STEREOCHEMISTRY - 1

ORGANIC CHEMISTRY

[B.sc – II (HONOURS)]

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18/07/2021

STEREOCHEMISTRY – 1

ISOMERISM

Iso – Same 18/07/2021

Merous – Molecules.

   When two or more than two organic compounds have same molecular formula but having different physical and chemical properties, the phenomenon is called as isomerism and the compounds are called as isomers.
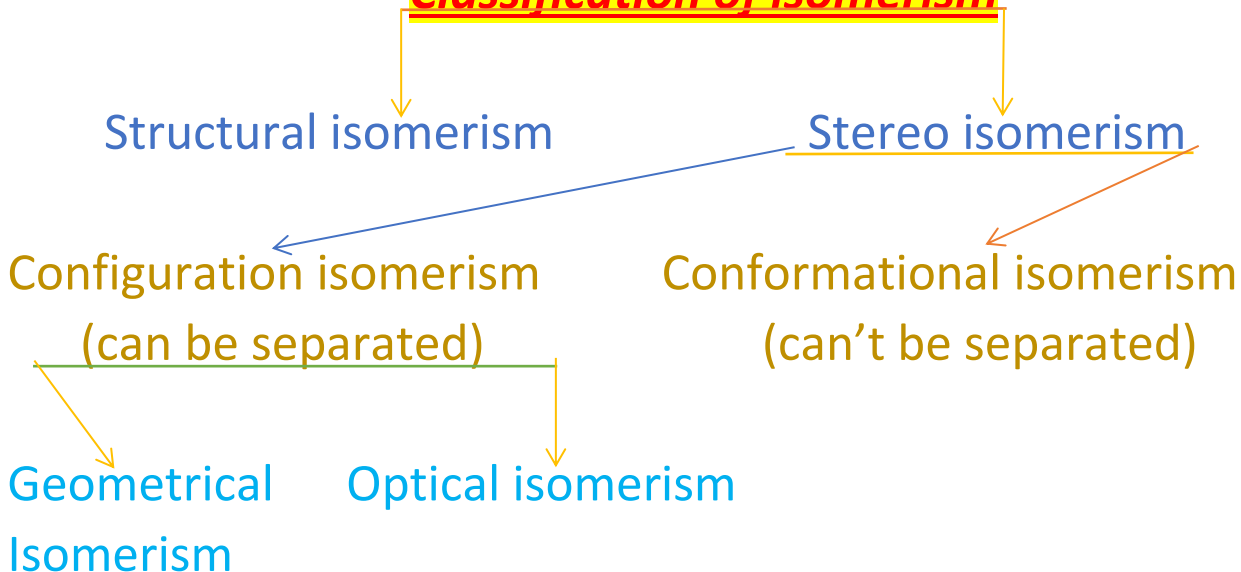
Ex :- (1). C_2H_5OH (2). $CH_3 – O – CH_3$

        Ethyl alcohol   Dimethyl ether

   Molecular formula – C_2H_6O

Classification of isomerism

Structural isomerism   Stereo isomerism

Configuration isomerism   Conformational isomerism
   (can be separated)   (can't be separated)
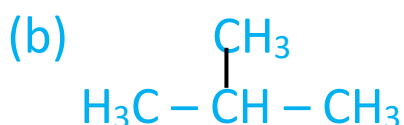
Geometrical   Optical isomerism
Isomerism

Structural isomerism:-

   When two or more than two organic compounds have same molecular formula but having different structural formula than the phenomenon is called as structural isomerism.

(a) C_4H_{10} – Butane

$H_3C - CH_2 - CH_2 - CH_3$

n – Butane

(b) CH_3
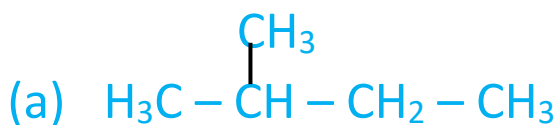$H_3C - CH - CH_3$

Iso – butane

Again structural isomerism is of following types:-
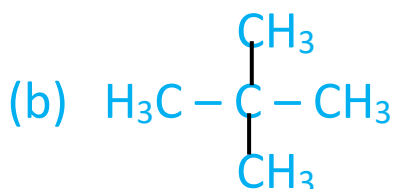
(1) *Chain isomerism or Nuclear isomerism.*

When two or more than two organic compounds have same molecular formula but having different type of carbon chain the phenomenon is called as chain isomerism.

Urea – (CH_4N_2O)   / Isomers/ Silver cyanate - (AgCNO)
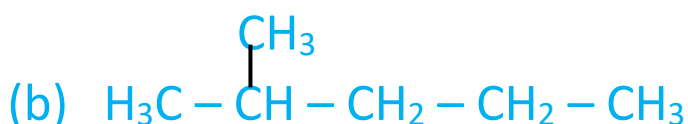
Silver fulminate - (AgCNO)

           CH_3
(a) $H_3C - CH - CH_2 - CH_3$

Iso – pentane

           CH_3
(b) $H_3C - C - CH_3$
           CH_3

2,2 – Dimethyl propane

➢ C_6H_{14}

(a) $H_3C - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$

n – Hexane

           CH_3
(b) $H_3C - CH - CH_2 - CH_2 - CH_3$

Iso – Hexane

(c)

$$CH_3$$
$$H_3C - C - CH_2 - CH_3$$
$$CH_3$$

Neo – Hexane

(d) $H_3C - CH - CH - CH_3$
$$CH_3 \quad CH_3$$
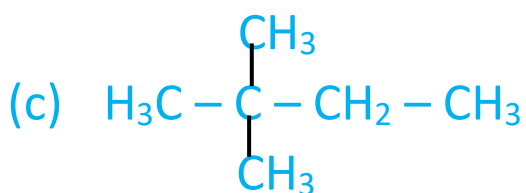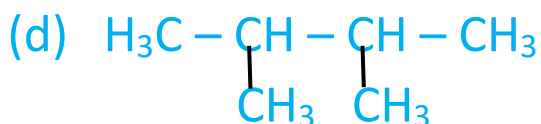
2,3 – Dimethyl butane

(e) $H_3C - CH_2 - CH - CH_2 - CH_3$
$$CH_3$$
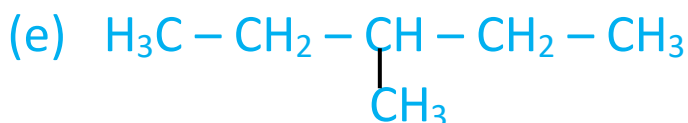
3 – Methyl pentane

(2) Ring chain isomerism:-
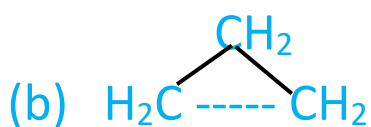
When two or more than two organic compounds having same molecular formula but having differ carbon chain or ring chain, the phenomenon is called as ring chain isomerism.
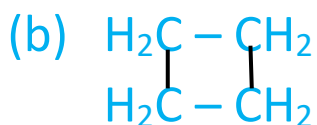
(i) $C_3H_6.$

(a) $H_3C - HC = CH_2$
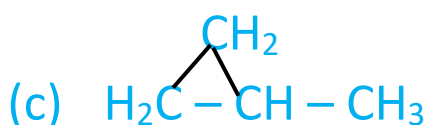
1 – Propene

(b)
$$CH_2$$
$$H_2C ----- CH_2$$

Cyclopropane

(ii) $C_4H_8.$

(a) $H_2C = CH - CH_2 - CH_3$

1 – Butene   or   But – 1 – ene

(b) $H_2C - CH_2$
$\quad H_2C - CH_2$

Cyclobutane

(c) $H_2C - \overset{\overset{\displaystyle CH_2}{\diagup}}{CH} - CH_3$

Methyl cyclopropane

(3)   *Positional isomerism:-*

When two or more than two organic compounds have same molecular formula but having different position of functional group, the phenomenon is called as positional isomerism.

(i) C_4H_8.

(a) $H_2C = CH - CH_2 - CH_3$

But – 1 – ene

(b) $H_3C - CH = CH - CH_3$

But – 2 – ene

(ii) C_4H_9OH.

(a) $H_3C - CH_2 - CH_2 - CH_2 - OH$

Butane – 1 – ol

(b) $H_3C - CH_2 - \overset{\overset{\displaystyle OH}{|}}{CH} - CH_3$
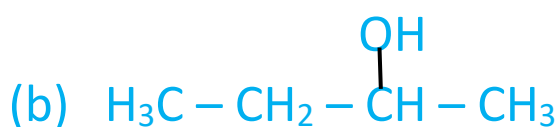
Butane – 2 – ol

(4)   *Functional group isomerism:-*

When two or more than two organic compounds have same molecular formula but having different type of functional group the phenomenon is called as functional group isomerism.

(i) C_2H_6O.

(a) C_2H_5OH

Ethanol

(b) $H_3C - O - CH_3$

   Diethyl either

(a) C_2H_5CHO

   Propanol

(b) $H_3C - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3$

   Propanone

(5) Allotropism or Kryptomerism.
Tautomerism or Desmotropism.

   When two or more than two compounds have same molecular formula but having different type of functional group, the phenomenon is called as Tautomerism.

   Tautomerism are inter conversable under same conditions.
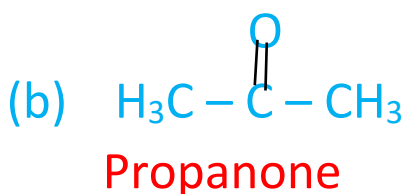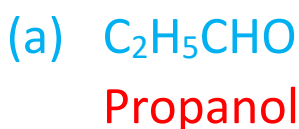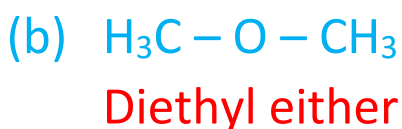
(I) $H_3C - \overset{\overset{\displaystyle O}{\|}}{C} = CH - COOC_2H_5$

   Ethyl acetoacetate (Keton form)

   $\updownarrow$(i)

   $H_3C - \overset{\overset{\displaystyle OH}{|}}{C} = COOC_2H_5$

      (ii)   (Enol form)

(II) $R - CH_2 - N\overset{\nwarrow O}{\underset{\searrow O}{}}$

   $\updownarrow$

   $R - CH = N\overset{\nwarrow OH}{\underset{\searrow O}{}}$

5
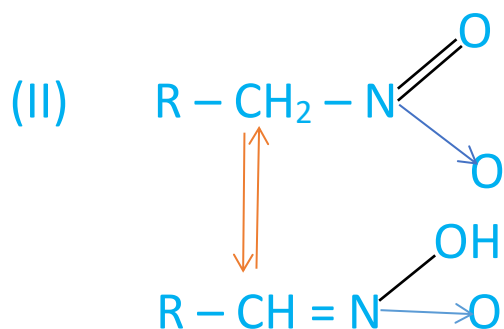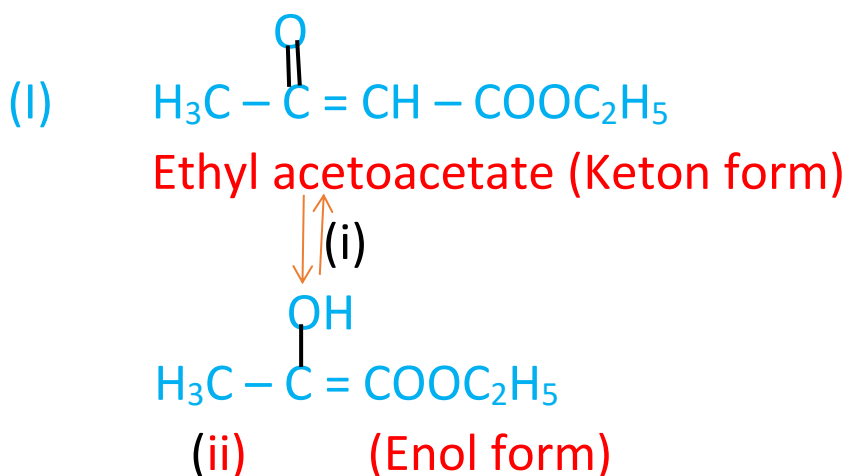
In Tautomerism shifting of only $\alpha - H -$ atoms take place.

(III) $R - C \equiv N \longleftrightarrow R - N \equiv C$

Alkyl cyanide

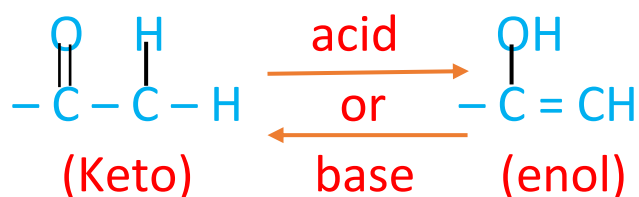## (6)   Isotopic isomerism:-

When two or more than two organic compounds have same molecular formula but having different arrangement of isotopes the phenomenon is called as isotopic isomerism.

Ex:- (a) CH_3COOH (b) $H_3C - COOH$

❖ Tautomerism :-

(i)   Tautomerism are in dynamic equilibrium.

(ii)   Conversions are acid or base catalysed.

(iii)   Keto – enol tautomerism.

$$\underset{(Keto)}{\overset{\overset{O}{\parallel}\quad\overset{H}{|}}{-C - C - H}} \quad \underset{base}{\overset{acid}{\underset{\longleftarrow}{\overset{\longrightarrow}{or}}}} \quad \underset{(enol)}{\overset{\overset{OH}{|}}{-C = CH}}$$

Tests:-

(a) Keto form   Forms oxine.

(b) Enol form   gives bromide

Water test

$$\overset{}{>}C = C\overset{}{<} \quad \xrightarrow[\text{Water (Red - brown)}]{Br} \quad \underset{(colourless)}{-\overset{\overset{Br}{|}}{C} - \overset{\overset{Br}{|}}{C} -}$$
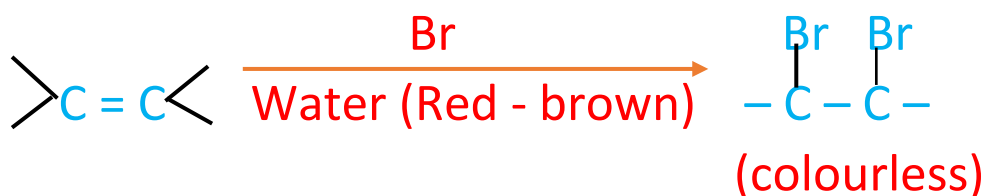
Mechanism :-

Acid catalysed.

$$H_3C - \overset{\overset{\displaystyle O}{\parallel}}{C} - CH_2R \longleftrightarrow H_3C - \overset{\overset{\displaystyle |\overline{O}|^{(+)}}{|}}{C}_{(+)} - \overset{\displaystyle |}{CH} - R$$

Keto

$$\downarrow +H^+$$

$$H_3C - \overset{\overset{\displaystyle OH}{|}}{C} = CH - R \longleftrightarrow H_3C - \overset{\overset{\displaystyle OH}{|}}{C}_{(+)} - \overset{\displaystyle |}{CH} - R$$

Enol
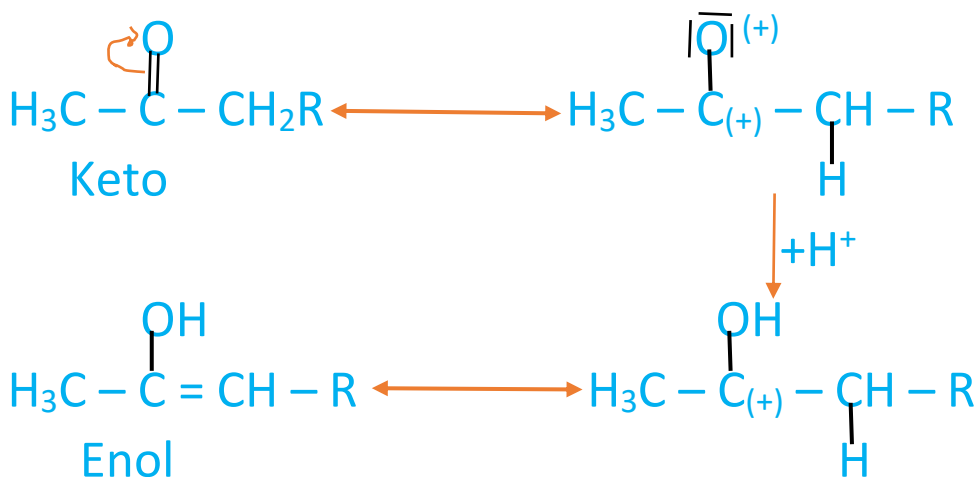
❖ Stereo isomerism :-

When two or more than two organic compounds have same molecular formula as well as structural formula but having different arrangements of atoms or groups in space the phenomenon is called as stereo isomerism and the compounds are called as stereo isomerism.
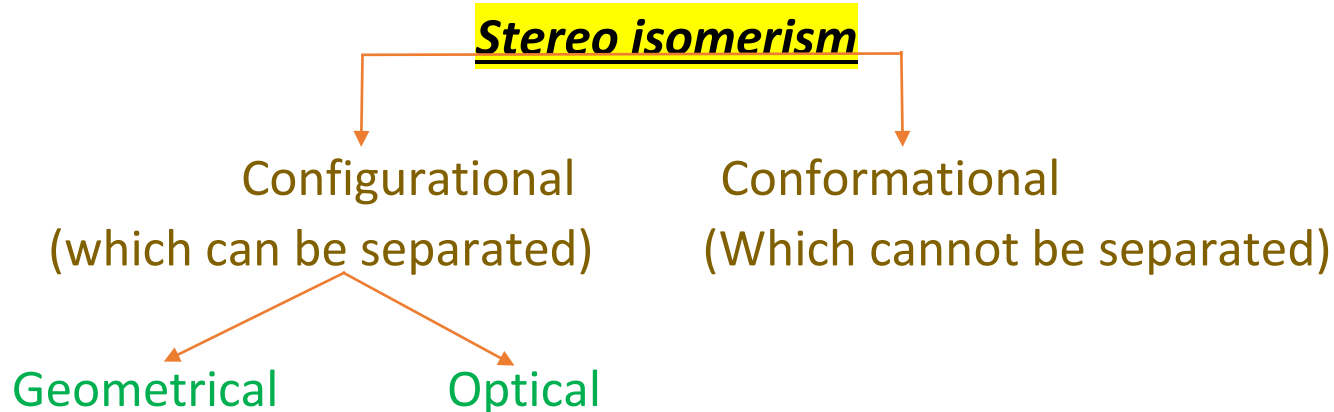
Stereo isomers have same chemical properties but different physical properties.

Stereo isomerism

Configurational
(which can be separated)

Conformational
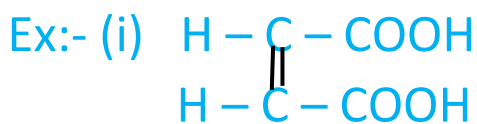(Which cannot be separated)

Geometrical   Optical

Geometrical isomerism:-

It was discovered by Van't Hoff and Le bel in 1874.

Definition:- When two or more than two organic compounds have same molecular formula and same structural formula but having different arrangement of atoms or group around double
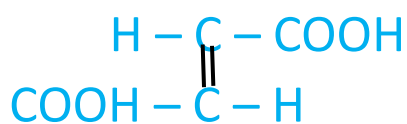
bond in space the phenomenon is called as geometrical isomerism.

Geometrical isomerism poeses different physical properties but having similar chemical properties (not identical).
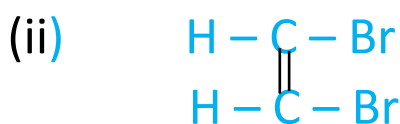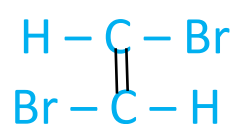
Ex:- (i)
$$H - \overset{\|}{\underset{\|}{C}} - COOH$$
$$H - C - COOH$$

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

Cis – maleic acid   Trans – fumaric acid

M.P – 130^0c   M.P – 286^0c

(ii)
$$H - \overset{\|}{\underset{\|}{C}} - Br$$
$$H - C - Br$$

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

Cis – 1,2-Dibromo ethene   Trans – 1,2-Dibromo ethene

M.P – -65^0c   M.P – -53^0c

(iii)
$$H_3C - \overset{\|}{\underset{\|}{C}} - H$$
$$H_3C - C - H$$

$$H - \overset{\|}{\underset{\|}{C}} - CH_3$$
$$H_3C - C - H$$
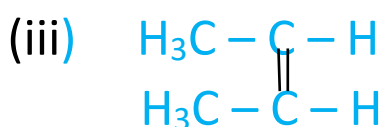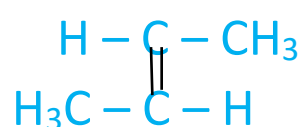
Cis – 2 – Butene   Trans – 2 – Butene

B.P – 4^0c   B.P – 1^0c

Types of geometrical isomerism:-

There are two types of geometrical isomerism.

(i)   Cis – isomers

(ii)   Trans – isomers

(i)   **Cis – isomers :-** When the similar groups lies on the same side it is called as cis-isomers.

Note:- Cis is a latin word which means same side.

(ii)   **Trans – isomers:-** When similar groups are on the opposite side, it is called as trans-isomers.
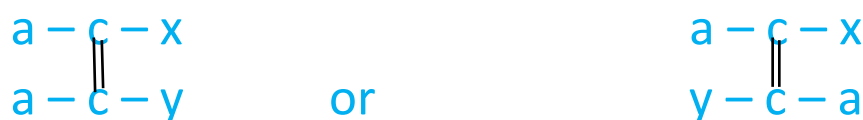
Note:- Trans is a latin word which means opposite side.
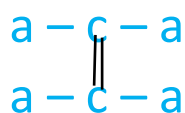
Cause of geometrical isomerism:-

The cause of geometrical isomerism is due to restricted rotation of atoms or group around double bond. Since the rotation about a C = C requires an energy of about 60 Kcal/mol to 70 Kcal/mol which is very high. Thus, rotation cannot take place at room temperature. Also, rotation around π – bond leads to decrease in overlap of π – bond due to which there is increase in energy which is energetically unfavourable.

Condition for geometrical isomerism:-

(i)   There must be at least one C = C present in the molecule.
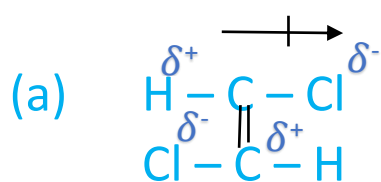
(ii) There must be following type of structure.

$$
\begin{array}{l}
b - c - a \\
\| \\
b - c - a
\end{array}
\qquad \text{or} \qquad
\begin{array}{l}
b - c - a \\
\| \\
a - c - b
\end{array}
$$

$$
\begin{array}{l}
a - c - x \\
\| \\
a - c - y
\end{array}
\qquad \text{or} \qquad
\begin{array}{l}
a - c - x \\
\| \\
y - c - a
\end{array}
$$

(iii) But there must not be following type of structure.

$$
\begin{array}{l}
a - c - a \\
\| \\
b - c - a
\end{array}
\qquad \text{or} \qquad
\begin{array}{l}
a - c - a \\
\| \\
b - c - b
\end{array}
$$

$$
\begin{array}{l}
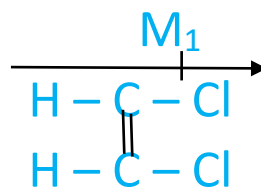a - c - a \\
\| \\
a - c - a
\end{array}
$$

Thus, geometrical isomerism is possible only when each of the double bonded carbon atoms have two different groups.

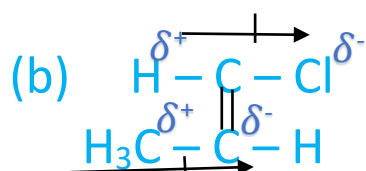Determination of configuration of geometrical isomerism:-

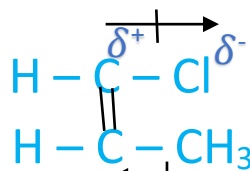*(1) By measurement of dipole momentum:-*

(a)

$$H \overset{\delta^+}{-} C - Cl^{\delta^-}$$
$$\overset{\delta^-}{\underset{||}{}} \overset{\delta^+}{}$$
$$Cl - C - H$$

Trans

M = 0

$$M_1$$
$$H - C - Cl$$
$$||$$
$$H - C - Cl$$

$M = m_1 + m_2, m_2$ Cis.

M = 1·8D

(b)

$$H \overset{\delta^+}{-} C - Cl^{\delta^-}$$
$$\overset{\delta^+}{\underset{||}{}} \overset{\delta^-}{}$$
$$H_3C - C - H$$

Trans, M = 1·97D

$$\overset{\delta^+}{H - C - Cl}^{\delta^-}$$
$$||$$
$$H - C - CH_3$$

Cis, M = 1·71D

(2)   (a) By measurement of melting point:-

In general atoms – isomers packs more easily in the crystal Lattice and hence higher density and M·P (melting point) than Cis compounds on the other hand Cis compounds have low M·P. Since they do not pack well in crystal lattice.

Eg:- (i) M·P of malic acid = 130^0c.

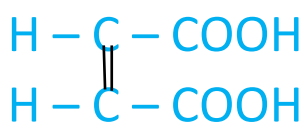(ii) M·P of fumaric acid = 286^0c.

(2) (b) By measurement of boiling point:-

Cis isomers have large B·P than trans isomer due to greater polarity and hence stronger inter molecular forces.

(3)   By measurement of solubility:-

The poor packing leads to weaker force of attraction between molecules in the crystal lattice. The weaker forces of attraction can be easily broken by the dielectric constant of solvents. Hence, the Cis – isomers, has greater solubility than its trans – isomers.
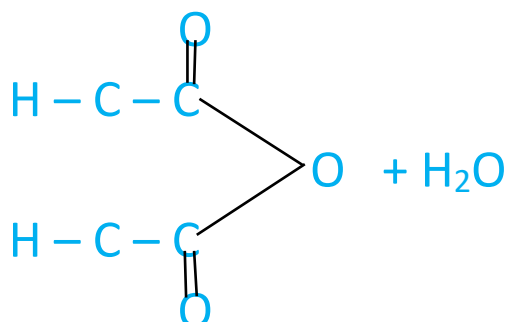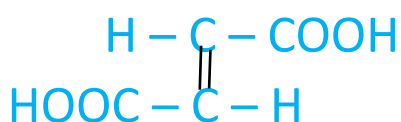
(4)   By chemical methods:-

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

Cis – maleic acid CH_3COCl P·T·O

             Acetyl chloride

$$H - C - \overset{O}{\overset{\|}{C}} \diagdown$$
$$\qquad\qquad O \; + H_2O$$
$$H - C - \underset{O}{\underset{\|}{C}} \diagup$$

Malic anhydride

$$H - \overset{\|}{\underset{\|}{C}} - COOH$$
$$HOOC - C - H$$

$\xrightarrow{CH_3COCl}$ No reaction

Trans – formic acid

     Malic acid readily forms cyclic anhydride where, as formic acid does not. This means that in maleic acid the two groups are nearer to each other than in formic acid. Obviously maleic acid is the Cis – form and formic acid is the trans form.

(5) *By acidic strength:-*

     We can explain very strong acidic character of maleic acid (Cis – form) than formic acid (Trans – form). It proton is removed from each of the acids, the corresponding ions are formed but the maleate ion can be stabilized by chelation ring formation because hydrogen and oxygen responsible for forming H – bond are very near to each other on the other hand fumarate ion cannot be stabilized by chelation because Hydrogen and Oxygen are on the opposite side to each other. This explains why maleic acid is stronger acid than formic acid.

H − C − COOH $\xrightarrow{\text{-H}^+}$ H − C − COO⁻ H⁺   bond

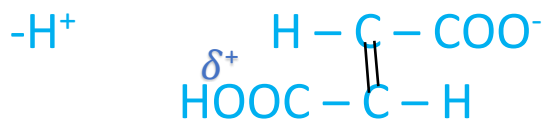H − C − COOH   H − C − COOH
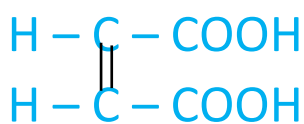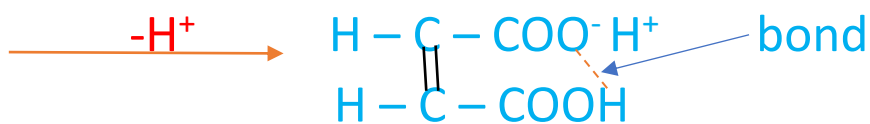
Maleic acid   **maleate ion (chelation) (more stable)**

H − C − COOH   -H⁺   H − C − COO⁻

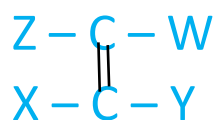HOOC − C − H δ^+ HOOC − C − H
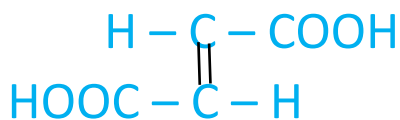
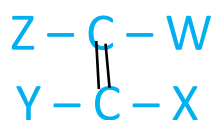**Fumaric acid**   **Fumarate ion (No chelation) (Less stable)**

(6) By stability :-

Trans – isomers are more stable than Cis – isomers.

Cahn – Ingold – Prelog system of geometrical isomerism.

Z − C − W   Z − C − W

X − C − Y   Y − C − X

    (I)   (II)

(i)   In the older method one isomer is called as Cis and the other Trans. When X = Z, (I) is the Cis and (II) is trans isomer.

(ii)   Unfortunately, there is no easy way to apply this method when the four groups are different. The newer method which can be applied to all cases is based on Cahn – Ingold – Prelog system.

        The group at each carbon is ranked by the sequence rule. Then that isomer which has the two higher ranking group on the same side of the double bond is called as Z – isomer (From German word zusammen meaning together) and the other is E – isomers (From entgegen meaning opposite).

Note:- Z – isomer is not necessary the one that would be called Cis under the older system.

(3) Like Cis and trans Z and E are used as prefixes.

Ex:-   Br – C – Cl   Cl – C – Br
        ‖   ‖
        H – C – Cl   H – C – Cl
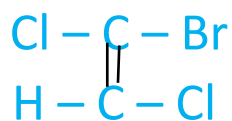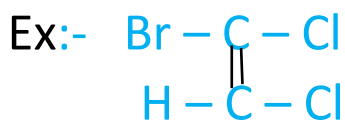
E-1-Bromo-1,2-Dichloro   Z-1-Bromo-1,2-Dichloroethane

Geometrical isomerism of compounds having more than one double bond:-
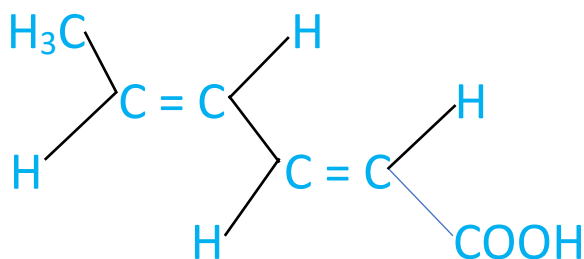
When there is more than one double bond fulfilling the condition for geometrical isomerism in a molecular the number of geometrical isomerism = 2^n where n = number of such double bonds.

Ex:-

$$\begin{array}{c} H_3C \\ \diagdown \\ \\ H \diagup \end{array} C = C \begin{array}{c} H \\ \\ \diagdown \\ C = C \end{array} \begin{array}{c} H \\ \diagup \\ \\ \diagdown COOH \end{array}$$

Number of double bonds = 2

∴ Total number of geometrical isomerism = $2^2 = 4$

Isomers of above example:-

(i)

$$\begin{array}{c} H_3C \\ \diagdown \\ \\ H \diagup \end{array} C = C \begin{array}{c} H \\ \\ \diagdown \\ C = C \end{array} \begin{array}{c} H \\ \diagup \\ \\ \diagdown COOH \end{array}$$

Trans – Trans

(ii)

$$\begin{array}{c} H_3C \\ \diagdown \\ \\ H \diagup \end{array} C = C \begin{array}{c} H \\ \\ \diagdown COOH \\ C = C \end{array} \begin{array}{c} \\ \\ \diagup \\ H \end{array}$$

Trans – Cis

(iii)

Cis – Trans

F.G | C = N – OH
Oxime

(iv)
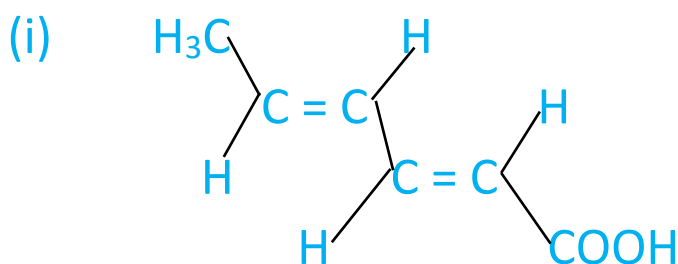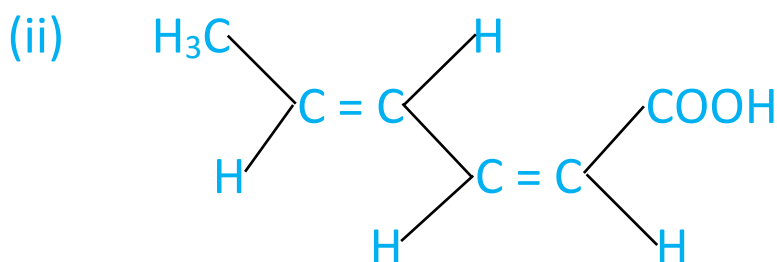
Cis – Cis
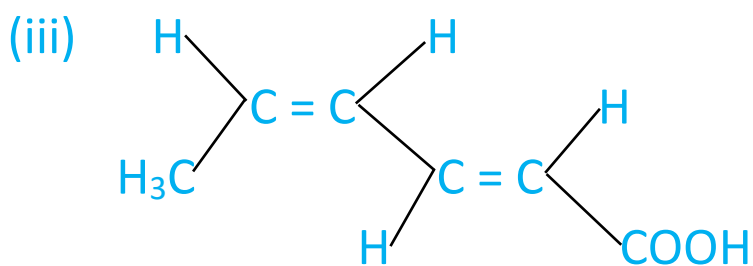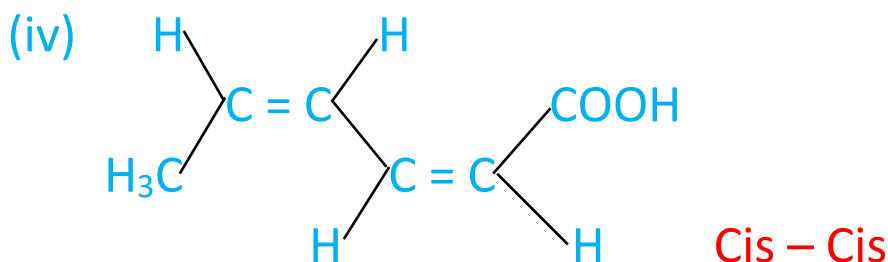
Geometrical isomerism in oximes:-

Aldoximes and ketoximes also show geometrical isomerism.

In aldoximes when hydrogen and –OH group are on the same side the isomer is called sys (analogous to Cis) and when these group are on opposite side the isomer is known as anti (analogous to trans).

Ex:- (i) $C_6H_5 – C – H$
$\quad\quad\quad\quad\quad\|$
$\quad\quad\quad\quad N – OH$

Sys – Benzaldoxime

(ii) $C_6H_5 – C – H$
$\quad\quad\quad\quad\|$
$\quad\quad HO – N$
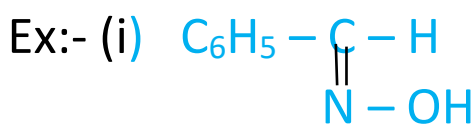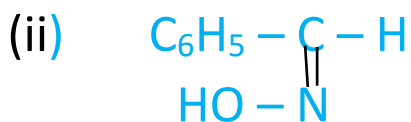
Anti – Benzaldoxime

In ketoximes the prefixes Sys and Anti indicate which group of ketoxime is Sys can the same side or Anti can the opposite side to OH group.

Ex:- (a) $H_3C - C_6H_4 - \overset{\displaystyle \|}{\underset{\displaystyle N-OH}{C}} - C_6H_5$

Sys – Phenyl – tolyl ketoxime

Or, Anti – tolyl – phenyl ketoxime

(b) $H_3C - C_6H_4 - \overset{\displaystyle \|}{\underset{\displaystyle HO-N}{C}} - C_6H_5$
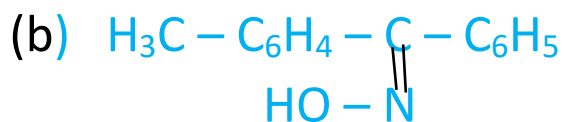
Sys – tolyl – phenyl ketoxime

Or, Anti – phenyl – tolyl ketoxime

Geometrical isomerism in cyclic compound:-

Rotation around a single bond is possible but when that bond is placed in a ring, the rotation around bond becomes impossible. Restricted rotation leads to geometrical 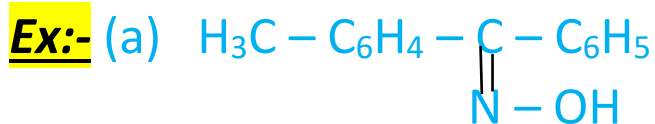isomerism provided when none of the two identical groups or atoms thus suitably substituted alicyclic compounds exhibits geometrical isomerism.
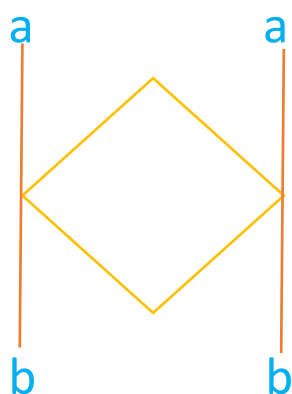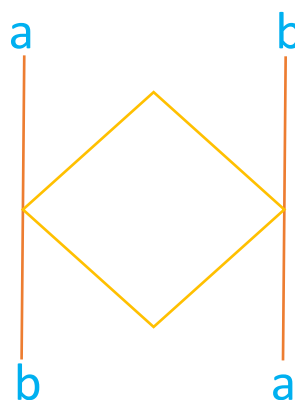
Cis   Trans

The ring is assumed as planar when the same substituents are on the same side it is called Cis – isomer and when similar groups are on the opposite it is called as trans – isomers.

When the geometrical isomerism arises in cyclic compounds it is often associated with optical activity, it is seen that Cis and

Trans – 2 – methyl – cyclopropane carboxylic acid also show optical isomerism.

The geometrical isomers of – 2 – methyl cyclopropane carboxylic acid are non – sub superimposable mirror image, they rotate PPL.

H_3C — C(H) — C(H) — CH_2 ... COOH   HOOC — C(H) — C(H) — CH_2 ... CH_3

H — C(H_3C) — C(H) — CH_2 ... COOH   HOOC — C(H) — C(CH_3) — CH_2 ... H
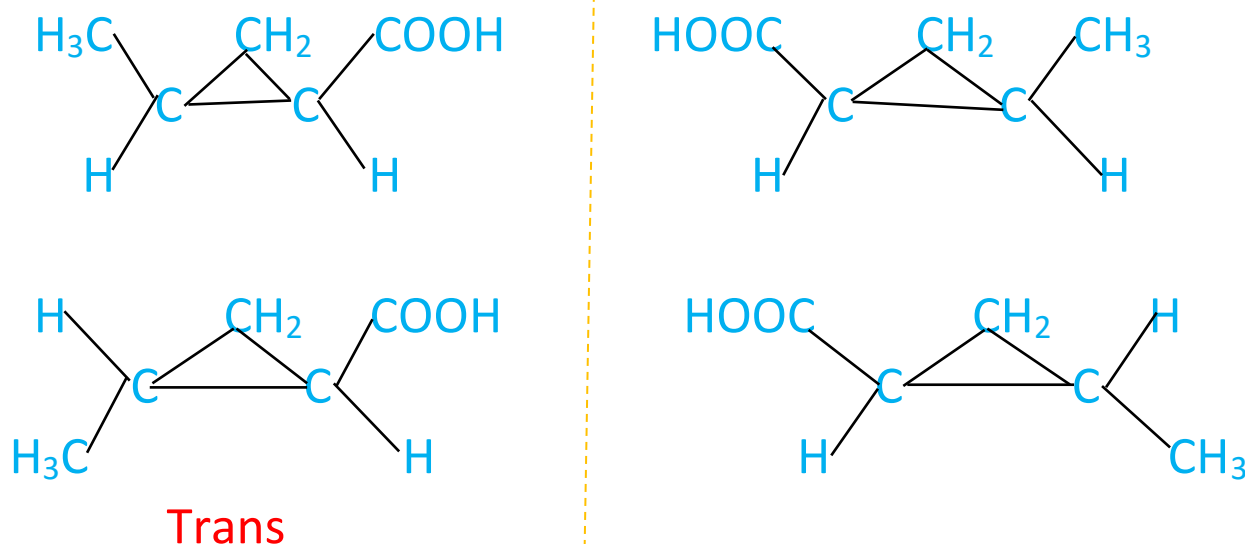
Trans

In case of even namferedring the molecule may have a plane of symmetry. There, fore no. optically active form, exist Although the may still exist in Cis and Trans isomerism.

(a)
COOH   COOH   COOH   H

H   H   H   COOH
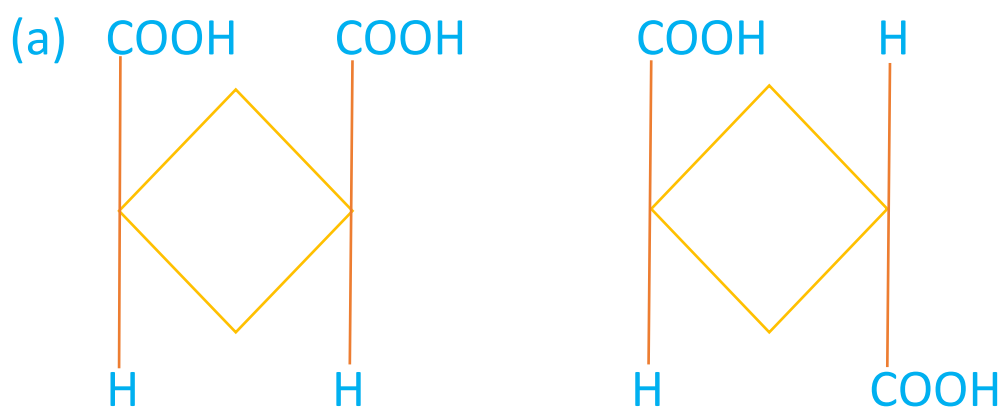
Cis   **Trans**

1,3 – cyclobutene dicarboxylic acid

(b)

COOH   COOH   COOH   H

H   H   H   COOH

      Cis   Trans
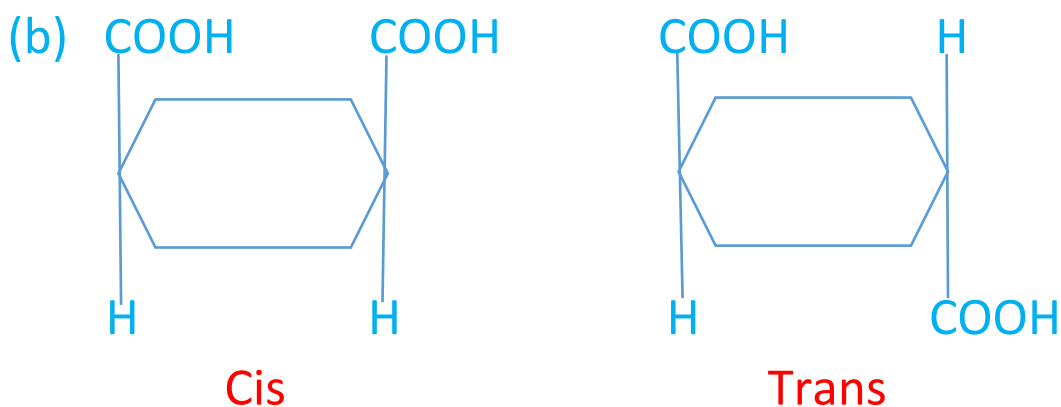
1,4 – Cyclohexane dicarboxylic acid

OPTICAL ISOMERISM

PLANE OF POLARISED LIGHT (PPL):-

The ray of light having rays of specific wavelength is called as monochromatic light (mono = one, or croma = colour). Ordinary monochromatic light vibrates in all possible planes.

Molus (in 1807) found that when such a monochromatic light is passed through **Nicol prism** or **germanium** crystal, the emerging light vibrates in a single plane which is **parallel** to the axis of crystal. This very light is called as plane polarised light.

Monochromatic   (PPL)

   Light   Nicol Prism
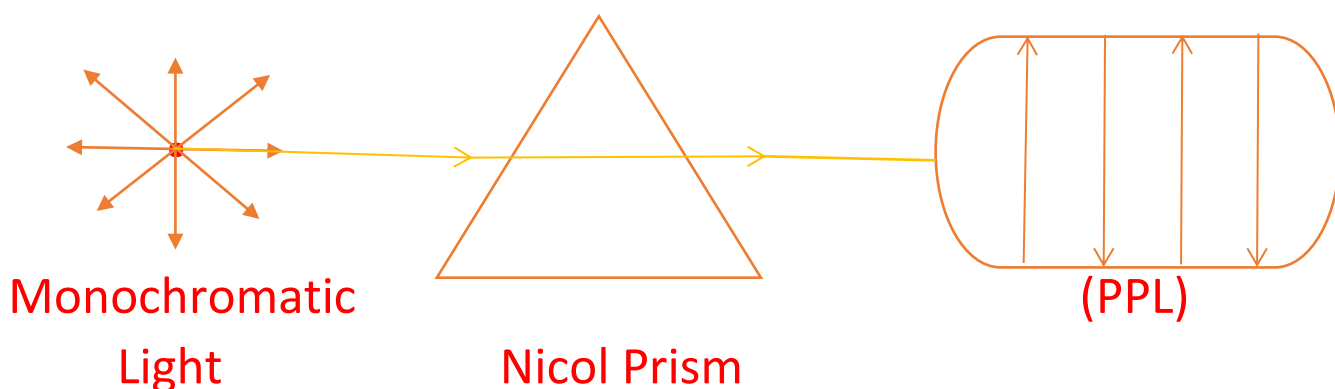
This plane polarised light is that monochromatic light which has been set to vibrate in a single plane.

The observed rotation of the plane polarised light is determined with the help of polarimeter.

According to Vont's Hoff and Le Bel, the four bonds of a C – atoms are directed towards the four corners of regular tetrahedral and the carbon atom, itself as situated at the centre. This gives us the idea non – planar structure of a carbon compound.

Vont's Hoff and Le Bel related the phenomenon of optical rotation to the presence of asymmetrically substituted carbon atoms when a carbon atom is joined to four different atoms or groups the carbon atom is called as asymmetric carbon atom or chiral centre and is represented as C*.

The molecule which has got chiral centre is called chiral molecule and this phenomenon is called as chirality.

Chirality is necessary and sufficient condition for existence of Enantiomers that is to say a compound whose molecule is chiral can exist as enantiomer and a compounds whose molecules are not chiral can't exist as **enantiomer**.

Enantiomer:-

A pair of optically active isomers related as object and mirror image and are not superimposable are called as enantiomer.

Ex:- Optical isomers is lactic acid are enantiomer.

$$CH_3 \qquad\qquad\qquad CH_3$$
$$H - C - OH \qquad\qquad HO - C - H$$
$$COOH \qquad\qquad\qquad COOH$$
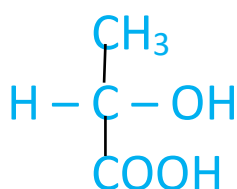
D – Lactic acid   (Mirror image)   L – Lactic acid

Or, (+) Dextro – Lactic acid   or, (-) Laevo – Lactic acid

The two forms represent the optically active isomers of lactic acid. These are related to one another by object and mirror image and are not superimposable. Thus, the pair of these two isomers are known as enantiomers. These two optical isomers are capable to rotate the planed polarised light one rotates the plane polarised light towards right known as dextro or (+) or D and the other rotate the PPL towards left and is called as laevo rotatory or L or (-).

Elements of symmetry :-

There are mainly three types of symmetry in the molecule.

(i)   Plane of symmetry.

(ii)   Centre of symmetry.

(iii)   Axis of symmetry.

(1)   Plane of symmetry:-

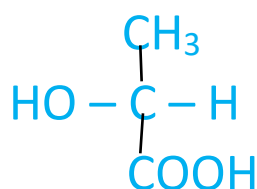It is defined as mirror plane which bisects an object so that one – half (1/2) of the object coincides with the reflection of the other half object having plane.

Note:- A carbon atom in a ring can be chord centre if.

(a) It bears two different substituents and.

(b) The path traced around the ring form that carbon in clock wise direction is different from that traced in anti-clock wise direction.

H   OH   H   OH   O   H
                                              CH₃

Achiral   Chiral
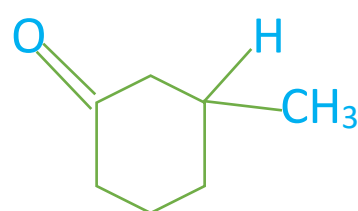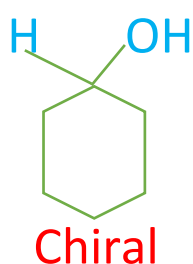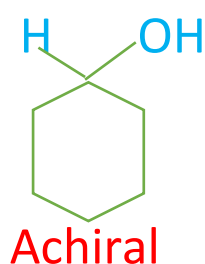
Of symmetry. They are superimposable on its mirror image.

(i)

$$H_3C\diagdown$$
$$C^*-H \qquad C^*-CH_3$$
$$H_3C\diagup \qquad \diagup H \qquad \diagdown C_2H_5$$

$$H_3C\diagdown$$
$$C^*-H \qquad C^*-CH_3$$
$$H_5C_2\diagup \qquad \diagup H \qquad \diagdown C_2H_5$$
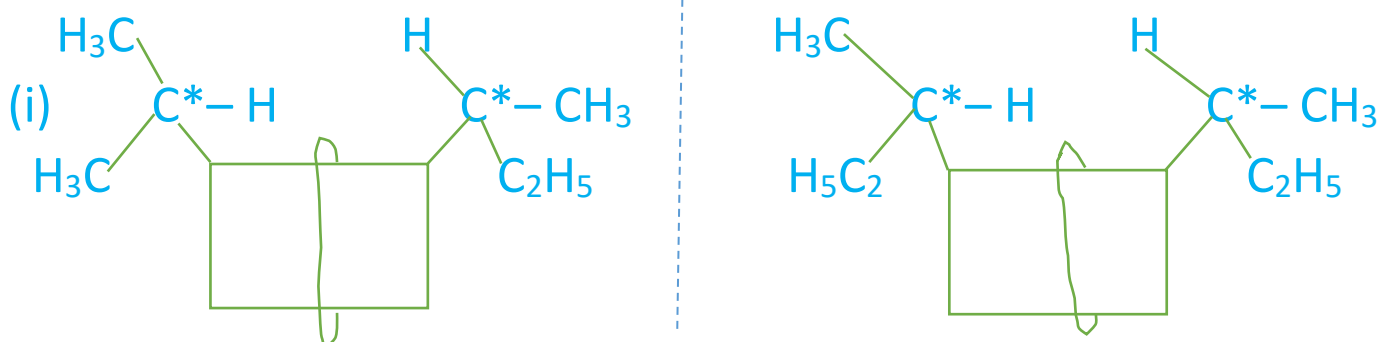
Object having plane of symmetry are superimposable on its mirror image.

(ii)

$$\begin{array}{c} CH_3 \\ | \\ H-C-Cl \\ | \\ \text{------------} \quad \text{Plane of symmetry} \\ | \\ H-C-Cl \\ | \\ CH_3 \end{array}$$
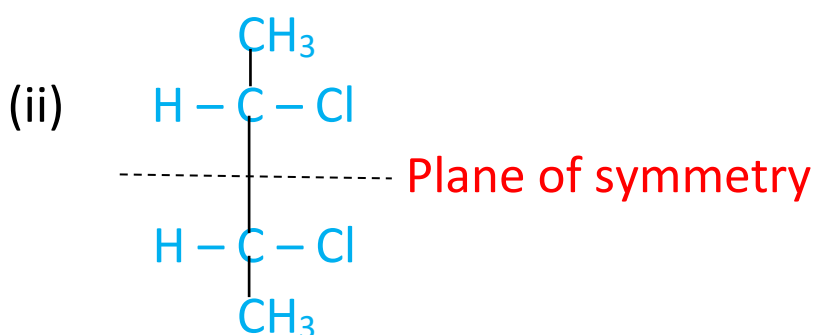
(2) <mark>*Centre of symmetry:-*</mark>

A centre of symmetry is a point such that if a line is drawn from any element to this point and then extended an equal distance beyond the point another identical element will be found at the end of the line.

$$H_3C \qquad COOH$$
$$H \quad \boxed{\begin{array}{c} H \\ \quad H \end{array}} \quad H$$
$$COOH \qquad CH_3$$

$$COOH \qquad CH_3$$
$$\qquad H$$
$$H \quad \boxed{\begin{array}{c} \quad \bullet \\ H \end{array}}$$
$$H_3C \qquad COOH \qquad H$$
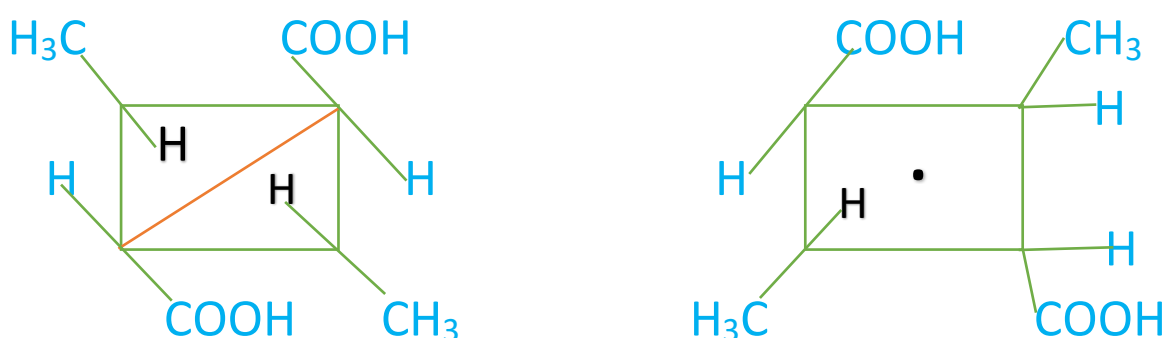
The molecule shown above have a centre of symmetry at the centre of ring. Its mirror image may be superimposable by turning the ring upside down.

Such type of molecules having centre of symmetry are also in active.

(3) *Axis of symmetry:-*

(a) *Axis of symmetry or Fourfold alternative:-*

A fourfold axis of symmetry is an axis such that when the structure possessing this is rotated around the axis by an angular of 90^0 identical structure results. Its mirror image is superimposable with the original molecule by turning the ring upside down and rotating it 90^0 around the axis.

$$H_3C \quad H \quad \xrightarrow{\ 90^0\ } \quad H_3C \quad H_3C \mid CH_3 \quad H$$
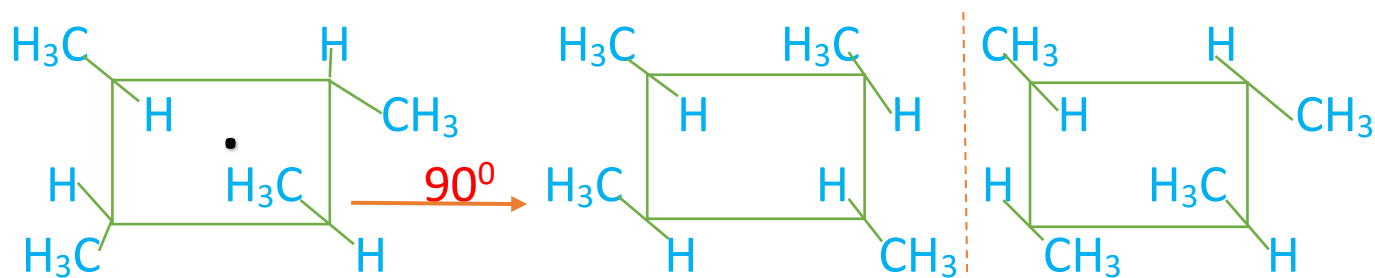
The molecule has a fourfold alternative axis of symmetry passing through centre of the ring and at right angle to it. Its mirror image is superimposable with the original by turning the molecule upside down and rotating it 90^0 around the axis. Such type of molecule, are also optically in active.

(b) *Two fold axis of symmetry:-*

There are molecules having only twofold axis of symmetry. It is not superimposable with its mirror image and both the molecules shows are optically active.

Molecule of this type which are non – superimposable mirror image, are called enantiomers. They rotate plane of polarised light in opposite direction but have the same absolute value of specific rotation.

H_5C_2

$C - CH_3$

H

H_5C_2

$H - C$

CH_3

CH_3

$H - C - C_2H_5$

C_2H_5

$C - H$

H_3C
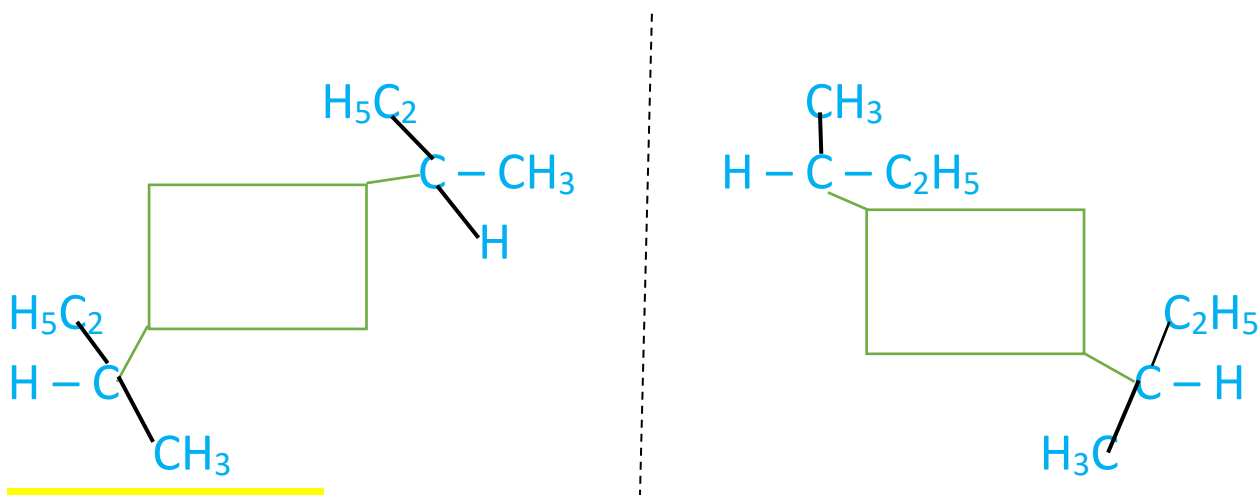
Conclusion:- Wheland has drawn attention to the fact that since a molecule may be optically active even through it has a simple axis of symmetry. It is not correct to say that optically active molecule, take the element of symmetry. There, fore the optically active and asymmetric has applied to molecules should not preferably be used in the same context. A new term is called for, to denote the absence of an alternating axis of symmetry (but not necessarily of a simple). This term is dissymmetric. A molecule that is dissymmetric lacks an alternating axis of symmetry and is usually optically active. A dissymmetric (and therefore usually active) a molecule may or may not be asymmetric. Asymmetric molecules is one which does not passes any element of symmetry and thus optically active.

Optically isomerism:-

When two or more than two compounds have same molecular formula, same structural formula, same physical and chemical properties but having different action of plane of polarised light (PPL) the phenomenon is called as of optical isomerism.

Those isomers which rotate PPL to the right direction are called as dextro or d or (+) form. Those isomers which rotate PPL

to the left are called as leavo isomers or L or (-) forms.

Ex:- Lactic acid.

$$CH_3$$
$$H-C-OH$$
$$COOH$$

$$CH_3$$
$$HO-C-H$$
$$COOH$$
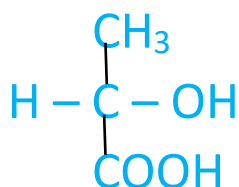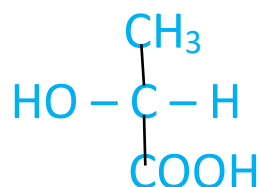
D – lactic acid (+) or D – form   L – lactic acid (-)

Above two isomers are enantiomers because these two or mirror image to each other.

Fisher projection formula:-

The drawings we have used so, for which indicate a molecule becomes increasing complex as more asymmetric carbon atoms are added. Thus, in discussing the stereochemistry of organic compounds it is difficult to use always the tetrahedral representation.

A more convenient representation in such cases is provided which is called as fisher projection formula often the name of this discover. In this case we take two, dimensional projection formula. Here carbon chain always written **Vertical** and **Horizontal** line represent the group above the plane of the paper where, as the vertical lines represents the plane below of the paper. Thus, the fisher projection formula of above two isomers of lactic acid can be written as.

$$CH_3$$
$$H-|-OH$$
$$COOH$$

$$CH_3$$
$$HO-|-H$$
$$COOH$$

Chiral – C – atom   Mirror image
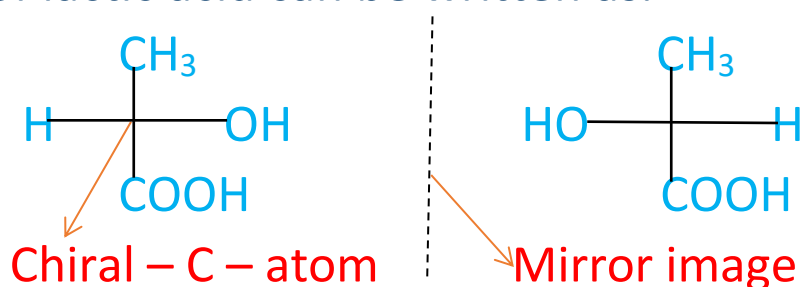
The chiral carbon is not shown by atomic symbol in the fisher projection.

Optical isomerism of compounds with unequal asymmetric carbon atom:-

Example:-

CHOC*HCOH) C*HCOH) CH_2OH

   (Aldotetrose)

Since, here there are two asymmetric carbon atoms for such type of organic compounds total number of optically active isomers – 2^n.

Here, for aldotetrose.

n = 2, Number of optical isomers = 2^2 = 4.
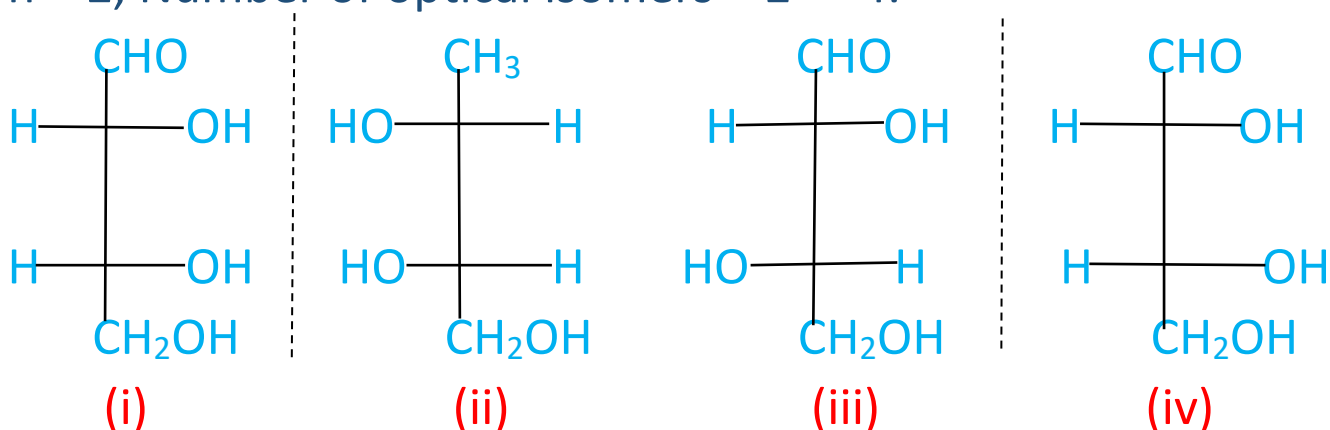
CHO	CH_3	CHO	CHO
H——OH	HO——H	H——OH	H——OH
H——OH	HO——H	HO——H	H——OH
CH_2OH	CH_2OH	CH_2OH	CH_2OH
(i)	(ii)	(iii)	(iv)
(-) Erythrose	(+) Erythrose	(-) Threose	(+) Threose

Erythrose:- When similar groups will be attached at the same side.

Threose:- When similar groups will be attached at the opposite side.

   It is found that configuration (i) and (ii), (iii) and (iv) are related to each other by object and mirror image which are not superimposable. Thus (i) and (ii); (iii) and (iv) are enantiomers.

Comparison to pair (i) and (ii); (i) and (iv); (ii) and (iii), (ii) and (iv) shown that they are not mirror images of each other. Such stereo isomers which are dissymmetric but which are not mirror image of each other are called as diastereomers.

Diastereomers:-

A pair of optically active isomers of a compound which are not related as object and mirror image of each other is called as diastereomers.

Enantiomers have both physical and chemical properties identical where, as diastereomers may differ widely in physical and chemical properties.

Difference between Enantiomer and Diastereomers:-

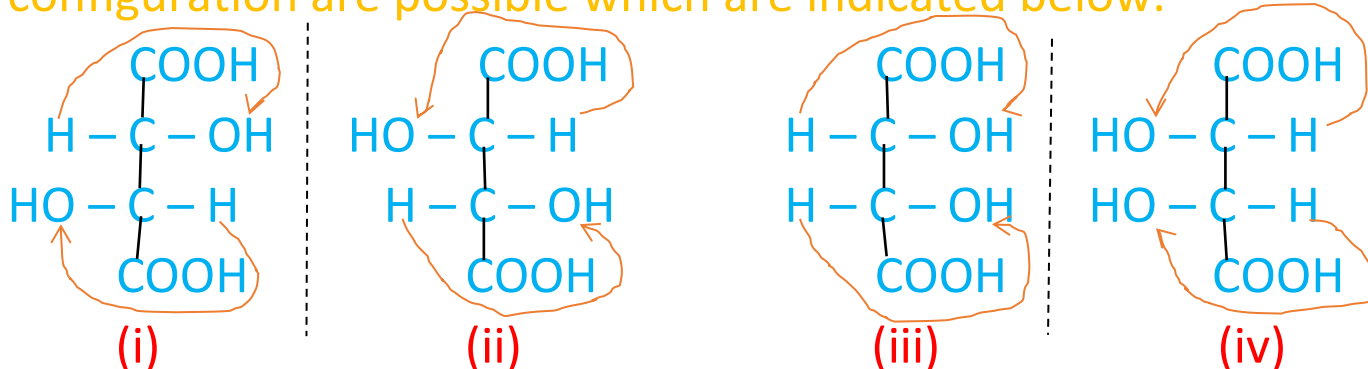| Enantiomer	Diastereomers
(a) Enantiomeric pair of optically isomer active are related as object and mirror.	(a) Diastereomers pair of optical isomers are not related as object and mirror image.
(b) In enantiomer all inter molecular distance between corresponding groups are same.	(b). Diastereomers may differ or may not in effect of plane of polarised light (PPL).
(c) Enantiomer differ in effect of plane of polarised light one isomer rotate it to left and other to right.	(c). Diastereomers may differ or may not in effect of PPL.
(d) The rate of reaction of Enantiomer pair with other reagent is identical.	(d). Different.

(e). Enantiomers have similar physical properties.	(e). Different.
(f). Enantiomers pairs have same free energy.	(f). Diastereomers have different free energy.

Optical isomerism of compounds having two similar asymmetric carbon atoms:-

When a compound contains two asymmetric C – atom which are alike (meaning that same atoms and groups are attached to both asymmetric C – atoms). Let us consider an example of tartaric acid having molecular formula (Tartaric acid).

HOOC C*H(OH) C*(OH) COOH

The four different arrangements of atoms and groups I,e. configuration are possible which are indicated below.

```
     COOH              COOH              COOH              COOH
  H – C – OH       HO – C – H        H – C – OH       HO – C – H
  HO – C – H        H – C – OH       H – C – OH       HO – C – H
     COOH              COOH              COOH              COOH
      (i)               (ii)             (iii)             (iv)
```

The configuration (i) and (ii) are dissymmetric. Thus, they represent two optically active form of tartaric acid. These two configurations are related as object and mirror image which are not superimposable. Thus, these two are enantiomers. In this compound, the rotatory power of each asymmetric centre is the same. In configuration (i) and (ii) arrangement of H, COOH and OH groups on upper and lower asymmetric C – atoms in the same direction. Thus, the rotation by upper and lower asymmetric C –

atoms will be the same degree and in the same direction. Now, one of the two configuration (i) and (ii) is dextro rotatory and the other is leavo.

The configuration (iii) and (iv) have a plane of symmetry because arrangement of H, COOH and OH on upper and lower asymmetric C – atoms are in opposite direction. There, fore rotation by upper and lower asymmetric C – atoms will be to the same degree but in opposite direction. Thus, the two tendencies will balance each other and it will be optically in active. Such forms of isomers are called as meso form.

Conclusion:- Thus in tartaric acid to total number of optically in active isomers = 2.

Meso form:- It is an optically in active stereo isomers of an optically active compound. In active is due to the presence of plane of symmetry within the molecules. This inactive arises due to internal compensation as it is not a mixture of D and L form. Thus, it cannot be resolved in to D and L compounds.

Number of optically active isomers:-

Case 1:- If the molecule cannot be divided in to two equal halves which are mirror image of each other the number of optically active isomers = 2^n.

Where, n = number of asymmetry C – atom.

Ex:- Morose.

Case 2:- If the molecule can be divided in to two halves which are mirror image of each other and n is even n = number of asymmetric C – atom then number of optically active isomers =2^{n-1}.

_Ex:-_ Tartaric acid.

In tartaric acid total number of optically active isomers
$= 2^{2-1} = 2^1 = 2$.

Case 3:- If the molecules can be divided in to two halves which are mirror images of each other and n is odd then number of optically active isomers $= 2^{n-1} - 2^{\frac{n-1}{2}}$
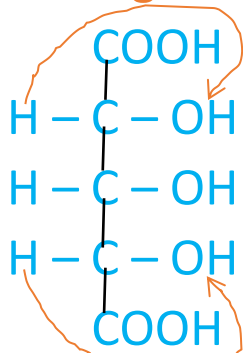
_Ex:-_ Trihydroxy glutaric acid.

HOOC C*H(OH) C*H(OH) C*H(OH) COOH

Here, n = 3

No. of optically active isomers $= 2^{3-1} - 2^{\frac{3-1}{2}} = 4 - 2 = 2$.

Following are the possible configuration of trihydroxy glutaric acid.
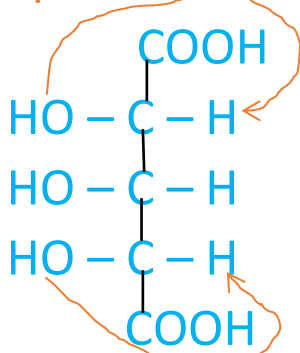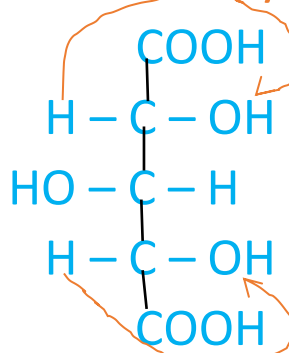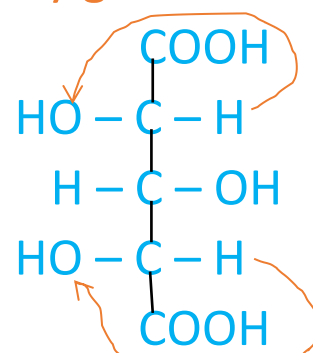
```
     COOH          COOH          COOH          COOH
 H – C – OH     HO – C – H    H – C – OH    HO – C – H
 H – C – OH     HO – C – H    HO – C – H    H – C – OH
 H – C – OH     HO – C – H    H – C – OH    HO – C – H
     COOH          COOH          COOH          COOH
      (i)           (ii)         (iii)          (iv)
```

Optically inactive   Optically inactive

```
     COOH          COOH          COOH          COOH
HO – C – H     H – C – OH     H – C – OH    HO – C – H
 H – C – OH    HO – C – H     H – C – OH    HO – C – OH
 H – C – OH    HO – C – H     HO – C – H    H – C – OH
     COOH          COOH          COOH          COOH
      (v)           (vi)        (vii)         (viii)
```

Optically active

28
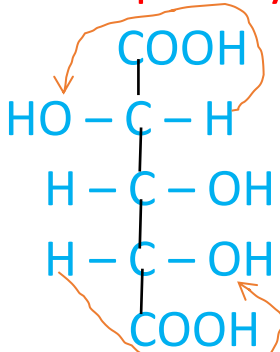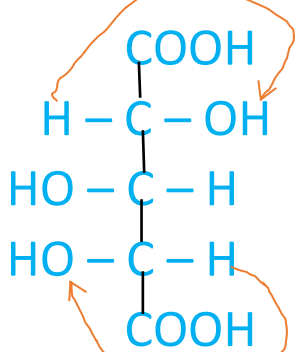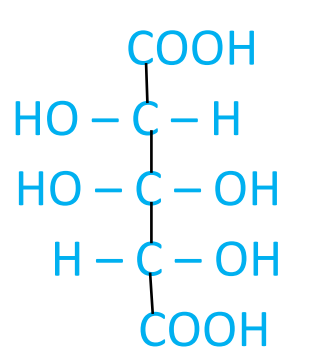
Configuration (vi) and (viii), (v) and (vii) are identical and represent the same form. Thus, trihydroxy glutaric acid has got only two optically active isomers.

 Differential the following racemization racemic modification and racemic mixture:-

(1) ***Racemic modification:-*** When two enantiomers are mixed in equimolar quantities it, resulting product becomes optically in active due to mutual or external compensation of the constituents. Such type of optically in active compounds is known as Racemic modification and is generally designated by prefix or ($\pm$). A racemic modification may be a purely mechanical mixture a compound or a solid solution for the reson it is better to use the term racemic modification than the racemic mixture.

Ex:- (a) Lactic acid.

```
      COOH              COOH
       |                 |
 H ————+——— OH    HO ———+——— H
       |                 |
      CH₃               CH₃
       D                 L
      50%               50%
```
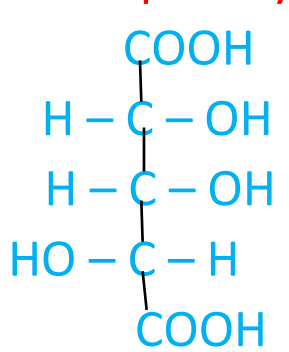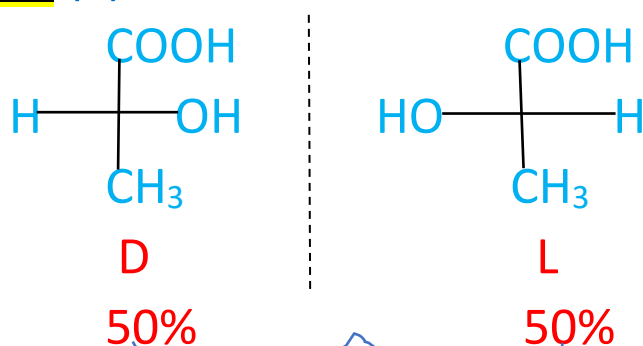
Racemic modification of Lactic acid.

```
      ⬡                      ⬡
      |                      |
 H — C — CH₃           H₃C — C — H
      |                      |
      OH    50%              OH   50%
```
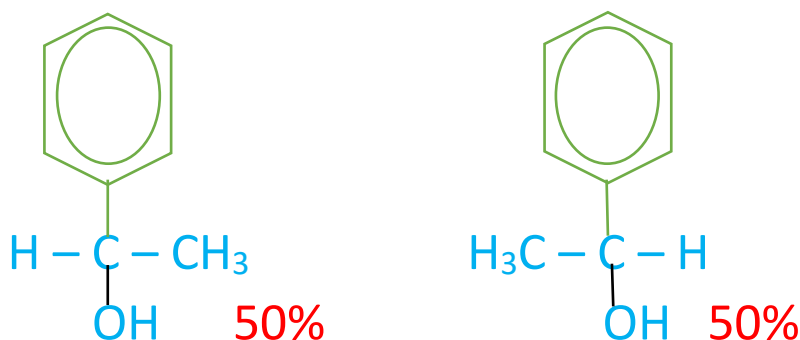
The racemic mixture is a mechanical mixture of the crystals of two enantiomers (+ and -). This is a solid state of racemic modification but not all racemic modification are racemic mixture.

The racemic modification in solution (liquid or gaseous state), have the same properties as the individual enantiomers (Racemic modification have same boiling point density refindex as the enantiomers).

But in solid state the racemic modification have same properties different from that of pure enantiomers. Three possible solid state of racemic modification.

(i)   Racemic mixture (Conglomerate)

(ii)   Racemic compounds (Racemate)

(iii)   Racemic solid solution

(1)   Racemic mixture (Conglomerate):-

It is a mechanical mixture of crystals of the two enantiomers (+ and -). It is formed when enantiomers have greater affinity for the molecule of its own type than that for its opposite enantiomers. In most respect its properties are similar to those of pure enantiomers but like an ordinary mixture is melting point is lower than that of pure components an solubility is higher.

Ex:- Sodium ammonium tartaric crystalised from water below 27^0c. Here, the crystals of two forms are mirror image of each other.

$$\begin{array}{c} COONa^+ \\ | \\ H-C-OH \\ | \\ HO-C-H \\ | \\ COONH_4^+ \end{array}$$ Sodium ammonium tartaric.
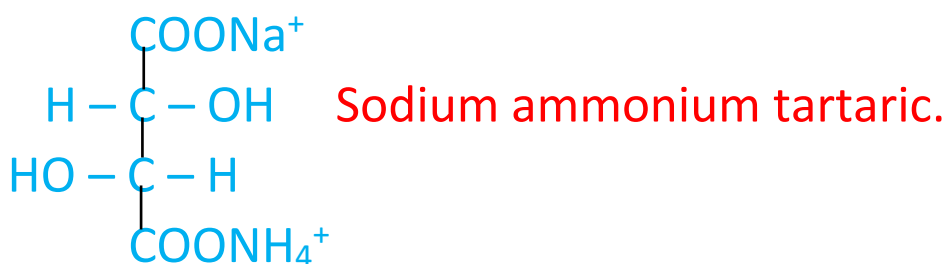
(2) Racemic compounds (Racemate):-

Unlike the racemic mixture when each isomers has greater affinity for molecules of other enantiomers than for its own kind a molecular compounds is formed which is known as racemic compounds.

In other words, we can say that a racemate is a molecular compound formed by the union of two enantiomers. Most of the physical properties of racemate are different from those of pure enantiomers.

$$\begin{array}{c} COOH \\ | \\ HO-C-H \\ | \\ H-C-OH \\ | \\ COOH(+) \end{array} \quad + \quad \begin{array}{c} COOH \\ | \\ H-C-OH \\ | \\ HO-C-H \\ | \\ COOH(-) \end{array} \longrightarrow$$

Racemic compound
or
Racemic (+) Tartaric acid

M.P = 170^0c 170^0c 206^0c

Density = $1.76g/cm^3$ $1.76g/cm^3$ $1.69g/cm^3$

Solubility = 151g/100   137g/100cc of HCl   206g/100cc of HCl
of HCl   cc of HCl
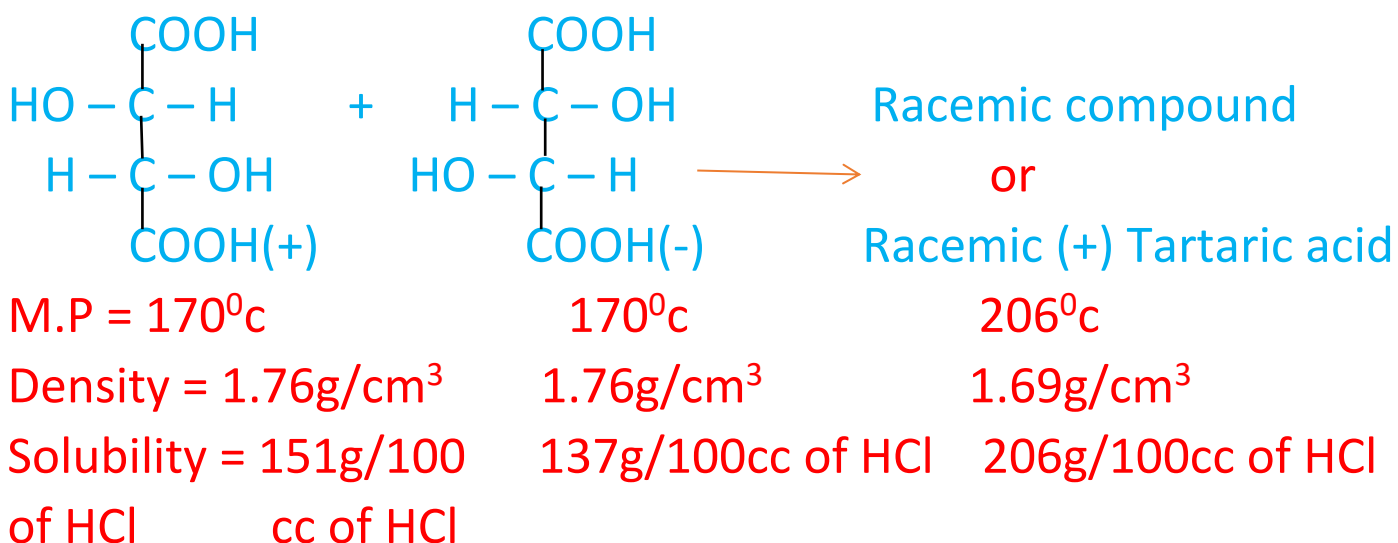
However, it must be clear that a racemic mixture may be converted in to racemic compound at a particular temperature.

Ex:- Sodium ammonium tartrate (Racemic mixture). Below 27^0c it remains racemic mixture.

Sodium ammonium tartrate $\xrightarrow[27^0c]{above}$ Racemic compound.
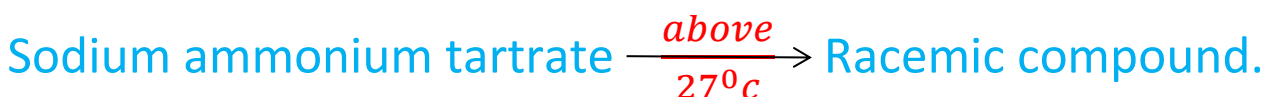
This temperature 27^0c is called as transition temperature.

(3)   _Racemic solid solution (Psedo – Racemic compound):-_

When a pair of isomers hors enantiomers crystallizes together the product form is called as racemic solid solution.

Iso – same morphous – molecule

This type of racemic modification is formed when there is a little difference in affinity between enantiomers between like or opposite configuration such racemic modification are identical with the enantiomers in all respects even the melting point and solubility.

Preparation of racemic modification:-

There are so many methods for the preparation of racemic modification.

(1) **_Racemization:-_** It is a process of converting an optically active (D or L) compounds in to the racemic modification. Hence in racemization we state with an optically active compounds D and get optically inactive compound. It is always accompanied by a change in optical rotation form a value characteristic of origin enantiomers to a value 0. This means that the (+) and (-) form of most optically active compounds are conversible one in to another. The final result being an, racemic modification. The racemization may be achieved by the application of heat light or chemical reagents. Thus, if the starting material is (+) form then after treatment half will have converted in to the (-) form. Similarly, when starting material is (-) form half will be

converted in to (+) form. In this way racemization takes place.

For ex:- (+) and (-) lactic acid can be converted in to racemic modification by the above method.

<u>**Resolution of racemic modification:-**</u>

The process of separation of racemic modification in to its compounds or two pure enantiomers (+) and (-) is known as resolution. This process is of immense importance in the synthetic organic chemistry.

Since the two enantiomers of a racemic modification are having the same physical properties. They cannot usually be separated by physical methods (I,e. fractional crystallization or distillation). Following are methods to separate them.

(1) <u>***Mechanical separation :-***</u> This method of historical importance only because it was the first method used by Pasteur for the resolution of sodium. Ammonium tartrate which crystalizes out in the racemic form below 27^0c.

This method is applicable to only a few cases and moreover only to racemic mixture. Where crystal shapes of two optical isomers are different. They can be separated with the help of a magnifying lens and a small forceps.

(2) <u>***Preferential crystallization by inoculation:-***</u>

This method involves the seeding of a saturated of the racemic mixture with a pure, crystals of one of the two enantiomer. The solution now, become super saturated with respect to added enantiomers and after same time of cooling it

begins crystallize out this method was developed by renee. Hard obtained total optical resolution of free α – amino acids with the help of L and D isomers.

Sometimes seeding with a crystal of optically active form of another molecule is also possible.

Ex:- A crystal of (-) asparagine.

($CH_3NCOCH_2C*HNH_2COOH$) crystallizes out (+) sodium ammonium tartrate, form a solution of racemic modification.

(3)   Biochemical separation (By Louis pasteur):-

This method is based on the fact that when certain micro – organism (becteria, guest fungus), are grown in dilute solution of racemic modification. They as similar one enantiomer rapidly than the other. The mould penicillium glaucum preferentially destroy the (+) isomer of racemic ammonium tartrate and thus values the (-) in solution. This is an example of biochemical asymmetric destruction. Thus, this method gives only D or L isomer not both from racemic modification.

(4)   By diastereomers (By Louis pasteur):-

It is best method for the resolution of racemic modification in which the enantiomers of racemic modification are converted in to diastereomer pure enantiomers are non – identical they have different physical properties and hence, they can easily be separated in to its two compounds by fractional crystallization. After the complete separation of two diastereomers they are converted back in to original chemical constituents by an appropriate reaction. Each diastereomers will produce an

enantiomers of other. Hence, successes of method depend upon the following point.

(i)   The diastereomers should easily be formed in a crystalline form.

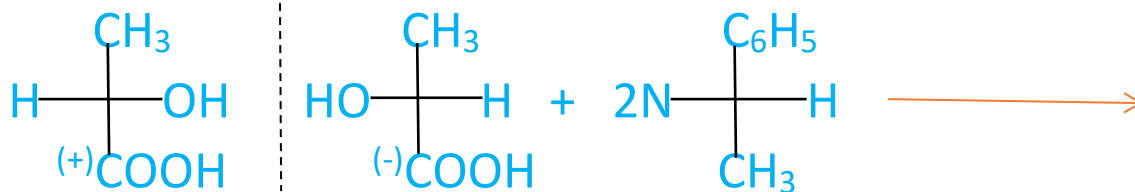(ii)   They must also be converted back in to parent compound by suitable reaction. Some of the group that have been resowed by this method are.

Ex:- Resolution of acid:-

Resolution of racemic modification of acids is carried out with the aid of optically active bases two diastereomers are obtained.

[L(acid) + D(base)] + 2D(base)

$$\frac{L(acid) + D(base)}{Diastereomers} + (L\ acid + D\ base)$$
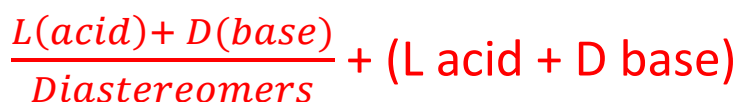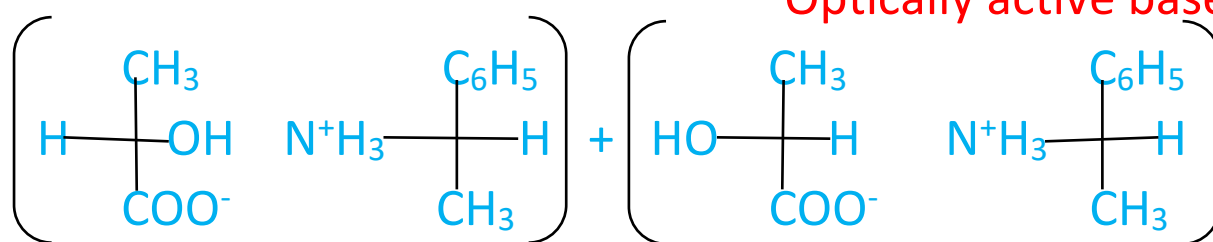
Example:-

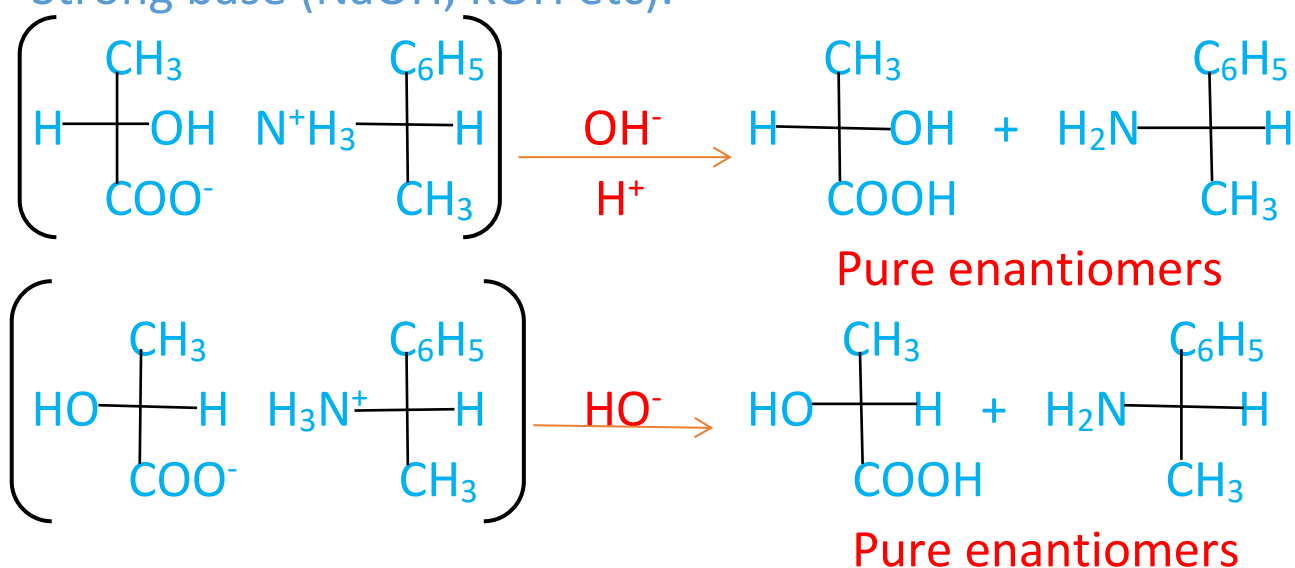Racemic modification   1 – phenylethyl amine or
                            Optically active base

Diastereomer pair (salt)

The diastereomeric pair of salt is separated by fractional crystallization due to their different solubility. Now pure enantiomers can be generated from each of the separated diastereomers by hydrolysis with strong acid (H_2SO_4, HCl etc). or

Strong base (NaOH, KOH etc).

$$\begin{bmatrix} \begin{array}{c} CH_3 \\ H - OH \\ COO^- \end{array} \quad \begin{array}{c} C_6H_5 \\ N^+H_3 - H \\ CH_3 \end{array} \end{bmatrix} \xrightarrow[H^+]{OH^-} \begin{array}{c} CH_3 \\ H - OH \\ COOH \end{array} + \begin{array}{c} C_6H_5 \\ H_2N - H \\ CH_3 \end{array}$$

Pure enantiomers

$$\begin{bmatrix} \begin{array}{c} CH_3 \\ HO - H \\ COO^- \end{array} \quad \begin{array}{c} C_6H_5 \\ H_3N^+ - H \\ CH_3 \end{array} \end{bmatrix} \xrightarrow{HO^-} \begin{array}{c} CH_3 \\ HO - H \\ COOH \end{array} + \begin{array}{c} C_6H_5 \\ H_2N - H \\ CH_3 \end{array}$$

Pure enantiomers

In this way enantiomeric pair of lactic acid are separated by this method.

Absolute configuration:-

A specific arrangement of atoms and groups in three, dimensional space around an atom is called as absolute configuration.

For ex:- (+) lactic acid and (-) lactic acid represent molecular of identical structure but different configuration.

$$\begin{array}{c} CH_3 \\ H - C - OH \\ COOH \end{array} \qquad \begin{array}{c} CH_3 \\ HO - C - H \\ COOH \end{array}$$
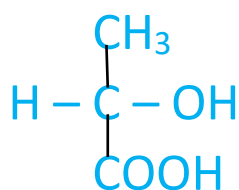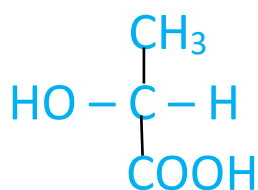
(+) lactic acid   (-) lactic acid

The question may, be arise why one needs a new concept. Absolute configuration to distinguish two lactic acids when there is already distinctive term namely rotation dextro(+) and laevo (-). Rotation is an experimental property where as configuration is a theoretical concept related to arrangement of atoms or groups in

space. When (+) lactic acid is dissolved in aqueous sodium hydroxide the resulting solution of sodium lactates is laevo rotary while the arrangement of groups about C* is not changed. Thus, it is clear that there is no significant relation between sing of rotation and configuration of enantiomers.

R – S configuration :-

This is a news systematic method of specifying absolute configuration of optically active compounds. Since, it has been proposed by R – S cahn and C – K in gold and V prolong this system is also called as cahn – ingold prolong system. This system of designating configuration has been used since early 1960s.

Cahn – in gold prolong system is based on the actual three dimensional or tetrahedral structure of compound.

In order to specific configuration about an asymmetric carbon C*, groups a, b, d, and e are first assigned and order of priority is determined by sequence rule.

Let us assign priorities 1, 2, 3, 4 to the groups a, b, d, e – the order of priority is written as.

a>b>d>e

1>2>3>4

Now, we can determine the R – S configuration with the following (conservation) rules.

(i)   If the eye while moving from a⟶b⟶d⟶e travels in a clockwise, the configuration is designated ''R''
         (Latin, rectus = right)

(ii)   If the eye while moving from a⟶b⟶d⟶e travels in a

anticlockwise the configuration is designated ''S''.
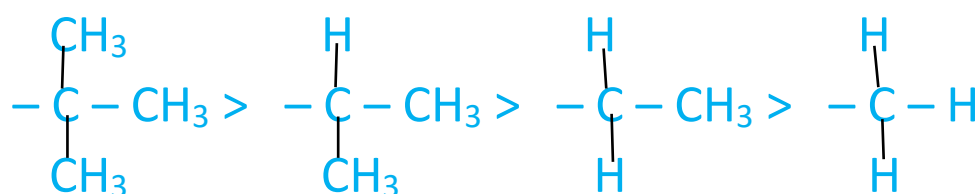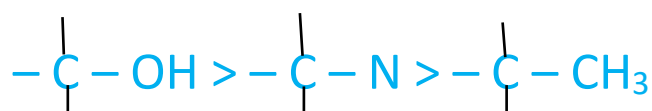
(Latin sinister means Left).

Sequence rule:-

According to this rule the following points must be taken in to account for the arrangement of four different groups around an asymmetric C – atom in a priority sequence.

(i)   Priority is given on the basis of atomic number

So, I > Br > Cl > F > O > N > C > H

(ii)   If priority is not, settle on the basis of atomic number of first atom (attached to C*) it is settled on the basis of next atom.

Thus,

$$-\overset{|}{\underset{|}{C}}-OH > -\overset{|}{\underset{|}{C}}-N > -\overset{|}{\underset{|}{C}}-CH_3$$

$$-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 > -\overset{H}{\underset{CH_3}{C}}-CH_3 > -\overset{H}{\underset{H}{C}}-CH_3 > -\overset{H}{\underset{H}{C}}-H$$

(iii)   If the first atoms of the two group have same substituent of higher atomic number the one with more substituent takes the priority.

$-CHCl_2 > -CH_2Cl$

(iv)   A doubly of triply bonded atom ''A'' present in a group attached to asymmetric carbon is considered equivalent to two or three singly bonded ''A'' s respectively.
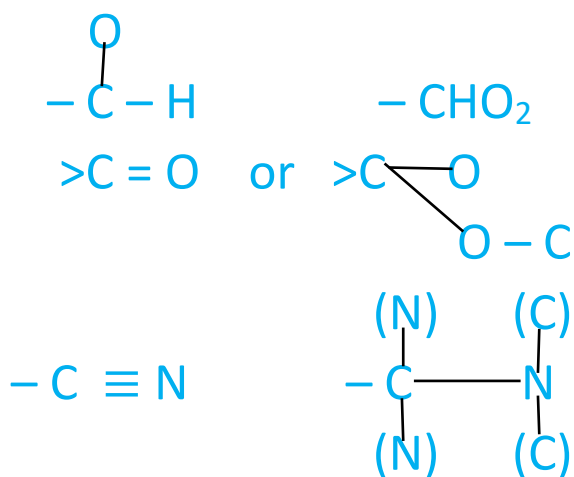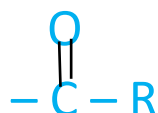
Ex:-   = A equals to

```
        A
      <
        A
```

38

$\equiv$ A equals to

A
A
A

Hence

$$O$$
$$- \overset{\parallel}{C} - H \qquad - CHO_2$$
$$>C = O \quad or \quad >C \underset{O-C}{\overset{O}{\diagdown}}$$

$$\qquad \qquad (N) \qquad (C)$$
$$- C \equiv N \qquad - \overset{(N)}{\underset{(N)}{C}} - \overset{(C)}{\underset{(C)}{N}}$$

Atoms in bracket are called as phantom atoms priority order.

$$O$$
$$- \overset{\parallel}{C} - R$$

Or, $\quad - CHO < COR < CONH_2 < COOH < COOR$

(v) The more highly oxidised groups, has higher priority order.
$\quad CH_3 < CH_2OH < CHO < COOH$

(vi) The lone pair has the lowest priority that is the lone pair is treated as having number = 0. In the group $= \overset{..}{N} - OH$ electron pair is of lower priority than OH.

(vii) The priority of is topic group is decided by the mass number. The atom with higher mass number has higher priority.
$\quad H < D < T$

Designating R and S configuration:-

(i)   Identical the four different substituents attached to stereogenic centre. Assign each of the four substituent a priority 1, 2, 3, 4 using the sequence rule such that.
1 > 2 > 3 > 4

(ii)   Mentally rotate the molecule with the stereogenic centre in the plane of paper until the group of lowest priority 4 directly behind the stereogenic centre.

(iii)   Look down the bond from the stereogenic centre to the substituent priority 4, three substituent 1, 2, 3 will appear radiating from the stereogenic centre like the spokes of wheel.

(iv)   Trace a path from 1⟶2⟶3. If the path describes clockwise motion, then the stereogenic centre is assigned R – configuration and if the path describes an anticlockwise motion, the stereogenic centre is called.
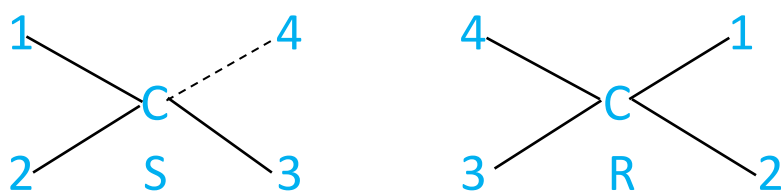
(v)   The descriptors R and S are it anglicised and place in parentheses, each is connected with a hyphen. They are used to denote the enantiomers and diastereomers.
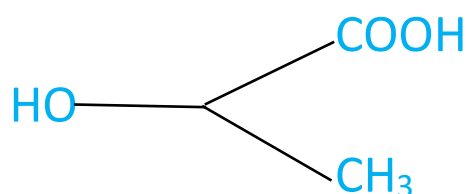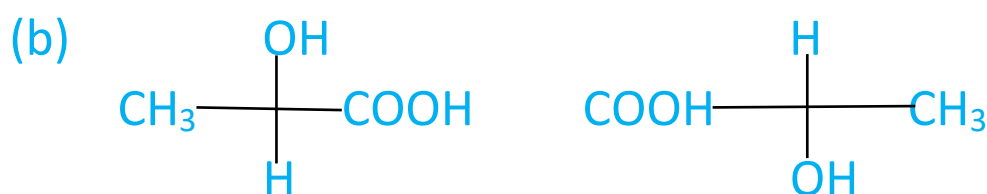
Ex:-

(a)
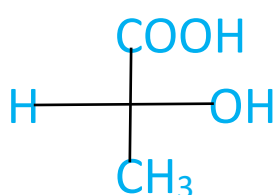
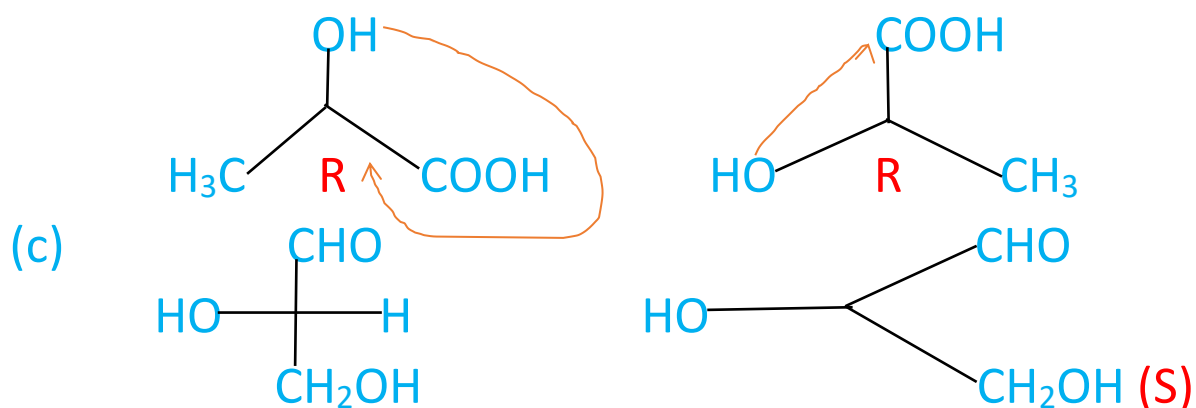| Groups	priority
OH	1
COOH	2
CH$_3$	3
H	4

Now the molecule is rotated so that H is just behind the stereogenic carbon away form, viewer below the plane of page. By doing so, the group on right will be transported to left and the group on the left will be transported to right.

$$HO-\overset{\displaystyle COOH}{\underset{\displaystyle CH_3}{\diagup\diagdown}}$$

The compounds lactic acid has R – configuration and written as R – lactic acid

(b)

$$CH_3-\overset{\displaystyle OH}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-COOH \qquad COOH-\overset{\displaystyle H}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}-CH_3$$

If the group of lowest priority 4 is either up or down in the fischer projection no rotation of the molecule is necessary.

$$H_3C-\overset{\displaystyle OH}{\underset{\displaystyle R}{\diagup\diagdown}}-COOH \qquad HO-\overset{\displaystyle COOH}{\underset{\displaystyle R}{\diagup\diagdown}}-CH_3$$

(c)

$$HO-\overset{\displaystyle CHO}{\underset{\displaystyle CH_2OH}{\overset{|}{\underset{|}{C}}}}-H \qquad HO-\overset{\displaystyle CHO}{\underset{\displaystyle CH_2OH}{\diagup\diagdown}} \text{ (S)}$$

It can be determined by another way.

It is convenient to use a fischer projection formula with the knowledge that interchange of pair of groups by an even no. of times reproduces the original keeping in mind the group of lowest priority 4 occupied the bottom position in fischer projection.
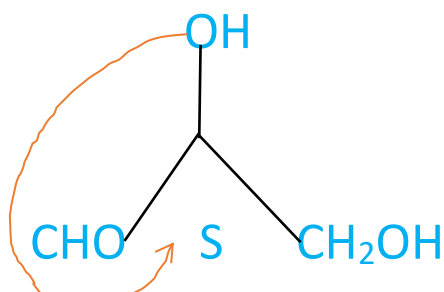
```
        CHO                    OH
  HO ——┼—— H      ≡ CHO——┼——CH₂OH
        CH₂OH                  H
```
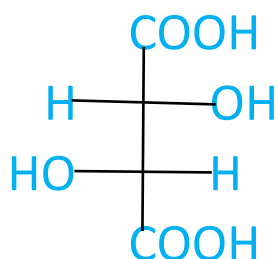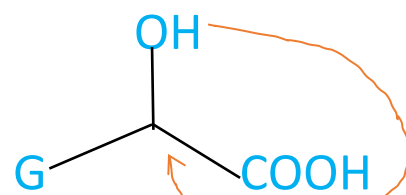
Groups   Priority

Groups	Priority
OH	1
CHO	2
CH₂OH	3

```
                    OH
                    |
                    C
                   / \
              CHO   S   CH₂OH
```

Thus, it is S – configuration.

(d)
```
        COOH
  H ——┼—— OH
  HO ——┼—— H
        COOH
```
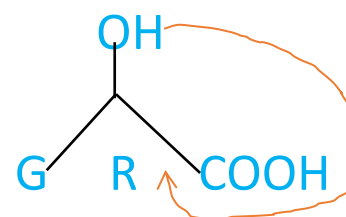When there is more than one stereogenic centre each is designated with configuration R or S.

Top stereogenic carbon.

```
        COOH                OH                    OH
  H ——┼—— OH    ≡ G——┼——COOH                     |
        G                H                        C
                                                 / \
                                                G   COOH
```

Bottom stereogenic carbon

```
        G                 OH                      OH
  HO ——┼—— H    ≡ G——┼——COOH                      |
        COOH             H                        C
                                                 / \
                                               G  R  COOH
```
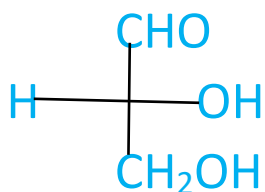
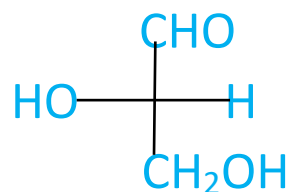The compound is (2R, 3R) – tartaric acid

==D – L Nomenclature:-==

It is applicable to the molecule of type RCHXR' where, R – C – R Constitutes the main chain of the molecule and is represented by vertical line. If X is to the right, the molecule is called as 'D' and if X is on the left. It is called as 'L' where, 'X' is heteroatom.

For ex:- Absolute configuration of (+) and (-) glyceraldehyde are, as.

$$
\begin{array}{ccc}
 & CHO & \\
H & \rule[0.5ex]{3em}{1pt} & OH \\
 & CH_2OH &
\end{array}
\qquad\qquad
\begin{array}{ccc}
 & CHO & \\
HO & \rule[0.5ex]{3em}{1pt} & H \\
 & CH_2OH &
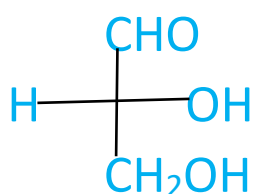\end{array}
$$

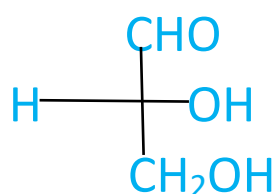D (+) glyceraldehyde   L (-) glyceraldehyde

The other stereo isomers can be assigned D or L natation by comparison with structural arrangement of D and L – glyceraldehyde. While comparison following convention should be followed.

(i)   The most oxidised carbon attached to chiral centre is placed on the top of the vertical line.

(ii)   The group with C – atom forming a part of the chain is kept at the bottom of the vertical line.

(iii)   The remaining group are assumed to be projected towards the viewer and are placed along horizontal line.
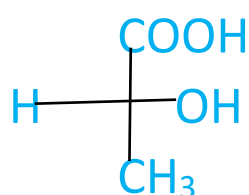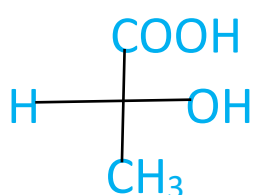
_Ex:-_ (a) Glyceraldehyde.

$$
\begin{array}{ccc}
 & CHO & \\
H & \rule[0.5ex]{3em}{1pt} & OH \\
 & CH_2OH &
\end{array}
\qquad\qquad
\begin{array}{ccc}
 & CHO & \\
H & \rule[0.5ex]{3em}{1pt} & OH \\
 & CH_2OH &
\end{array}
$$

D(+)   L(-)

(b)   Lactic acid.

$$
\begin{array}{ccc}
 & COOH & \\
H & \rule[0.5ex]{3em}{1pt} & OH \\
 & CH_3 &
\end{array}
\qquad\qquad
\begin{array}{ccc}
 & COOH & \\
H & \rule[0.5ex]{3em}{1pt} & OH \\
 & CH_3 &
\end{array}
$$
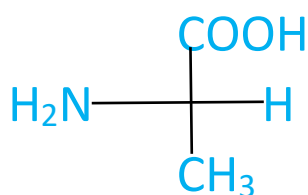
D   L
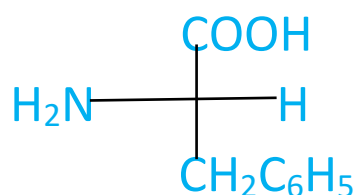
It may be noted that D and L do not pertains to dextro or laevo as it clear, from following examples.

$$\begin{array}{c} COOH \\ | \\ H_2N - C - H \\ | \\ CH_3 \end{array} \qquad \begin{array}{c} COOH \\ | \\ H_2N - C - H \\ | \\ CH_2C_6H_5 \end{array}$$

L (+) Alanine   L (-) Phenyl alanine

$$\begin{array}{c} CHO \\ | \\ HO - C - H \\ | \\ H - C - OH \\ | \\ CH_2OH \end{array}$$
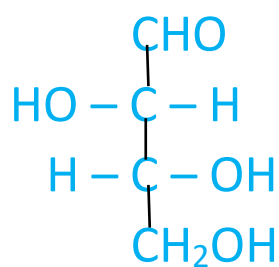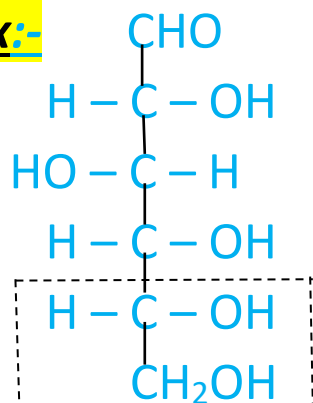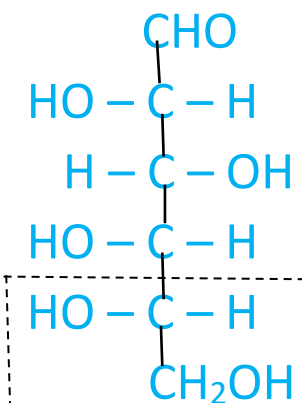
An addition convention has been developed according to which in the sugar the configuration on the lowest dissymmetric C – atom l,e. next to primary alcohol is the denote configuration of sugar

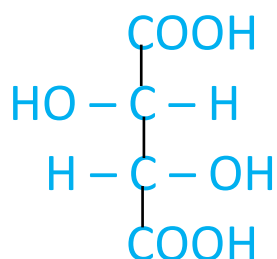Thus, the (-) threose has D – configuration and (+) threose has L – configuration.

For ex:-

$$\begin{array}{c} CHO \\ | \\ H - C - OH \\ | \\ HO - C - H \\ | \\ H - C - OH \\ | \\ H - C - OH \\ | \\ CH_2OH \end{array} \qquad \begin{array}{c} CHO \\ | \\ HO - C - H \\ | \\ H - C - OH \\ | \\ HO - C - H \\ | \\ HO - C - H \\ | \\ CH_2OH \end{array}$$
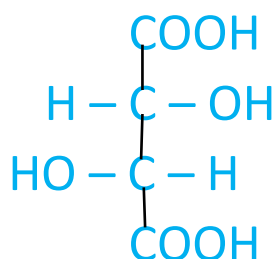
D (+) Glucose   L (-) Glucose

Demerits:- D – L – Nomenclature can't be generalised to the compound having two asymmetric carbon atom identical.
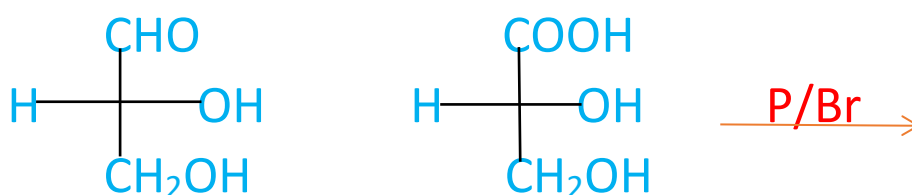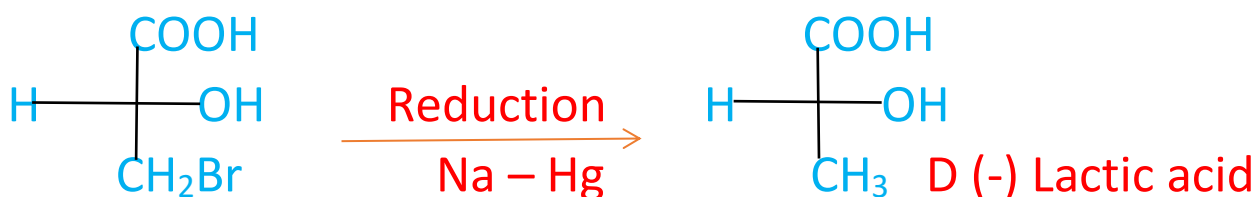
For ex:- Tartaric acid

$$\begin{array}{c} COOH \\ | \\ H - C - OH \\ | \\ HO - C - H \\ | \\ COOH \end{array} \qquad \begin{array}{c} COOH \\ | \\ HO - C - H \\ | \\ H - C - OH \\ | \\ COOH \end{array}$$

Configuration of one optically active compound can be Co – related to another compound with already established configuration. The compound with already established configuration is transferred in to whose configuration is designed in such a way that no chemical bond around the chirality centre is cleared.

For ex:- Let us study the trans formation of D (+) glyceraldehyde.

$$\begin{array}{ccc}
\text{CHO} & \text{COOH} & \\
\text{H}\!-\!\!\!-\!\!\!-\!\text{OH} & \text{H}\!-\!\!\!-\!\!\!-\!\text{OH} & \xrightarrow{\ P/Br\ } \\
\text{CH}_2\text{OH} & \text{CH}_2\text{OH} &
\end{array}$$

D (+) glyceraldehyde

$$\begin{array}{ccc}
\text{COOH} & & \text{COOH} \\
\text{H}\!-\!\!\!-\!\!\!-\!\text{OH} & \xrightarrow[\text{Na – Hg}]{\text{Reduction}} & \text{H}\!-\!\!\!-\!\!\!-\!\text{OH} \\
\text{CH}_2\text{Br} & & \text{CH}_3 \quad \text{D (-) Lactic acid}
\end{array}$$

Optical isomerism in compounds containing no. asymmetric carbon atom.

The basic requirement for a compound to be optically active is its non – superimposable on its mirror image. Although the largest number of optically active compounds are known which are optically active due to presence of an asymmetric carbon atom. Some compounds are also known which do not passes any asymmetric carbon atom but they are optically active.

Ex :- They are Allenes, spiranes biphenyls etc. Show optically activity but these have not any asymmetric carbon atom.

<mark>*Optical isomerism of Allenes:-*</mark>

(i)   Von't Hoff pointed out that an unsymmetrically substituted allenes should exist in two enantiomeric from.
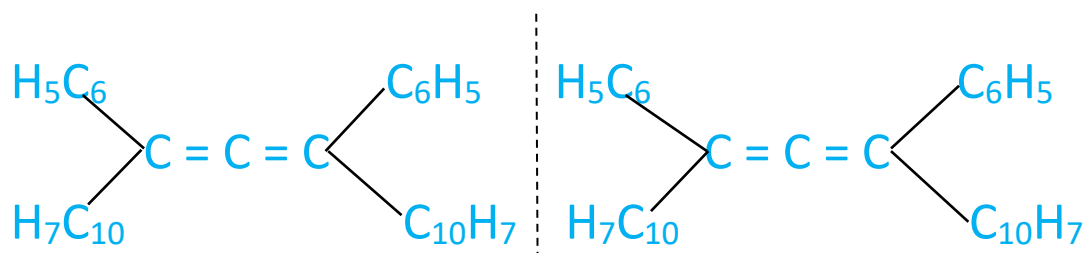
(ii)   A general rotation is shown below.

$$a \diagdown \qquad a \diagup$$
$$C = C = C$$
$$b \diagup \qquad b \diagdown$$
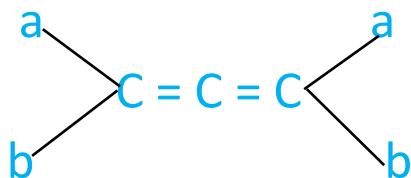
(iii)   The necessary and sufficient condition for such an allene to be asymmetric is that a $\neq$ b.

(iv)   In allene two terminal C – atoms are Sp^2 hybridised. Three Sp^2 hybrid orbitals are directed in a plane at 120^0 angle and one unhybrid P – orbital remains perpendicular to the plane of Sp^2 orbitals and the middle C – atom is Sp – hybrid and two unhybrid P – orbitals, remains perpendicular to the Sp – orbitals and each other also.

(v)   The central C – atom linked linearly to terminal C – atom through Co – linear σ – bonds due to Sp – Sp^2 overlap and two π – bonds are in a plane perpendicular to each other. There, fore the plane of Sp^2 orbitals of one terminal carbon atom is right angle to those at other and. Thus, the substituents of terminal C – atom is not planer to that of other. So, this type of molecule possesses neither plane of symmetry nor – centre of symmetry and forms a non – superimposable mirror image. Hence the asymmetry.

$$H_5C_6 \diagdown \atop H_7C_{10} \diagup C = C = C \diagup^{C_6H_5} \diagdown_{C_{10}H_7} \qquad H_5C_6 \diagdown \atop H_7C_{10} \diagup C = C = C \diagup^{C_6H_5} \diagdown_{C_{10}H_7}$$

1,3 – di – α – dapthyl – 1,3 – diphenyl allene.