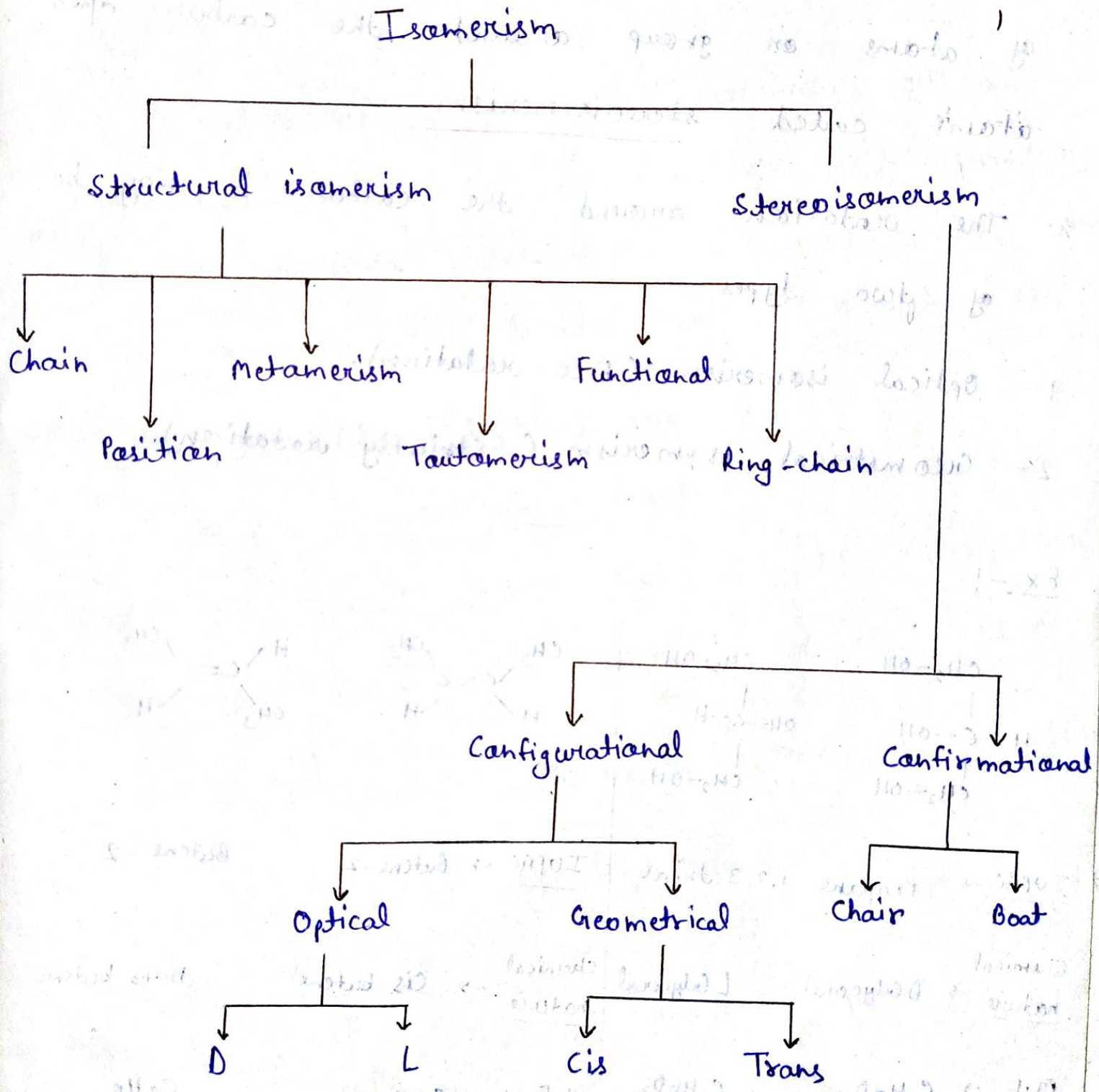
Unit – I

Stereo isomerism



Stereo isomerism

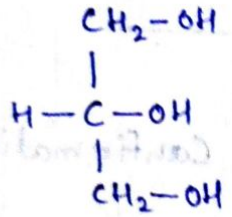
When molecular formula and IUPAC name of compound are same but their chemical nature and properties are different due to rotation of atoms or group around the carbon then it is called stereoisomerism.

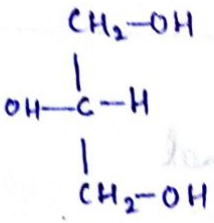
* The rotation around the carbon is may be of two types —

1- Optical isomerism (Free rotation).

2- Geometrical isomerism (Strictly rotation).

Ex -1



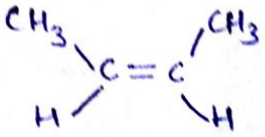


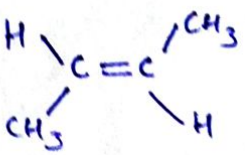
IUPAC → Propane 1,2,3 trial

Chemical nature → D Glyceral L Glyceral

M.F → $C_3H_8O_3$ $C_3H_8O_3$

Free rotation (optical)





IUPAC → Butene-2 Butene-2

Chemical nature → Cis butene trans butene

M.F. → C_4H_8 C_4H_8

Strictly rotation (Geometrical)

Optical activity

* The power of any substance to rotate the plane polarised light from it's axis to clock wise or anticlock wise direction is called optical activity.

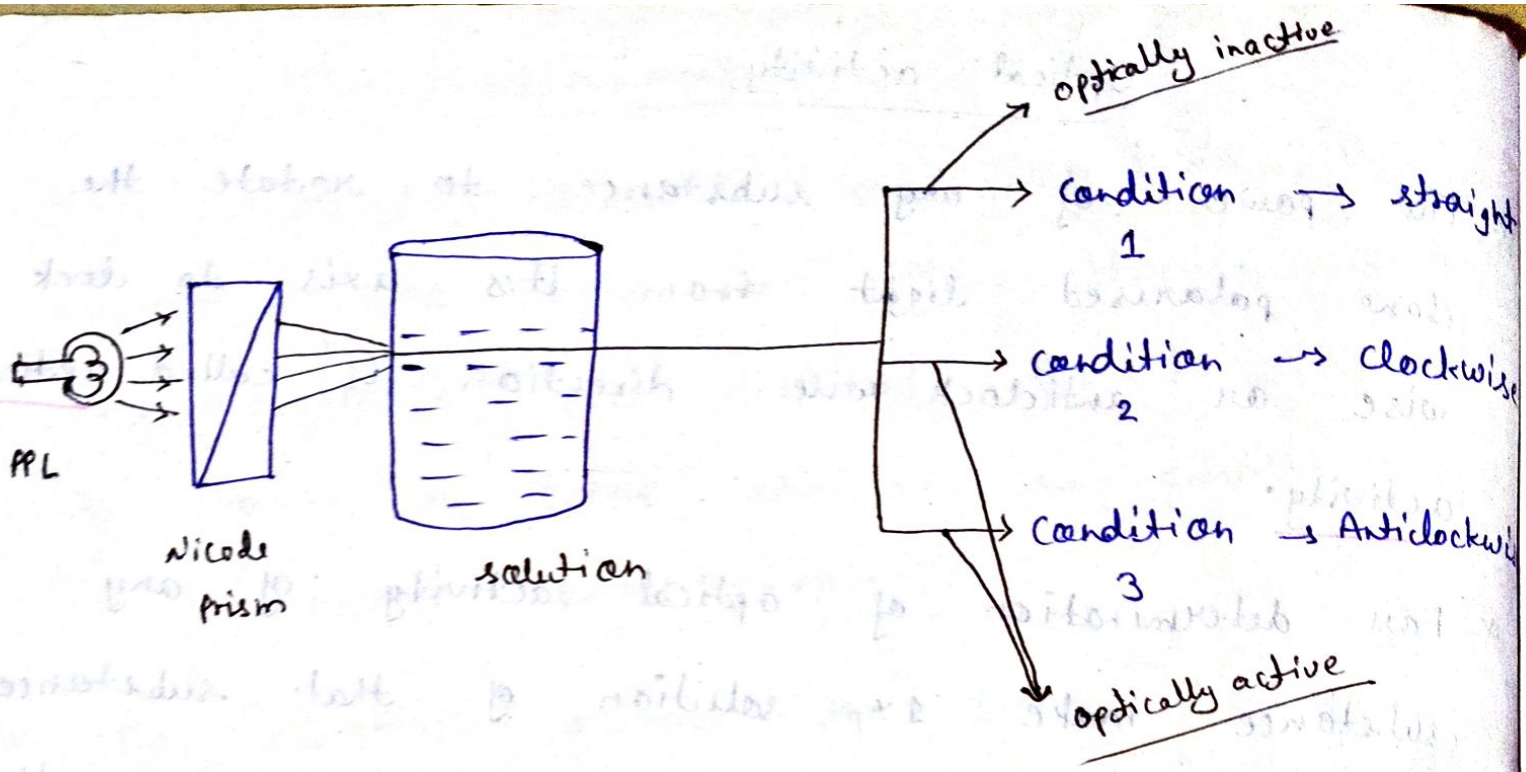
* For determination of optical activity of any substance make 1% solution of that substance in a particular solvent, and now pass the PPL across the nicole prizm through soln.

* If the PPL light goes instrate light then compound is optically inactive but if the PPL deviate from it's axis in any direction then compound is called optically active.

* Optically active compounds are of 2 types -

(i) Dextro (clock wise) (+) (D).

(ii) Levo (Anti clock wise) (-) (L).



Racemic mixture :-

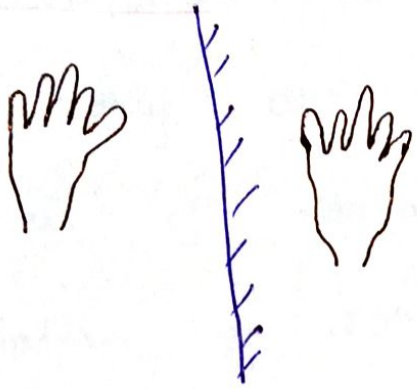
The equimolar mixture of Dextro and levo substance is called racemic mixture.

Chirality

* The term chirality is derived from chier which means hand like structure.
* The concept of chirality was given by kelvin in 1884.
* Any two structure which are mirror image of each other but they are non - super

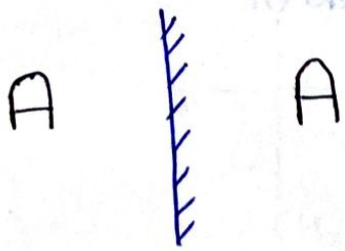
imposible to each other then they are called chiral compound and this property is k/as chirality.

* If two compounds are mirror image of each other but they are super imposible then compound is called achiral.

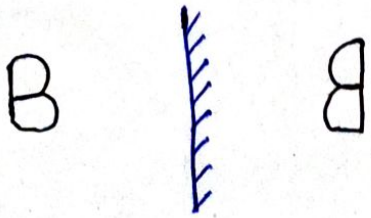


(I) Mirror image

(II) Non super imposible



A → Achiral



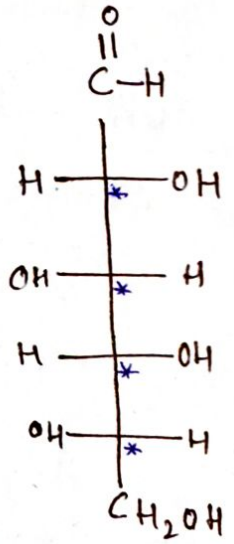
B → Chiral

Chiral compound

* Those organic compound in which four different atom or group are attached with carbon by single bond, they are called chiral compound.

* That carbon which is chiral in the compound is called chiral centre or stereogenic centre.

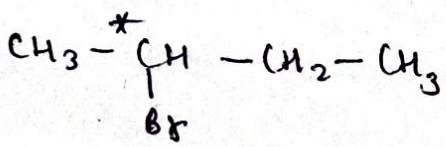
Ex -:



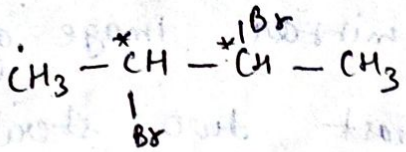
Glucose = 4* chiral center

$CH_3-CH_2-CH_2-CH_3$

Butane = Achiral



2 Bromo butane = 1

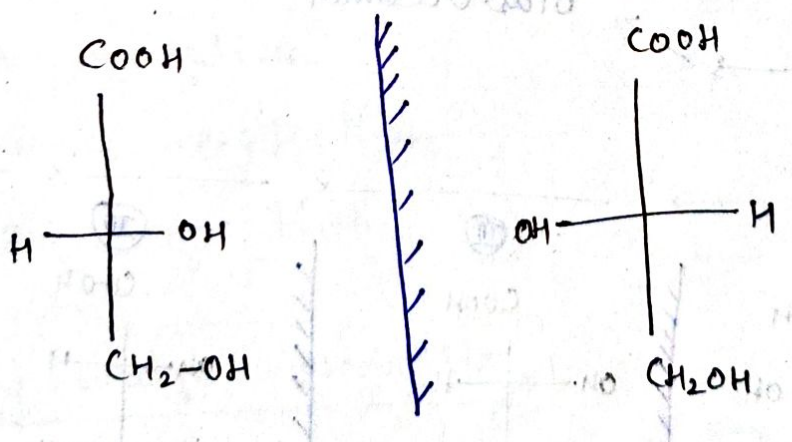


2,3 dibromobutane = 2

Enantiomer

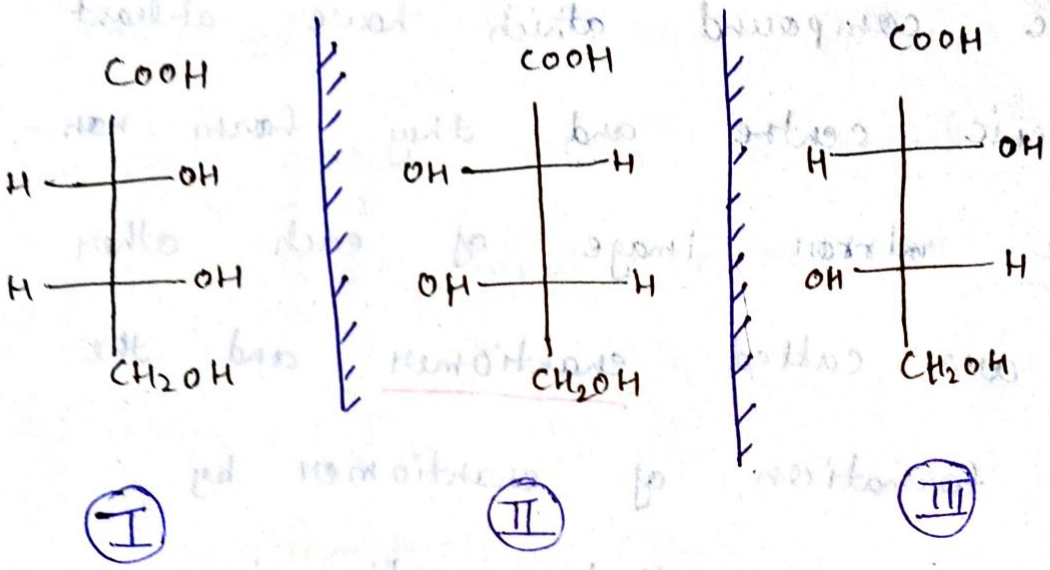
Those organic compound which have atleast one stereogenic centre and they form non-superimpossible mirror image of each other then they are called enantiomer and the process of formation of enantiomer by rotation of 180° is called enantiomerism.

Eg-:



Diastereomer :-

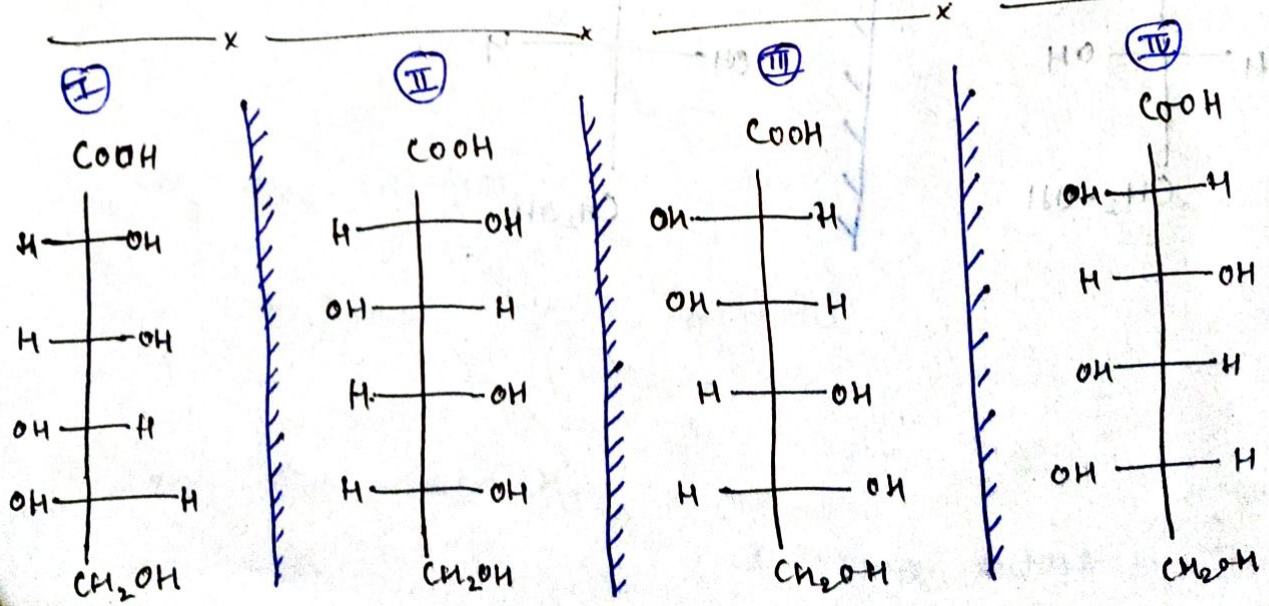
Those structure which are not mirror image of each other and they have atleast two stereogenic centre then they are called diastereomer of each other.



I II III

I & II → Enantiomer

I & III →
II & III → Diastereomer



I & II = D

I & III = E

I & IV = D

II & III = D

II & IV = E

III & IV = D

Representation of 3D structure of molecules

It is very difficult or impossible to draw 3D structure of molecule on 2D paper so there were different method to represent the 3D structure on 2D paper —

(I) Flywedge projection.
(II) Fisher projection.
(III) Sawhorse projection.
(IV) Newman projection.

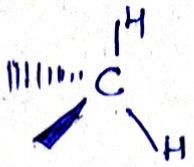
(I) Flying wedge projection -:

This projection is for tetrahedral structure.

In tetrahedral structure 2 atom or group are arranged in the plane, and other two

atom or group is present above the plane. and below the plane.

Ex -: CH_4



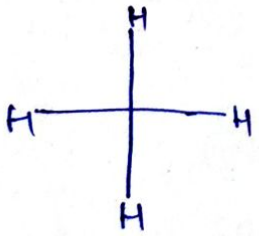
— Above the plains wedge

|||||||.... Dotted line below the plain

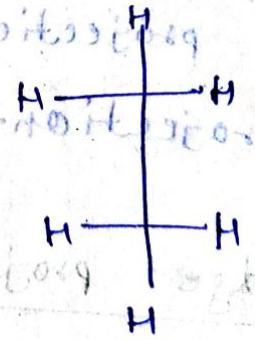
(ii) Fisher projection -:

This is the simplest method which is used in stereochemistry, In this method molecules are represented by cross lines and the centre of line is assumed as carbon.

Ex -: CH_4



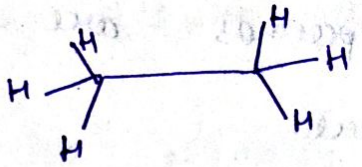
CH_3-CH_3



(iii) Sawhorse projection -:

In this method the structure of molecule is represented as by chair or stool.

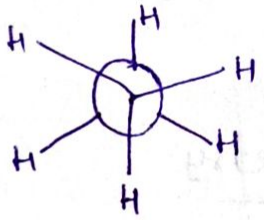
Ex-: $CH_3 - CH_3$



(iv) Newman projection -:

In this method structure of molecule is shown in the form of above the plane structure and below the plain structure.

Ex-: $CH_3 - CH_3$ Ethane



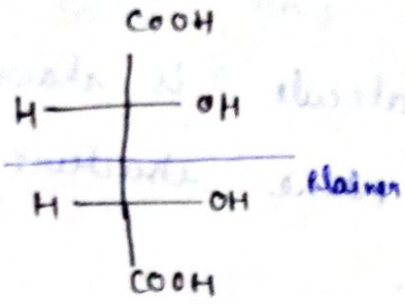
Elements of symmetry

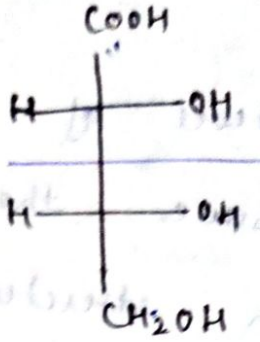
Those compound which can be divided into 2 equal parts from any plane they are called symetrical compounds and vice - versa.

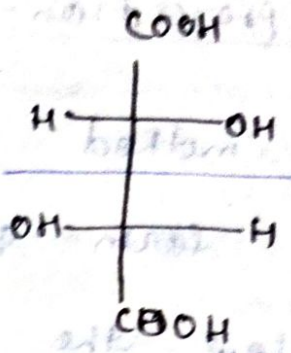
meso compound

Those compounds which are planner symetrical and after dividing both part are the mirror image of each other then they are called mesocompound.

* All the meso compounds are achical and optically inactive in nature.







Tartaric acid
Symmetrical
Meso ✓

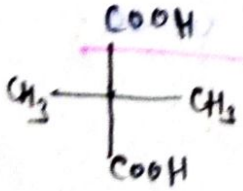
Asymmetrical
Meso ✗

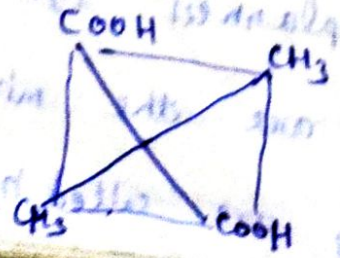
Symmetrical
No mirror
Not meso compo

Centre of symmetry

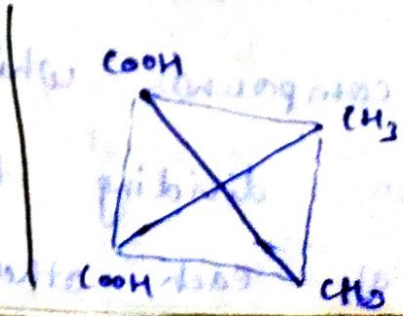
The centre of symmetry is a point in a molecule which if lines are drawn on one side and extended to an equal distance on the other side will meet the same atom

Ex -1





Symmetrical

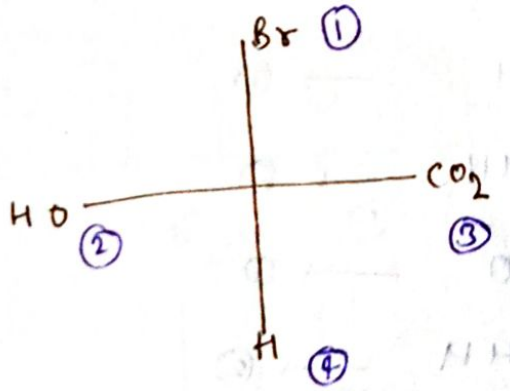


Cohn Ingold prelog sequence Rule (CIP rule)

CIP rule decides the preority of atom or group attach with the chiral carbon —

Rule-1 → — The preority of atom or group is decided on the basis of their atomic number.

— The atom or group of highest atomic number is always given higher preority.



According to Z

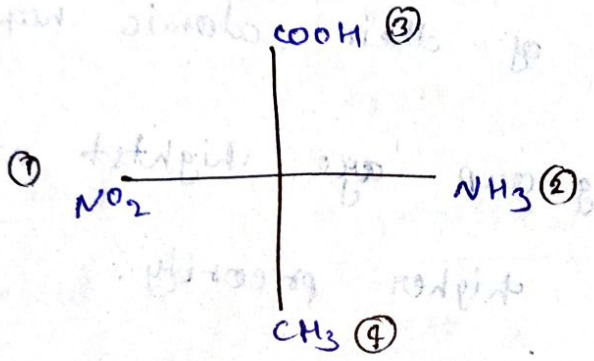
H → ①

OH → 8

C → 6

Br → 35

Rule-2 If in any group the first atom are similar then we compair with the second atom and if second is also same, then we move forward so on.



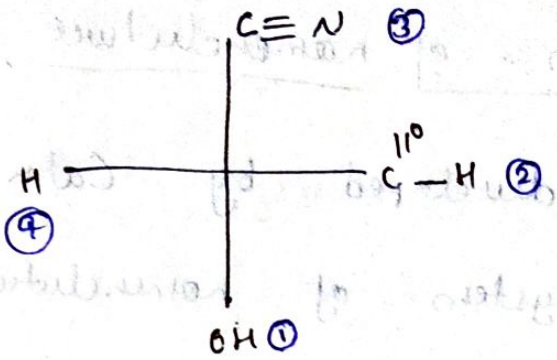
COOH —— ~~C~~OOH → ③

CH_3 —— ~~C~~HHH → ④

NO_2 —— ~~N~~OO → ①

NH_3 —— ~~N~~HHH → ②

Rule-3 If in any atom or group double or triple bond is present then the respective atom written the number of times as per bond.



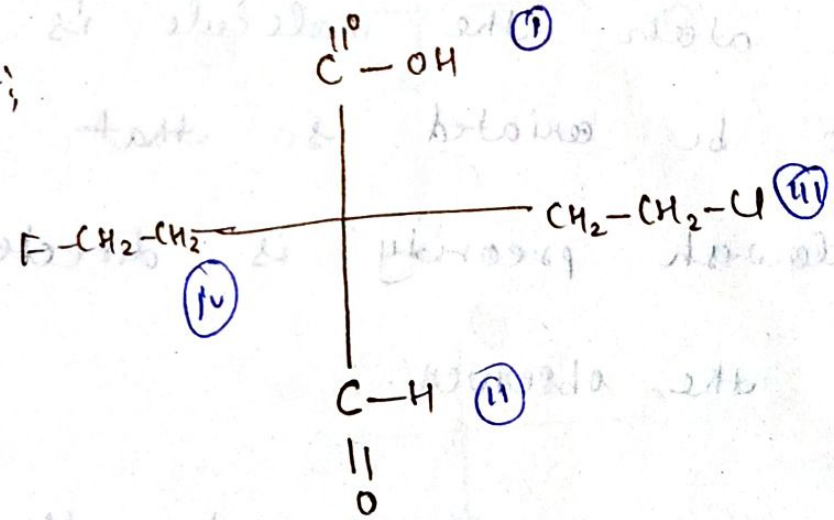
C≡N → CNNN → ③

C=O
H → COOH → ②

H → ④

OH → ①

Eg –;



COOOH → ①

CCHHHHCl → (iii)

COOH → (ii)

CCHHHHF → (iv)

R – S system of nomenclature

* This system was developed by Cahn. et al in 1956, this system of nomenclature is based on the actual configuration.

* The R – S nomenclature system involve 2 step-

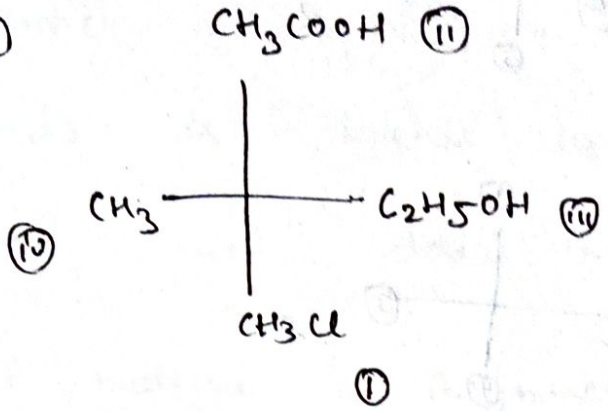
Step – 1 → The 4 atom or group attached to the chiral centre are assigned a sequence of precority according to the sequence of

Step-2 → After assigning the precority of atoms to the carban atom the molecule is to amezing to be oriated so that the group of lowest precority is directed away from the observer.

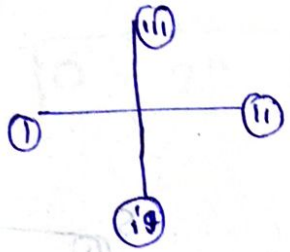
* Now the arrangement of remaining three group is wiped in the ding order of their precority, If the orientation is clock wise then is called R or D, and if the orientation is anti clock wise then it

will be L or S.

Ex -: (i)

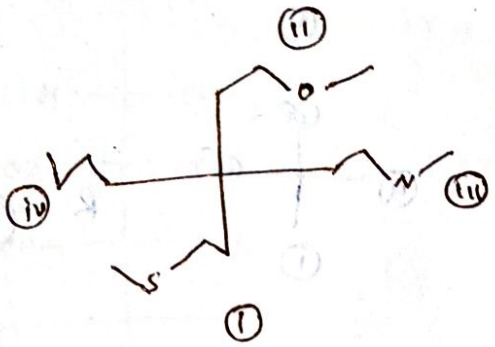


C C O O O H
C C O H
C Cl
C H H H

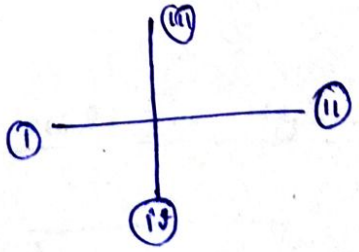


= L

(ii)

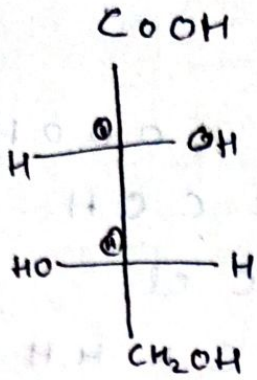


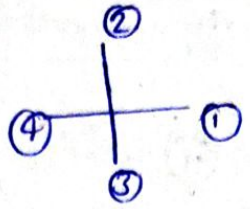
C C O C
C C N C
C C S C
C C C C



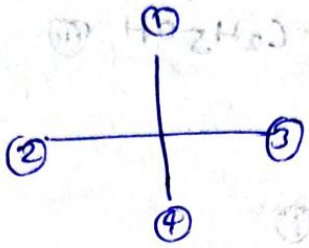
= L

(iii)





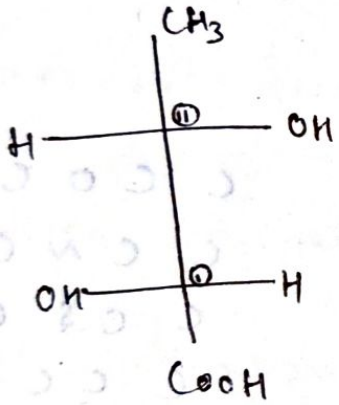
R

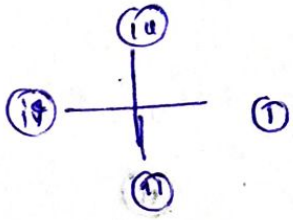


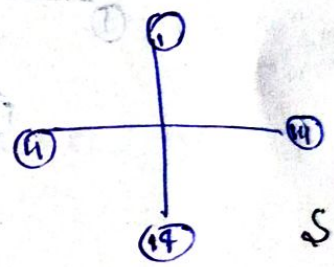
S

2R, 3S

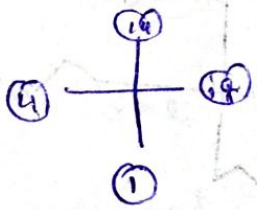
(iv)

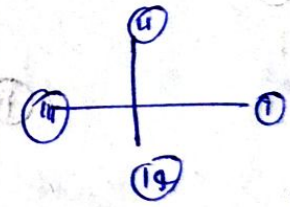






S





S

2S, 3S

No. of optical isomer

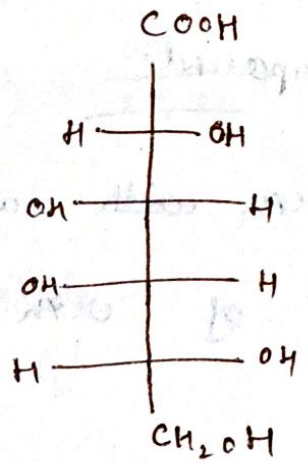
The number of optical isomer of organic compounds is depends upon the symmetry of compound and total number of chiral carbon.

1 → If molecule is Asymmetrical —

$$a = 2^n$$

where → n = number of chiral carbon.

Ex →



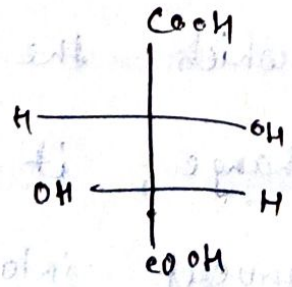
$n = 4$

$a = 2^4 = 16$

2 → If molecule is symmetrical

$$a = 2^{n-1}$$

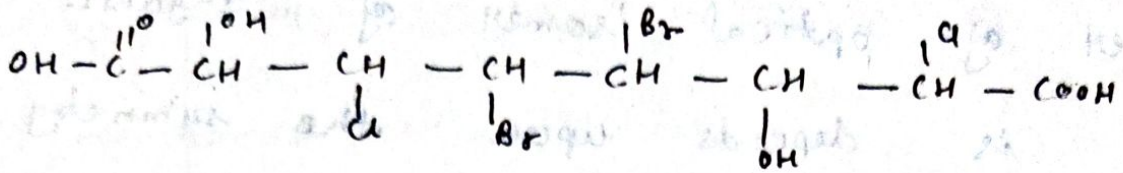
Ex →



$a = 2^{2-1}$

$a = 2$

Example



$a = 2^{n-1}$

$a = 2^{6-1}$

$\boxed{a = 32}$

Rxn of chiral compounds

Chiral compounds after rxn ~~with~~ at chiral centre shows 3 types of rxn —

1- Inversion.

2- Racemisation.

3- Retention.

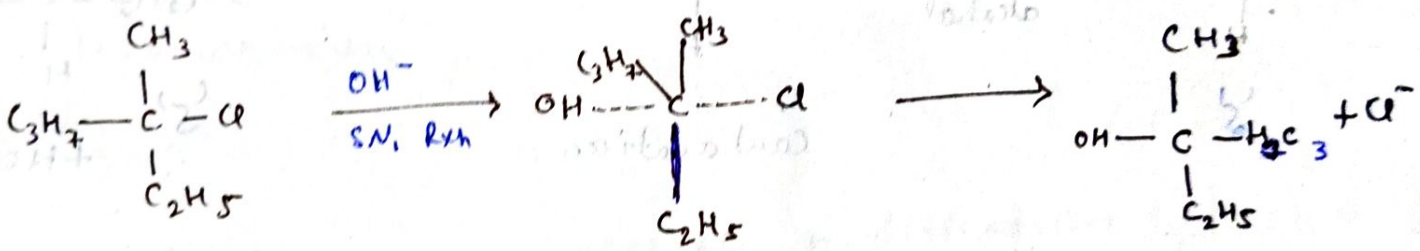
1- Inversion →

Such chemical rxn after which the rotation of chiral compound is change, it means dextro compound (R) is convert into two

compound (S) or levo compound is convert into dextro this is called inversion rxn.

eg → → S_N1 rxn show the example of inversion rxn.

→ when butyl chloride after rxn with alcohol convert into butyl alcohol then 'S' form is change into 'R' form.



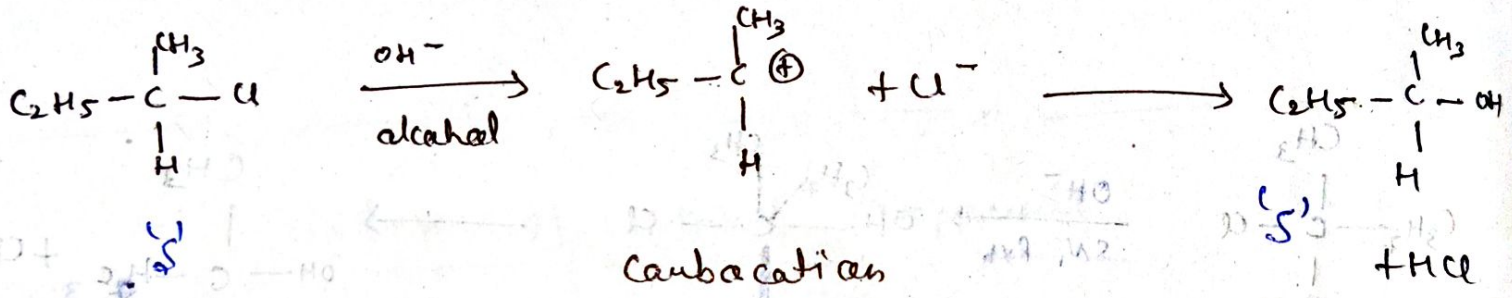
Butyl chloride 'S' or 'L'

Butyl alcohol 'R' or 'D'

2- Racemisation rxn —!

Such chemical rxn after which the optically active compound is convert into optically inactive compound or inert compound then it is called racemisation rxn.

Ex → In S_N2 rxn when secondary alkyl halide is convert into secondary alcohol then in intermediate step they form carbocation which is neutral in nature so S_N2 rxn is an example of racemisation rxn.

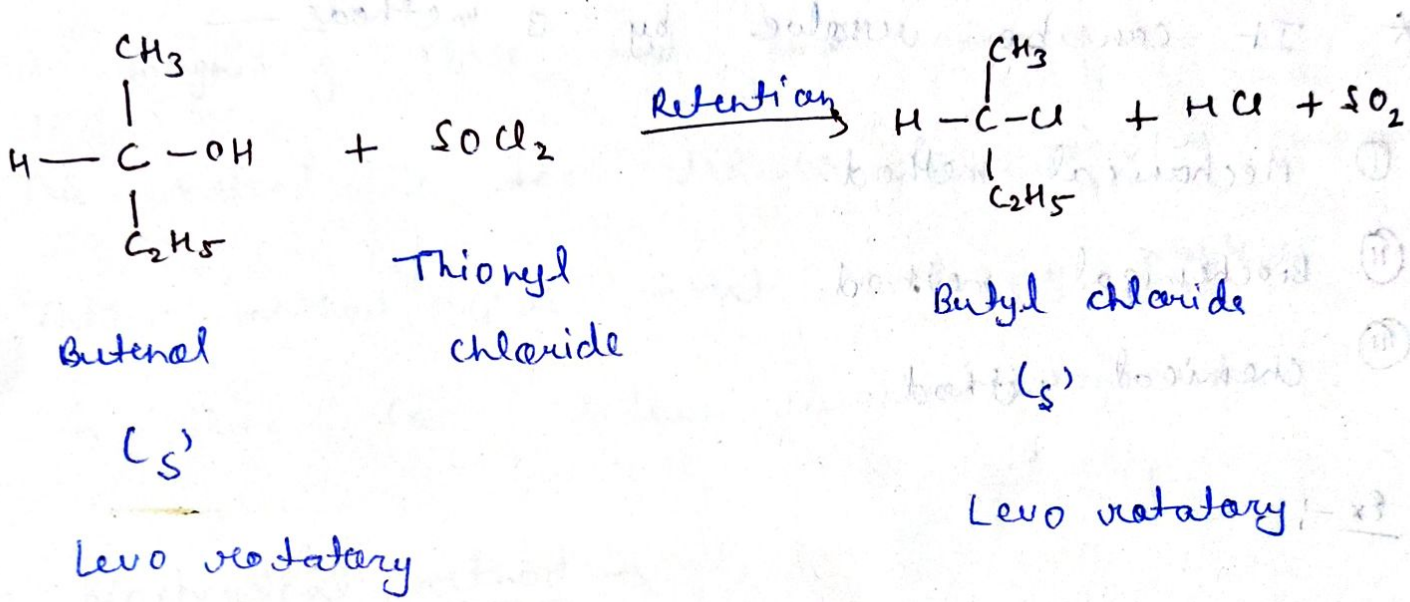


3 → Retention rxn →

A few reaction at chiral carbon atom gives product that have the same configuration as the starting material this rxn is called retention rxn.

* For example butanol which is ~~dextro~~ levo rotatory after reaction with thionyl

chloride it form butyl chloride which is also levo rotatory. so it is the example of retention rxn.



Resolution of recemic modification

* The separation of a recemic modification into it's constituents enentiomer is k/as resolution.

* Meso compounds are optically inactive and the method by which we convert the optically inactive compound into optically active compound by change in the

orientation of one atom or group at one chiral centre is called resolution of racemic modification.

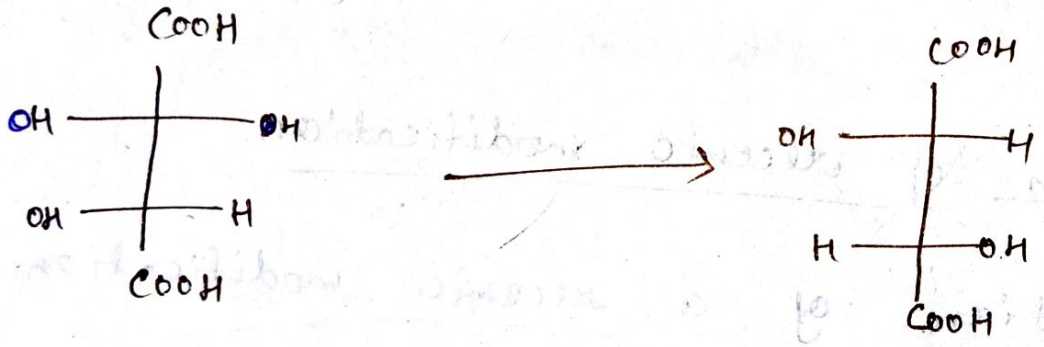
* It can be resolve by 3 methods —

(i) Mechanical method.

(ii) Biochemical method.

(iii) Chemical method.

Ex -;



Tartric acid

Meso compound

(opticaly inactive)

Non meso

opticaly active.

1- Mechanical method →

Some enentiomeric compounds form left handed and right handed crystals which allow their separation by hand using a magnifing class and small forces.

* This method is too tedious for practical purpose.

This method was first used by pasture in 1848 for sodium ammonium tartarate.

2- Biochemical method →

when certain bacteria are allow to grow in a solⁿ of recemic modification, they destroy one enentiomer selectively from the other.

Ex-: Penicillium can be used to remove D-ammonium tartrate from the mixture of recemic ammonium tartrate.

3- chemical method →

This is the best method of resolution and was introduced pasture in

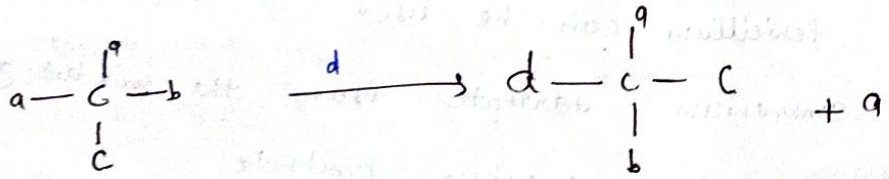
1858.

* In this method a racemic modification is converted into a mixture of diastereomer of another compound.

Ex → Acid - base rxn are often used for resolution of racemic ~~acid~~ alkaloids like quinine, morphine, strychnine.

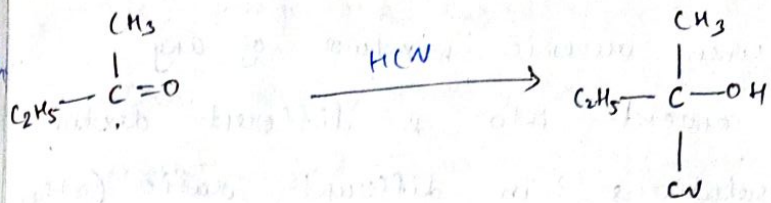
Asymmetric synthesis

The conversion of achiral molecule or symmetric molecule into chiral or asymmetric molecule by chemical rxn is called asymmetric synthesis.



chiral achiral

Glucose (dl) 50% D 50% L → Glucose D - 80% + glucose L 20%
D - 40% L 60%



Achiral chiral

* In a racemic mixture the dextro and levo compounds are present in equimolar ratio so they are optically inert.

* By the asymmetric synthesis racemic mixture change into dextro or levo rotatory compound. By changing the ratio of dextro and levo compound.

Types of asymmetrical synthesis

It is of 2 types —

① - Partial asymmetric synthesis.

② - Absolute asymmetric synthesis

① - Partial →

when racemic mixture of any compound is convert into 2 different dextro and levo solutions in different ratio (other than 50-50) then it is called partial asymmetrical synthesis.

* The ratio of D and L solution will never be same but both of them are present in the mixture.

Glucose (±) (dl) racemic $\xrightarrow{A.S.}$ D Glucose (+) 70% + L Glucose (−) 30%

Asymmetric

② - Absolute →

When racemic mixture of any compound is completely convert into any one either dextro or levo 100%. then it is called absolute asymmetrical synthesis.

* This phenomena needs high amount of energy. After this process only one type of salt is present and other is completely disappear.

Glucose	$\xrightarrow{A.S.}$	D Glucose	+ L Glucose
(±)		(+)	(−1)
(dl)		100 %	0%
(Racemic)			