **Wurtz reaction** : Ethyl bromide on treatment with metallic sodium forms butane, ethane and ethylene by involving free radical mechanism.

(iv) **Allylic bromination by NBS** (*N*-Bromosuccinimide) : NBS is a selective brominating agent and it normally brominates the ethylenic compounds in the allylic $(CH_2 = CH - CH_2-)$ position. This type of reaction involving substitution at the alpha carbon atom with respect to the double bond is termed Allylic substitution. It is also used for benzylic bromination. Some examples are:

$$\underset{\text{Propene}}{CH_3 - CH = CH_2} + \underset{\text{NBS}}{\begin{array}{c} CH_2 - CO \\ | \\ CH_2 - CO \end{array}} N - Br \xrightarrow{CCl_4}$$

$$\underset{\text{Allylbromide}}{Br - CH_2 - CH = CH_2} + \underset{\text{Succinimide}}{\begin{array}{c} CH_2 - CO \\ | \\ CH_2 - CO \end{array}} NH$$
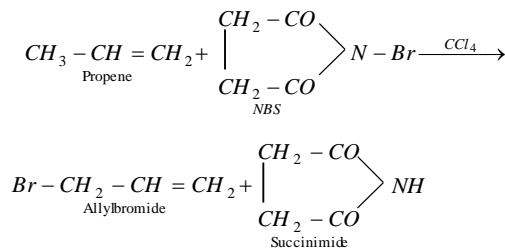
Addition reactions

These reactions are given by those compounds which have at least one π bond,

i.e., $(> C = C <, -C \equiv C-, -\overset{O}{\overset{\|}{C}}-, C \equiv N)$. In such reaction there is loss of one π bond and gain of two σ bonds. Thus product of the reaction is generally more stable than the reactant. The reaction is a spontaneous reaction.

Types of addition reactions : Addition reactions can be classified into three categories on the basis of the nature of initiating species.

(1) Electrophilic additions

(2) Nucleophilic additions

(3) Free radical additions

(1) **Electrophilic addition reactions**

(i) Such reactions are mainly given by alkenes and alkynes.

(ii) Electrophilic addition reactions of alkenes and alkynes are generally two step reactions.

(iii) Alkenes and alkynes give electrophilic addition with those reagents which on dissociation gives electrophile as well as nucleophile.

(iv) If the reagent is a weak acid then electrophilic addition is catalysed by strong acids (Generally H_2SO_4).

(v) Unsymmetrical alkenes and alkynes give addition reactions with unsymmetrical reagents according to Markownikoff's rule.

The negative part of the addendum adds on that doubly bonded carbon of the alkene which has least number of hydrogen atom.

This rule can be used only in those alkenes which fulfil the following conditions:

(a) Alkene should be unsymmetrical.

(b) Substituent/substituents present on doubly bonded carbon/(*s*) should only be +*I* group.

(c) If phenyl group is present on doubly bonded carbon, then both doubly bonded carbons should be substituted by phenyl groups.

For example, the following alkenes will give addition according to the Markownikoff's rule.

$$CH_3 - CH = CH_2, \quad \begin{array}{c} CH_3 \\ \diagdown \\ CH_3 \end{array} C = CH_2,$$

$$\begin{array}{c} C_6H_5 \\ \diagdown \\ C_6H_5 \end{array} C = CH - C_6H_5, \quad C_6H_5 - CH = CH_2$$
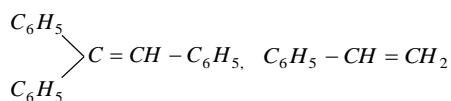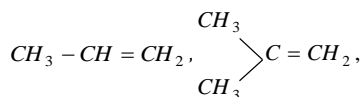
Following alkenes will not give addition reaction according to Markownikoff's rule.

$$CH_2 = CH_2, \quad R - CH = CH - R, \quad \begin{array}{c} R \\ \diagdown \\ R \end{array} C = C \begin{array}{c} R \\ \diagup \\ R \end{array},$$

$$\begin{array}{c} C_6H_5 \\ \diagdown \\ C_6H_5 \end{array} C = C \begin{array}{c} C_6H_5 \\ \diagup \\ C_6H_5 \end{array}$$
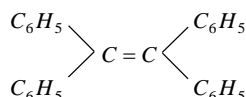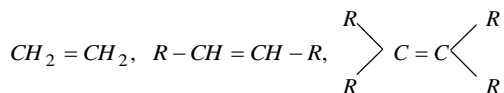
(vi) Unsymmetrical alkenes having the following general structure give addition according to anti Markownikoff's rule.

$CH_2 = CH - G$, where *G* is a strong −*I* group such as

$$- CX_3, -NO_2, - CN, -CHO, -COR, -COOH, -\overset{O}{\overset{\|}{C}} - Z$$

$$(Z = Cl, OH, OR, NH_2)$$

Example:

$$CH_2 = CH - CHO + HCl \xrightarrow{\text{Anti-Markownikoff's addition}} \overset{\overset{Cl}{\overset{|}{}}}{CH_2 - CH_2 - CHO}$$
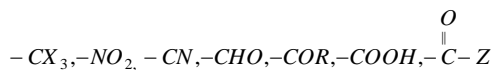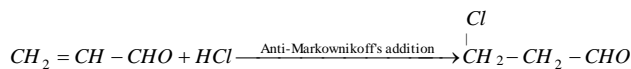
(vii) Mechanism of electrophilic addition reactions is as follows,

$$\underset{\text{Olefin}}{\diagup C = C \diagdown} + \underset{\text{Electrophile}}{\overset{\oplus}{E}} \xrightarrow{\text{Slow}} \underset{\text{Carbonium ion}}{\overset{+}{\diagup}C - \overset{|}{C} - E}$$

$$\overset{\oplus}{\diagup}C - \overset{|}{C} - E + \underset{\text{Nucleophile}}{\overset{\ominus}{X}} \xrightarrow{\text{Fast}} \underset{\text{Addition product}}{\diagup C - \underset{X}{\overset{|}{C}} - E}$$
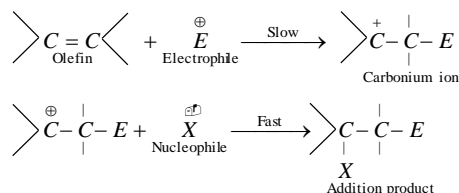
(2) **Nucleophilic addition reactions :** When the addition reaction occurs on account of the initial attack of nucleophile, the reaction is said to be a nucleophilic addition reaction. Due to presence of strongly electronegative oxygen atom, the π -electrons of the carbon-oxygen double bond in carbonyl group ($C = O$) get shifted towards the oxygen atom and thereby such bond is highly polarised. This makes carbon atom of the carbonyl group electron deficient.

$$\diagup C \overset{\frown}{=} O \quad \leftrightarrow \quad \overset{\oplus}{\diagup}C - \overset{\ominus}{O} \quad \equiv \quad \overset{\delta+}{\diagup}C - \overset{\delta-}{O}$$
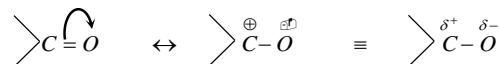
Example : The addition of *HCN* to acetone is an example of nucleophilic addition.

$$\underset{\text{Acetone}}{\begin{array}{c} CH_3 \\ \diagdown \\ CH_3 \end{array} C = O} + HCN \rightarrow \underset{\text{Acetone cyanohydrin}}{\begin{array}{c} CH_3 \\ \diagdown \\ CH_3 \end{array} C \begin{array}{c} OH \\ \diagup \\ CN \end{array}}$$
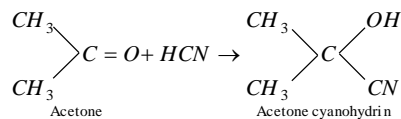
The mechanism of the reaction involves the following steps:

Step 1. *HCN* gives a proton $(\overset{\oplus}{H})$ and a nucleophile, cyanide ion $(\overset{\ominus}{CN})$.

$$HCN \rightarrow H^{\oplus} + CN^{\ominus}$$

Step 2. The nucleophile $(CN^{\ominus})$ attacks the positively charged carbon so as to form an anion [$H^{\oplus}$ does not initiate the negatively charged oxygen as anion is more stable than cation].

$$\overset{\ominus}{CN} \underset{CH_3}{\overset{CH_3}{>}} C = O \rightarrow CN \underset{CH_3}{\overset{CH_3}{>}} C - O^{\ominus} \text{ or } \underset{CH_3}{\overset{CH_3}{>}} C \overset{O^{\ominus}}{\underset{CN}{<}}$$
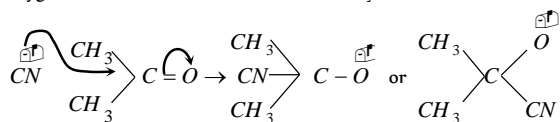
Step 3. The proton (H^+) combines with anion to form the addition product.

$$CN \underset{CH_3}{\overset{CH_3}{>}} C - O^{\ominus} + H^{\oplus} \rightarrow NC - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - OH \text{ or } \underset{CH_3}{\overset{CH_3}{>}} C \overset{OH}{\underset{CN}{<}}$$
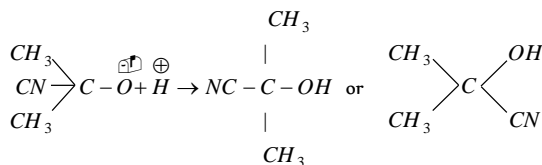
In $>C = O$ compounds, the addition of liquid HCN gives cyanohydrin and the addendum is CN^- ion and not HCN directly (addition is catalysed by bases or salts of weak acids and retarded by acids or unaffected by neutral compounds).

$$>C \overset{\delta^+ \ \delta^-}{\underset{(A.R.)}{+ H - CN}} \rightarrow >\overset{\oplus}{C} - \overset{\ominus}{O} \overset{\overset{\ominus}{CN}}{\longrightarrow} >C \overset{O^{\ominus}}{\underset{CN}{<}} \overset{\overset{\oplus}{H}}{\longrightarrow} >C \overset{OH}{\underset{CN}{<}}$$
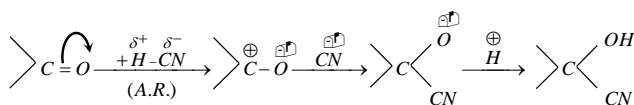
Nucleophilic addition (A) reactions on carbonyl compounds will be in order:

$$\underset{H}{\overset{H}{>}} C = O \ > \ \underset{H}{\overset{H_3C}{>}} C = O \ > \ \underset{H_3C}{\overset{H_3C}{>}} C = O$$
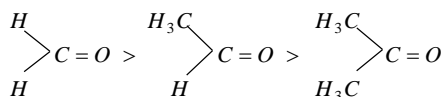
Decreasing order of nucleophilic addition in some species.

$$C_6H_5CH_2COCH_3 > CH_3COCH_3 > C_6H_5 - \overset{\overset{O}{||}}{C} - CH_3 > C_6H_5 - \overset{\overset{O}{||}}{C} - C_6H_5 - CHO >$$
$$-COCH_3 > -COCl > -COOCH_3 > -CONH_2 > -COOH$$
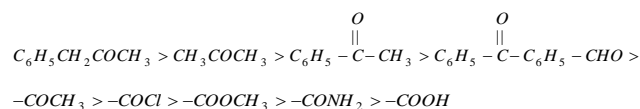
(3) **Free radical addition reactions :** Those reactions which involve the initial attack by a free radical are known as free radical reactions. Addition of hydrogen bromide to alkenes (say, propylene) in the presence of peroxide (radical initiator) follows free radical mechanism. Free radical reactions generally take place in non-polar solvents such as CCl_4, high temperature, in presence of light or a free radical producing substance like O_2 and peroxides.

Elimination reactions

Elimination reactions are formally the reverse of addition reactions and involve the removal of the two groups (Generally, one being a proton) from one or two carbon atoms of a molecule to form an unsaturated linkage or centre.

Elimination reaction is given by those compounds which have a nucleophilic group as leaving group,

$$i.e., \ X, \ OH, \ OR, \ \overset{\oplus}{N_2}, N_3, \overset{\oplus}{H_3}O, \overset{\oplus}{N} \underset{R}{\overset{R}{<}} \overset{R}{\underset{R}{>}} \overset{\oplus}{R}, S \overset{R}{\underset{R}{<}}$$
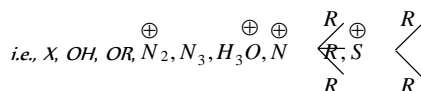
Elimination reactions are generally endothermic and take place on heating.

Elimination reactions are classified into two general types,

(I) α- elimination reactions or 1, 1-elimination reactions.

(II) β- elimination reaction or 1, 2-elimination reactions.

(I) ***α-elimination reactions or 1,1-elimination reactions:*** A reaction in which both the groups or atoms are removed from the same carbon of the molecule is called α- elimination reaction. This reaction is mainly given by gem dihalides and gem trihalides having at least one α- hydrogen.

$$CHX_3 \xrightarrow{Alc. KOH/\Delta} \overset{..}{C}X_2 + \overset{\ominus}{X} + \overset{\oplus}{H}$$

Product of the reaction is halocarbenes or dihalocarbenes. which are key intermediates in a wide variety of chemical and photochemical reactions.

(II) ***β-elimination reactions or 1, 2-elimination reactions:*** Consider the following reactions,

$$CH_3 - \underset{\beta}{CH_2} - \underset{\alpha}{CH_2} - L \rightarrow CH_3 - CH = CH_2 + \overset{\oplus}{H} + \overset{\ominus}{L}$$
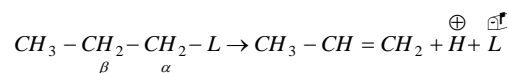
A reaction in which functional group (*i.e.,* leaving group) is removed from α- carbon and other group (Generally hydrogen atom) from the β- carbon is called β- elimination reaction. In this reaction there is loss of two σ bonds and gain of one π bond. Product of the reaction is generally less stable than the reactant.

(1) **Types of β- elimination reactions :** In analogy with substitution reactions, β- elimination reactions are divided into three types:

(i) E_1 (Elimination unimolecular) reaction, (ii) E_2 (Elimination bimolecular) reaction and (iii) E_{1cb} (Elimination unimolecular conjugate base) reaction

(i) E_1 (Elimination unimolecular) **reaction :** Consider the following reaction,

$$CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - Cl \xrightarrow{C_2H_5\overset{\ominus}{O}/\Delta} CH_2 = C \underset{CH_3}{\overset{CH_3}{<}} + C_2H_5OH + \overset{\ominus}{Cl}$$
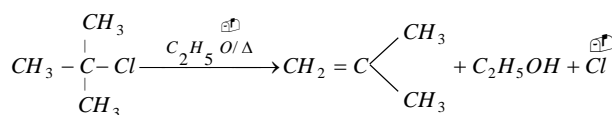
(a) Reaction velocity depends only on the concentration of the substrate; thus reaction is unimolecular reaction.

$$Rate \propto [Substrate]$$

(b) Product formation takes place by the formation of carbocation as reaction intermediate (*RI*).

(c) Since reaction intermediate is carbocation, rearrangement is possible in E_1 reaction.

(d) Reaction is carried out in the presence of polar protic solvent.

(e) The E_1 reaction occurs in two steps,

Step 1.

$$CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - Cl \rightarrow CH_3^{+\delta} \overset{\overset{CH_3}{|\delta^+}}{\underset{\underset{CH_3}{|}}{C}} \cdots Cl^{-\delta} \xrightarrow{Slow step} CH_3 - \overset{\oplus}{\underset{\underset{CH_3}{|}}{C}} - CH_3 + \overset{\ominus}{Cl}$$
$$(TS_1) \qquad\qquad (RI)$$

Step 2.

$$B + \overset{\curvearrowright}{H} - CH_2 - \overset{\oplus}{\underset{\underset{CH_3}{|}}{C}} - CH_3 \rightarrow \left[B ---- H ---- CH_2 ---- \underset{\underset{CH_3}{|}}{C} - CH_3 \right]_{TS_2}$$

$$\xrightarrow{fast} \overset{\oplus}{B}H + CH_2 = C \big\langle \begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

(ii) **E_2 (Elimination bimolecular) reaction** : Consider the following reaction,

$$CH_3 - CH_2 - CH_2 - Br \xrightarrow[\Delta]{Base\,(B)} CH_3 - CH = CH_2 + \overset{\oplus}{H} + \overset{\ominus}{Br}$$

(a) Reaction velocity depends only on the concentration of the substrate and the base used; thus reaction is bimolecular reaction. Rate $\propto$ [Substrate] [Base]

(b) Since the reaction is a bimolecular reaction, the product formation will take place by formation of transition state (TS).

(c) Rearrangement does not take place in E_2 reaction but in case of allylic compound rearrangement is possible.

(d) Reaction is carried out in the presence of polar aprotic solvent.

(e) The E_2 reaction occurs in one step,

$$\underset{\underset{\underset{Br}{|}}{\underset{H}{|}}{CH_3 - \overset{\curvearrowright}{C} \overset{H \, H}{\underset{\,}{\,}} C - H}} \xrightarrow{Slow\,step} \left[\begin{matrix} B^{-\delta} ---- H^{+\delta} & H \\ CH_3 - \underset{\underset{H}{|}}{C} ===== \underset{\underset{Br}{}}{C} - H \\ TS \end{matrix} \right]$$

$$\xrightarrow{fast} CH_3 - CH = CH_2 + BH + \overset{\ominus}{Br}$$

(2) **Orientation in β - elimination reactions** : If substrate is unsymmetrical, then this will give more than one product. Major product of the reaction can be known by two emperical rules.

(i) **Saytzeff rule** : According to this rule, major product is the most substituted alkene *i.e.,* major product is obtained by elimination of $\overset{\oplus}{H}$ from that β- carbon which has the least number of hydrogen. Product of the reaction in this case is known as Saytzeff product.

$$CH_3 - \overset{\beta_2}{\underset{\underset{CH_3}{|}}{CH}} - \overset{\overset{Cl}{|}}{\underset{\alpha \quad \beta_1}{CH}} - CH_3 \xrightarrow[-HCl]{Alc.KOH/\Delta} CH_3 - \underset{\underset{CH_3}{|}}{C} = CH - CH_3$$
$$\text{Saytzeff product}$$

(ii) **Hofmann rule** : According to this rule, major product is always least substituted alkene *i.e.,* major product is formed from β- carbon which has maximum number of hydrogen. Product of the reaction in this case is known as Hofmann product.

$$CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - \overset{\beta_2}{CH_2} - \overset{\overset{Br}{|}}{\underset{\alpha \quad \beta_1}{CH}} - CH_3 \xrightarrow{Alc.KOH/\Delta} CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - CH_2 - CH = CH_2$$
$$\text{Hofmann product}$$

□ In E_1 reactions, product formation always takes place by Saytzeff rule.

□ In E_{1b} reactions, product formation always takes place by Hofmann rule.

□ In E_2 reactions, product formation takes place by Saytzeff as well as Hofmann rule. In almost all E_2 reactions product formation take place by Saytzeff rule.

(3) **Examples of β - elimination reactions**

(i) **Dehydrohalogenation** is removal of HX from alkyl halides with alcoholic KOH or KNH_2 or ter- BuOK (Potassium tertiary butoxide) and an example of α-β elimination,

e.g.,
$$CH_3 - CH_2 X \xrightarrow[(-HX)]{Alc.KOH} \underset{Ethene}{H_2C = CH_2} \ ;$$

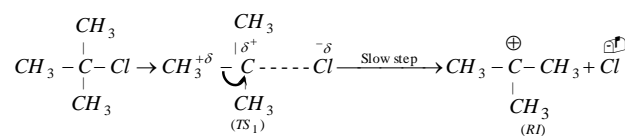$$CH_3 - \overset{\overset{}{|}}{\underset{\underset{X}{|}}{CH}} - CH_3 \xrightarrow[(-HX)]{Alc.KOH} \underset{Propene}{CH_3 CH = CH_2}$$

$$CH_3 - CH_2 - \overset{}{\underset{\underset{X}{|}}{CH}} - CH_3 \xrightarrow[(-HX)]{Alc.KOH} \underset{2\text{- Butene (Major)}}{CH_3 - CH = CH - CH_3} +$$

$$\underset{1\text{- Butene (Minor)}}{CH_3 - CH_2 - CH = CH_2}$$

(ii) **Dehydration** of alcohol is another example of elimination reaction. When acids like conc. H_2SO_4 or H_3PO_4 are used as dehydrating agents, the mechanism is E_1. The proton given by acid is taken up by alcohol.

Dehydration is removal of H_2O from alcohols,

e.g.,
$$CH_3 - CH_2 - OH \xrightarrow[(-H_2O)]{Conc.\ H_2SO_4,170°C} H_2C = CH_2$$

$$\underset{Propan\text{ -1-ol}}{CH_3 - CH_2 - CH_2 - OH} \xrightarrow[(-H_2O)]{Conc.\ H_2SO_4,170°C} \underset{Propene}{CH_3 - CH = CH_2}$$

□ Dehydration of alcohols is in the order:
$$\underset{(3°)}{Tertiary} > \underset{(2°)}{Secondary} > \underset{(1°)}{Primary}$$

□ 2° and 3° alcohol by E_1 process and 1° alcohol by E_2 process. Alcohols leading to conjugated alkenes are more easily dehydrated than the alcohols leading to non-conjugated alkenes. $CH_2 = CH - \underset{\underset{OH}{|}}{CH} - CH_3$ is easily dehydrated than

$$CH_3 - CH_2 - \underset{\underset{OH}{|}}{CH} - CH_3 \text{ and so}$$

(iii) **Dehalogenation** : It is removal of halogens, *e.g.,*

$$\underset{\underset{Br \quad Br}{|\qquad |}}{CH_2 - CH_2} + Zn\,dust \xrightarrow[(-ZnBr_2)]{in\,CH_3OH,\,heat} \underset{Ethylene}{H_2C = CH_2}$$
$$\text{Ethylene bromide}$$

(iv) *Dehydrogenation* **:** It is removal of hydrogen, *e.g.*,

$$CH_3 - CH - CH_3 \xrightarrow[(-H_2)]{Cu, 300°C} CH_3 - C - CH_3$$

$$\underset{\text{Isopropyl alcohol}}{\overset{|}{OH}} \qquad \qquad \underset{\text{Acetone}}{\overset{||}{O}}$$
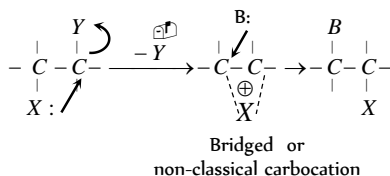
Rearrangement reactions

The reactions, which involve the migration of an atom or group from one site to another within the molecule (nothing is added from outside and nothing is eliminated) resulting in a new molecular structure, are known as rearrangement reactions. The new compound is actually the structural isomer of the original one.

It is convenient to divide rearrangement reactions into following types:

(1) Rearrangement or migration to electron deficient atoms (Nucleophilic rearrangement) **:** Those rearrangement reactions in which migrating group is nucleophilic and thus migrates to electron deficient centre which may be carbon, nitrogen and oxygen.


Bridged or
non-classical carbocation

X = Nucleophilic species, *Y* = Electronegative group, *B* = Another nucleophile.

(2) Rearrangement or migration to electron rich atoms (Electrophilic rearrangement) **:** Those rearrangement reactions in which migrating group is electrophile and thus migrates to electron rich centre.

(3) Rearrangement or migration to free radical species (Free radical rearrangement) **:** Those rearrangement reactions in which the migrating group moves to a free radical centre. Free radical rearrangements are comparatively rare.

(4) Aromatic rearrangement : Those rearrangement reactions in which the migrating group moves to aromatic nucleus. Aromatic compounds of the type (*I*) undergo rearrangements in the manner mentioned below,
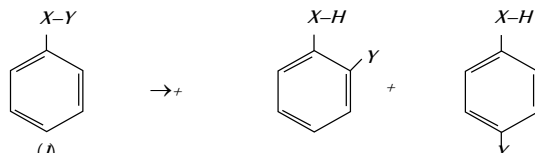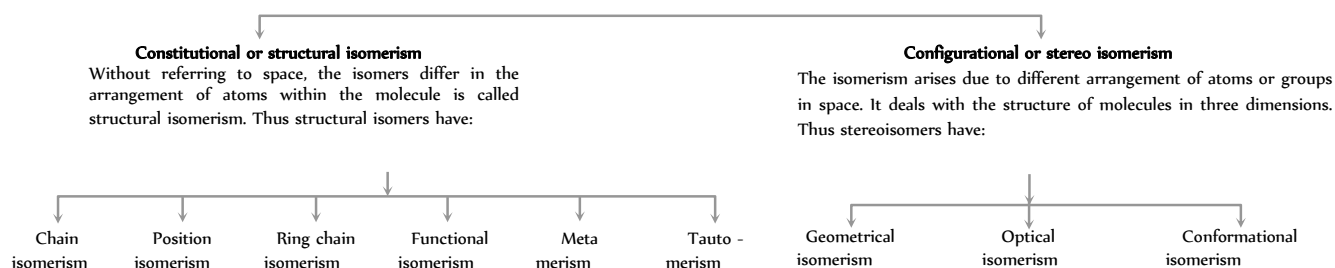

The (*I*) element *X* from which group *Y* migrates may be nitrogen or oxygen.

Isomerism

Organic compounds having same molecular formula but differing from each other at least in some physical or chemical properties or both are known as isomers (Berzelius) and the phenomenon is known as isomerism.

The difference in properties of isomers is due to the difference in the relative arrangements of various atoms or groups present in their molecules. Isomerism can be classified as follows:
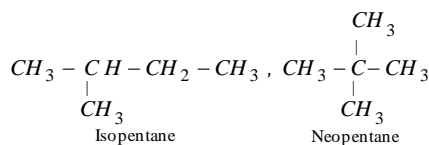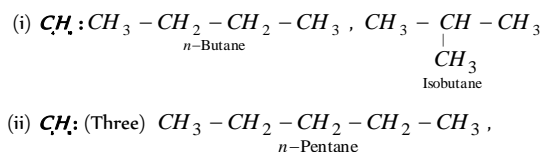
Isomerism

Constitutional or structural isomerism
Without referring to space, the isomers differ in the arrangement of atoms within the molecule is called structural isomerism. Thus structural isomers have:

Configurational or stereo isomerism
The isomerism arises due to different arrangement of atoms or groups in space. It deals with the structure of molecules in three dimensions. Thus stereoisomers have:

| Chain isomerism | Position isomerism | Ring chain isomerism | Functional isomerism | Meta merism | Tauto - merism | Geometrical isomerism | Optical isomerism | Conformational isomerism |

Constitutional or structural isomerism

(1) Chain, nuclear or skeleton isomerism : This type of isomerism arises due to the difference in the nature of the carbon chain (*i.e.,* straight or branched) which forms the nucleus of the molecule.

Examples :

(i) $\underset{\centerdot\centerdot}{C_4H_{10}} : CH_3 - CH_2 - CH_2 - CH_3$, $CH_3 - \underset{\underset{\text{Isobutane}}{\overset{|}{CH_3}}}{CH} - CH_3$
$\quad\quad\quad\quad\quad\quad\underset{n-\text{Butane}}{}$

(ii) $\underset{\centerdot\centerdot}{C_5H_{12}}$ (Three) $CH_3 - CH_2 - CH_2 - CH_2 - CH_3$,
$\quad\quad\quad\quad\quad\quad\quad\quad\underset{n-\text{Pentane}}{}$

$$CH_3 - \underset{\underset{\text{Isopentane}}{\overset{|}{CH_3}}}{CH} - CH_2 - CH_3 \; , \; CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{\text{Neopentane}}{\overset{|}{CH_3}}}{C}} - CH_3$$
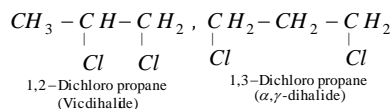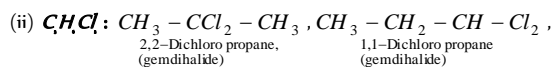
❏ Except alkynes chain isomerism is observed when the number of carbon atoms is four or more than four.

❏ Chain isomers differ in the nature of carbon chain, *i.e.,* in the length of carbon chain.

❏ The isomers showing chain isomerism belong to the same homologous series, *i.e.,* functional group, class of the compound (Cyclic or open) remains unchanged.

❏ Chain and position isomerism cannot be possible together between two isomeric compounds. If two compounds are chain isomers then these two will not be positional isomers.

(2) **Position isomerism :** It is due to the difference in the position of the substiuent atom or group or an unsaturated linkage in the same carbon chain.

(ii) $C_3H_6Cl_2$: $CH_3 - CCl_2 - CH_3$, $CH_3 - CH_2 - CH - Cl_2$,

<div style="margin-left:2em">
2,2–Dichloro propane,
(gemdihalide)   1,1–Dichloro propane
          (gemdihalide)
</div>

$$CH_3 - \underset{\underset{Cl}{|}}{C}H - \underset{\underset{Cl}{|}}{C}H_2 \ , \ \underset{\underset{Cl}{|}}{C}H_2 - CH_2 - \underset{\underset{Cl}{|}}{C}H_2$$

<div style="margin-left:2em">
1,2–Dichloro propane   1,3–Dichloro propane
(Vicdihalide)   (α,γ-dihalide)
</div>

❑ Aldehydes, carboxylic acids (and their derivatives) and cyanides do not show position isomerism.

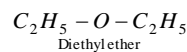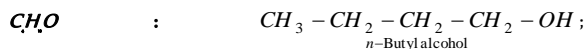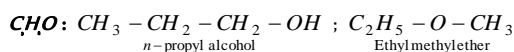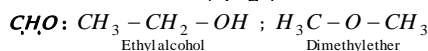❑ Monosubstituted alicylic compounds and aromatic compounds do not show position isomerism.

❑ Structural isomers which differ in the position of the functional group are called regiomers. For example, (i) $CH_3 - CH_2 - CH_2 - OH$

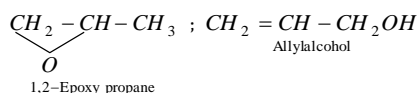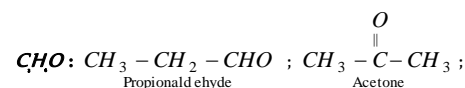(ii) $CH_3 - \underset{\underset{OH}{|}}{C}H - CH_3$
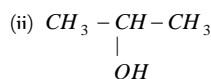
(3) **Functional isomerism :** This type of isomerism is due to difference in the nature of functional group present in the isomers. The following pairs of compounds always form functional isomers with each other.
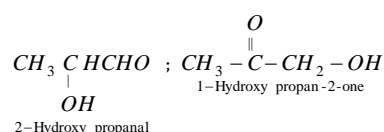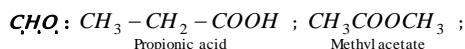
Examples :

(i) *Alcohols and ethers ($C_nH_{2n+2}O$)*
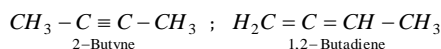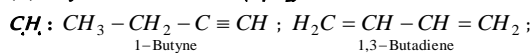
C_2H_6O : $CH_3 - CH_2 - OH$; $H_3C - O - CH_3$

<div style="margin-left:2em">Ethylalcohol   Dimethylether</div>

C_3H_8O : $CH_3 - CH_2 - CH_2 - OH$; $C_2H_5 - O - CH_3$

<div style="margin-left:2em">n–propyl alcohol   Ethylmethylether</div>

$C_4H_{10}O$: $CH_3 - CH_2 - CH_2 - CH_2 - OH$;

<div style="margin-left:6em">n–Butyl alcohol</div>

$C_2H_5 - O - C_2H_5$

<div style="margin-left:2em">Diethyl ether</div>

(ii) *Aldehydes, ketones and unsaturated alcohols ...etc. ($C_nH_{2n}O$)*

C_3H_6O : $CH_3 - CH_2 - CHO$; $CH_3 - \overset{\overset{O}{\|}}{C} - CH_3$;

<div style="margin-left:2em">Propionaldehyde   Acetone</div>

$\underset{O}{\overset{CH_2 - CH - CH_3}{\diagdown\diagup}}$; $CH_2 = CH - CH_2OH$

<div style="margin-left:2em">1,2–Epoxy propane   Allylalcohol</div>
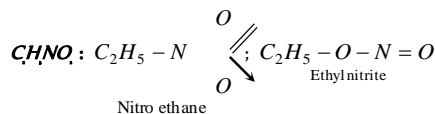
(iii) *Acids, esters and hydroxy carbonyl compounds ...etc. ($C_nH_{2n}O_2$)*

$C_2H_4O_2$: CH_3COOH ; $HCOOCH_3$

<div style="margin-left:2em">Aceticacid   Methyl formate</div>

$C_3H_6O_2$: $CH_3 - CH_2 - COOH$; CH_3COOCH_3 ;

<div style="margin-left:2em">Propionic acid   Methyl acetate</div>

$CH_3 \underset{\underset{OH}{|}}{C}HCHO$; $CH_3 - \overset{\overset{O}{\|}}{C} - CH_2 - OH$

<div style="margin-left:6em">1–Hydroxy propan-2-one</div>

<div style="margin-left:2em">2–Hydroxy propanal</div>

(iv) *Alkynes and alkadienes (C_nH_{2n-2})*

C_4H_6 : $CH_3 - CH_2 - C \equiv CH$; $H_2C = CH - CH = CH_2$;

<div style="margin-left:2em">1–Butyne   1,3–Butadiene</div>

$CH_3 - C \equiv C - CH_3$; $H_2C = C = CH - CH_3$

<div style="margin-left:2em">2–Butyne   1,2–Butadiene</div>

(v) *Nitro alkanes and alkyl nitrites ($-NO_2$ and $-O - N = O$)*

$C_2H_5NO_2$: $C_2H_5 - \overset{\overset{O}{\|}}{\underset{\underset{O}{\big\downarrow}}{N}}$; $C_2H_5 - O - N = O$

<div style="margin-left:2em">Nitro ethane   Ethylnitrite</div>

(vi) *Amines (Primary, secondary and tertiary)*

C_3H_9N : $CH_3 - CH_2 - CH_2 - NH_2$;

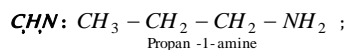<div style="margin-left:2em">Propan -1- amine</div>

$$CH_3 - CH_2 - N \diagup^{H}_{\diagdown CH_3}$$

<div style="margin-left:2em">N–Methyl ethanamine</div>

$CH_3 - \underset{\underset{NH_2}{|}}{C}H - CH_3$; $CH_3 - CH_2 - N \diagup^{CH_3}_{\diagdown CH_3}$

<div style="margin-left:2em">Propan -2- amine N,N–Dimethyl methanamine</div>
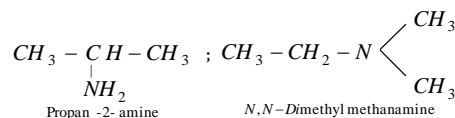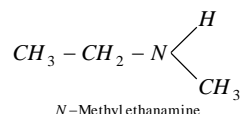
(vii) *Alcohols and phenols*

C_7H_8O ; Benzyl alcohol ($C_6H_5CH_2OH$) ; o-Cresol

(viii) *Oximes and amides*

C_2H_5NO : $CH_3 - CH = NOH$; $CH_3 - \overset{\overset{O}{\|}}{C} - NH_2$

<div style="margin-left:2em">Acetaldoxime   Acetamide</div>
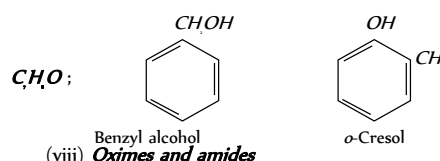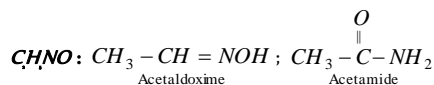
(4) **Ring-chain isomerism :** This type of isomerism is due to different modes of linking of carbon atoms, *i.e.,* the isomers possess either open chain or closed chain sturctures.

C_6H_{12} : Cyclohexane ;

$\underset{\underset{CH_2 - CH_2}{|}}{CH_2 - CH_2} \diagdown CHCH_3$; $CH_3CH_2CH_2CH_2CH = CH_2$

<div style="margin-left:2em">Methyl cyclopentane   1–Hexene</div>
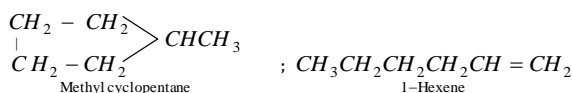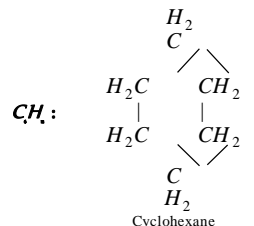
❑ Ring – chain isomers are always functional isomers.

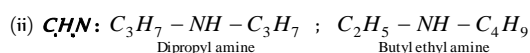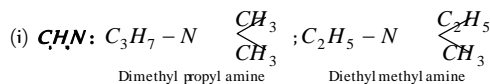(5) **Metamerism :** This type of isomerism is due to the difference in the nature of alkyl groups attached to the polyvalent atoms or functional group. Metamers always belong to the same homologous series. Compounds like ethers, thio-ethers ketones, secondary amines, *etc.* show metamerism.

(i) $C_5H_{13}N$: $C_3H_7 - N \diagup^{CH_3}_{\diagdown CH_3}$; $C_2H_5 - N \diagup^{C_2H_5}_{\diagdown CH_3}$

<div style="margin-left:2em">Dimethyl propyl amine   Diethylmethyl amine</div>

(ii) $C_6H_{15}N$: $C_3H_7 - NH - C_3H_7$; $C_2H_5 - NH - C_4H_9$

<div style="margin-left:2em">Dipropyl amine   Butyl ethyl amine</div>

❑ If same polyvalent functional group is there in two or more organic compounds, then chain or position isomerism is not possible, there will be metamerism *e.g.,*

(a) $CH_3 - \overset{\overset{\|}{O}}{C} - CH_2 - CH_2 - CH_3$;

<div style="margin-left:2em">(Pentan −2−one)</div>

$$CH_3CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2CH_3 \quad \text{are metamers and not position isomers.}$$
(Pentan −3−one)

(b) $CH_3 - \overset{\overset{\displaystyle }{\underset{\underset{\displaystyle O}{\|}}{C}}}{} - CH_2CH_2CH_3$;

(Pentan −2−one)

$$CH_3 - \overset{\overset{\displaystyle }{}}{C} - \overset{\overset{\displaystyle }{}}{C}H - CH_3 \quad \text{are metamers and not chain isomers.}$$
$$\underset{O \quad CH_3}{\|}$$
(3-Methylbutan-2-one)
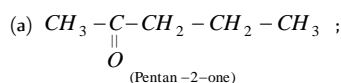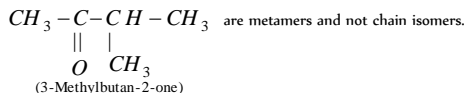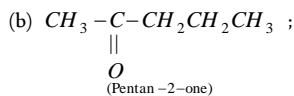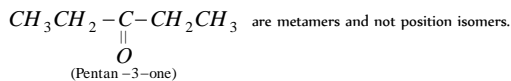
❏ Alkenes does not show metamerism.

(6) Tautomerism

(i) The type of isomerism in which a substance exist in two readily interconvertible different structures leading to dynamic equilibrium is known as tautomerism and the different forms are called **tautomers** (or tautomerides).

The term **tautomerism** (Greek: *tauto* = same; *meros* = parts) was used by **Laar** in 1885 to describe the phenomenon of a substance reacting chemically according to two possible structures.
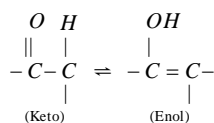
(ii) It is caused by the wandering of hydrogen atom between two polyvalent atoms. It is also known as **Desmotropism** (Desmos = bond and tropos = turn). If the hydrogen atom oscillates between two polyvalent atoms linked together, the system is a **dyad** and if the hydrogen atom travels from first to third atom in a chain, the system is a **triad**.

(a) *Dyad system* : Hydrocyanic acid is an example of dyad system in which hydrogen atom oscillates between carbon and nitrogen atoms. $H - C \equiv N \rightleftharpoons C \cong N - H$
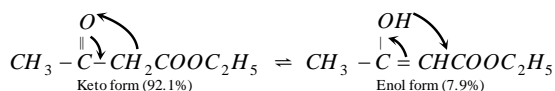
(b) *Triad system*

Keto-enol system : Polyvalent atoms are oxygen and two carbon atoms.

Examples :

$$-\overset{\overset{\displaystyle O}{\|}}{C} - \overset{\overset{\displaystyle H}{|}}{\underset{|}{C}} - \rightleftharpoons -\overset{\overset{\displaystyle OH}{|}}{C} = \overset{}{\underset{|}{C}} -$$
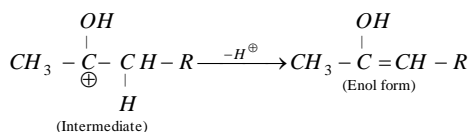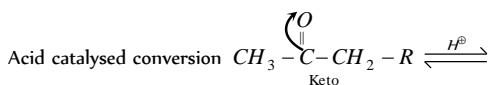(Keto)   (Enol)

Acetoacetic ester (Ethyl acetoacetate) :

$$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2COOC_2H_5 \rightleftharpoons CH_3 - \overset{\overset{\displaystyle OH}{|}}{C} = CHCOOC_2H_5$$
Keto form (92.1%)   Enol form (7.9%)
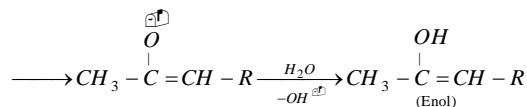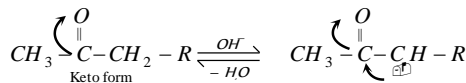
Acetoacetic ester gives certain reactions showing the presence of keto group (Reactions with HCN , H_2NOH , $H_2NNHC_6H_5$, *etc.*) and certain reactions showing the presence of enolic group (Reactions with $Na, CH_3COCl, NH_3, PCl_5, Br_2$ water and colour with neutral $FeCl_3$, *etc.*).
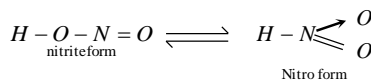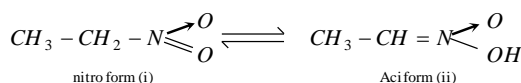
Enolisation is in order
$$CH_3COCH_3 < CH_3COCH_2COOC_2H_5 < C_6H_5COCH_2COOC_2H_5$$
$$< CH_3COCH_2COCH_3 < CH_3COCH_2CHO$$

Acid catalysed conversion $CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2 - R \underset{}{\overset{H^{\oplus}}{\rightleftharpoons}}$
Keto

$$CH_3 - \overset{\overset{\displaystyle OH}{|}}{\underset{\oplus}{C}} - \overset{}{\underset{|}{C}}H - R \xrightarrow{-H^{\oplus}} CH_3 - \overset{\overset{\displaystyle OH}{|}}{C} = CH - R$$
$$\underset{H}{}$$ (Enol form)
(Intermediate)

Base catalysed conversion

$$CH_3 \overset{\curvearrowleft}{-}\overset{\overset{\displaystyle O}{\|}}{C} - CH_2 - R \underset{-H_2O}{\overset{OH^-}{\rightleftharpoons}} CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - \overset{\ominus}{C}H - R$$
Keto form

$$\longrightarrow CH_3 - \overset{\overset{\displaystyle \ominus O}{|}}{C} = CH - R \xrightarrow[-OH^{\ominus}]{H_2O} CH_3 - \overset{\overset{\displaystyle OH}{|}}{C} = CH - R$$
(Enol)
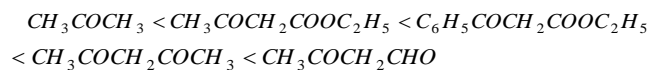
(c) Triad system containing nitrogen : Examples
Nitrous acid exists in 2 forms

$$H - O - N = O \rightleftharpoons H - N \overset{\diagup O}{\diagdown O}$$
nitrite form   Nitro form

Nitro acinitro system

$$CH_3 - CH_2 - N \overset{\diagup O}{\diagdown O} \rightleftharpoons CH_3 - CH = N \overset{\diagup O}{\diagdown OH}$$
nitro form (i)   Aci form (ii)

(iii) *Characteristics of tautomerism*

(a) Tautomerism (cationotropy) is caused by the oscillation of hydrogen atom between two polyvalent atoms present in the molecule. The change is accompanied by the necessary rearrangement of single and double bonds.

(b) It is a reversible intramolecular change.

(c) The tautomeric forms remain in dynamic equilibrium. Hence, their separation is a bit difficult. Although their separation can be done by special methods, yet they form a separate series of stable derivatives.

(d) The two tautomeric forms differ in their stability. The less stable form is called the labile form. The relative proportion of two forms varies from compound to compound and also with temperature, solvent etc. The change of one form into another is also catalysed by acids and bases.

(e) Tautomers are in dynamic equilibrium with each other and interconvertible ($\rightleftharpoons$).

(f) Two tautomers have different functional groups.

(g) Tautomerism has no effect on bond length.

(h) Tautomerism has no contribution in stabilising the molecule and does not lower its energy.

(i) Tautomerism may occur in planar or nonplanar molecules.

❏ Keto=enol tautomerism is exhibited only by such aldehydes and ketones which contain at least one α -hydrogen.

For example

$CH_3CHO, CH_3CH_2CHO, CH_3COCH_2COCH_3$ etc,.
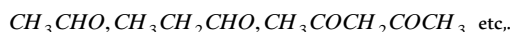
❏ Tautomerism is not possible in benzaldehyde (C_6H_5CHO), benzophenone ($C_6H_5COC_6H_5$), tri methyl acetaldehyde, $(CH_3)_3C - CHO$ and chloral $CCl_3 - CHO$ as they do not have $\alpha - H$.

Number of structural isomers

Molecular formula	Number of isomers
Alkanes	
C_4H_{10}	Two
C_5H_{12}	Three
C_6H_{14}	Five
C_7H_{16}	Nine
C_8H_{18}	Eighteen
C_9H_{20}	Thirty five

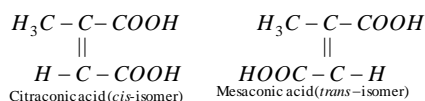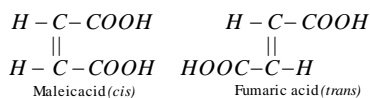|	
$C_{10}H_{22}$	Seventy five
Alkenes and cycloalkanes	
C_3H_6	Two (One alkene + one cycloalkane)
C_4H_8	Six (Four alkene + 2 - cycloalkane)
C_5H_{10}	Nine (Five alkenes + 4 – cycloalkanes)
Alkynes	
C_3H_4	Two
C_4H_6	Six
Monohalides	
C_3H_7X	Two
C_4H_9X	Four
$C_5H_{11}X$	Eight
Dihalides	
$C_2H_4X_2$	Two
$C_3H_6X_2$	Four
$C_4H_8X_2$	Nine
$C_5H_{10}X_2$	Twenty one
Alcohols and ethers	
C_2H_6O	Two (One alcohol and one ether)
C_3H_8O	Three (Two alcohols and one ether)
$C_4H_{10}O$	Seven (Four alcohols and three ethers)
$C_5H_{12}O$	Fourteen (Eight alcohols and six ethers)
Aldehydes and ketones	
C_3H_6O	Two (One aldehyde and one ketone)
C_4H_8O	Three (Two aldehydes and one ketone)
$C_5H_{10}O$	Seven (Four aldehydes and three ketone)
Monocarboxylic acids and esters	
$C_2H_4O_2$	Two (One acid and one ester)
$C_3H_6O_2$	Three (One acid and two esters)
$C_4H_8O_2$	Six (Two acids and four esters)
$C_5H_{10}O_2$	Thirteen (Four acids and nine esters)
Aliphatic amines	
C_2H_7N	Two (One 1°-amine and one 2°-amine)
C_3H_9N	Four (Two 1°-amines, one 2°-amine and one 3°-amine)
$C_4H_{11}N$	Eight (Four 1°-amines, three 2°-amines and one 3°-amines)
Aromatic compounds	
C_8H_{10}	Four
C_9H_{12}	Nine
C_7H_8O	Five

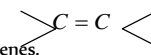## Geometrical or cis-trans isomerism

The compounds which have same molecular formula but differ in the relative spatial arrangement of atoms or groups in space are known as geometrical isomers and the phenomenon is known as geometrical isomerism. The isomer in which same groups or atoms are on the same side of the double bond is known as *cis* form and the isomer in which same groups or atoms are on the opposite side is called *trans*-isomer.
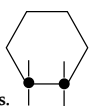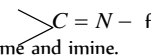
Examples :

$$H-C-COOH \qquad H-C-COOH$$
$$\| \qquad\qquad \|$$
$$H-C-COOH \qquad HOOC-C-H$$
Maleic acid *(cis)*   Fumaric acid *(trans)*

$$H_3C-C-COOH \qquad H_3C-C-COOH$$
$$\| \qquad\qquad\qquad \|$$
$$H-C-COOH \qquad HOOC-C-H$$
Citraconic acid *(cis-isomer)*   Mesaconic acid *(trans–isomer)*

(1) **Conditions for geometrical isomerism :** Compound will show geometrical isomerism if it fulfils the following two conditions

(i) There should be frozen rotation about two adjacent atoms in the molecule.

(a) $\diagup C = C \diagdown$ frozen rotation about carbon, carbon double bond in alkenes.

(b) frozen rotation about carbon, carbon single bond in cycloalkanes.

(c) $\diagup C = N-$ frozen rotation about carbon, nitrogen double bond in oxime and imine.

(ii) Both substituents on each carbon should be different about which rotation is frozen.

If these two conditions are fulfilled, then compound will show geometrical isomerism.

❏ The compounds of the following type will not show geometrical isomerism.

$$a-C-a \qquad x-C-a \qquad a-C-a$$
$$\| \qquad\qquad \| \qquad\qquad \|$$
$$x-C-y \qquad a-C-a \qquad x-C-x$$
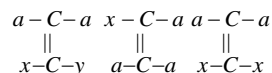
(2) **Distinction between *cis-* and *trans-* isomers**

(i) **By cyclization method :** Generally, the *cis*-isomer (*e.g.* maleic acid) cyclises on heating to form the corresponding anhydride while the *trans*-isomer does not form its anhydride.

$$H-C-COOH \xrightarrow{\text{Heat}} H-C-CO$$
$$\| \qquad\qquad\qquad \| \qquad\qquad \diagdown O$$
$$H-C-COOH \qquad\qquad H-C-CO \diagup$$
Maleic acid *(cis)*   Maleic anhydride
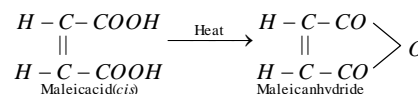
❏ Note that the two reacting groups (*–COOH*) are near to each other.

$$H-C-COOH \xrightarrow{\text{Heat}} \text{No anhydride}$$
$$\|$$
$$HOOC-C-H$$
Fumaric acid *(trans)*
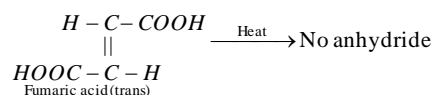
❏ Note that the two reacting groups (*–COOH*) are quite apart from each other, hence cyclisation is not possible.

(ii) **By hydroxylation** (Oxidation by means of $KMnO_4, OsO_4$ or H_2O_2 in presence of OsO_4) **:** Oxidation (Hydroxylation) of alkenes by means of these reagents proceeds in the *cis*-manner. Thus the two geometrical isomers of an alkene leads to different products by these reagents. For example,

$$H-C-COOH$$
$$\|$$
$$H-C-COOH$$
Maleicacid(*cis*)

$\xrightarrow{KMnO_4}$

$$H \underset{OH}{\overset{OH}{\rule{0pt}{1.2em}}} COOH$$
$$H \;\; COOH$$
meso –Tartaricacid

$$H-C-COOH$$
$$\|$$
$$HOOC-C-H$$
Fumaric acid(trans)

$\xrightarrow{KMnO_4}$

$$H \underset{OH}{\overset{OH}{\rule{0pt}{1.2em}}} COOH$$
$$HOOC \;\; H$$
(+)–Tartaricacid

$+$

$$HOOC \underset{OH}{\overset{OH}{\rule{0pt}{1.2em}}} H$$
$$H \;\; COOH$$
(–)–Tartaricacid
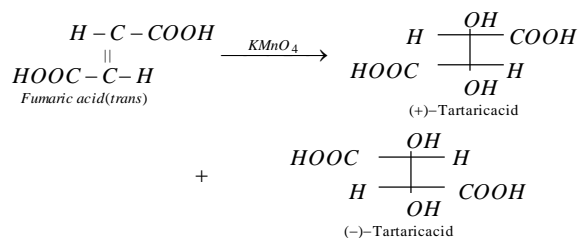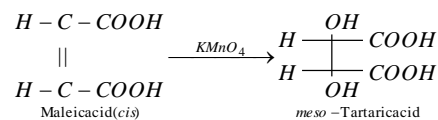
(iii) **By studying their dipole moments :** The *cis*-isomer of a symmetrical alkene (Alkenes in which both the carbon atoms have similar groups) has a definite dipole moment, while the *trans*-isomer has either zero dipole moment or less dipole moment than the *cis*-isomer. For example, 1,2-dichloroethylene and butene-2.

$$H-C-Cl$$
$$\|$$
$$H-C-Cl$$
cis–Dichloroethylene
(μ=1.9 D)

$$H-C-Cl$$
$$\|$$
$$Cl-C-H$$
trans–Dichloroethylene
(μ=0.0 D)

$$H-C-CH_3$$
$$\|$$
$$H-C-CH_3$$
cis–Butene–2

$$H-C-CH_3$$
$$\|$$
$$CH_3-C-H$$
trans–Butene–2
(μ=0.0 D)
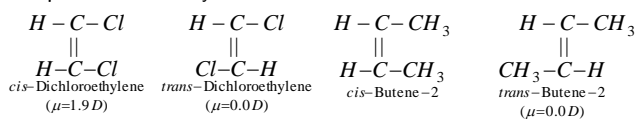
In *trans*-isomer of the symmetrical alkenes, the effect produced in one half of the molecule is cancelled by that in the other half of the molecule.

In case of unsymmetrical alkenes, the *cis*-isomer has higher dipole moment than the corresponding *trans*-isomer.

For Example,

$$H_3C - C - Cl$$
$$||$$
$$CH_3 - CH_2 - C - Cl$$

cis−2,3−Dichloropentene−2
(High dipolemoment)

$$CH_3 - C - Cl$$
$$||$$
$$Cl - C - CH_2CH_3$$

trans−2,3−Dichloropentene−2
(*Less dipolemoment*)
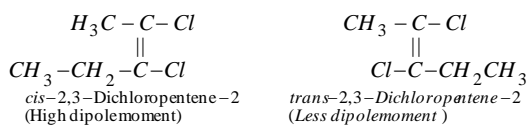
Similar is the case with hexene-2.

$$\begin{matrix} H_3C \\ H \end{matrix} > C = C < \begin{matrix} CH_2CH_2 - CH_3 \\ H \end{matrix}$$

cis−Hexene −2(more polar)

$$\begin{matrix} H \\ CH_3 \end{matrix} > C = C < \begin{matrix} CH_2CH_2 - CH_3 \\ H \end{matrix}$$

trans−Hexene −2(Less polar)

(iv) *By studying other physical properties*: (*a*) The *cis*-isomer of a compound has higher boiling point due to higher polarity, higher density and higher refractive index than the corresponding *trans*-isomer (*Auwers-skita rule*).

$$CH_3 - C - H$$
$$||$$
$$CH_3 - C - H$$

cis−2−Butene
b.p   4°C
m.p.   −139°C

$$CH_3 - C - H$$
$$||$$
$$H - C - CH_3$$

trans−2Butene
1°C
−106°C

$$H - C - Cl$$
$$||$$
$$H - C - Cl$$
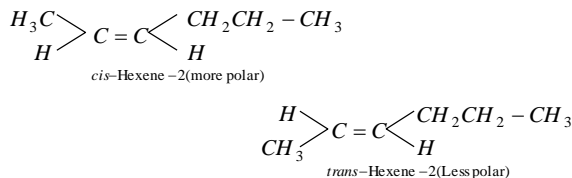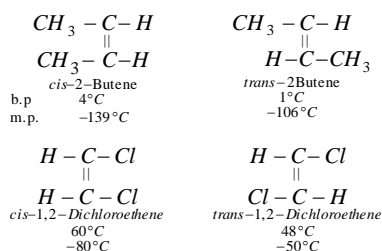
cis−1,2−Dichloroethene
60°C
−80°C

$$H - C - Cl$$
$$||$$
$$Cl - C - H$$

trans−1,2−Dichloroethene
48°C
−50°C

(b) The *trans*-isomer has higher melting point than the *cis*-isomer due to symmetrical nature and more close packing of the *trans*-isomer.

(v) *Stability* : *Trans*-isomer is more stable than *cis*-isomer due to symmetrical structure.

❑ *Terminal alkenes such as propene, 1-butene and 2-methyl propene do not show geometrical isomerism.*

❑ *Cis-trans* isomers are configurational isomers but not mirror images, hence *cis* and *trans* isomers are always *diastereomers*.

❑ Non-terminal alkenes with the same atoms or groups either on one or both the carbon atoms of the double bond such as 2-methyl-2-butene, 2,3-dimethyl −2 − butene etc. do not show geometrical isomerism.

(3) *E* and *Z* system of nomenclature : '*Cis*' and '*Trans*' designations cannot be used if four different atoms or groups are attached to the carbon atoms of a double bond.

$$\begin{matrix} a \\ b \end{matrix} > C = C < \begin{matrix} d \\ e \end{matrix}$$
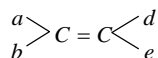
In such cases, *E* and *Z* system of nomenclature is used. This system is based on a priority system developed by *Cahn, Ingold* and *Prelog*.

In this system, the two atoms or groups attached to each of the doubly bonded carbon are put in order of preference on the basis of sequence rules.

The symbol '*E*' is assigned to an isomer in which the atoms or groups of higher preference are on the opposite side (*E* from German word *Entgegen* = across or opposite).

The symbol '*Z*' is assigned to an isomer in which the atoms or groups of higher preference are on the same side (*Z* from German word, *Zusammen* = together).
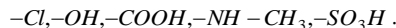

E−isomer   *Z*−isomer
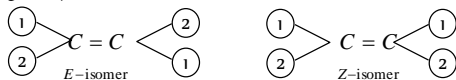
❑ 1 signifies higher preference and 2 signifies lower preference. Preference in most of the cases '*Z*' corresponds to *cis*-form and '*E*' to *trans*-form. However, there are many exceptions.

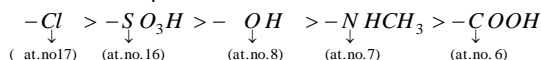The following rules are followed for deciding the precedence order of the atoms or groups;

(i) Higher priority is assigned to the atoms of higher atomic number. For example, the order of preference in the following atoms, H, Cl, I, Br is : I (at. no. 53)> Br (at. no. 35)>Cl (at. no. 17)>H (at. no. 1).

(ii) If isotopes of the same element are attached, the isotope with higher mass number is given higher order of preference. For example, deuterium $\left(^2_1 D\right)$ is assigned higher priority in comparison to hydrogen $\left(^1_1 H\right)$.

(iii) In the groups, the order of preference is also decided on the basis of atomic number of first atom of the group. For example, in the following set,

$$-Cl, -OH, -COOH, -NH - CH_3, -SO_3 H .$$

The order of the precedence is :

$$-Cl > -SO_3H > -OH > -NHCH_3 > -COOH$$
$$(\text{at.no}17)\quad(\text{at.no. }16)\quad(\text{at.no. }8)\quad(\text{at.no. }7)\quad(\text{at.no. }6)$$

When the order of preference of the groups cannot be settled on the first atom, the second atom or the subsequent atoms in the groups are considered. For example, in the set $-CH_2 - CH_3, -CH_3, -COOH$, the order cannot be decided on the basis of first atom as it is same in all the groups. However, in $-CH_2 - CH_3$, the second atom is carbon, in $-CH_3$, the second atom is hydrogen while in $-COOH$, the second atom is oxygen. Hence, the order of preference is :

$$-COOH > -CH_2 - CH_3 > -CH_3$$
$$(\text{at.no.}8)\qquad(\text{at.no.}6)\qquad(\text{at.no.}1)$$
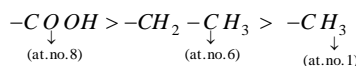
(iv) A doubly or triply bonded atom is considered equivalent to two or three such atoms. For example,

The group $>C = O$ is equal to $>C - O$ and the group $-C \equiv N$
$$\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\quad O$$

$$N$$
$$|$$
is equal to $- C - N .$
$$|$$
$$N$$
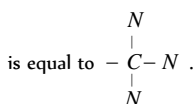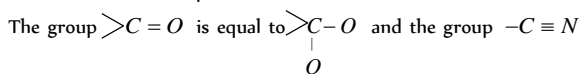
(4) Number of geometrical isomers in polyenes

(i) When a compound has *n* double bonds and ends of a polyene are different, the number of geometrical isomers $= 2^n$

$$C_6H_5 - CH = CH - CH = CH - CH = CH - CH = CH - Cl$$

The given compound has four double bonds and the two ends are different (One is C_6H_5 and other is *Cl*). Therefore, number of geometrical isomers $= 2^n = 2^4 = 16$.

(ii) When the ends of polyene are same.

Case 1 : When number of double bonds ($=n$) is even then the number of geometrical isomers $= 2^{n-1} + 2^{[(n/2)-1]}$

$$Cl - CH = CH - CH = CH = CH - CH = CH - CH = CH - Cl$$
$$\qquad\qquad\qquad\qquad n=4,\text{even}$$
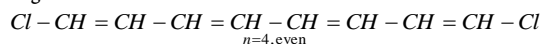
Number of geometrical isomers $= 2^{n-1} + 2^{(n/2)-1} = 2^3 + 2^1 = 8 + 2 = 10$.

Case II : When number of double bonds ($=n$) is odd.

Number of geometrical isomers $= 2^{n-1} + 2^{\left[\frac{n+1}{2}\right]-1}$

$$C_6H_6 - CH = CH - CH = CH - CH = CH - C_6H_5$$
$$\qquad\qquad\qquad(n=3,\text{ odd})$$
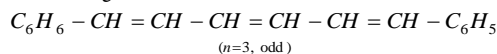
Number of geometrical isomers $= 2^2 + 2^{2-1} = 2^2 + 2^1 = 4 + 2 = 6$.

(5) Geometrical Isomerism in nitrogen compounds

(i) Geometrical isomerism due to $\diagdown C = N -$ bond.

The important class of compounds exhibiting geometrical isomerism due to $C = N -$ bond are oximes, nitrones, hydrazones and semicarbazones. But the most common compound is oxime.

Oximes : In aldoxime, when hydrogen and hydroxyl groups are on the same side, the isomer is known as syn. (analogous to *cis*) and when these groups are on the opposite side, the isomer is known as anti

(analogous to *trans*)

$$C_6H_5 - C - H \atop \| \atop N - OH$$
Syn-benzaldoxime

$$C_6H_5 - C - H \atop \| \atop HO - N$$
Anti−benzaldoxime

In ketoximes the prefixes **syn** and **anti** indicate which group of ketoxime is syn or anti to hydroxyl group. For example:

$$CH_3 - C - C_2H_5 \atop \| \atop N - OH$$ this compound will be named as;

(a) Syn-ethyl methyl ketoxime $\Rightarrow HO$ and C_2H_5 are syn or

(b) Anti-methyl ethyl ketoxime $\Rightarrow HO$ and C_2H_5 are anti.

Similarly consider the following structure

$$C_2H_5 - C - CH_3 \atop \| \atop N - OH$$
Syn −methylethylketoxime
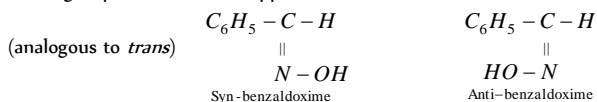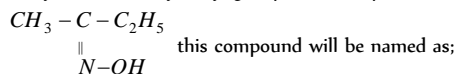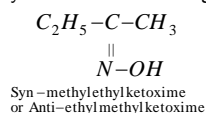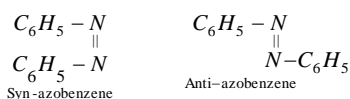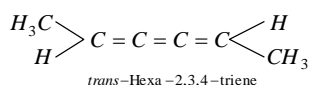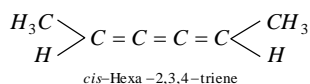or Anti−ethylmethylketoxime

(ii) Geometrical isomerism due to $N = N$ bond.

$$C_6H_5 - N \atop \| \atop C_6H_5 - N$$
Syn -azobenzene

$$C_6H_5 - N \atop \| \atop N - C_6H_5$$
Anti−azobenzene

(6) **Geometrical isomerism show by cumulatrienes :** Cumulatrienes (Trienes with three adjacent double bonds) show only geometric isomerism. This is because their molecule is planar, as such the terminal $-CH_3$ groups and H- atoms lie in the same plane. Therefore, in this case their planar structure can exist in two diastereoisomeric forms, *cis*- and *trans*- but no enantiomeric forms are possible.

$$H_3C \atop H \diagup C = C = C = C \diagdown CH_3 \atop H$$
cis−Hexa −2,3,4−triene

$$H_3C \atop H \diagup C = C = C = C \diagdown H \atop CH_3$$
trans−Hexa −2,3,4−triene

(7) **Geometrical isomerism in cycloalkanes :** Disubstituted cycloalkanes show geometrical isomerism.

Cis-1,2-dimethylcyc
lopropane

Cis-1,2-cyclohexanediol

Trans-1,2-cyclopent
anediol
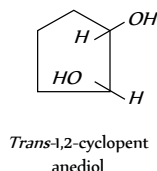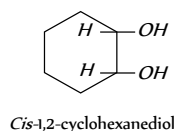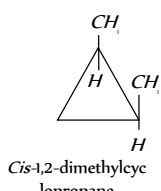
❑ Certain compounds show geometrical as well optical isomerism. Such type of isomerism is known as **geometrical enantiomerism**.

Optical isomerism

(1) Compounds having similar physical and chemical properties but they have the ability to rotate the plane of polarised light either to the right (Clockwise) or to the left (Anticlockwise) are termed as optically active or optical isomers and the property is called optical activity or optical isomerism.

The optical activity was first observed in organic substances like quartz, rock-crystals and crystals of potassium chlorate $(KClO_3)$, potassium bromate $(KBrO_3)$ and sodium periodate $(NaIO_4)$.

(2) **Measurement of optical activity :** The measurement of optical activity is done in terms of *specific rotation which is defined as the rotation produced by a solution of length of 10 centimetres (One decimetre) and unit concentration (1 g/mL) for the given wavelength of the light at the given temperature.*

$$\text{Specific rotation, } [\alpha]^{t°C}_{\text{wavelength}} = \frac{\alpha_{obs}}{l \times C}$$

Where α_{obs} is the rotation observed, *l* is the length of the solution in decimeters and C is the number of grams in $1mL$ of solution. The specific rotation of the sucrose at 20°C using sodium light (*D*-line, λ=5893$\mathring{A}$) is +66.5°C and is denoted as: $[\alpha]^{20°C}_D = +66.5°C(C = 0.02\,g/mL\text{ water})$

+ sign indicates the rotation in clockwise direction.

(3) On the basis of the study of optical activity, the various organic compounds were divided into four types :

(i) The optical isomer which rotates the plane of the polarised light to the right (Clockwise) is known as dextrorotatory isomer (Latin: *dextro = right*) or *d*-form or indicated by +*ve* sign.

(ii) The optical isomer which rotates the plane of the polarised light to the left (Anticlockwise) is known as laevorotatory isomer (Latin; *laevo = left*) or *l*-form or indicated by −*ve* sign.

(iii) The optical powers of the above two isomers are equal in magnitude but opposite in sign. An equimolar mixture of the two forms, therefore, will be optically inactive due to external compensation. This mixture is termed as racemic mixture or *dl*-form or (±) mixture.

(iv) Optical isomer with a plane of symmetry is called *meso* form. It is optically inactive due to internal compensation, *i.e.,* the rotation caused by upper half part of molecule is neutralised by lower half part of molecule.

(4) **Chirality,** (i) *Definition* : A molecule (or an object) is said to be chiral or dissymmetric, if it is does not possess any element of symmetry and not superimposable on its mirror image and this property of the molecule to show non-superimposability is called chirality.

On the other hand, a molecule (or an object) which is superimposable on its mirror image is called achiral (non-dissymmetric or symmetric).

To understand the term chiral and achiral let us consider the alphabet letters '*P*' and '*A*' whereas '*P*' is chiral, '*A*' is achiral as shown in fig.

Mirror

Non-superimposable
(Chiral or dissymmetric)

Mirror

Superimposable
(Achiral or non-dissymmetric)
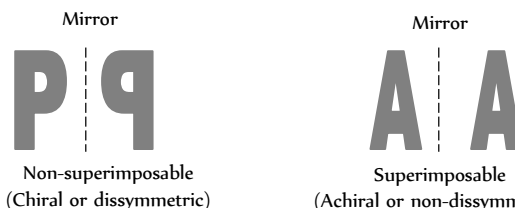
(ii) *Elements of symmetry* : There are three elements of symmetry,

(a) *Plane of symmetry* : It may be defined as a plane which divides a molecule in two equal parts that are related to each other as an object and mirror image. e.*g.,*

$$
\begin{array}{c}
COOH \\
| \\
H-C-OH \\
| \\
\overline{H-C-OH} \;\text{----------- Plane of symmetry} \\
| \\
COOH
\end{array}
$$
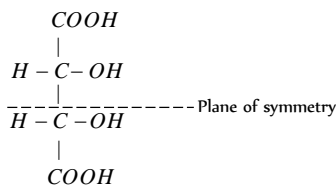
(b) *Centre of symmetry* : It may be defined as a point in the molecule through which if a line is drawn in one direction and extended to equal distance in opposite direction, it meets another similar group or atom, *eg.*

$$
\begin{array}{c}
CH_3 \qquad\qquad CH_3 \\
| \quad NH-CO \quad | \\
C \!<\!\! \!\!>\! C \qquad \text{and} \\
| \quad CO-NH \quad | \\
H \qquad\qquad H \\
cis-\text{Dimethyl diketo piperazine}
\end{array}
\qquad
\begin{array}{c}
\text{Centre of symmetry} \\
CH_3 \qquad\qquad H \\
| \quad NH \!\!\mid\!\! CO \quad | \\
C \!<\! \bullet \!>\! C \\
| \quad CO-NH \quad | \\
H \qquad\qquad CH_3 \\
Trans-\text{Dimethyl diketo piperazine}
\end{array}
$$

Since *trans* form contains a centre of symmetry, it is optically inactive.

(c) *Alternating axis of symmetry* : A molecule is said to possess an alternating axis of symmetry if an oriention indistinguishable from the original is obtained when molecule is rotated Q degree around an axis passing through the molecule and the rotated molecule is reflected in a mirror that is perpendicular to the axis of rotation in step (1).

Reflection perpendicular to axis rotation
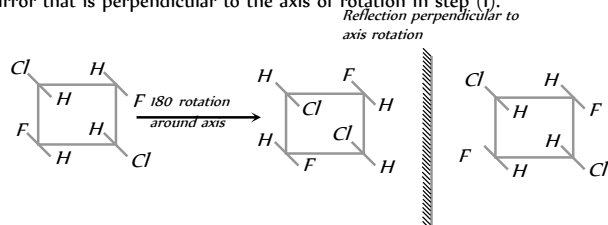
(iii) *Symmetric, Asymmetric and Dissymmetric molecules*

(a) *Symmetric molecules :* If any symmetry is present in the molecule then molecule will be symmetric molecule.

(b) *Dissymmetric molecules* : Molecule will be a dissymmetric molecule if it has no plane of symmetry, no centre of symmetry and no alternating axis of symmetry.

(c) *Asymmetric molecules* : Dissymmetric molecule having at least one asymmetric carbon is known as asymmetric molecule. All asymmetric molecules are also dissymmetric molecules but the reverse is not necessarily true.

$$
\begin{array}{c}
COOH \\
| \\
H-C^*-OH \\
| \\
H-C^*-OH \\
| \\
C_6H_5 \\
\text{No plane of symmetry} \\
\Downarrow \\
\text{Dissymmetric molecule} \\
\Downarrow \\
\text{Asymmetric molecule}
\end{array}
\qquad
\begin{array}{c}
CHO \\
| \\
H-C^*-OH \\
| \\
CH_3 \\
\text{No plane of symmetry} \\
\Downarrow \\
\text{Dissymmetric molecule} \\
\Downarrow \\
\text{Asymmetric molecule}
\end{array}
$$
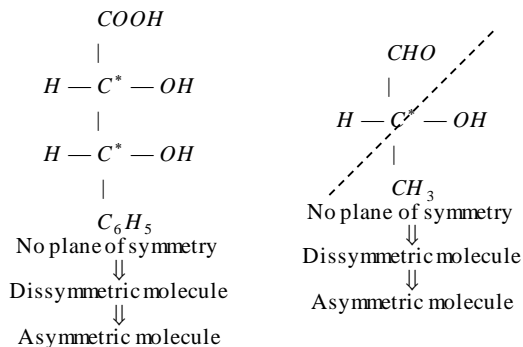
(iv) *Chiral or asymmetric carbon atom* : A carbon bonded to four different groups is called a chiral carbon or a chirality centre. The chirality centre is indicated by asterisk. *e.g.,*

$$
\begin{array}{c}
a \\
| \\
d-C^*-b \\
| \\
c
\end{array}
\qquad
\begin{array}{c}
CH_3 \\
| \\
HO-C^*-H \\
| \\
COOH \\
\text{Lactic acid}
\end{array}
$$
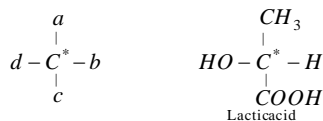
❏ Carbons that can be chirality centres are sp^3-hybridised carbons; sp^2 and sp-hybridised carbons cannot be chiral carbons because they cannot have four group attached to them.

❏ Isotopes of an atom behave as different group in stereoisomerism.

$$
\begin{array}{c}
D \\
| \\
H-C^*-T \\
| \\
Br
\end{array}
\qquad
\begin{array}{c}
H_1 \\
| \\
Cl^{35}-C^*-Cl^{37} \\
| \\
H_2 \\
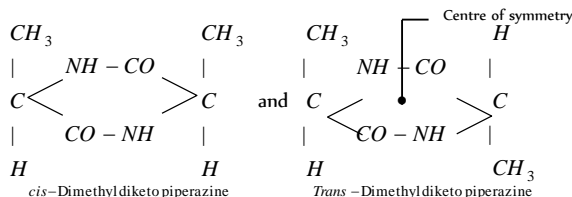\text{Lactic acid}
\end{array}
$$
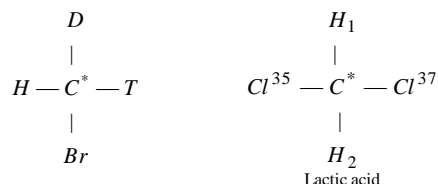
❏ Carbon of the following groups will not be a chiral carbon

$$
-CH_3,\; -CH_2OH,\; -CHX_2,\; -CHO,\; -\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}-Z
$$
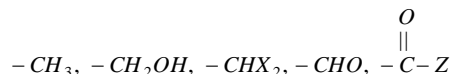
❏ Maleic acid $(HOOC-CH=CH-COOH)$ show geometrical isomerism while malic acid $(HOOC-CH_2-CHOH-COOH)$ show optical isomerism.

(5) **Calculation of number of optical isomers**

(i) If molecule is not divisible into two identical halves and molecule has n asymmetric carbon atoms then

Number of optically active forms $=2^n=a$

Number of enantiomeric pair $=a/2$

Number of racemic mixture $=a/2$

Number of *meso* form $=0$

(ii) If molecule is divisible into two identical halves, then the number of configurational isomers depends on the number of asymmetric carbon atoms.

Case 1 : When compound has even number of carbon atoms, i.e., $n=2,4,8,10,12,.....$:

(i) Number of optically by active forms $=a=2^{n-1}$

(ii) Number of enantiomeric pairs $=a/2$

(iii) Number of racemic mixture $=a/2$

(iv) Number of *meso* forms $=m=2^{(n/2)-1}$

(v) Total number of configurational isomers $=a+m$

Case II : When compound has odd number of carbon atoms, *i.e.,* $n=3,5,7,9,11,......$:

(i) Number of optically active forms $=a=2^{n-1}-2^{(n-1)/2}$

(ii) Number of enantiomeric pairs $=a/2$

(iii) Number of racemic mixutre $=a/2$

(iv) Number of *meso* forms $=m=2^{(n-1)/2}$

(v) Total number of configurational isomers $=a+m$

(6) **Optical activity of compounds containing one asymmetric carbon**

Examples :

$$CH_3 - \overset{*}{C}HOH - COOH \; ; \; CH_3 - \overset{*}{C}HOH - CHO$$
<center>Lacticacid</center>

$$CH_2OH - \overset{*}{C}HOH - CHO \; ; \quad C_6H_5 - \overset{*}{C}HCl - CH_3$$
<center>Glyceraldehyde   1-chloro-1-phenylethane</center>
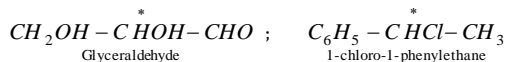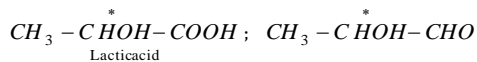
Any molecule having one asymmetric carbon atom exists in two configurational isomers which are nonsuperimposible mirror images.

$$\begin{array}{ccc}
COOH & | & COOH \\
| & | & | \\
H-C-OH & | & HO-C-H \\
| & | & | \\
CH_3 & | & CH_3 \\
(I) & | & (II)
\end{array}$$

(I) and (II) have the same molecular formula, the same structure but different configurations, hence (I) and (II) are known as configurational isomers. (I) and (II) are nonsuperimposable mirror images, hence (I) and (II) are optical isomers. Configurational isomers which are nonsuperimposable mirror images are known as **enantiomers**. Thus (I) and (II) are enantiomers. Pair of (I) and (II) is known as enantiomeric pair.

(i) *Properties of Enantiomers* : All chemical and physical properties of enantiomers are same except two physical properties.

Mode of rotation : One enantiomer rotates light to the right and the other by an **equal magnitude** to the left direction.

(ii) *Racemic Mixture* : An equimolar mixture of two enantiomers is called a racemic mixture (or racemate, $\pm$ form, (*dl*) form or racemic modification). Such a mixture is optically inactive because the two enantiomers rotate the plane polarised light equally in opposite directions and cancel each other's rotation. This phenomenon is called **external compensation**.

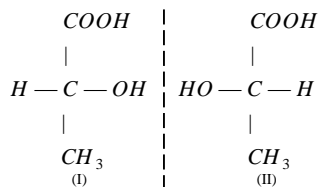$\Rightarrow$ Racemic mixture can be separated into (+) and (−) forms. The separation is known as **resolution**.

$\Rightarrow$ The conversion of (+) or (−) form of the compound into a racemic mixture is called **racemisation**. It can be caused by heat, light or by chemical reagents.

$\Rightarrow$ Racemic mixture is designated as being ($\pm$) or (*dl*).

(7) **Optical activity of compounds containing two asymmetric carbon**

Case 1 : When molecule is not divisible into two identical halves.

The number of optical isomers possible in this case is four $(a = 2^2 = 4)$. Further there will be two pairs of enantiomers and two racemic modifications. In practice also it is found to be so.

Configurational isomers which are not mirror images are known as **diastereomers**.

Properties of Diastereomers : Diastereomers have different physical properties, *e.g.*, melting and boiling points, refractive indices, solubilities in different solvents, crystalline structures and specific rotations. Because of differences in solubility they often can be separated from each other by fractional crystallisation; because of slight differences in molecular shape and polarity, they often can be separated by chromatography.

Diastereomers have different chemical properties towards both **chiral** and **achiral** reagents. Neither any two diastereomers nor their transition states are mirror images of each other and so will not necessarily have the same energies. However, since the diastereomers have the same functional groups, their chemical properties are not very dissimilar.

Case II : *When molecule is divisible into two identical halves.*

Number of optical isomers $= a = 2^{2-1} = 2$

Number of meso forms $= m = 2^0 = 1$

Total number of configurational isomers $= 3$

(8) **Optical activity in compounds containing no assymmetric carbon** : Although the largest number of known optically active compounds are optically active due to the presence of chiral carbon atom, some compounds are also known which do not possess any chiral carbon atom, but on the whole their molecules are chiral (such molecules were earlierly called **dissymmetric**); hence they are optically active. Various types of compounds belonging to this group are allenes, alkylidene cycloalkanes, spiro compounds (spirans) and properly substituted biphenyls.

(i) *Allenes* : Allenes are the organic compounds of the following general formulae.

$$>C=C=C<$$
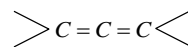
Allenes exhibit optical isomerism provided the two groups attached to each terminal carbon atom are different, *i.e.,*

$$\begin{array}{ccc}
\overset{a}{\underset{b}{>}}C=C=C\overset{a}{\underset{b}{<}} & or & \overset{a}{\underset{b}{>}}C=C=C\overset{x}{\underset{y}{<}}
\end{array}$$
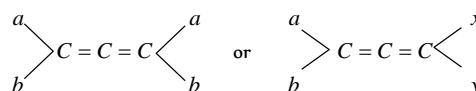
(ii) *Alkylidene cycloalkanes and spiro compounds* : When one or both of the double bonds in allenes are replaced by one and two rings, the resulting systems are respectively known as alkylidene cycloalkanes and spirans.

<center>1-Methylcyclohexylidene-4- acetic acid
(Alkylidene cycloalkane)</center>

<center>Spirans</center>
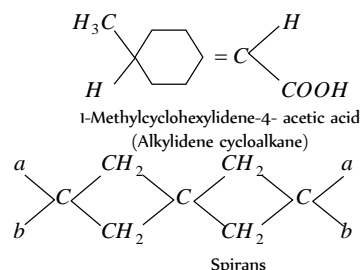
(iii) *Biphenyls* : Suitably substituted diphenyl compounds are also devoid of individual chiral carbon atom, but the molecules are chiral due to restricted rotation around the single bond between the two benzene nuclei and hence they must exist in two non-superimposable mirror images of each other. *Such types of stereoisomerism which is due to restricted rotation about single bond, is known as atropisomerism and the stereoisomers are known and* **atropisomers**. Examples
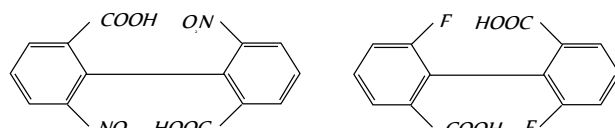
The above discussion leads to the conclusion that the *essential condition for optical isomerism is the molecular disymmetry or molecular chirality* and not the mere presence of a chiral centre. However, it may be noted that the *molecules having only one chiral centre are always chiral and exhibit optical isomerism.*

(9) **Fischer projection formulae :** The arrangement of the atoms or groups in space that characterises a stereoisomer is called its configuration.

Emil Fischer (1891) provided an easy method to represent the three dimensional formulae of various organic molecules on paper. *Fischer projection is, thus, a planar representation of the three dimensional structure.*

By convention, the following points are followed in writing the Fischer formula.

(i) The carbon chain of the compound is arranged vertically, with the most oxidised carbon at the top.

(ii) The asymmetric carbon atom is in the paper plane and is represented at the interaction of crossed lines.

$$\text{Asymmetric Carbon atom}$$
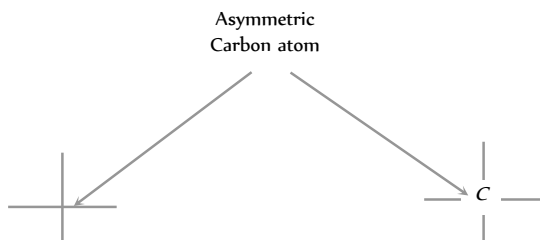
(iii) Vertical lines are used to represent bonds going away from the observer, i.e., groups attached to the vertical lines are understood to be present behind the plane of the paper.

(iv) Horizontal lines represent bonds coming towards the observer, i.e., groups attached to the horizontal lines are understood to be present above the plane of the paper.

(10) **Name of optical isomers :** Following three nomenclatures are used for optically active compounds,

(i) *D,L. System of nomenclature* : This nomenclature is mainly used in sugar chemistry or optically active polyhydroxy carbonyl compounds. This nomenclature was given by Emil Fischer to designate the configurations of various sugars relative to the enantiomeric (+) and (−) glucose as reference.

All sugars whose Fischer projection formula shows the OH group on the chiral carbon atom adjacent to the terminal CH_2OH group on the right hand side belong to the D-series. Similarly if OH is on the left hand side, then the sugars belong to the L-series.

$$H - C - OH \qquad HO - C - H$$
$$CH_2OH \qquad\qquad CH_2OH$$
$$\text{D−series} \qquad\qquad \text{L−series}$$

Examples :

$$CHO \qquad\qquad CHO$$
$$H - C - OH \qquad HO - C - H$$
$$CH_2OH \qquad\qquad CH_2OH$$
$$D(d)\text{glyceraldehyde} \qquad L(l)\text{glyceraldehyde}$$
$$\text{or} \qquad\qquad \text{or}$$
$$D(+)\text{glyceraldehyde} \qquad L(-)\text{glyceraldehyde}$$
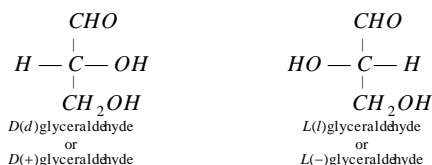
⇒ It must be noted that there is no relation between the sign of rotation (+, − or *d, l*) and the configuration (*D* and *L*) of an enantiomer.

⇒ Any compound that can be prepared from, or converted into $D(+)$ glyceraldehyde will belong to D-series and similarly any compound that can be prepared from, or converted into $L(-)$ glyceraldehyde will belong to the L-series.

⇒ This nomenclature is also used in α-amino acids.

(ii) *Erythro and Threo system of nomenclature* : This nomenclature is used only in those compounds which have

(a) Only two chiral carbons and

(b) The following structure, $R' - Cab - Cbc - R''$

i.e., out of six substituents on two asymmetric carbons, at least two should be same.

When two like groups in Fischer projection formula are drawn on the same side of the vertical line, the isomer is called *erythro* form; if these are placed on the opposite sides, the isomer is said to be *threo* form.

$$R' \qquad\qquad CH_3 \qquad\qquad CH_3$$
$$a - C - b \qquad H - C - Cl \qquad H - C - Cl$$
$$c - C - b \qquad H - C - Br \qquad Br - C - H$$
$$R'' \qquad\qquad C_6H_5 \qquad\qquad C_6H_5$$
$$\text{Erythro form} \qquad \text{Erythro form} \qquad \text{Threo form}$$
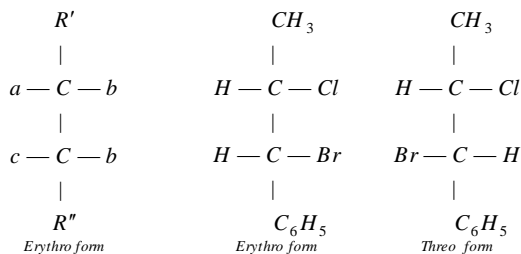
(c) *R,S Nomenclature* (Absolute configuration)

The order of arrangement of four groups around a chiral carbon (stereocentre) atom is called the absolute configuration around that atom. System which indicates the absolute configuration was given by three chemists **R.S. Cahn, C.K. Ingold** and **V. Prelog**. This system is known as (R) and (S) system or the **Cahn-Ingold Prelog** system. The letter (R) comes from the latin **rectus** (means right) while (S) comes from the latin **sinister** (means left). Any chiral carbon atom has either a (R) configuration or a (S) configuration. Therefore, one enantiomer is (R) and other is (S). A racemic mixture may be designated (R) (S), meaning a mixture of the two. (R) (S) nomenclature is assigned as follows :

Step 1 : By a set of sequence rules given below the atoms or groups connected to the chiral carbon are assigned a priority sequence.

Sequence Rules for Order of Priority

Rule 1 : If all four atoms directly attached to the chiral carbon are different, priority depends on their atomic number. The atom having highest atomic number gets the highest priority, i.e., (1). The atom with the lowest atomic number is given the lowest priority, i.e., (2), the group with next higher atomic number is given the next higher priority (3) and so on. Thus,

$$Cl \qquad\qquad ③$$
$$F - C - I \equiv ④ - C - ①$$
$$Br \qquad\qquad ②$$
$$\overrightarrow{F \ Cl \ Br \ I}$$
$$\text{Increasing atomic number}$$
$$\overrightarrow{④ \ ③ \ ② \ ①}$$
$$\text{Increasing priority}$$

$$COOH \qquad\qquad ④$$
$$H_2N - C - Br \equiv ③ - C - ①$$
$$OH \qquad\qquad ②$$
$$\overrightarrow{C \quad N \quad O \quad Br}$$
$$\text{Increasing priority with atomic number}$$

Rule 2 : If two or more than two isotopes of the same element is present, the isotope of higher atomic mass receives the higher priority.

$$_1H^1 \ _1H^2 \ _1H^3$$
$$\overrightarrow{\text{Increasing priority}}$$
$$③ \qquad ② \qquad ①$$

Rule 3 : If two or more of the atoms directly bonded to the chiral carbon are identical, the atomic number of the next atoms are used for priority assignment. If these atoms also have identical atoms attached to them, priority is determined at the first point of difference along the chain. The atom that has attached to it an atom of higher priority has the higher priority.

$$I - H_2C - H_2C - \overset{\overset{\displaystyle I \quad 2H\,and\,Br}{|}}{\underset{\underset{\displaystyle 2H\,and\,C}{CH_2 - CH_2 - CH_3}}{\overset{\uparrow}{C}}} - CH_2 - Br$$

In this example the atoms connected directly to the chiral carbon are iodine and three carbons. Iodine has the highest priority. Connected, to the three carbons are 2*H* and *Br*, 2*H* and *C* and 2*H* and *C*. Bromine has the highest atomic number among *C*,*H* and *Br* and thus CH_2Br has highest priority among these three groups (*i.e.,* priority no. 2).The remaining two carbons are still identical (*C* and 2*H*) connected to the second carbons of these groups are 2*H* and *I* and 2*H* and *C*. Iodine has highest priority among these atoms, so that $-CH_2 - CH_2 - I$ is next in the priority list and $CH_2 - CH_2 - CH_3$ has the last priority.

$$I - CH_2 - CH_2 - \underset{CH_2-CH_2-CH_3}{\overset{\overset{\displaystyle I}{|}}{C}} - CH_2 - Br \qquad \equiv \qquad$$

Rule 4 : If a double or a triple bond is linked to chiral centre the involved atoms are duplicated or triplicated respectively.

$$-C = O \equiv -\underset{|}{\overset{|}{C}}- O \; ; \; -C \equiv N \equiv -\underset{N}{\overset{|}{C}}- N \; ; \; -\overset{\overset{\displaystyle O}{||}}{C}- OH \equiv -\underset{O}{\overset{|}{C}}- OH$$

By this rule, we obtained the following priority sequence :

$$-CH = CR_2, \quad \langle \bigcirc \rangle \quad -CN, \; CH_2OH, \; CHO, \; CO, COOH$$

→ Increasing priority

Step 2 : The molecule is then visualised so that the group of lowest priority (4) is directed away from the observes (At this position the lowest priority is at the bottom of the plane). The remaining three groups are in a plane facing the observer. If the eye travels clockwise as we look from the group of highest priority to the groups of second and third priority (*i.e.,* $1 \rightarrow 2 \rightarrow 3$ with respect to 4) the configuration is designated as *R*. If arrangement of groups is in anticlocwise direction, the configuration is designated as *S*.

For example:

Clockwise arrangement of ①, ② and ③ ⇒ *R*   Anticlockwise arrangement of ①, ② and ③ ⇒ *S*

Let us apply the whole sequence to bromochlorofluoro methane.

$$Br - \underset{Cl}{\overset{\overset{\displaystyle F}{|}}{C}} - H \equiv$$

In this Fischer projection the least priority number is not at the bottom of the plane.

In such cases the Fischer projection formula of the compound is converted into another equivalent projection formula in such a manner that atom or group having the lowest priority is placed vertically downward. This may be done by two **interchanges** between four priority numbers. The first interchange involves the two priority numbers, one is the least priority number and other is the priority number which is present at the bottom of the plane. In the above case first interchange will takes place between 2 and 4.

First interchange Between ② and ④

(A)   (B)

First interchange of two groups at the chiral centre inverts the configuration and this gives enantiomer of the original compound. Thus (*A*) and (*B*) are enantiomer. The second interchange involves the remaining two groups.

Second interchange between remaining groups, *i.e.,* ① and ③

(B)   (A)

Example :

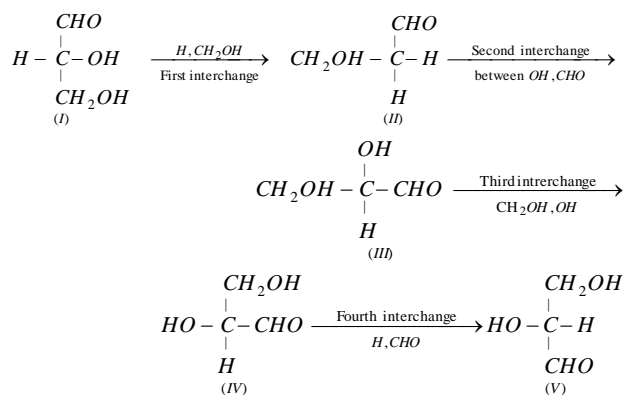$$\underset{CH_2OH}{\overset{\overset{\displaystyle CHO}{|}}{\underset{|}{H - C - OH}}}$$
D-glyceraldehyde

Arrangement of ①, ② and ③ are clockwise, hence configuration is *R*

$$\equiv \qquad H - C - OH \equiv$$

First interchange Between ③ and ④

Second interchange Between ① and ②

⇓ Clockwise R-configuration

$$\underset{CH_2OH}{\overset{\overset{\displaystyle CHO}{|}}{\underset{|}{HO - C - H}}} \equiv$$
L-Glyceraldehyde

(i) First interchange between ③ and ④
(ii) Sec. interchange between ① and ②

Anticlockwise ⇓ S-configuration

Glyceraldehyde (For example) has one asymmetric carbon, hence it has two configurational isomers (I) and (II).

$$\underset{CH_2OH}{\overset{\overset{\displaystyle CHO}{|}}{\underset{|}{H - C - OH}}} \qquad\qquad \underset{CH_2OH}{\overset{\overset{\displaystyle CHO}{|}}{\underset{|}{HO - C - H}}}$$
(*R*)glyceraldehyde   (*S*)glyceraldehyde
(I)   (II)

One can draw a number other configurations for glyceraldehyde but each of them will be a repetition of either (I) or (II). In this connection it is

important to note that if two projection formulae differ by an odd number of interchanges (1, 3, 5, 7, ...) of positions of groups on the chiral carbon, they are different. But if the two differ by an even number of interchanges (2, 4, 6, ...) they are identical.

For example :

$$H - \underset{\underset{(I)}{\overset{|}{CH_2OH}}}{\overset{\overset{CHO}{|}}{C}} - OH \xrightarrow[\text{First interchange}]{H,\,CH_2OH} CH_2OH - \underset{\underset{(II)}{\overset{|}{H}}}{\overset{\overset{CHO}{|}}{C}} - H \xrightarrow[\text{between } OH,\,CHO]{\text{Second interchange}}$$

$$CH_2OH - \underset{\underset{(III)}{\overset{|}{H}}}{\overset{\overset{OH}{|}}{C}} - CHO \xrightarrow[CH_2OH,\,OH]{\text{Third interchange}}$$

$$HO - \underset{\underset{(IV)}{\overset{|}{H}}}{\overset{\overset{CH_2OH}{|}}{C}} - CHO \xrightarrow[H,\,CHO]{\text{Fourth interchange}} HO - \underset{\underset{(V)}{\overset{|}{CHO}}}{\overset{\overset{CH_2OH}{|}}{C}} - H$$

Thus (*I*), (*III*) and (*V*) are identical. Similarly (*II*) and (*IV*) are identical.
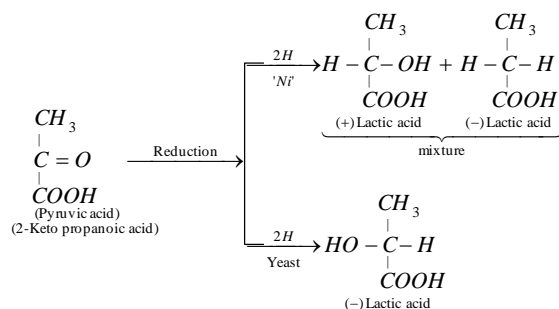
(11) **Resolution of racemic modifications :** The separation of racemic mixture into its enantiomers is known as resolution.

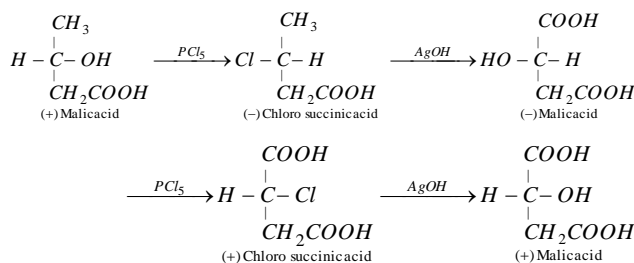❑ Group *X* reacts with group *O* to give new group *W*.

(12) **Asymmetric synthesis and Walden inversion**

(i) **Asymmetric synthesis :** The synthesis of an optically active compound (asymmetric) from a symmetrical molecule (having no asymmetric carbon) without resolution to form (+) or (−) isomer directly is termed **asymmetric synthesis**. For example the reduction of pyruvic acid $(CH_3 - \overset{\overset{O}{||}}{C} - COOH)$ in presence of nickel catalyst gives (±) lactic acid (racemic mixture). On the other hand, pyruvic acid is reduced to (−) lactic acid only by yeast.

$$\underset{\substack{\text{(Pyruvic acid)}\\\text{(2-Keto propanoic acid)}}}{\overset{\overset{CH_3}{|}}{\underset{\underset{COOH}{|}}{C}} = O} \xrightarrow{\text{Reduction}} \begin{cases} \xrightarrow[\text{'}Ni\text{'}]{2H} H - \underset{\underset{COOH}{|}}{\overset{\overset{CH_3}{|}}{C}} - OH + H - \underset{\underset{COOH}{|}}{\overset{\overset{CH_3}{|}}{C}} - H \\ \qquad \underbrace{\;\;(+)\text{Lactic acid} \qquad (-)\text{Lactic acid}\;\;}_{\text{mixture}} \\ \xrightarrow[\text{Yeast}]{2H} HO - \underset{\underset{COOH}{|}}{\overset{\overset{CH_3}{|}}{C}} - H \\ \qquad (-)\text{Lactic acid} \end{cases}$$

(ii) **Walden inversion:** The conversion of (+) form into (−) form and vice-versa is called **Walden inversion**. When an atom or group directly linked to an asymmetric carbon atom is replaced; the configuration of the new compound may be opposite to (inverse) that of the original, *i.e.,*

$$\underset{(+)\text{Malic acid}}{H - \underset{\underset{CH_2COOH}{|}}{\overset{\overset{CH_3}{|}}{C}} - OH} \xrightarrow{PCl_5} \underset{(-)\text{Chloro succinic acid}}{Cl - \underset{\underset{CH_2COOH}{|}}{\overset{\overset{CH_3}{|}}{C}} - H} \xrightarrow{AgOH} \underset{(-)\text{Malic acid}}{HO - \underset{\underset{CH_2COOH}{|}}{\overset{\overset{COOH}{|}}{C}} - H}$$

$$\xrightarrow{PCl_5} \underset{(+)\text{Chloro succinic acid}}{H - \underset{\underset{CH_2COOH}{|}}{\overset{\overset{COOH}{|}}{C}} - Cl} \xrightarrow{AgOH} \underset{(+)\text{Malic acid}}{H - \underset{\underset{CH_2COOH}{|}}{\overset{\overset{COOH}{|}}{C}} - OH}$$

Conformational isomerism

(1) **Definition :** The different arrangement of atoms in a molecule which can be obtained due to rotation about carbon-carbon single bond are called conformational isomers (conformers) or rotational isomers (rotamers). This type of isomerism is found in alkanes and cycloalkanes and their substituted derivatives.

It may be noted that rotation around a $C - C$ sigma bond is not completely free. It is in fact hindered by an energy barrier of 1 to 20 $kJ\ mol^{-1}$ in different bonds. There is a possibility of weak repulsive interactions between the bonds or electron pairs of the bonds on adjacent carbon atoms. Such type of repulsive interaction is known as **torsional strain**.

(2) **Difference between conformation and configuration :** The term conformation should not be confused with the *configuration which relates to those spatial arrangements of the atoms of a molecule that can be changed only by the breaking and making of bonds whereas the spatial arrangements in conformation are changed simply by rotation about a single bond.*

(3) **Representation of conformations :** Conformers can be represented in two simple ways. These are : (i) Saw horse representation and (ii) Newman projection

(i) *Saw horse representation* : In this projection, the molecule is viewed along the axis of the model from an oblique angle. The central carbon-carbon bond ($C - C$) is draw as a straight line slightly tilted to right for the sake of clarity. The front carbon is shown as the lower left hand carbon and the rear carbon is shown as the upper right hand carbon. The three bonds around each carbon atom ($C - H$ in ethane or $C - C$ in higher alkanes) are shown by three lines.


Saw horse representation   Newman projection
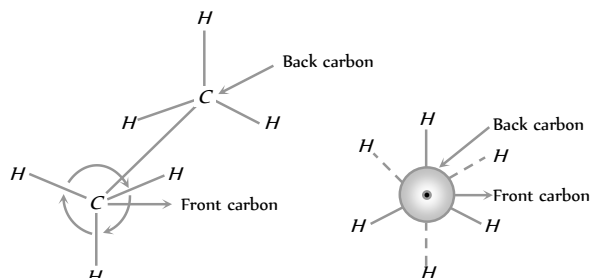
(ii) *Newman projection* : This is a simple method to represent the conformations. In this method, the molecule is viewed from the front along the carbon-carbon bond axis. The two carbon atoms forming the σ-bond are represented by two circles; one behind the other so that only the front carbon is seen. The front carbon atom is shown by a point whereas the carbon further from the eye is represented by the circle. Therefore, the $C - H$ bonds of the front carbon are depicted from the centre of the circle while $C - H$ bonds of the back carbon are drawn from the circumference of the circle at an angle of 120° to each other.

(4) **Conformation in alkanes**

(i) *Conformations of ethane* : When one of the carbon atom is kept fixed and other is rotated about $C - C$ bond an infinite numbers of isomers are possible. Out of all the conformations for ethane, only two extreme conformations are important and these are:

(a) Staggered conformation

(b) Eclipsed conformation

Staggered conformation   Eclipsed conformation
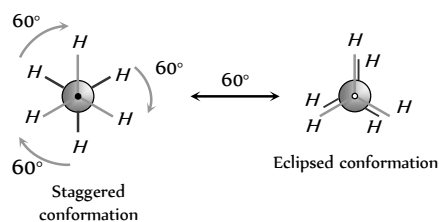
Staggered conformation of ethane is more stable than eclipsed.

(ii) **Conformations of propane** : The next higher member in alkane series, propane $(CH_3 - CH_2 - CH_3)$ also has two extreme conformations, the energy barrier in propane is 14 $kJmol$, which is slightly higher than that in ethane.

Staggered propane   Eclipsed propane

Newman projection of propane
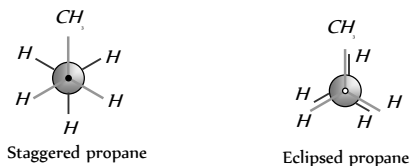
(iii) **Conformations of butane** : As the alkane molecule becomes larger, the conformation situation becomes more complex. In butane $(CH_3 - CH_2 - CH_2 - CH_3)$, for example, the rotation about the single bond between two inner atoms (C_2 and C_3) is considered. In this case, all the staggered as well as eclipsed conformations will not have same stability and energy because of different types of interaction between $C - C$ (of methyl) and $C - H$ bonds.

The lowest energy conformation will be the one, in which the two methyl groups are as far apart as possible *i.e.,* 180° away form each other.

This conformation will be maximum staggered, most stable and is called **anti or trans conformation** (marked I). Other conformations can be obtained by rotating one of the C_2 or C_3 carbon atoms through an angle of 60° as shown ahead.

I   II   III
Anti   Eclipsed   Skew or Gauche

IV   V   VI
Fully eclipsed   Skew or Gauche   Eclipsed
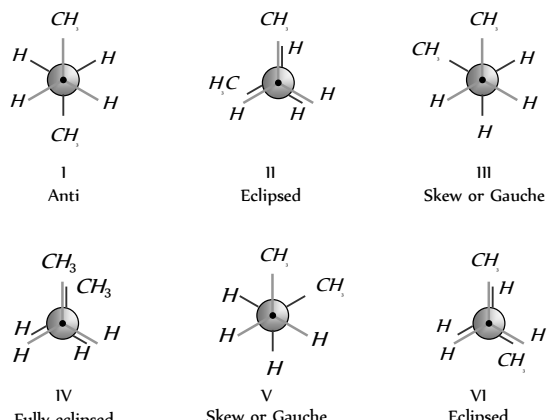
As is clear from the above Newman projection, the Gauche or Skew conformations (III and V) are also staggered. However, in these conformations, the methyl groups are so close that they repel each other. This repulsion causes gauche conformations, to have about 3.8 $kJ\ mol$ more energy than anti conformation. This conformations II and VI are **eclipsed conformations**. These are unstable because of repulsions. These are 16 $kJ\ mol$ less stable than anti conformation. Conformation IV is also eclipsed and it is least stable having energy 19 $kJ\ mol$ more than anti conformation. This is because of repulsion between methyl-methyl groups which are very closed together. It is called **fully eclipsed conformation**.

The **order of stability** of these conformations is, Anti > Skew or Gauche > Eclipsed > Fully eclipsed.

(5) **Conformations in cycloalkanes**

(i) **Stability of cycloalkanes** : Compounds with three and four membered rings are not as stable as compounds with five or six membered rings.

The German chemist Baeyer was the first to suggest that the instability of these small rings compounds was due to angle strain. This theory is known as **Baeyer-strain theory**.

Baeyer strain theory was based upon the assumption that when an open chain organic compound having the normal bond angle 109.5° is convert into a cyclic compound, a definite distortion of this normal angle takes place leading to the development of a strain in the molecule.
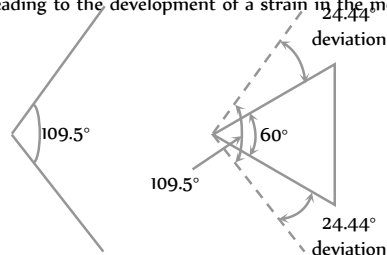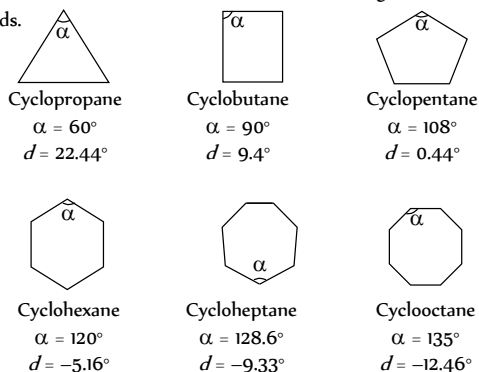

Baeyer assumed that cyclic rings are planar. Assuming that the rings are planar, the amount of strain in various cycloalkanes can be expressed in terms of angle of deviation (d).

$$d = \frac{1}{2}\left[109.5 - \frac{2(n-2)}{n} \times 90\right] \quad \text{or} \quad d = \frac{1}{2}[109.5 - \alpha]$$

Where n = number of carbon-carbon bonds in cycloalkane ring; α = inner bond angle in the cycloalkane ring.

$$\text{Angle strain} \propto d \propto \frac{1}{\text{inner angle}} ; \text{ Stability} \propto \frac{1}{d} \propto \text{inner angle}(\alpha)$$

Now let us take the case of three to eight membered cyclic compounds.

Cyclopropane	Cyclobutane	Cyclopentane
$\alpha = 60°$	$\alpha = 90°$	$\alpha = 108°$
$d = 22.44°$	$d = 9.4°$	$d = 0.44°$

Cyclohexane	Cycloheptane	Cyclooctane
$\alpha = 120°$	$\alpha = 128.6°$	$\alpha = 135°$
$d = -5.16°$	$d = -9.33°$	$d = -12.46°$

The positive and negative values of (d) indicate whether the inner angle is less than or more than the normal tetrahedral value.

Beayer thus predicted that a five membered ring compound would be the most stable. He also predicted that six membered ring compounds would be less stable and as the cyclic compounds become larger than five membered ring, then they would become less and less stable.

Contrary to what Baeyer predicted, however cyclohexane is more stable than cyclopentane. Furthermore, cyclic compounds do not become less and less stable as the number of sides increase. Thus Baeyer strain theory is applicable only to **cyclopropane, cyclobutane and cyclopantane**.

The mistake that Baeyer made was to assume that all cyclic compounds are planar. But only cyclopropane is planar and other cycloalkanes are not planar. Cyclic compounds **twist** and **bend** in order to

achieve structure that minimises the three different kinds of strain and that can destabilise a cyclic compound.

(a) **Angle strain** is the strain that results when the bond angle is different from desired tetrahedral bond angle of $109.5°$.

(b) **Torsional strain** is caused by repulsion of the bonding electrons of one substituent with bonding electrons of a nearby substituent.

(c) **Steric strain** is caused by atoms or groups of atoms approaching each other too closely.

(ii) *Conformation of cyclohexane* : Despite Baeyer's prediction that five-membered cyclic compounds would be the most stable, the six membered cyclic compound is the most stable. Six membered cyclic compound are most stable because they can exist in a conformation that is almost completely free of strain. This conformation is called the **chair conformation**. In a chair conformation of cyclohexane all bond angles are $109.38°$ which is very close to the $109.5°$ and all the adjacent carbon-hydrogen bonds are staggered.


Chair conformation of cyclohexane

Newmann projection of the chair conformation
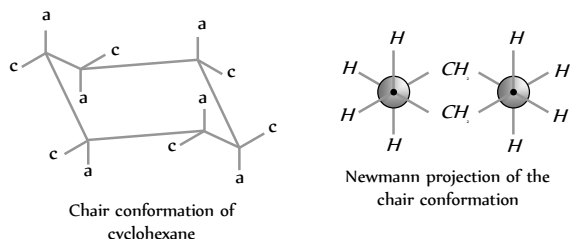
$\Rightarrow$ Each carbon in chair conformation has an axial bond and an equatorial bond.

$\Rightarrow$ Axial bonds are perpendicular to the plane of the ring and equatorial bonds are in the plane of the ring.

$\Rightarrow$ If axial bond on carbon-1 is above the plane of the ring then axial bond on carbon-2 will be below the plane of the ring. Thus
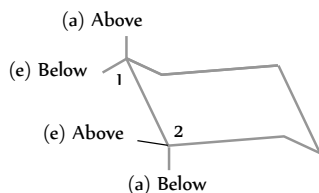
$C-1, C-3$ and $C-5$ axial bonds are above the plane

$C-2, C-4$ and $C-6$ axial bonds are below the plane
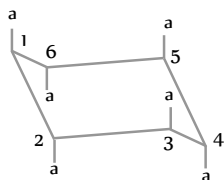
$\Rightarrow$ Thus $C-1$ axial and $C-2$ axial are *trans* to each other. Similarly $C-1$ and $C-5$ axials are *cis* to each other.

$\Rightarrow$ If axial bond on carbon-1 will be above the plane then equatorial bond on this carbon will be below the plane.

(a) Thus $C-1$ equatorial and $C-2$ equatorial bonds are *trans*.

(b) $C-1$ axial and $C-2$ equatorial will be *cis*.

$\Rightarrow$ As a result of rotation about carbon-carbon single bonds cyclohexane rapidly interconverts between two stable chair conformations. This interconversion is known as ring –flip. When the two chair forms interconvert, axial bonds become equatorial and equatorial bonds become axial.
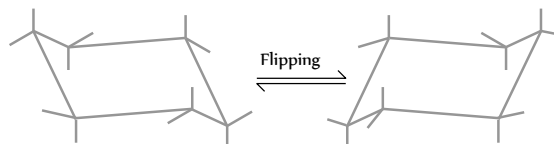
$\Rightarrow$ Cyclohexane can also exist in a boat conformation. Like the chair conformation, the boat conformation is free of angle strain. However, the boat conformation is less stable than the chair conformation by 11 *kcal/mole.* Boat conformation is less stable because some of the carbon-hydrogen bonds in boat conformation are eclipsed.

The boat conformations is further destabilised by the close proximity of the flagpole hydrogens. These hydrogens are 1.8 $Å$ apart but the vander Waal's radii is 2.4 $Å$. The flagpole hydrogens are also known as *trans* nuclear hydrogens.

❒ The relative stabilities of the four conformations of cyclohexane decrease in the order:

Chair > twist boat > boat > half chair.

⊤ Tips & Tricks

✍ Wohler synthesised the first organic compound urea in the laboratory.

✍ The number of optical isomers of a compound depends on its structure and number of asymmetric carbon atoms present in its molecule.

✍ Stereoisomers that are not mirror images of each other are called diastereomers.

✍ Order of priority for both asymmetric carbon atoms using sequence rules is

$$-OH > -COOH > -CH(OH)COOH > -H$$
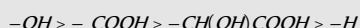
✍ The nitration and sulphonation of alkanes involve free radicals.

✍ Carbenes undergo insertion reactions.

✍ Alkanes usually undergo free radical substitution when hydrogen is replaced by a halogen. It is catalysed by benzoyl peroxide $(C_6H_5COO)_2$.

✍ The polymerisation of alkenes is free radical addition reaction.

✍ Allyl free radical $(CH_2 = CH - \overset{\cdot}{C}H_2)$ is more stable than n-propyl free radical $(CH_3CH_2\overset{\cdot}{C}H_2)$.

✍ The stability of free radicals is explained on the basis of hyperconjugation or conjugation.

✍ Propene is more reactive than ethene towards electrophilic addition reaction due to the formation of more stable 2° carbocation.

✍ The reactivity of alkyl halides in SN^1 is 3°> 2°>1°>methyl while SN^2 is methyl > 1°> 2°> 3°.

✍ Polar solvents favour SN^1 while non polar solvents favour SN^2 reactions.

✍ Dipole moment of $CHCl_3$ is less than that of CH_2Cl_2. This is because in CH_2Cl_2 all bond moments reinforce each other while in $CHCl_3$ the bond moment of one of the Cl opposes the net moment of the other two.

✍ Low concentration of nucleophiles favour SN^1 while high concentration favour SN^2.

✍ In SN^1 the attack of the nucleophile may be from either side and so recimization takes place. However, in SN^2 the attack of the nucleophile takes place from back side. So it leads to inversion of configuration.

✍ Hunsdieker reaction proceeds via free radical mechanism.

✍ Propene reacts with chlorine at 673 K to form allyl chloride and the intermediate is allyl free radical.