

ISOMERISM: Compds which have same mol formula but different physical & chemical properties are called isomers.

→ Phenomenon is called Isomerism

Types

Structural Isomerism

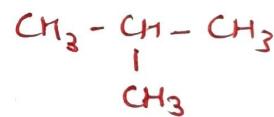
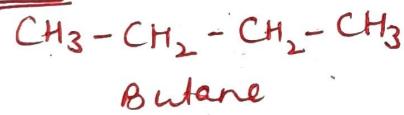
Same mol formula different arrangements of atom/gp in the molecule or different structural formulae.

Stereoisomerism

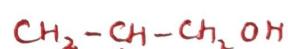
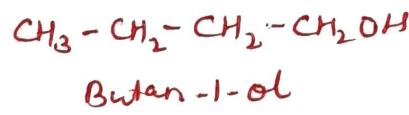
Same mol formula & same structural formula but differ in arrangement of atom/gps in space

→ Skeletal / chain Isomerism: When 2 or more compds have same mol formula but differ in - the difference in carbon chains, i.e., straight or branched.

for eg: C₄H₁₀

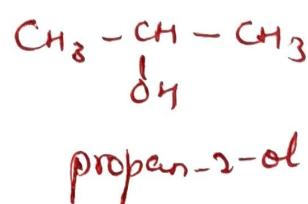
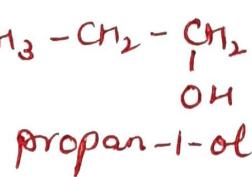


C₄H₉O



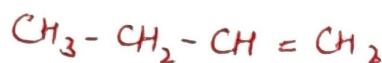
→ Position Isomerism: When 2 or more compds have same mol formula but differ in - the position of the functional gp, C-C multiple bonds, substituent gp.

eg. C₃H₈O

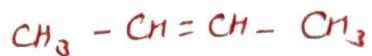


Sph
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C₄H₈

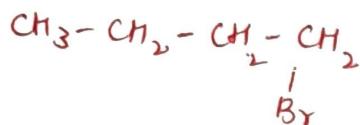


But-1-ene

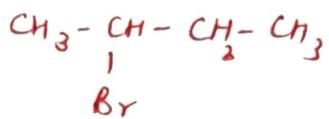


But-2-ene

C₄H₉Br



1-Bromobutane



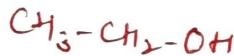
2-Bromobutane

→ Functional Isomerism:

→ different functional groups in the molecule.

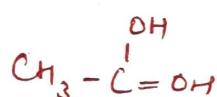
same mol. formula

C₂H₆O



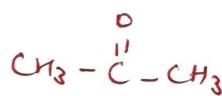
Ethyl alcohol

C₂H₄O₂



Acetic acid

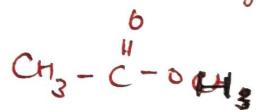
C₃H₆O



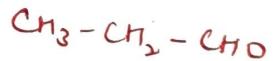
Acetone



Dimethyl ether



Methyl formate

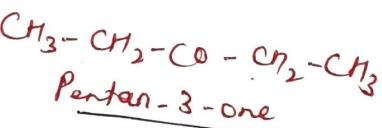


Propionaldehyde

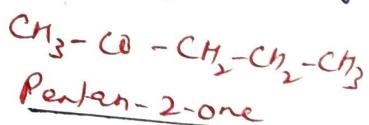
→ Metamerism:

same mol. formula, different alkyl group attached to the same functional group (bridging gp)

C₅H₁₀O -

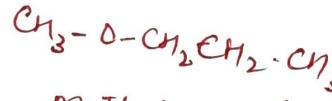


Pentan-3-one



Pentan-2-one

C₅H₁₀O -



Methyl propyl ether



Diethyl ether

[R] + [O]

Stereoisomers

Same mol. formulae, different spatial arrangements of atoms / gps.

Configurational Isomerism

Conformational Isomerism

→ Isomers are non-superimposable & non-convertible by rotⁿ around single bond.

Isomers are non-superimposable but easily convertible by rotⁿ around single bond.

OPTICAL
(ENANTIOMERS)

GEOMETRICAL
(DIASEREOISOMERS)

→ mirror image of each other

→ not the mirror of each other

→ Isomers have the same phys. properties but they differ in their behaviour towards plane polarized light.

→ Diastereomers ~~also~~ may / may not be optically active.

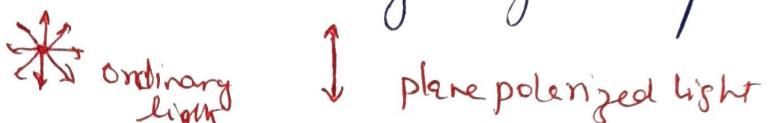
→ Have the ability to rotate plane polarized light.

if rotates plane-polarized light to the right (clockwise dirⁿ) → dextrorotatory isomer (+)

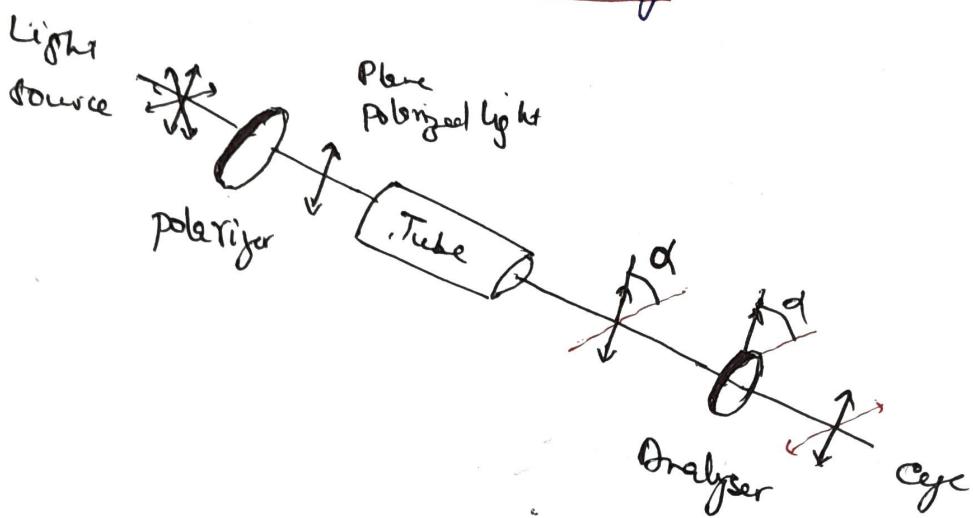
and
if left (anticlockwise) → levo-rotatory (-) isomer

OPTICAL (ROTATION) ACTIVITY :-

When a beam of ordinary light ~~of~~ waves of diff. wavelengths (vibrating in all dirⁿ) is passed thru a Nicol prism (special type of prism made up of crystalline CaCO_3) then light after coming out of it becomes plane polarized light. Nicol prism is known as polariser as it converts ordinary light to plane polarized light.



When the solⁿ of certain org. compds are placed in the path of plane polarized light. They rotate the path of the plane-polarized light ~~each~~ either to the left or to the right. Such compds are known as optically active substances. e.g. lactic acid, tartaric acid, glucose, fructose etc. and this property of a substance is known as optical activity.



The molecule which is not superimposable on its mirror image \rightarrow Chiral or dissymmetric molecule.

\rightarrow The dissymmetric molecule does not have any plane of symmetry.

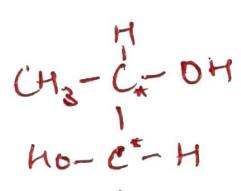
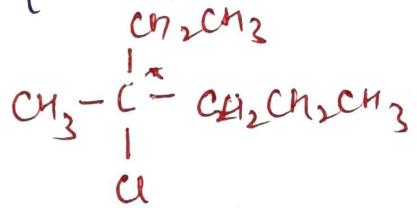
\rightarrow The property of non-superimposability of a structure on its mirror image \rightarrow Chirality or dissymmetry.

On the other hand, molecule which is superimposable on its mirror image \rightarrow Achiral or symmetric molecule and this property is called \rightarrow achirality or symmetry.

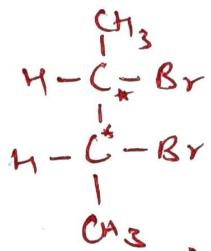
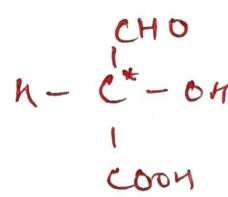
\rightarrow Symmetric molecule have plane of symmetry.

Dissymmetry is the essential condition for optical activity.

\rightarrow Organic compds / molecules which are chiral in nature contain atleast one C-atom which is bonded to 4-different atoms / gpc of atoms. The carbon which is bonded to four different atoms / gpc of atoms is called chiral / asymmetric carbon atom, indicated by C^* . Eg.



butane, 2,3-diol



2,3 dibromobutene.

molecule C
One chiral
C-atom

molecule E
two
chiral C-atom



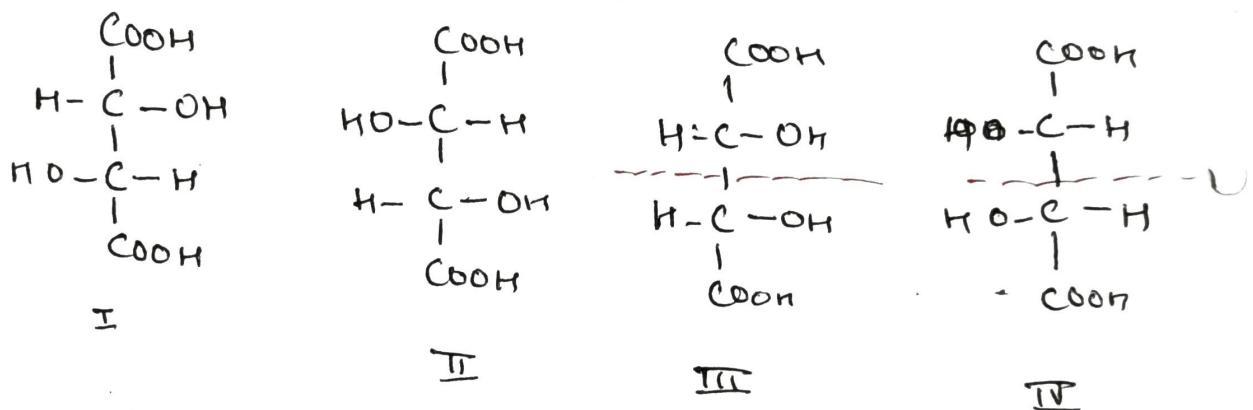
Eg:-

All molecules \bar{C} one Chiral C-atom \rightarrow Chiral
(no plane of symmetry) molecule

Molecules \bar{C} two or more chiral C-atom may be
Optically inactive.

Eg - Tartaric Acid : $\text{CH}(\text{OH})\text{COOH} \cdot \text{CH}(\text{OH})\text{COOH}$

\downarrow
2 chiral C atom
 \downarrow
No. of isomers $\cdot 2^n = 4$



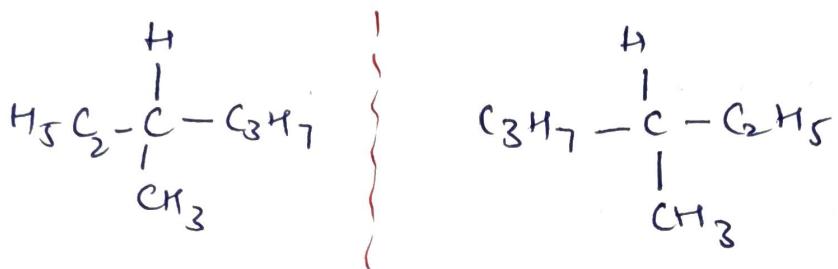
I & II \rightarrow Non superimposable mirror image \rightarrow dissymmetric
 III & IV \rightarrow No plane of symmetry \rightarrow optically active &
Chiral molecules
Have plane of symmetry \rightarrow symmetric molecule
 \rightarrow achiral molecule.

* Optical activity is due to presence of dissymmetry
not due to chiral C-atom.

Enantiomers

- Non superimposable mirror images
- Rotate plane polarized light equally in opp. direction.
- optically active
- dissymmetry / chirality involved.
- represented by d/(+) or l/(-)
- also known as optical isomers.

Eg. 3-methyl hexane:



Not superimposable
mirror image
Enantiomer

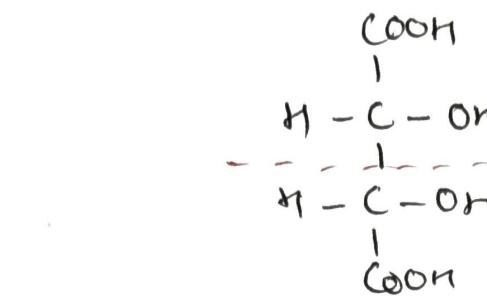
Properties → have same physical properties but differ in dirⁿ of rotⁿ of plane polarized light.
→ When equal量 of enantiomers are mixed an optically inactive racemic modification denoted by (±) & dl is obtained.

Racemic Mixtures - An equimolar mixture of the enantiomers (dextro and laevo forms) is called racemic mixture. → represented by ~~(D,L)~~ ± or all forms and are optically inactive.

The process of converting d- or l-form of an optically active compd in racemic form (dl) is called Racemisation. Eg. on mixing equal amounts of (+) and (-) 2-chlorobutane, we get (±) 2-chlorobutane racemic mixture.

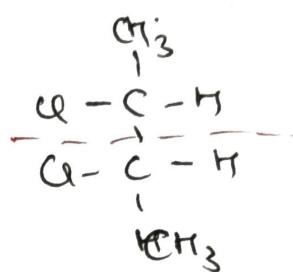
Meso Compds - Compds w/ 2 or more similar C-atom which are optically inactive due to presence of plane of symmetry are chiral meso compds.

Tartaric acid



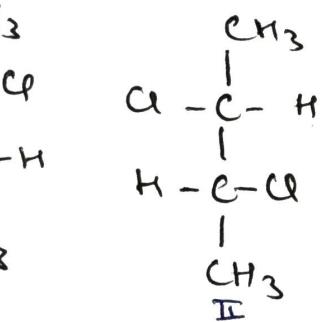
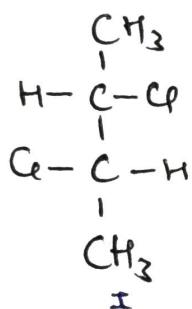
Dichlorobutene

- Plane of Symmetry.

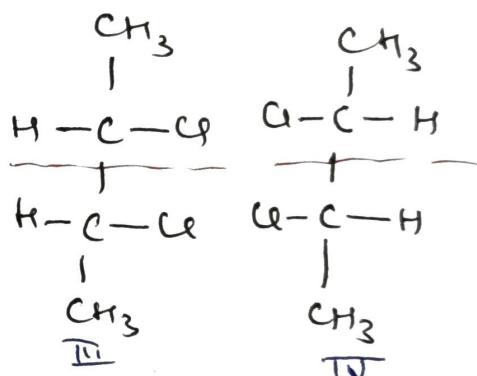


Optical activity of upper half of H molecule is neutralized by the lower half.

Eg:- Dichlorobutene 2 chiral C-atom \rightarrow 4 isomers

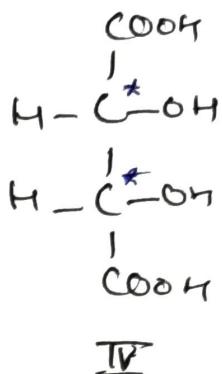
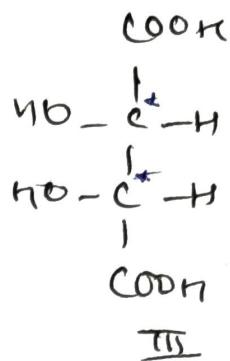
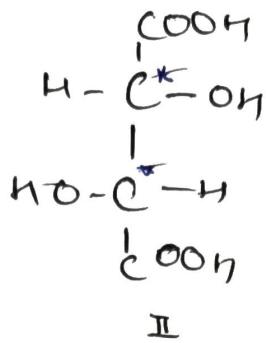
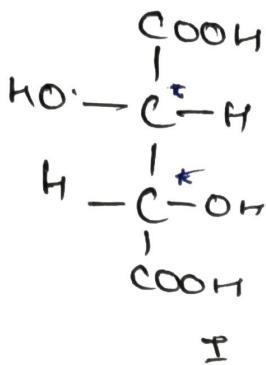


optically active
chiral molecule



optically inactive
achiral molecule
Meso molecule.

Find out enantiomers, diastereomers, meso compd.
of tartaric acid.



I & II → Enantiomers, optically active, Non superimposable mirror image

III → Meso compds, optically inactive
 IV → Meso compds, " "

~~III~~ I & III → Diastereomers, non superimposable mirror image

II & IV → Diastereomers

III & IV → Mirror image but are superimposable on each other. So ~~not~~^{can be} enantiomers.
 but have plane of symmetry.

∴ optically inactive.
 not enantiomers.

Find the ^{specific} type of isomerism

a) Diethyl ether & Methyl propyl ether



~~Functional isomerism~~ \rightarrow Metamerism

b) n-butyl alcohol & Diethyl ether



functional isomerism

c) Maleic acid & fumaric acid



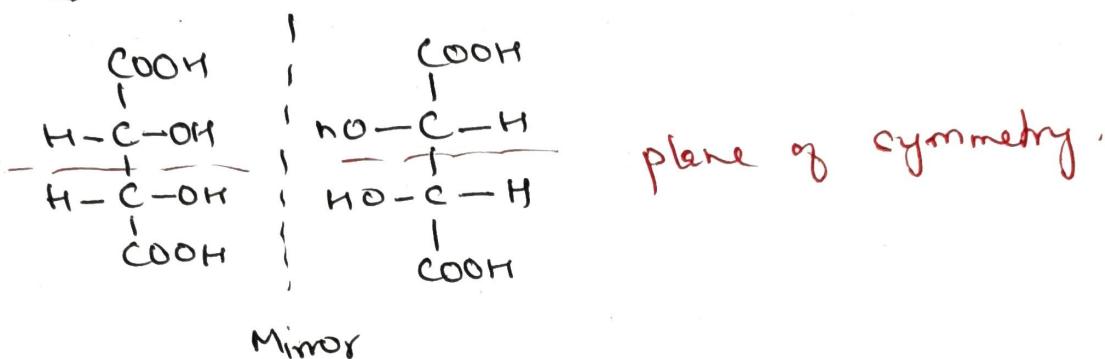
cis-trans butenedioic acid

Geometrical isomers

Elements of Symmetry:

1) Plane of Symmetry: when a molecule is divided into 2 equal halves in any plane, it is said that molecule has plane of symmetry. The atoms/groups on one side of the plane form mirror image of those on the other side.

Example Meso tartaric acid

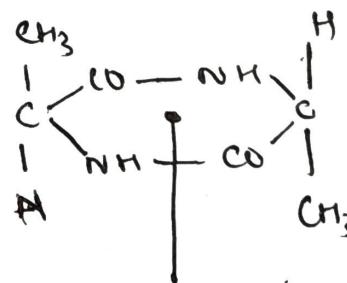
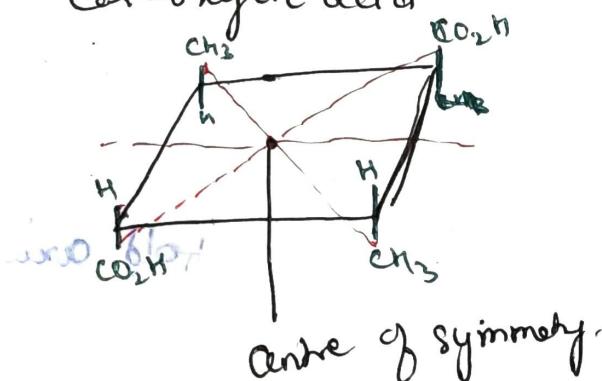


2) Centre of symmetry: A centre of symmetry is an imaginary pt in the centre of molecule from which if straight lines are drawn, they join identical points in the molecule cross each other.

→ It usually ~~not~~ only in an even membered ring

For e.g. 2,4-dimethyl dimethylcyclobutane-1,3-di-

carboxylic acid

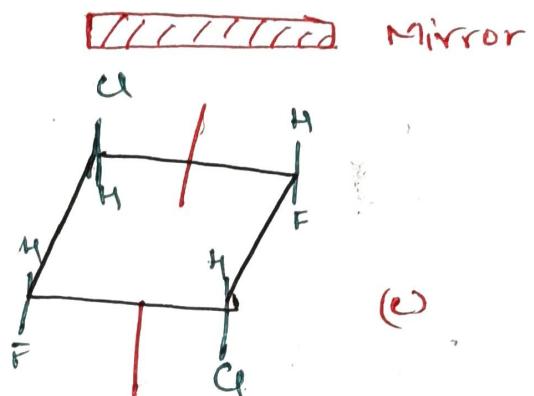
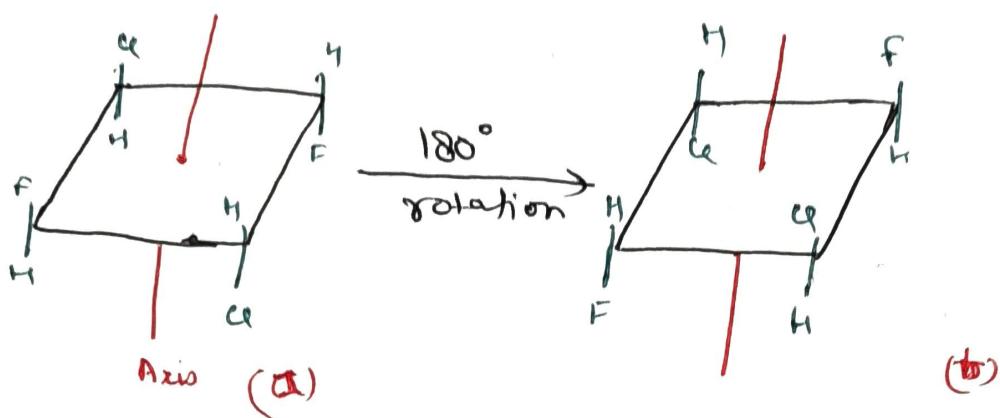


Centre of sym.

3) Alternating axis of symmetry:

A molecule is said to possess an alternating axis of symmetry if an arrangement identical to the original is obtained when the molecule is rotated thru an angle $\frac{360^\circ}{n}$ about the axis followed by reflection in a plane perpendicular to this axis. A molecule having n-fold axis of sy. is optically inactive.

Ex.



The molecule (a) is rotated thru 180° about the axis passing thru the centre of molecule & then reflected via mirror \perp to this axis, then an arrangement superimposable on (a), c is obtained.

\therefore Molecule is said to possess $\frac{360^\circ}{2} = 2$ fold axis of symmetry & will be optically inactive.

Symmetry axis - An axis around which a rotation by $\frac{360^\circ}{n}$ results in a molecule indistinguishable from the original. This is called n -fold rotation axis (C_n).

e.g. C_2 axis in water & C_3 axis in ammonia.

A molecule can have more than one symmetry axis, the one with the highest n is called principal axis.

NOMENCLATURE OF ENANTIOMERS (P2S SYSTEM)

The rotation axis of highest order is called as principal axis of symmetry.

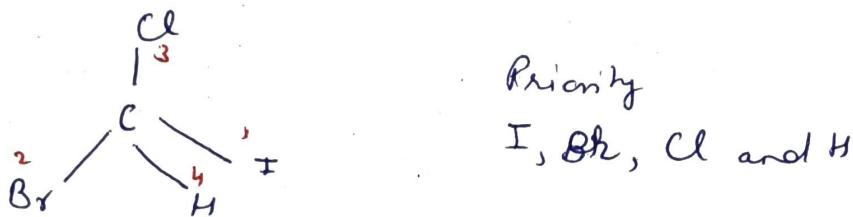
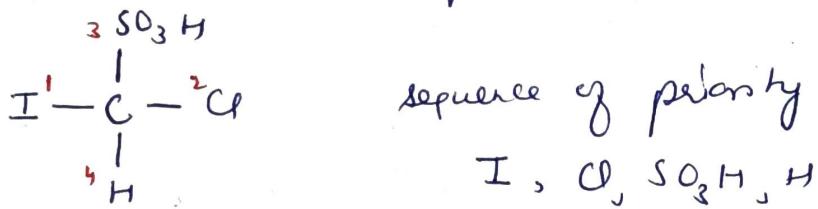
R S S nomenclature :

- Developed by Cahn, Ingold & Prelog
- designed to designate the conf' of all the molecules containing chiral centre (asymmetric centre)
- known as Cahn-Ingold-Prelog system or R.S.S system (Carbon atom)
- involves 2 steps:

Step 1 : four atoms/gps attached to asymmetric C-atom are assigned a sequence of priority acc to the following set of exp rules.

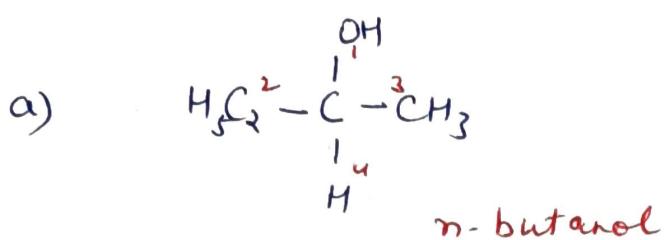
Seg. Rule 1: If the 4 atoms, attached to chiral c-atom, are all different, the priority depends on their atomic no. The atom of higher atomic number gets higher priority.

Eg : Chlorobromo methanesulphonic acid.

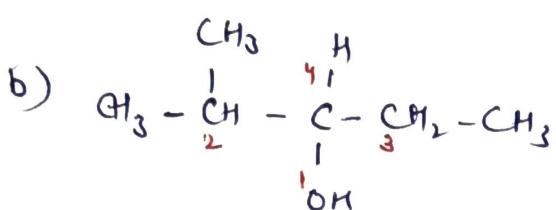


Seg. Rule 2 : If rule I fails to decide the relative priority of two atoms, it is determined by similar comparison of next atoms in the gp & so on.

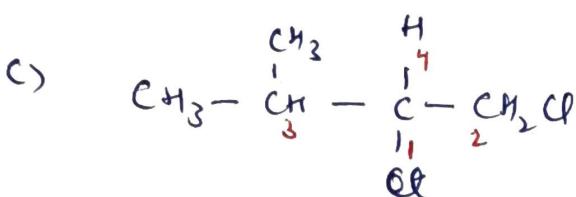
e.g.: 1,2-butanol, 2 of the atoms directly attached to chiral centre are C-themselves. Priority b/w $-CH_3$ & $-C_2H_5$



\rightarrow methyl C attached to 3 H-atom \rightarrow atomic no is 3 whereas methylene C of the ethyl gp is linked to 2 H's & one C-atom \rightarrow at.no. is 8 \therefore ethyl gp gets the priority over methyl



3-methyl-3-pentenol

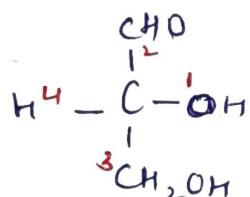


1,2 dichloro-3-methylbutane

See Rule 3: A doubly / triply bonded atom is considered equivalent to two / three such atoms.



e.g.: Glyceraldehyde:

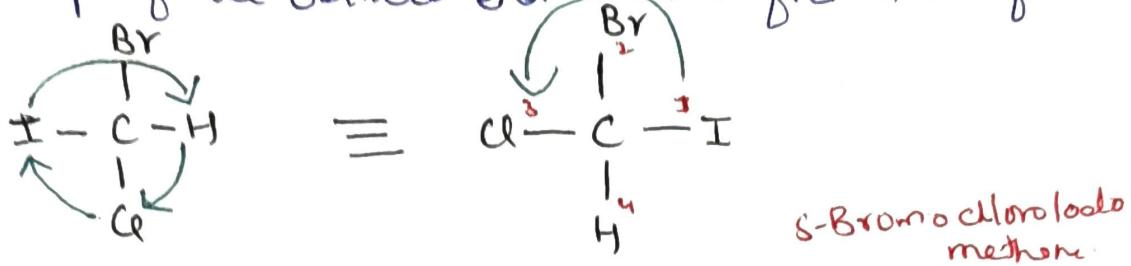


$-CHO$ gets priority
C atom is linked to O, O, H whereas
in $-CH_2OH$, C-atom is linked to O, H, H

STEP 2 After deciding the sequence of priority for 4-atoms/gps attached to asymmetric C-atom, the molecule is visualised in such a way that the atom or gp of lower or last (i.e. 4) priority is directed away from us; while the 3 remaining atoms or gps are pointing towards us. Then we trace the

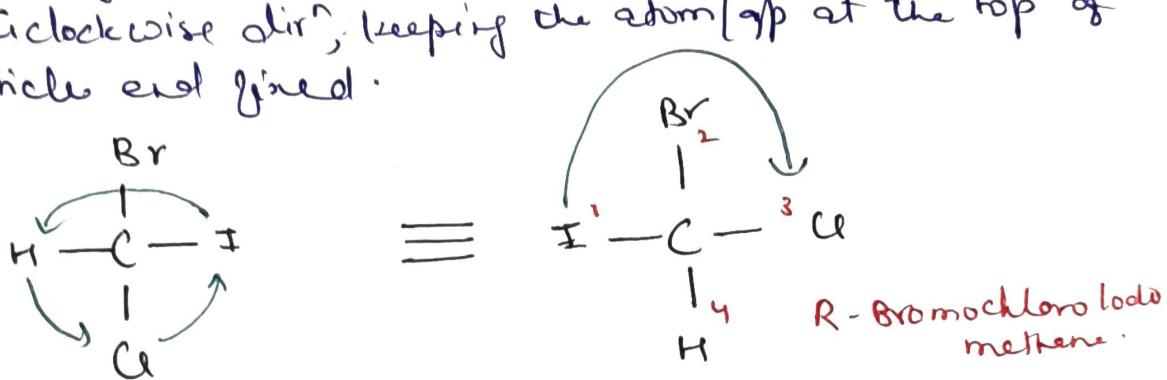
3) Atom/group of lowest priority is at the right hand side of horizontal line:

In such case: Change the position of atoms/groups in clockwise dirⁿ, so that atom/group of lowest priority comes at the bottom; but do not change the position of top atom/group at the top of the vertical end. Then find dirⁿ of order

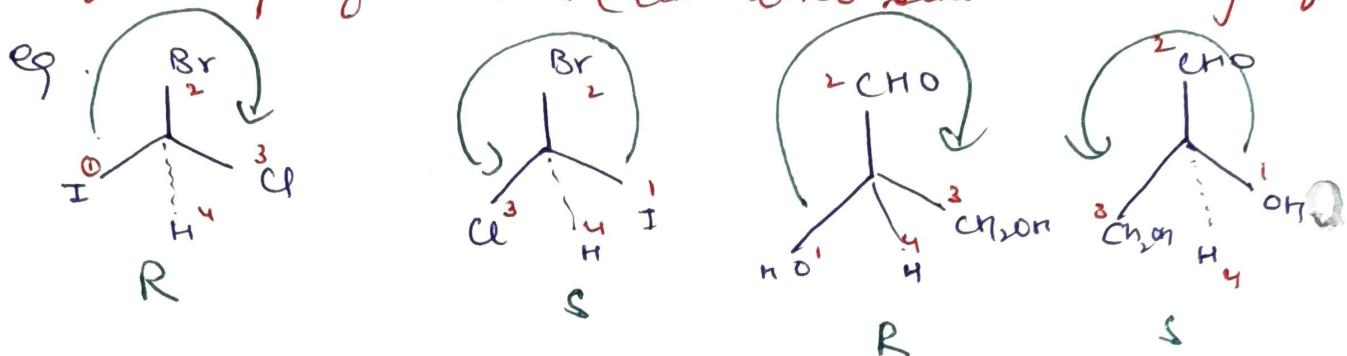


4) Atom/group of lowest priority is at the left hand side of horizontal line:

Similarly as above, change the position of atoms/groups in anticlockwise dirⁿ, keeping the atom/group at the top of vertical end fixed.



trace the path from the atom grp in the decreasing order priority (i.e. from 1 to 2 to 3) In doing so, if our eye travels in a clockwise dirⁿ the confⁿ is specified as R (Latin word rectus meaning right) & on the other hand if our eye moves in anticlockwise dirⁿ, the confⁿ is specified as S (Latin word sinister meaning left)

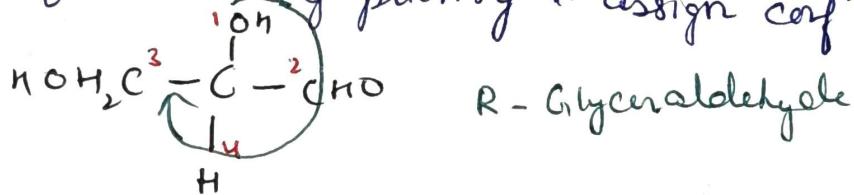


Confⁿ on the basis of ^{fisher} projection formula:-

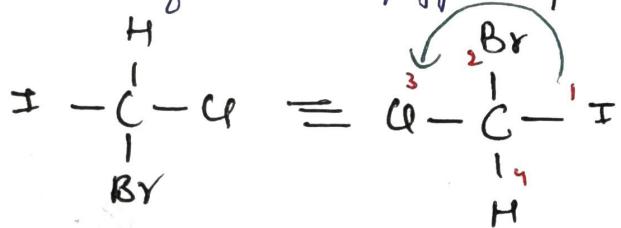
Four situations arise:

1) Atom/gp of lowest priority is at the bottom:

In such case simply rotate the eye in the order of decreasing priority & assign confⁿ (R or S)

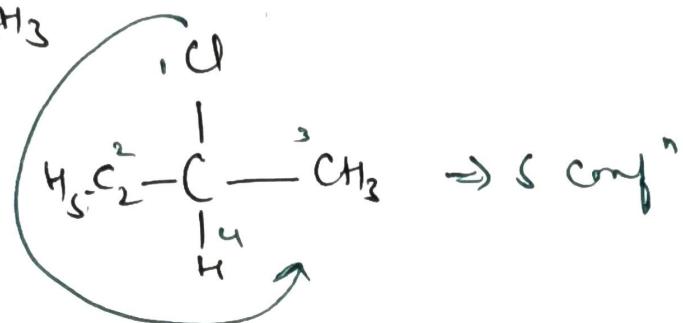
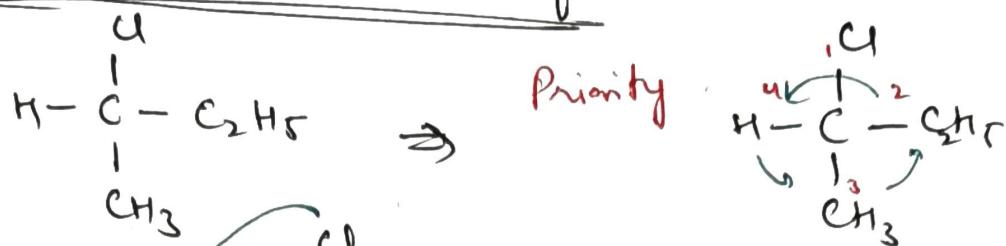


2) Atom/gp of lowest priority is at the top: In such case, rotate molecule 180°, so as to bring lowest priority atom or gp at the bottom. This can be done by reversing the positions of all atom/gps. e.g. CHBClI

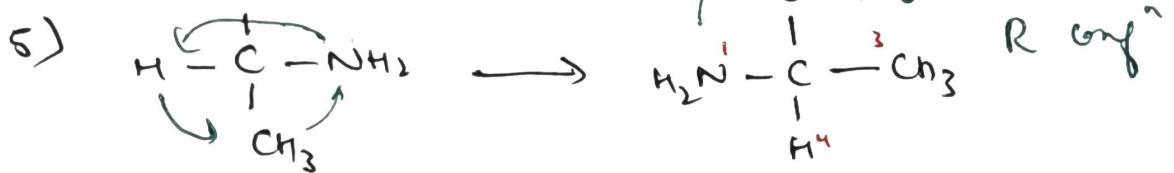
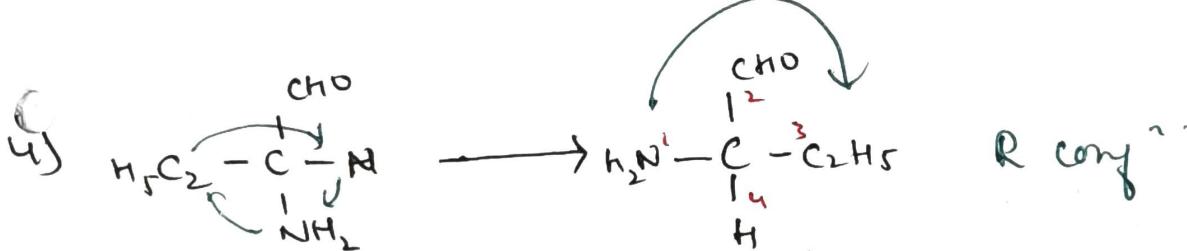
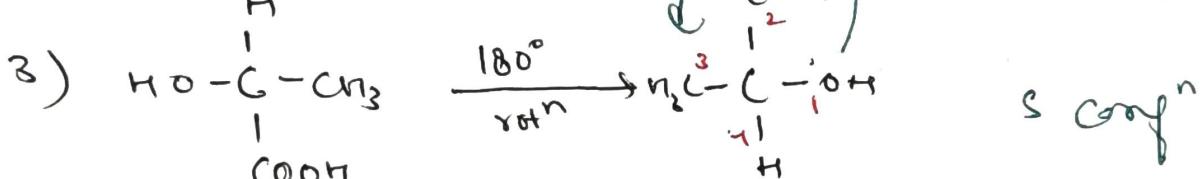
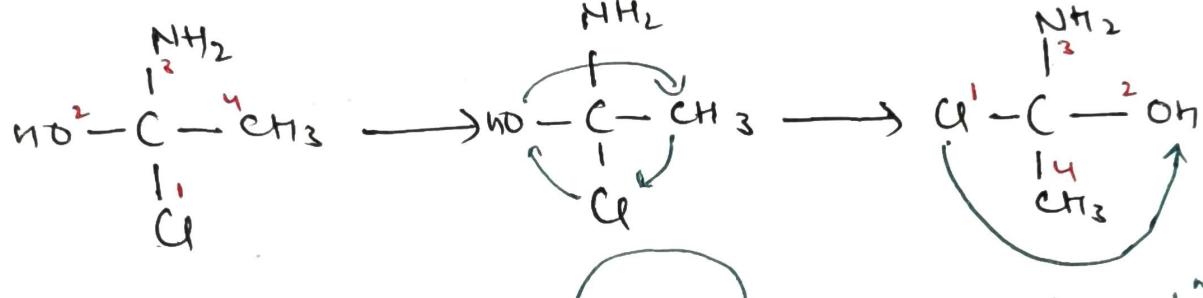


Assign R & S Confⁿ -

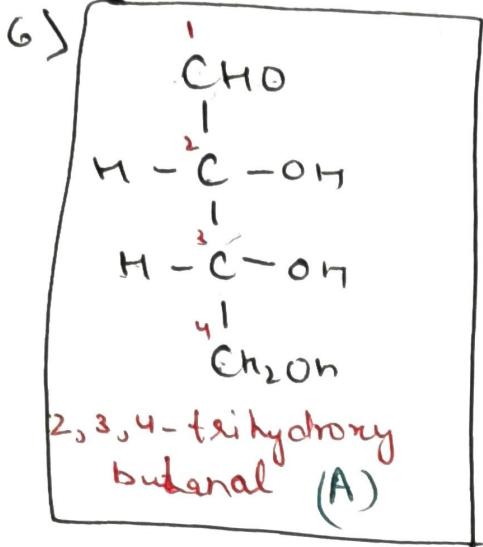
1)



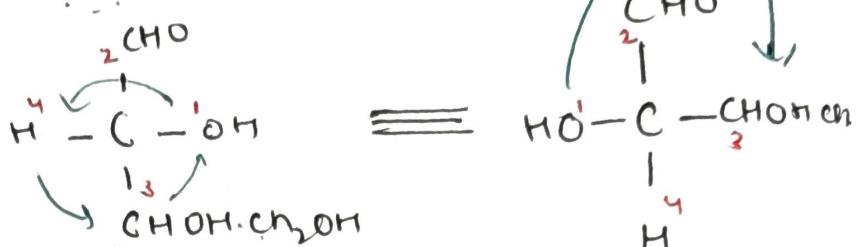
2)



when there are 2-Chiral C-atm -

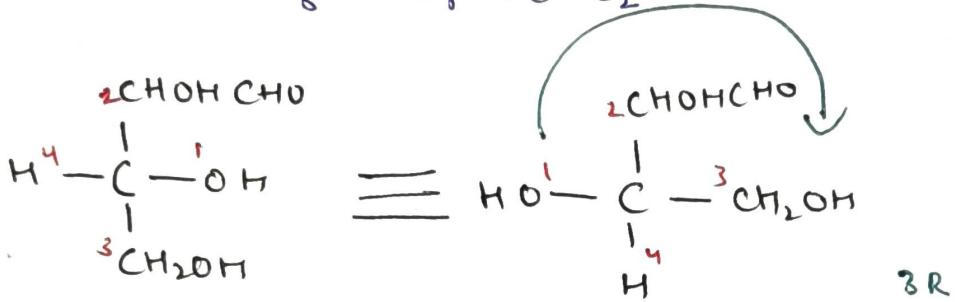


First fin specification, first let consider C_2 & ignore C_3



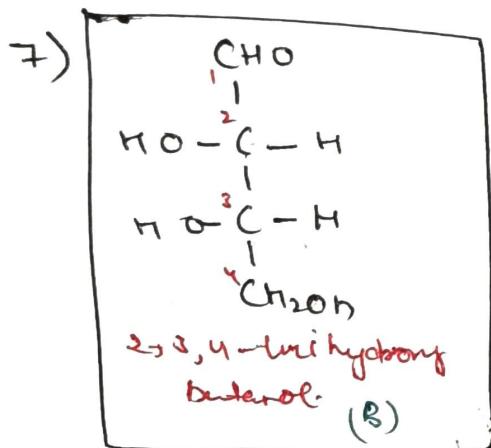
2R

Now Consider C_3 & ignore C_2

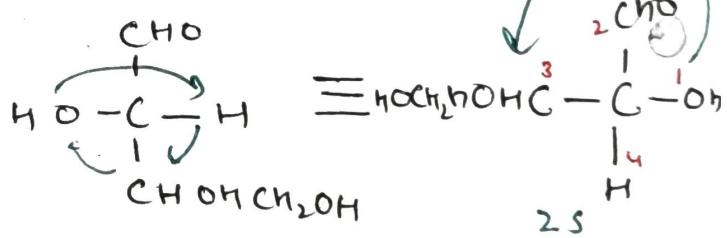


3R

\therefore Confⁿ of compd A is $\rightarrow (2R, 3R)-2,3,4\text{-trihydroxy butenal}$.

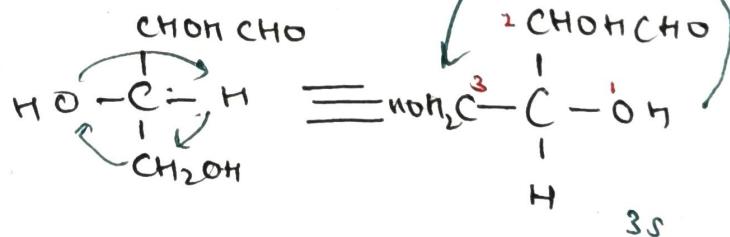


consider C_2 & ignore C_3



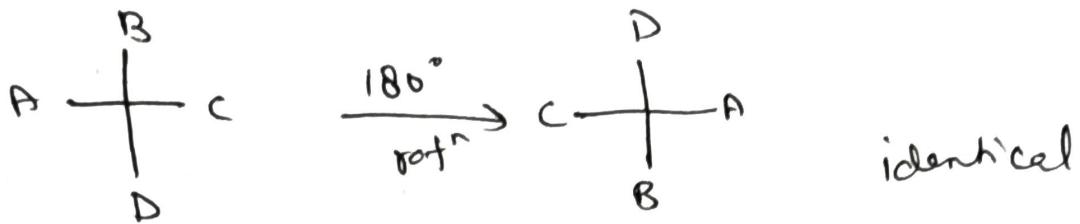
2S

Consider C_3 & ignore C_2



3S

\therefore Confⁿ of compd B is $= (2S, 3S)-2,3,4\text{-trihydroxy butenal.}$



Newman Representation :

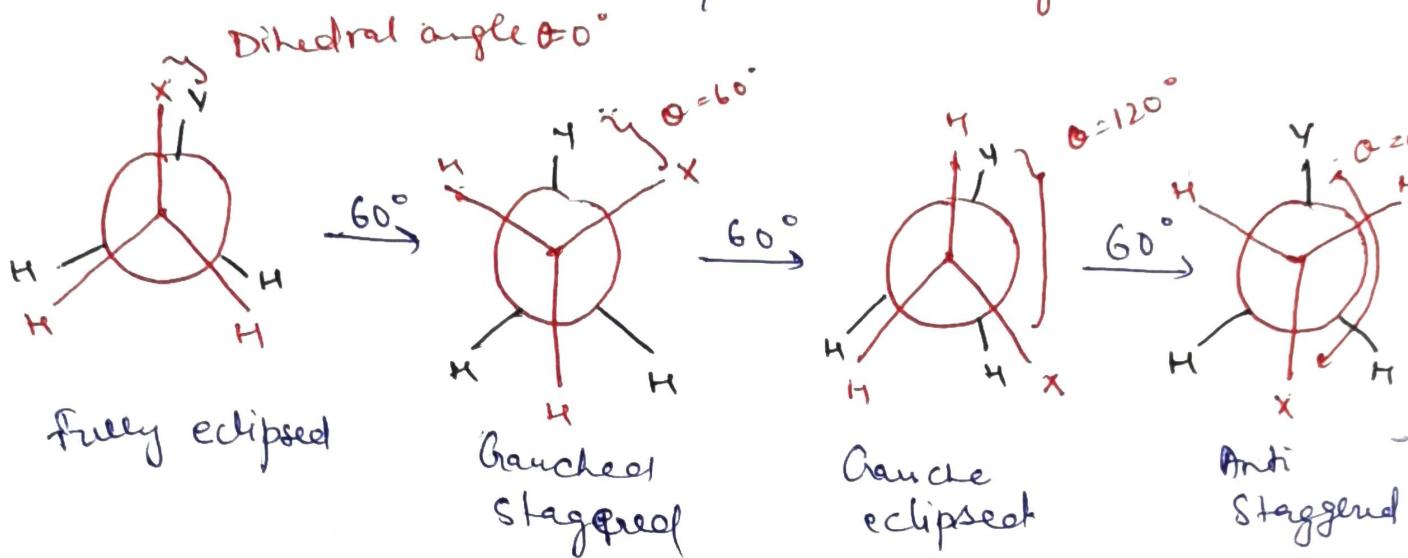
- Molecule is viewed from front to back in the dirⁿ of C-C single bond.
- Near Carbon is denoted by $\begin{array}{c} \text{H} & \text{H} \\ | & | \\ \text{C}^1 & -\text{C}^2 \\ | & | \\ \text{H} & \text{H} \end{array}$
- 1 Carbon - Near Carbon
- 2 Carbon - Rear Carbon
- Rear Carbon is denoted by O
- Carbon nearer to the eye is represented by a point & 2 H attached to it are shown by three lines at an angle of 120° to each other.
- Carbon atom away from the eye is represented by circle & 3 H atom are shown by shorter lines at an angle of 120° to each other.
- Newman projection for two extreme cases of



Eclipsed

- Angle b/w the two C-atom is 109° dihedral angle [$0=0^\circ$] is eclipsed
- The conformation in which H-atoms of two carbon are far apart as possible is staggered conformation
- The conformation in which H-atom of rear/back C are just overlapping behind as those of the front C is H/d Eclipsed Conf.

→ These are converted into one another by 1-Carbon against the other thru 60° . The other conformations, in b/w these two are k/d Skew conformations.

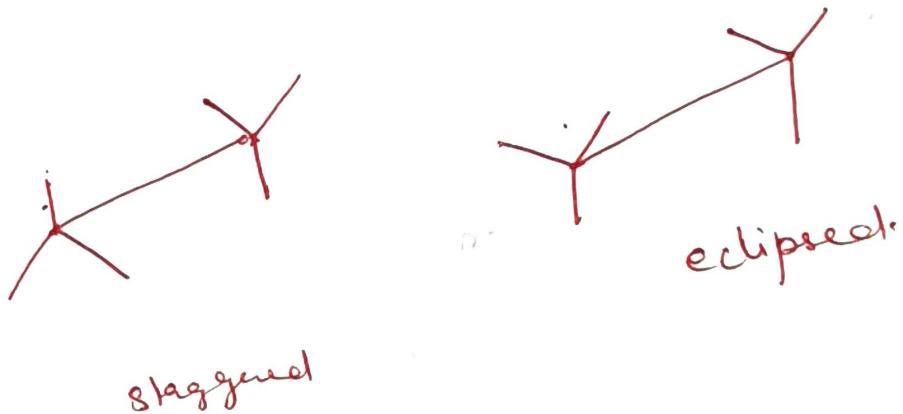
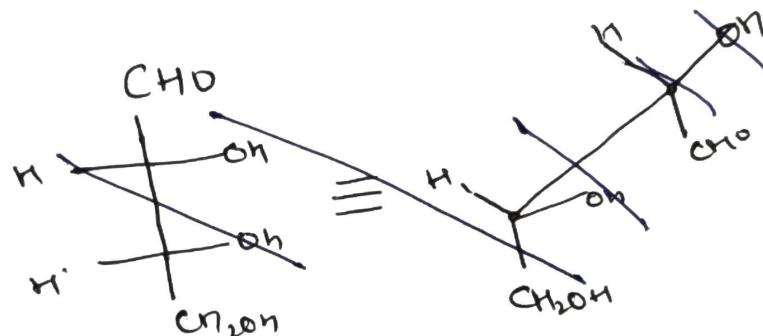
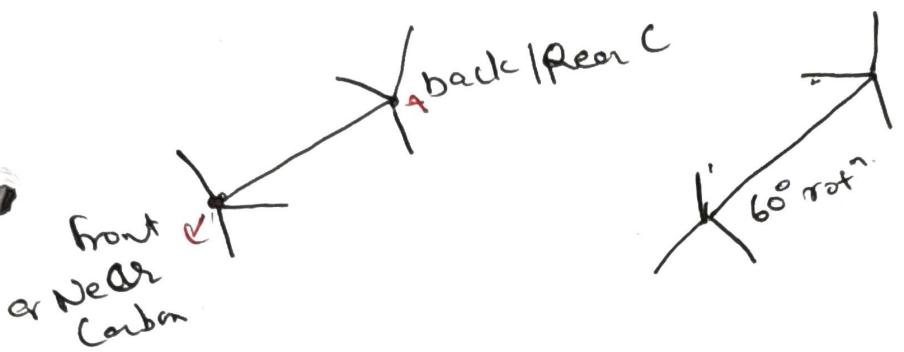


Different forms of a molecule due to free rotⁿ along C-C σ bond, which leads to different spatial arrangements of atoms in space are k/d conformational isomerism.

Saw horse projection [representation]:

- It is a 3d convention in which 2-atom under consideration are taken as the 2 pts where four lines intersect & the remaining pts are attached at the free ends.
- In this, the molecule is visualized slightly above and from the right & then projected on paper.
- Bond b/w two C-atom is drawn diagonally & is bit longer for sake of clarity.

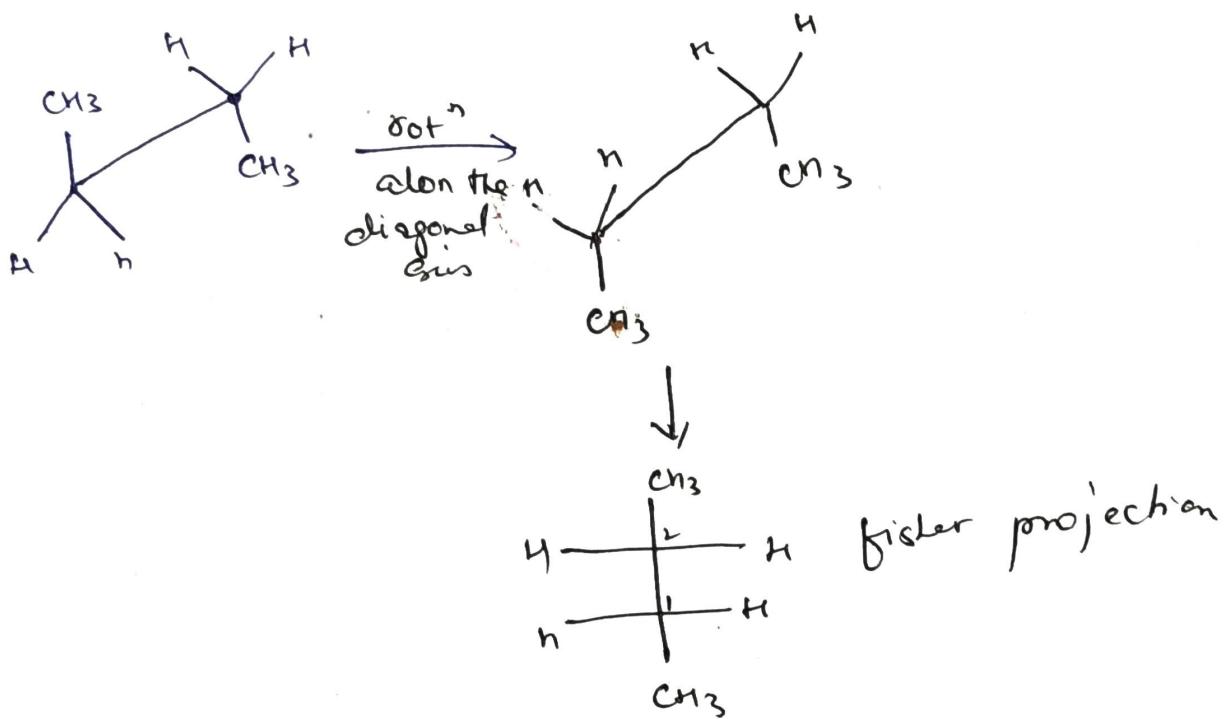
- lower left hand C is taken as front carbon.
- Upper right u u u - a back/rear carbon.
- There is free rotⁿ about the C-C bond & the three gp attached rotated may be clockwise or in anticlockwise dirⁿ.



Interconversion of Sawhorse to Fisher -

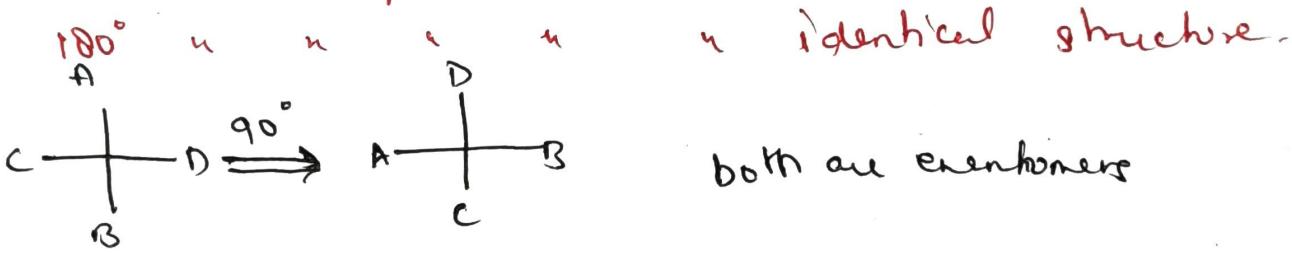
Involves 3-steps -

- 1) Near C-atom in sawhorse formula is regarded to the lowest Chiral C-atom in the respective Fisher's formula.
- 2) The given sawhorse is duly converted to eclipsed sawhorse - by rotⁿ the diagonal line upto least no. of degree.
- 3) The resulting sawhorse representⁿ as obtol in step 2 is now flattened to get desired Fisher's projection formula.



Fisher Projection:

- Simple method of representing 3d molecule in 2d or in one plane
- The chiral molecule is imagined in such a way that 2 gp pt towards the observer & 2 away from the observer.
- Molecule should be shown in the corrosus (+) i.e meeting pt. of vehicle & horizontal line
- Cross lines should be given only for asymmetric centres.
- Arrange max. no. of carbons on vehicle line
- Carbon skeleton unsymmetrical, highly oxidisable gp should be taken top of vehicle line
(i.e., gp having max. no. of O-atom & minimum no. of H-atom) [-CH₂, CH₂OH, CHO, COOH]
- Gp. attached to the vehicle line, away from the observer
- Gp attached to the horizontal line, nearer to the observer.
- All fisher projections are default eclipsed.
- * 90° rotⁿ in plane fisher gives enantiomers.

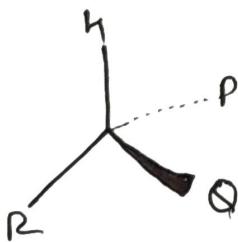
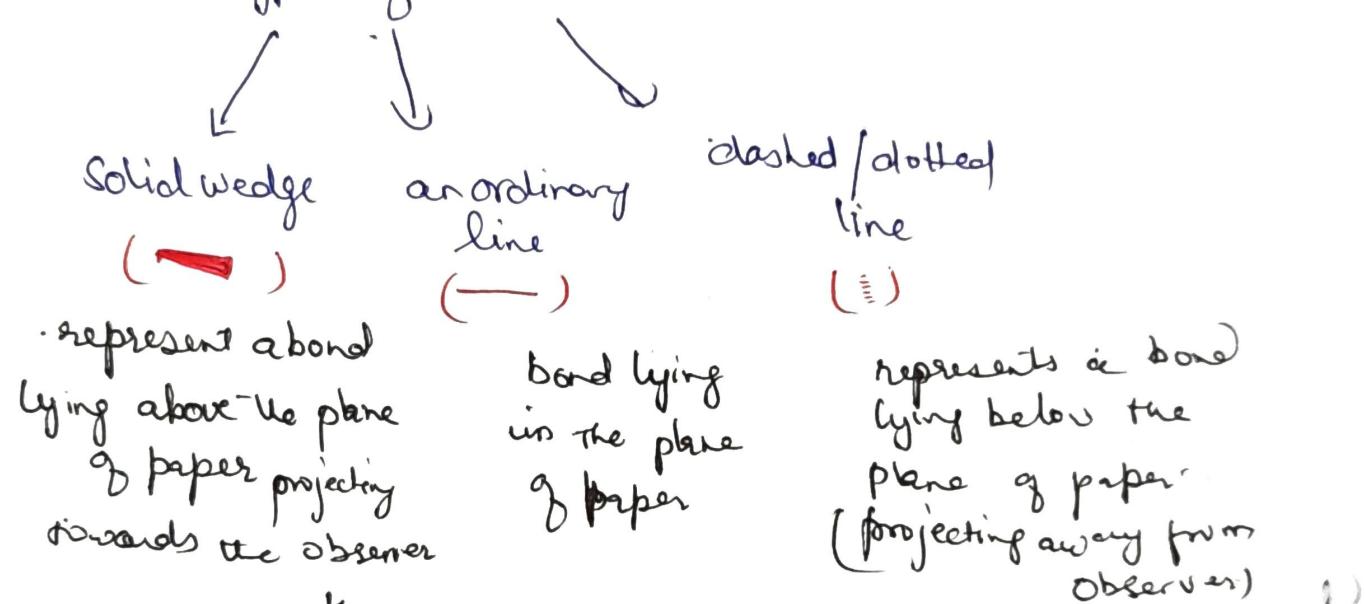


Conformational Isomers:

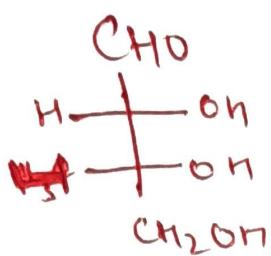
- Also known as rotational isomers or conformers
- Rotation of one ~~end~~ against other is possible without breaking of bond (sigma / single covalent)

Flying wedge Representation: three dimensional structure of an org. molecule may be represented by flying wedge model.

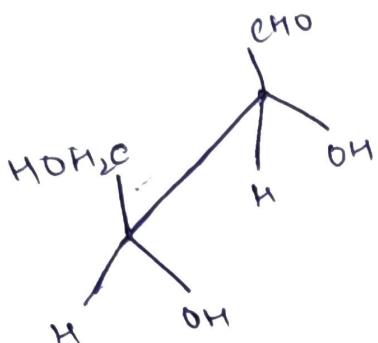
- Three types of lines are involved



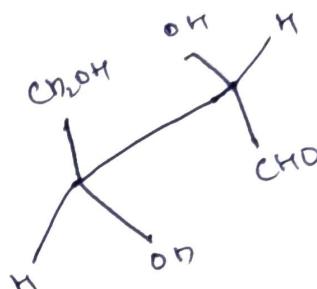
Convert D(-)-erythrose sugar



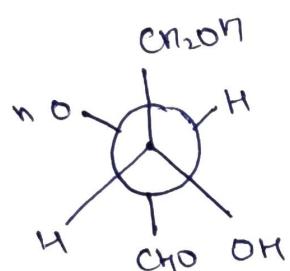
a) sawhorse eclipsed form



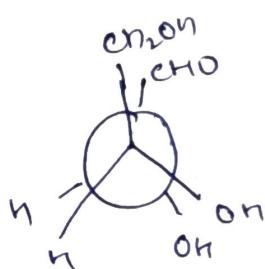
Sawhorse eclipsed



b) Newmann staggered



Newmann staggered



Optical purity: A pair of enantiomers are distinguished by their optical activities because they rotate the plane of polarized light by equal amounts in opp dirⁿ. The net specific rotⁿ of such a mixture will be zero i.e., optically inactive. A sample of a pure chiral compd uncontaminated by its enantiomers is said to be optically pure.

$$O.P = \frac{\text{observed optical rot}^n \text{ of the sample}}{\text{Optical rot}^n \text{ of pure sample}} \times 100$$

OR

$$O.P = \frac{\text{rot}^n \text{ of an optically compd}}{\text{Specific rot}^n} \times 100 \%$$

Enantiomeric Excess: A pair of enantiomers are distinguished by their optical activity as they rotate the plane. Optically purity (O.P) is synonymous to enantiomeric excess (ee). These term find use in the case of mixture which are neither optically pure nor racemic. The O.P of a mixture is the ratio of its rotation to the rotⁿ of the pure. The percentage optical yield or optical purity or enantiomeric excess

$$ee\% = \frac{\text{specific rot}^n \text{ of product}}{\text{specific rot}^n \text{ of pure enantiomer}} \times 100$$

$$ee\% = \frac{\text{Y. Enantiomer}^1 - \text{Y. Enantiomer}^2}{\text{Y. Enantiomer}^1 + \text{Y. Enantiomer}^2} \times 100$$

$$ee\% = \frac{[R] - [S]}{[R] + [S]} \times 100$$

$[R] = \text{conc}^n \text{ of } R \text{ isomer}$
 $[S] = \text{conc}^n \text{ of } S \text{ isomer}$