

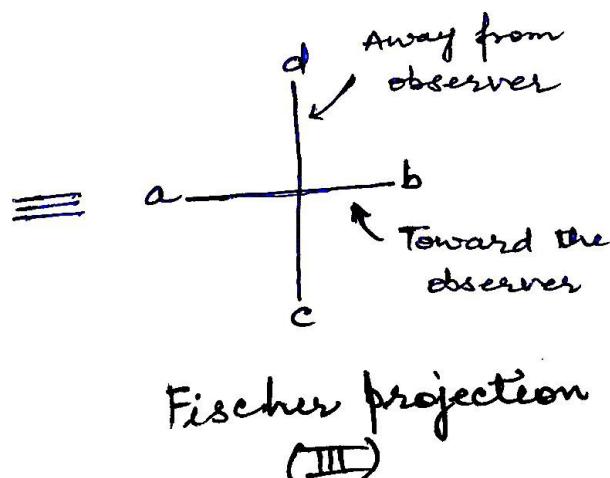
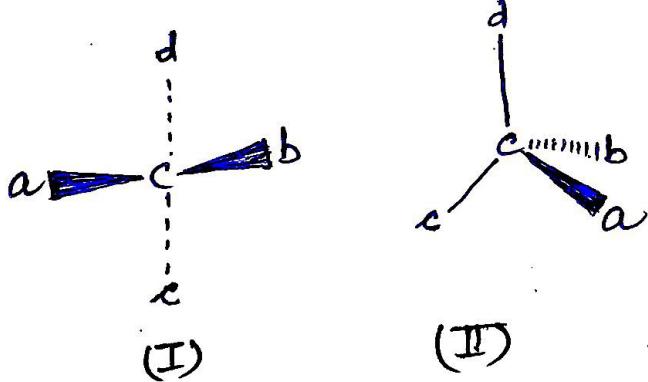
## Representation of three-dimensional molecules

Various methods have been developed for the two-dimensional representation of three-dimensional structures.

### (i) The Flying-Wedge Representation.

One of the most commonly used model is the flying-wedge representation (I & II).

- \* A solid wedge (or a thick line) represents a bond projecting above the plane of the paper (i.e. a bond pointing towards the observer) and
- \* A broken wedge (or a dashed line) a bond below the plane (i.e. a bond pointing away from the observer).
- \* Continuous lines (solid lines) are bonds in the plane of the paper.



### (ii) The Fischer Projection

In Fischer projection, all bonds are drawn as solid lines. The horizontal bonds point towards the observer and vertical bonds point away from the observer. The central tetrahedron

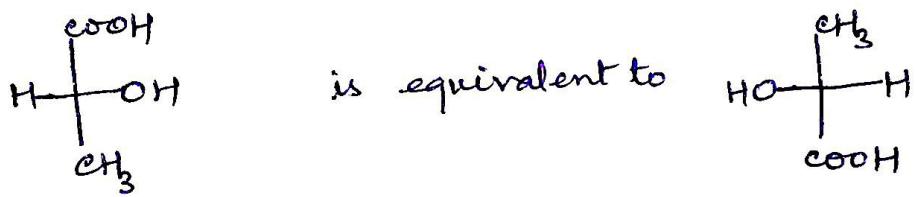
Carbon is omitted.

Usually, the projection is drawn so that the longest carbon chain in the molecule is vertical with the highly oxidized function at the top.

The Fischer projection formula of any compound containing more than one stereocentre is least stable fully eclipsed conformation of the molecule.

### Manipulation of projection formula

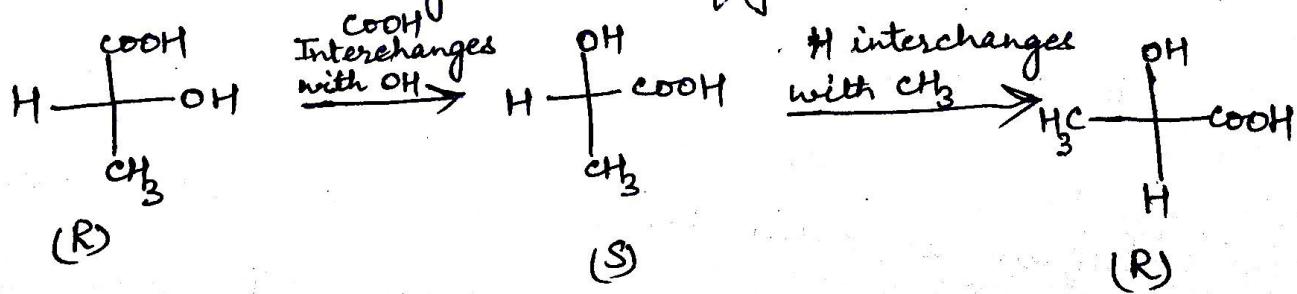
(i) Fischer projection may be rotated  $180^\circ$  in the plane of the paper.



(ii) Any odd number of interchanges of the ligands at one chiral centre inverts the configuration.

(iii)  $90^\circ$  rotation of the projection formula about the chiral centre inverts the configuration.

(iv) Any even number of interchanges of ligands at one chiral centre does not change the configuration.

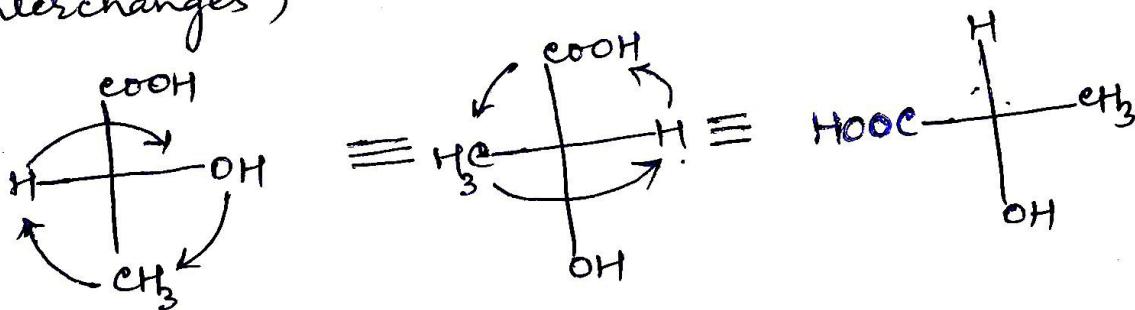


⑤ It is not permitted to lift projection formulae out of the plane of the paper and flip them over or view them from the opposite side of the paper



⑥ Fischer projections can be manipulated by rotating a group of any three ligands in a clockwise or anticlockwise direction; the fourth ligand does not change its position.

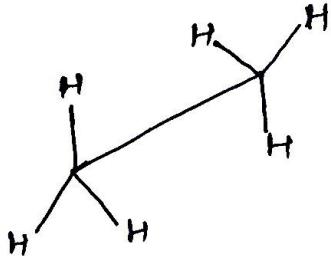
(This manipulation is equivalent to two interchanges)



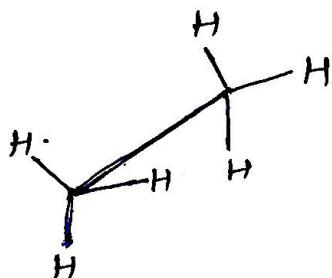
### The sawhorse (perspective) formula

The sawhorse formula indicates the spatial arrangement of all the ligands on two adjacent atoms. The bond between the adjacent carbon atoms is represented by a diagonal line, usually from lower left to upper right. The left hand bottom end represents the atom nearest to the observer and the right hand top end represents

the atom that is farther away. Two of the remaining bonds to the two atoms are drawn vertically (one at each atom) and the other four at  $+120^\circ$  or  $-120^\circ$  angles to these two as shown below:-



Staggered conformation of ethane



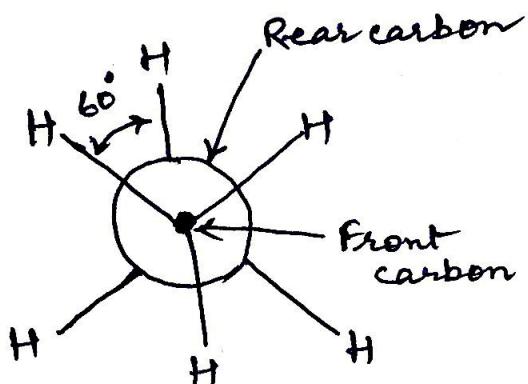
Eclipsed conformation of ethane

### Newman Projection

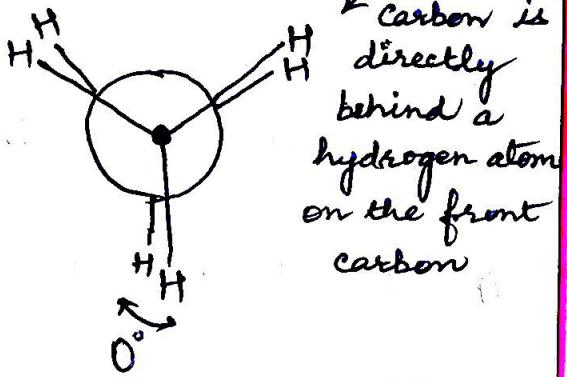
Just as the Fischer projection is a planar projection of the flying-wedge formula, the Newman projection is a planar projection of the saw-horse formula.

Similar to saw-horse projection, Newman projection represents the spatial arrangement of all the ligands on two adjacent atoms. Here a molecule is viewed along the axis of a carbon-carbon bond.

The carbon atom towards the front is represented by a dot and the carbon atom towards the rear side is shown by a circle. The substituents/groups on the carbon atoms are shown as being bonded to the dot or circle.



Staggered conformation  
of ethane



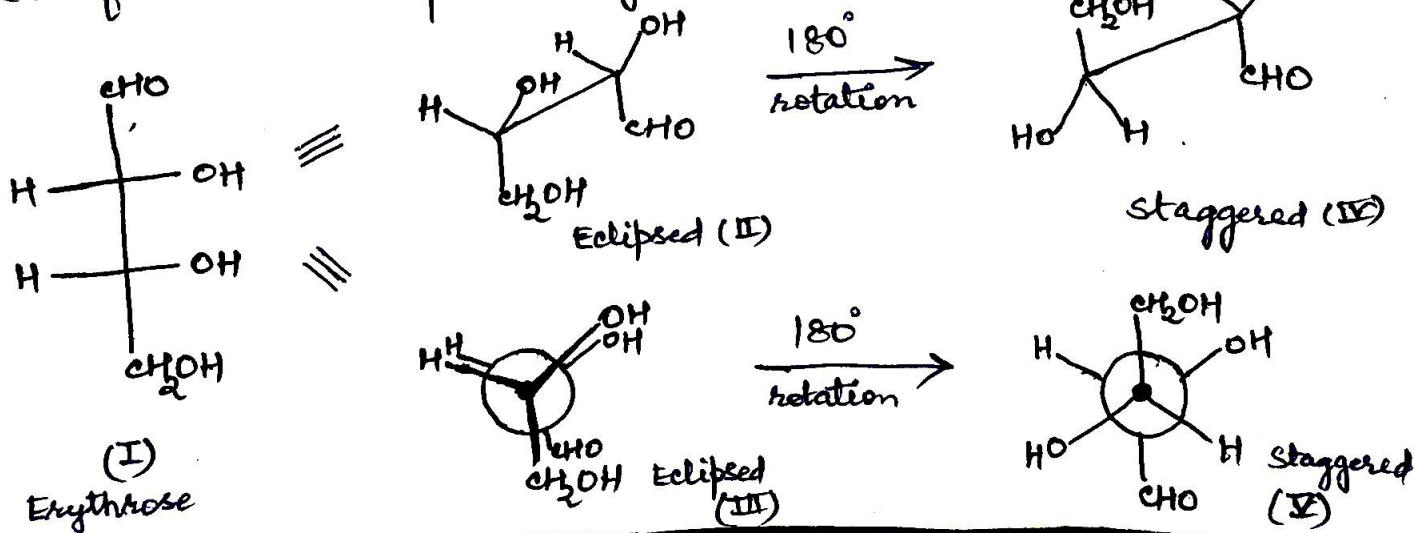
Eclipsed conformation  
of ethane

## Interconversion of Projection and Perspective Formulae

fischer projection can be directly translated  
<sup>(I)</sup> into sawhorse or Newman formula (both eclipsed)  
<sup>(II)</sup> <sup>(III)</sup>

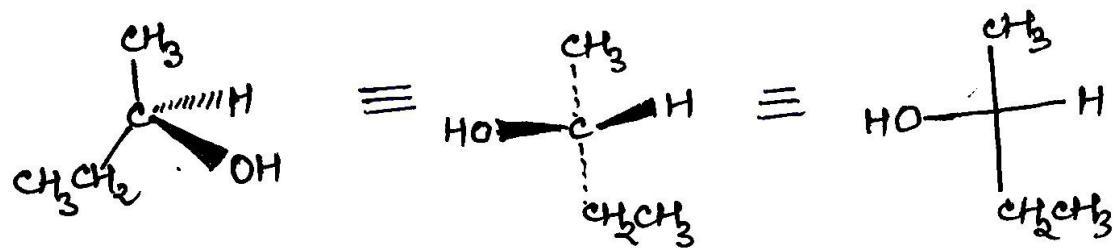
keeping in mind that the fischer projection  
represents eclipsed conformation of the molecule.

The front of the (II) and (III) can be rotated  
 $180^\circ$  about C<sub>2</sub>-C<sub>3</sub> bond with respect to the rear to  
give more stable staggered sawhorse (IV) an Newman  
(V) formulae respectively.

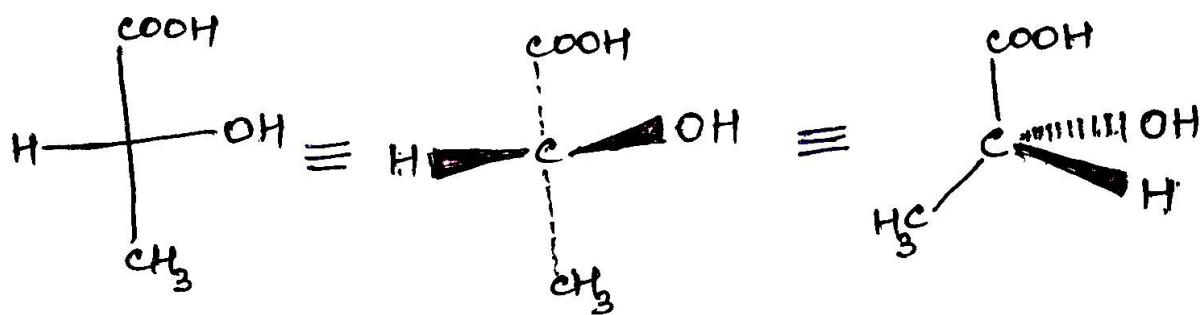


The method of converting the flying-wedge formula to the Fischer projection and vice-versa is shown here with the help of an example:

(R)-2-butanol : Flying wedge  $\rightarrow$  Fischer



(R)-Lactic acid : Fischer  $\rightarrow$  Flying wedge



\* Steps for interconversion

Fischer	$\rightleftharpoons$	Eclipsed Sawhorse or Eclipsed Newman	$\rightleftharpoons$	Staggered Sawhorse or staggered Newman	
		(less stable) generally			(More stable) generally

# Isomerism

## Structural Isomerism

- ✓ Chain Isomerism
- ✓ Positional Isomerism
- ✓ Functional Isomerism
- ✓ Metamerism
- + Tautomerism
- + Ring-chain Isomerism

## Stereoisomerism

### Geometric

(Isomers differ in their spatial arrangement about a double bond)

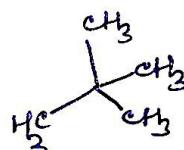
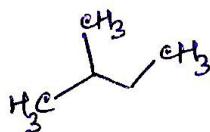
### Optical

(Isomers differ in the arrangement of atoms in 3D space creating mirror images)

## Structural Isomerism

① Chain Isom<sup>n</sup>: It occurs when carbon atoms are linked to the main chain in different ways.

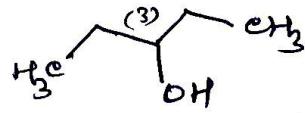
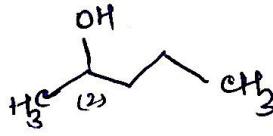
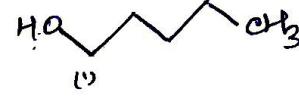
(C<sub>5</sub>H<sub>12</sub>) e.g.



## Position Isomerism

It occurs when functional groups are attached on different positions on a carbon chain.

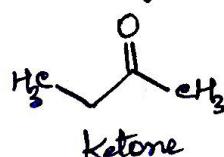
(C<sub>5</sub>H<sub>11</sub>OH) e.g.



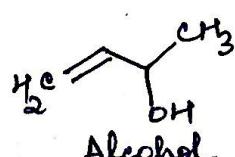
## Functional Isomerism

The compounds are different due to different arrangements of atoms leading to different functional groups.

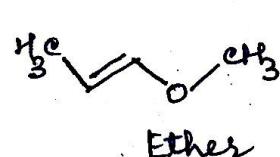
(C<sub>4</sub>H<sub>8</sub>O)



Ketone



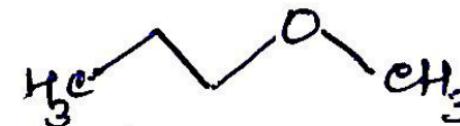
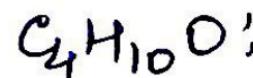
Alcohol



Ether

#### (4) Metamerism

This form of isomerism is rare and is limited to molecules having a divalent atom like O or S and alkyl groups around it. The type of groups present on around the divalent atom differ in this kind of isomerism.



## Geometrical (cis-trans) isomerism:-

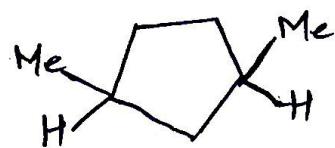
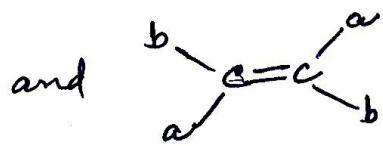
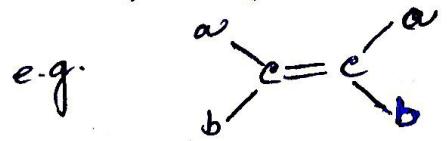
The isomerism which arises due to restricted rotation about a bond in a molecule is known as geometrical or cis-trans isomerism. Geometrical isomers are configurational isomers.

conditions for geometrical isomerism:-

- \* There should be restricted rotation about a bond in the molecule.
- \* Both substituents on each carbon, about which rotation is frozen (restricted) should be different.

Geometrical (cis-trans) isomerism is exhibited by a variety of compounds which may be classified as follows:-

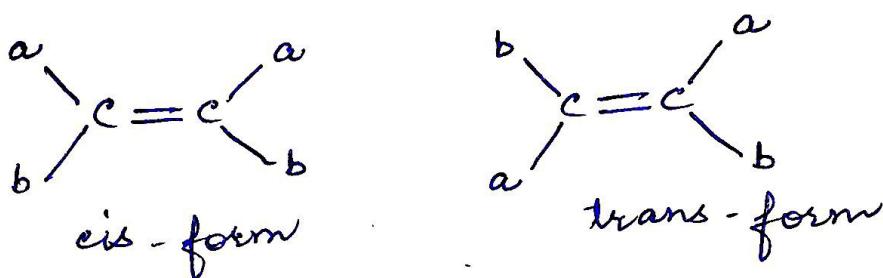
- (i) compounds containing double bond  
 $C=C$ ,  $C=N$ ,  $N=N$
- (ii) compounds containing cyclic structures i.e. ring systems
- (iii) compounds having restricted rotation about a single bond due to steric hindrance; some biphenyls.



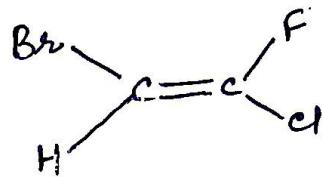
Geometrical isomers are not related as "object and mirror image" hence they are called diastereomers.  
( Stereoisomers which are not mirror images of each other are called diastereomers).

### cis-trans nomenclature

The isomer in which the identical groups are on the same side of the double bond is called 'cis' and the isomer in which the identical groups are on the opposite sides is called trans.



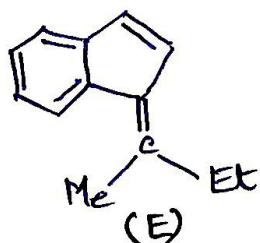
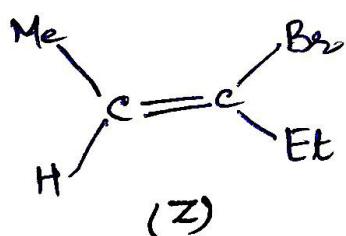
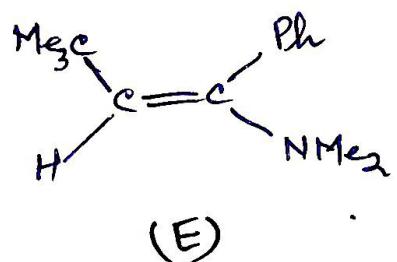
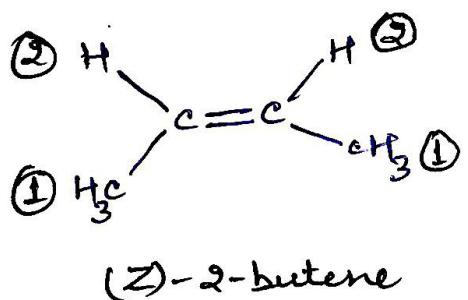
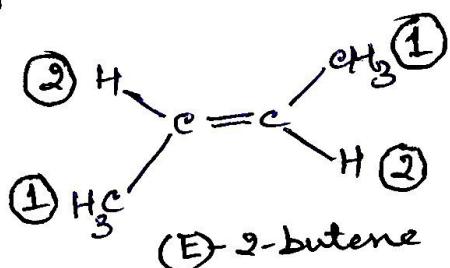
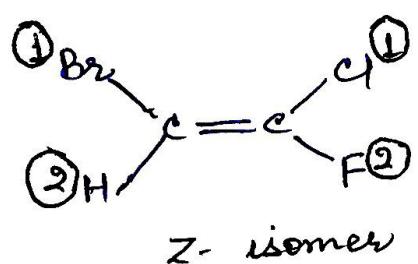
cis-trans nomenclature can be used only in those compounds in which only two or three types of ligands are attached to both the double bonded carbons. When all the four ligands are different, this nomenclature can not be used. e.g.



### E-Z nomenclature

This nomenclature is more general and can be applied to all compounds. It is based on Cahn-Ingold-Prelog system. In this system, the group of highest priority on each carbon atom is

identified by sequence rules (as in R,S nomenclature). If the highest priority groups are on the same side of the double bond, the configuration is Z (German: zusammen = together), and if they are on the opposite sides, the configuration is E (German: entgegen = opposite). for example:-



It should be noted that there is no relation between cis, trans and E,Z configurations, i.e. all the 'cis' compounds may not be Z and all the 'trans' may not be E.