

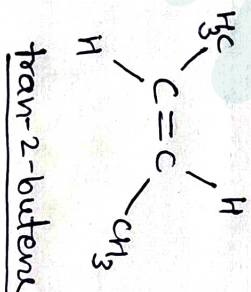
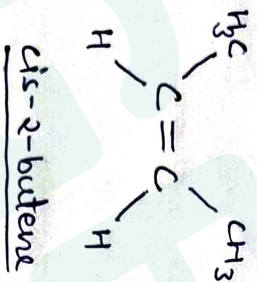
UNIT-2

Geometrical Isomerism

The isomers which are having same structural formula but are differing in spatial arrangement of the groups or atoms around the double bond are called geometrical isomers.

The differing spatial arrangement arises due to restricted rotation about the double bond, or single bond in cyclic compounds.

For example,



The two forms are not interconvertible due to restricted rotation of double bond. In cis isomer, two methyl groups are arranged on the same side of double bond, while in trans isomer, they are on opposite sides.

Nomenclature of Geometrical Isomers

Following nomenclature systems are used :

- (i) cis and trans nomenclature
- (ii) E and Z nomenclature
- (iii) Syn and Anti nomenclature.

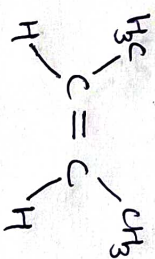
1) Cis-Trans Nomenclature

→ Nomenclature is done on the fact that rotation is restricted about the double bond.

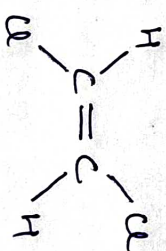
→ Presence of a double bond is mandatory.

cis → atoms/groups on same side of double bond
trans → atoms/groups on opposite side of double bond

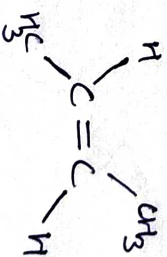
Examples,



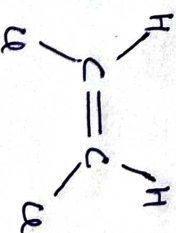
cis-2-butene



trans-1,2-dichloroethane



trans-2-butene



cis-1,2-dichloroethane

2) E and Z nomenclature

- EZ nomenclature is applied on the compounds in which all the four substituents attached to the carbon atoms of double bond are different and do not obey the cis-trans nomenclature.
- EZ nomenclature is applied on all compounds.
- E and Z are derived from two German words, *Eutgegen* and *Zusammen* respectively.

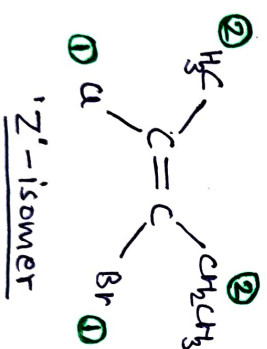
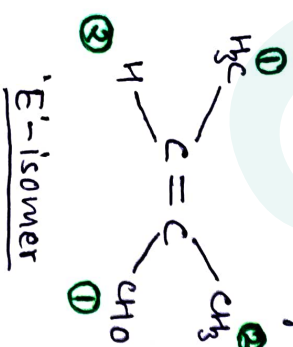
Rules for E and Z nomenclature.

- (1) In this system, the two groups on each carbon atom are assigned as priority number ① and ② on the basis of following rules:

Rule (a) The atom with higher atomic number is given the higher priority.

'E' → If the highest priority group is on opposite side of double bond.

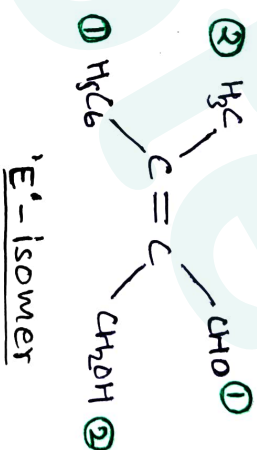
'Z' → highest priority group on same side.



Rule (b) If the two atoms attached to the

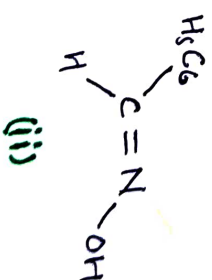
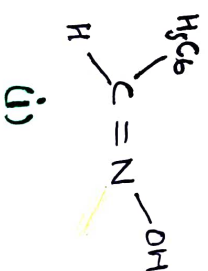
double bond have same atomic number then priority is decided by comparing the next elements in the group.

example,



3) Syn and Anti Nomenclature

This nomenclature is for those compounds which have C=N and N=N double bonds.



- In the first structure, 'C₆H₅' is 'syn' (same side to 'OH'), and 'H' is 'anti' to 'OH' group (opposite side).

→ In second structure, 'C₆H₅' is 'anti' to 'OH' and 'H' is 'syn' to 'H'.

Methods of determination of configuration of geometrical isomers

There are following methods:

- (i) Cyclisation method
- (ii) Conversion method
- (iii) Optical Activity methods
- (iv) Method based on physical properties

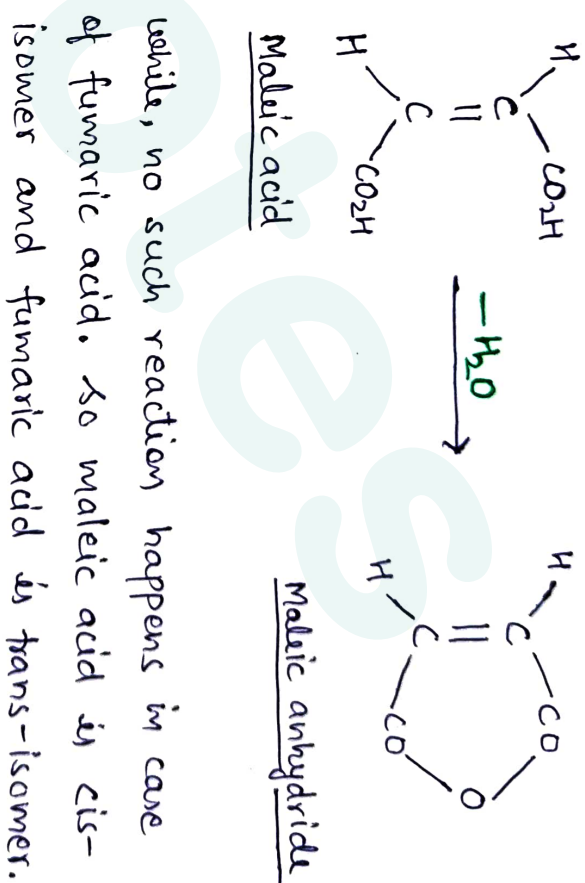
1) Method of cyclisation

→ This method is based on the principle that the intermolecular reaction occur easily when the reacting groups are closed together.

→ A cis-isomer undergoes cyclisation more readily than the trans-isomer.

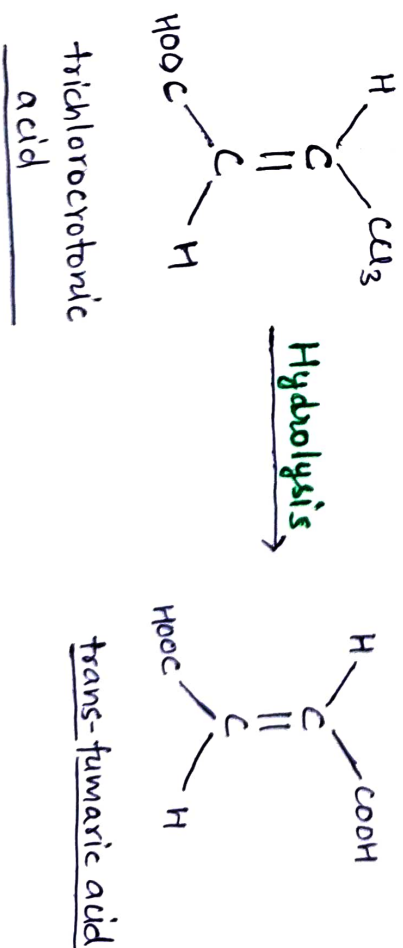
For example,

Malic acid, on heating, gives cyclic anhydride readily, while fumaric acid does not.



2) Conversion method

The configuration of geometrical isomers is determined by converting them into compounds whose configuration is already known.



→ In the above reaction, one isomeric form of trichlorocrotonic acid is converted into fumaric acid on hydrolysis. So, this isomeric form of trichlorocrotonic acid is trans-isomer because fumaric acid is a trans-isomer.

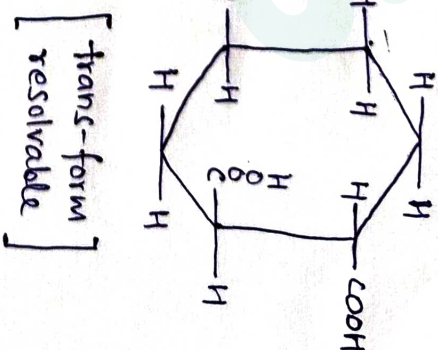
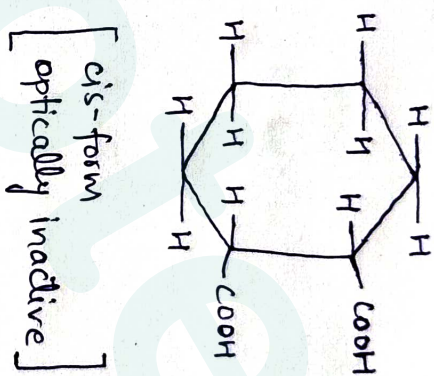
→ The other isomeric form does not give fumaric acid on hydrolysis. So, this will automatically be determined as cis-isomer.

3) Optical Activity

In some pairs of geometrical isomers, one form may show optical activity but the other form may not. In these cases, the configuration is determined by the successful resolution of one form.

For example, there are two hexahydrophthalic acids and the cis-form has a plane of symmetry and thus is optically inactive.

However the trans-form has no elements of symmetry.



4) Method based on physical properties

By comparing the physical properties of geometrical isomers:

- (i) The melting point and intensity of absorption of the trans-isomer is higher than the cis-isomer.
- (ii) The boiling point, solubility, heat of combustion, heat of hydrogenation, density, refractive index, dipole moment and dissociation constant of the trans-isomer are smaller than the cis-isomer.

Conformational Isomerism

→ These are the isomers resulting from different arrangements of atoms in space due to the rotation of groups around C-C single bonds.
→ conformational isomers called conformers or rotamers.

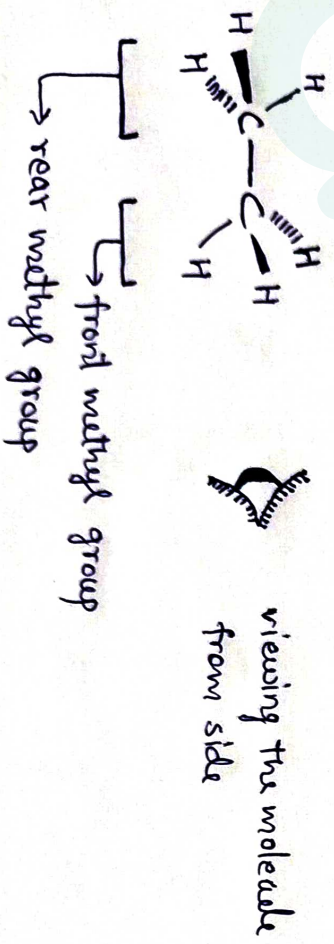
To understand conformers in detail, let's take some examples of Ethane, n-butane, cyclohexane.

Ethane

Before discussing particularly about ethane, let's take some general things:

Newman Projection → Newman projection is a drawing that helps to visualise the 3-dimensional structure of a molecule.

Let's take the example of ethane:

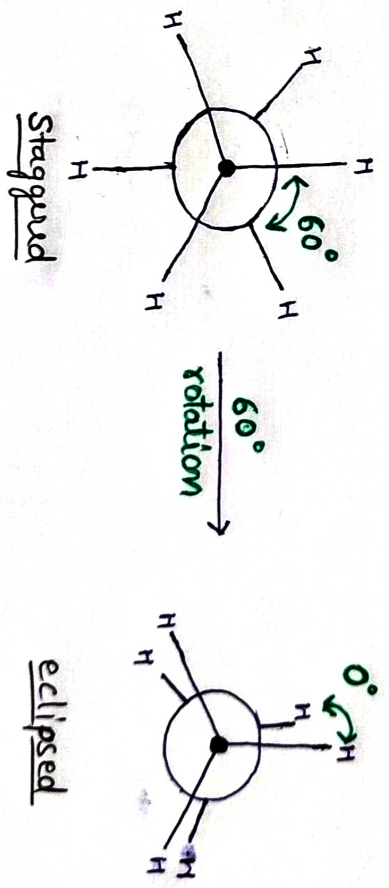


→ the front carbon is represented by the intersection of bonds from it, whereas the rear (back) carbon is represented in the form of circle.



→ Now, the ethane can occur in two conformational structures.

eclipsed form → torsional angle is 0° ,
staggered form → torsional angle is 60° .



During this rotation, energy is used, so, clearly, eclipsed conformation is higher in energy than staggered conformation.

Also, there is repulsion between hydrogen atoms in eclipsed conformation.

That is why, eclipsed is less stable than staggered conformation.

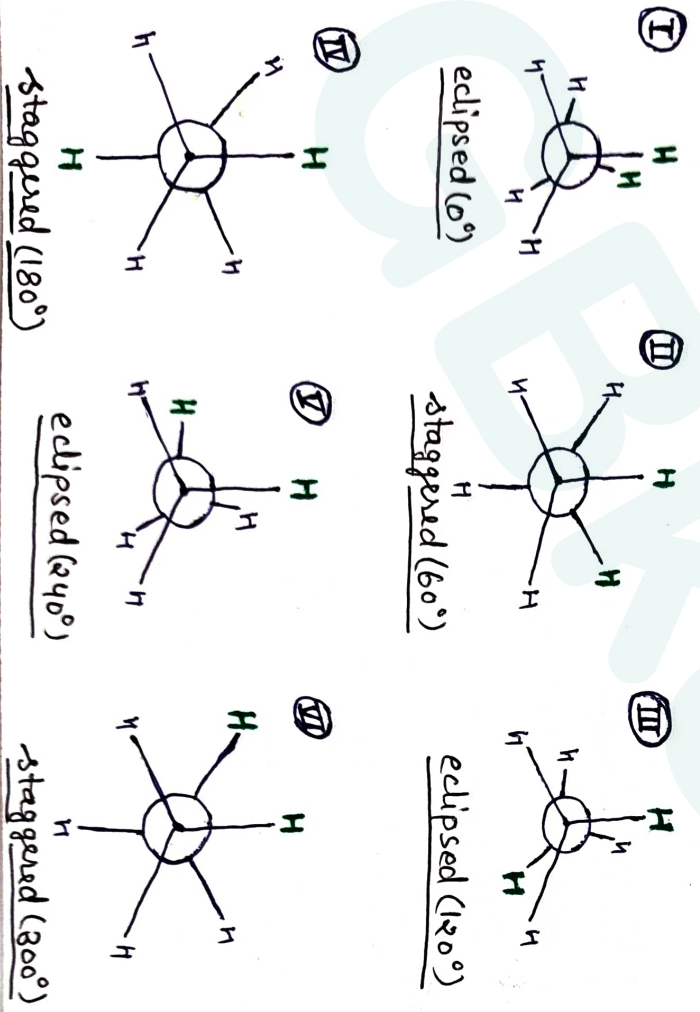
Rotations of ethane

Rotational energy acts as barrier in case of single bond rotation. It has to overcome this barrier to interconvert one conformer to another.

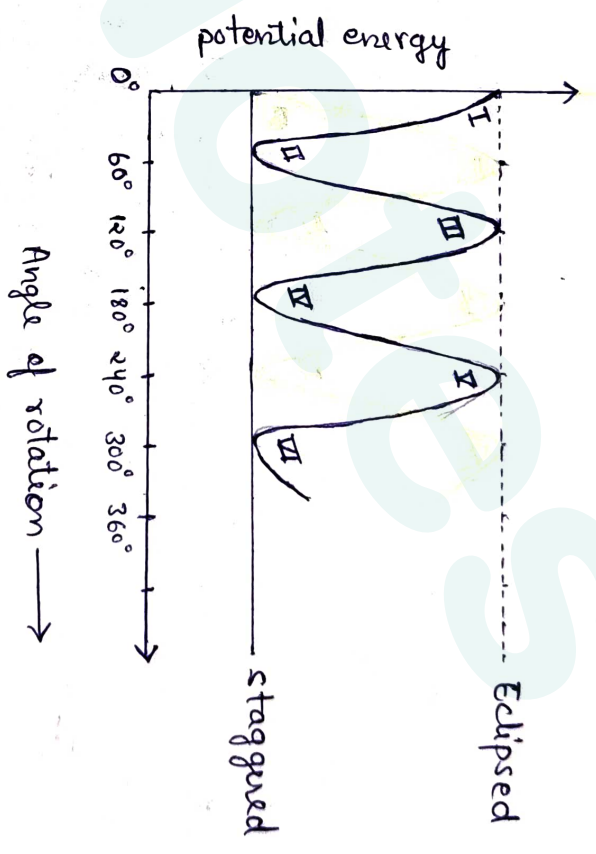
The energy barrier must be small.

Below are the rotations of ethane:

- (i) Torsional angle defined by green hydrogens
- (ii) Rotating the back carbon clockwise.

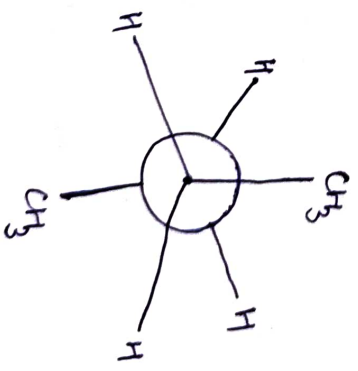
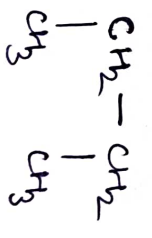


Energy graph of ethane

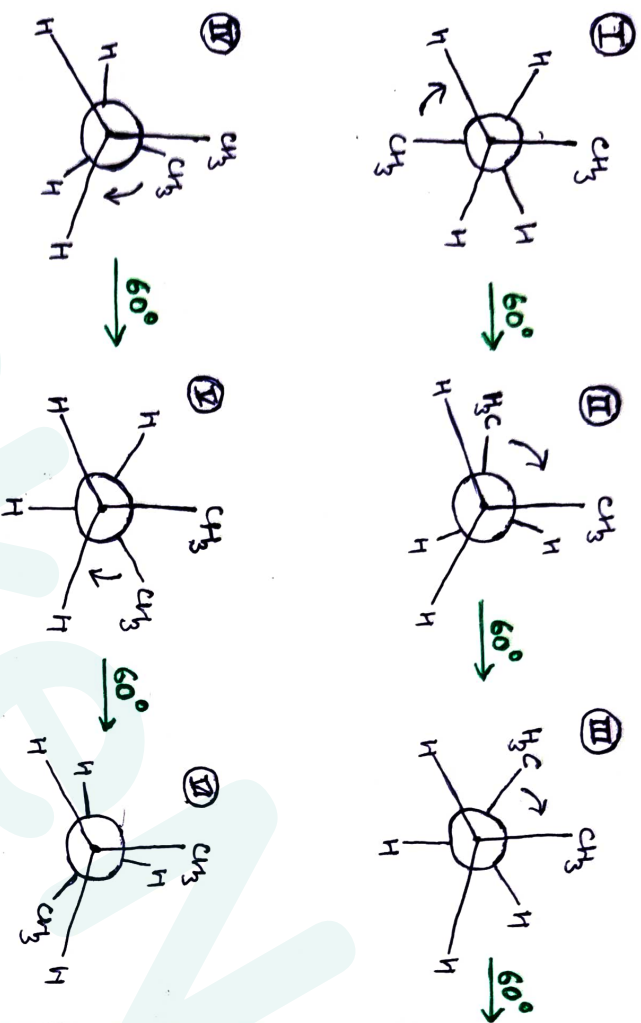


Energy difference = 3 kcal/mole

2) Butane



Rotation of Butane



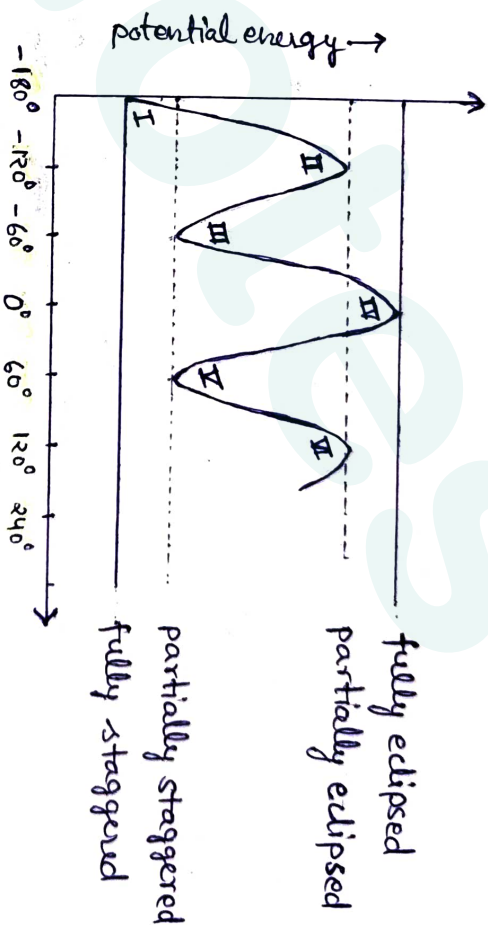
Conformer-I → most stable staggered conformer because methyl groups are at far distance → fully staggered (F.S.)

Conformer-II & III → eclipsed partially (P.E.)

Conformer-IV & V → partially staggered (gauche conformers)

Conformer-VI → fully eclipsed (least stable)

Energy graph of butane

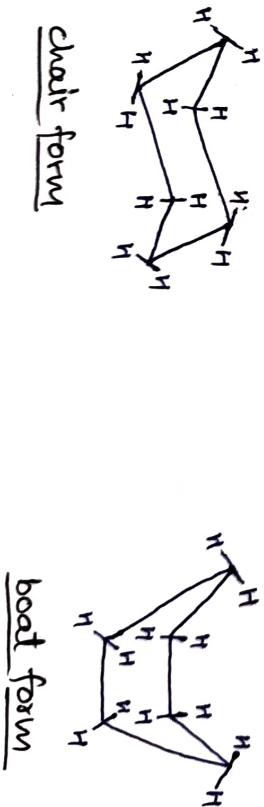


stability order

fully staggered > gauche > eclipsed > fully eclipsed

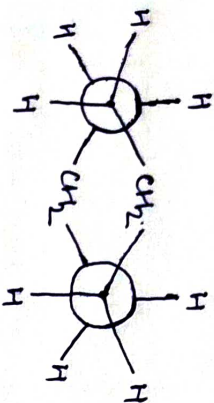
3) Cyclohexane or

cyclohexane shows two forms of conformers,

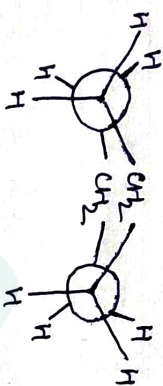


→ chair form is the staggered form of conformer, hence more stable.

→ boat form is eclipsed form, (less stable).



Chair (staggered)

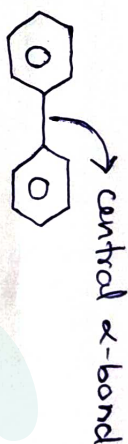


Boat (eclipsed)

Atropisomerism

→ It is a type of isomerism that happens when a single bond cannot rotate due to the presence of a steric hindrance that is caused by the presence of a bulky substituent.

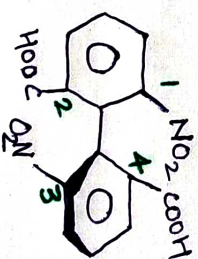
→ Biphenyls are compounds whereby a phenyl ring is connected to another phenyl ring through a central α -bond.



→ In unsubstituted biphenyl, there is sufficient amount of freedom to rotate around the central sigma bond.

→ However, biphenyls with large substituents at ortho positions on both sides of the central α -bond experience restricted rotation along this bond due to steric hindrance.

→ Both phenyl rings lie in different planes which are perpendicular, making the molecules chiral and exhibit enantiomerism.



Conditions for optical activity

→ There should be any atom/functional group at ortho position of rings such as, Cl, Br, COOH, NO₂, SO₃H, etc.

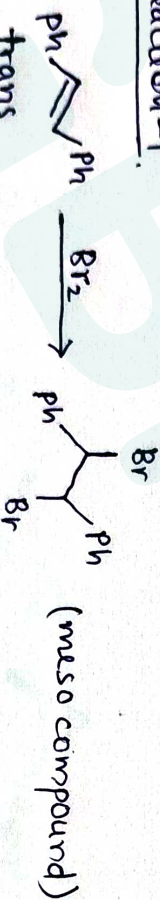
→ Both the rings must be resolvable and for that both ortho positions of a ring cannot be substituted with the same functional group.
 → For atropisomerism, $1 \neq 2$ & $3 \neq 4$.

Stereospecific and Stereoselective Reactions

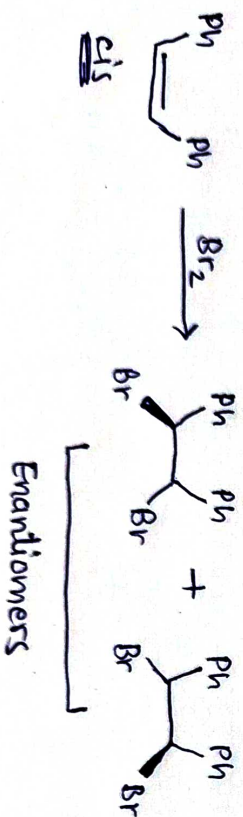
In stereospecific reactions, two diastereomeric forms of a compound react with a substance differently in a way that the products formed in both the conditions are also diastereomers to each other.

For example,

Reaction-1.



Reaction-2.



→ the trans-starting material gives a specific stereoisomer for a product (a meso compound).
 → And the cis-starting material gives a pair of enantiomers.

So, if the reaction is stereospecific and the starting materials (SM_1) are diastereomeric, the products will also be diastereomers.

Stereospecificity:

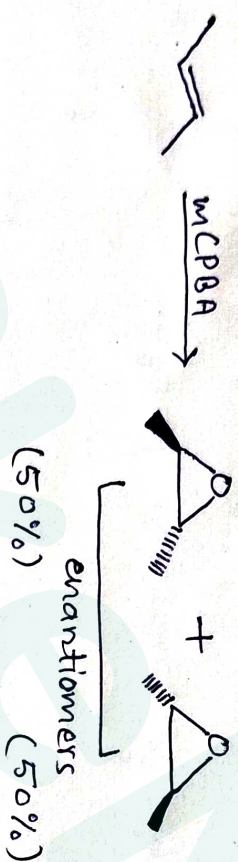


SM_1 and SM_2 are diastereomers of each other. Likewise, Product (1) and Product (2) are also diastereomers of each other.

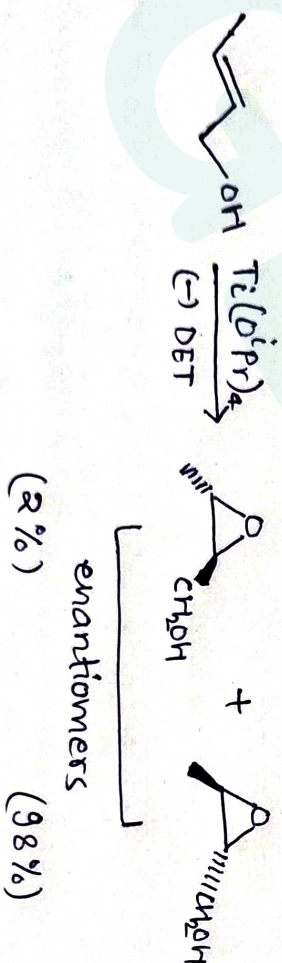
Stereoselective reactions

These are reactions that can give two different stereoisomers but one of those stereoisomers is major and the other one is minor. Lets get it by an example,

Reaction-1: epoxidation



Reaction-2: Sharpless epoxidation



→ The first reaction gives two stereoisomers, those are enantiomers. The first reaction gives no preference to one stereoisomer or the other. So its NOT stereoselective.

→ The second reaction, however is more selective towards one stereoisomer. Thus, we call it stereoselective.