

# UNIT-2

## Stereo Isomerism (Geometrical isomerism)

### Points to be covered in this topic

- ❖ GEOMETRICAL ISOMER
- ❖ NOMENCLATURE OF GEOMETRICAL ISOMERS
- ❖ METHODS OF DETERMINATION OF CONFIGURATION OF GEOMETRICAL ISOMERS
- ❖ CONFORMATIONAL ISOMERISM IN ETHANE, n-BUTANE AND CYCLOHEXANE
- ❖ ATROPISOMERISM
- ❖ STEREOSPECIFIC AND STEREOSELECTIVE REACTIONS

#### 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 termed as **geometrical isomers** and the phenomenon is termed as **geometrical isomerism**.



Maleic acid

Fumaric acid

(cis-butenedioic acid) (trans-butenedioic acid)

- The carbon atoms of the **carbon-carbon double bond** are  **$sp^2$  hybridized**.
- The carbon-carbon double bonds consist of  **$\sigma$  bond and  $\pi$  bond**.
- The **presence of  $\pi$  bond** locks the molecule in **one position**, therefore rotation around the C=C bond is not possible.
- This **restriction of rotation** about the **carbon-carbon double bond** is responsible for **Geometric Isomerism**.

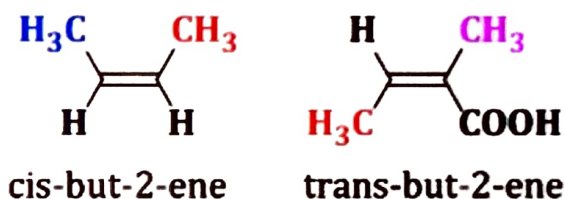
### ✓ Condition for Geometrical isomerism

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

## ☐ NOMENCLATURE SYSTEMS GEOMETRICAL ISOMERS

### ❖ CIS - TRANS SYSTEM

The designation **cis** (Latin word : same side), is used to denote the **presence of like atoms or groups** on the **same side** and **trans** (Latin word, across) is used when they are **on opposite sides**

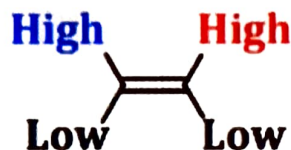


### ✓ COMPARISON OF CIS TRANS ISOMER

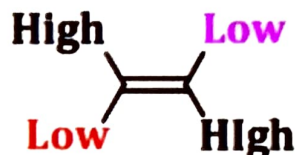
Properties	Cis, trans	Reason
Stability	Trans > cis	Trans have less mutual repulsion between the group
Dipole moment	Cis > trans	Trans have zero dipole moment
Boiling point	Cis > trans	Cis is more polar so BP is more
Melting point	Trans > cis	Trans is symmetrical molecule therefore better packing in crystal, more MP
Polarity	Cis > trans	Cis have more dipole moment so more polar

## ❖ E - Z SYSTEM

- E-Z isomerism is one type of stereoisomerism, which is applicable to **alkenes** and other organic compounds that **contain C=C bonds**.
- If the **two groups which has higher properties** are on the **same side of the double bond** which is described as the (Z) isomer,
- Where (E) isomer **takes place when the two groups with higher properties** are on opposite side of the double bond.



Z - Configuration

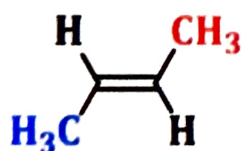


E - Configuration

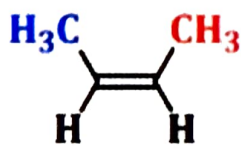
- **The EZ nomenclature is determined by the sequence rule**

According to Cahn-Ingold-Prelog rules:

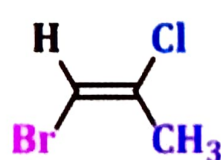
- **Each substituent** on a **double bond** is assigned a **priority**, then the positions of the **higher of the two substituents** on the carbon are **compared to each other**.
- If the **two groups of the higher priority** are on the **opposite sides** of the **double bond**, this bond assigns the E configuration.
- If the **two groups of higher priority** are on the **same side of the double bond** which is assigned as Z configuration.



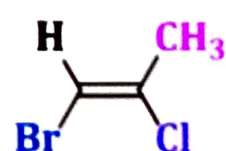
(E)-but-2-ene



(Z)-but-2-ene



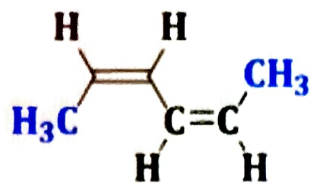
(E)



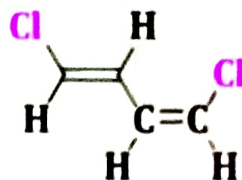
(Z)

## ❖ For molecules with multiple double bonds

- For molecules with **multiple double bonds**, it is necessary to **indicate the alkene location** for each E or Z symbol.



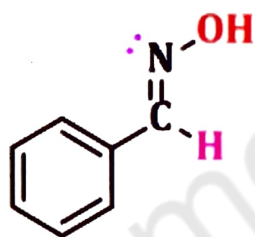
(2Z, 4Z)-2,4-hexadiene



(1E, 3Z)-1,4-dichloro-1,3-butadiene

## ❖ SYN - ANTI SYSTEM

- Syn - anti nomenclature is based upon **two substituents** in an **acyclic molecule**.
- The geometrical isomerism in **oximes** occurs due to **restricted rotation of C = N bond**.
- In **syn-aldoximes**, both the **hydrogen and the hydroxyl group** are on the **same side** of the C=N
- In anti-form, they are on both the **hydrogen and the hydroxyl group** on the **opposite side** of the C=N



syn benzaldoxime



anti benzaldoxime

## ❑ DETERMINATION OF CONFIGURATION OF GEOMETRICAL ISOMERISM

The methods of determination of configuration of geometrical isomerism are classified as:

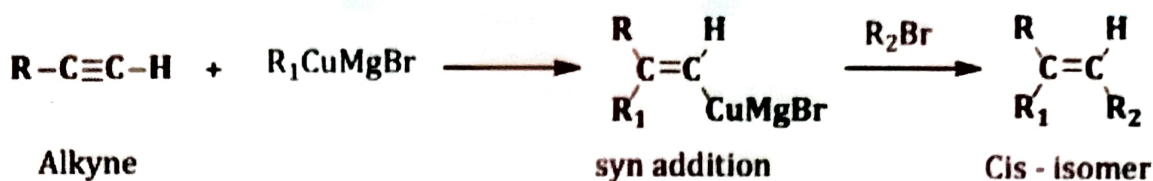
- (I) **Chemical methods**
- (II) **Physical methods**

## ❖ CHEMICAL METHODS

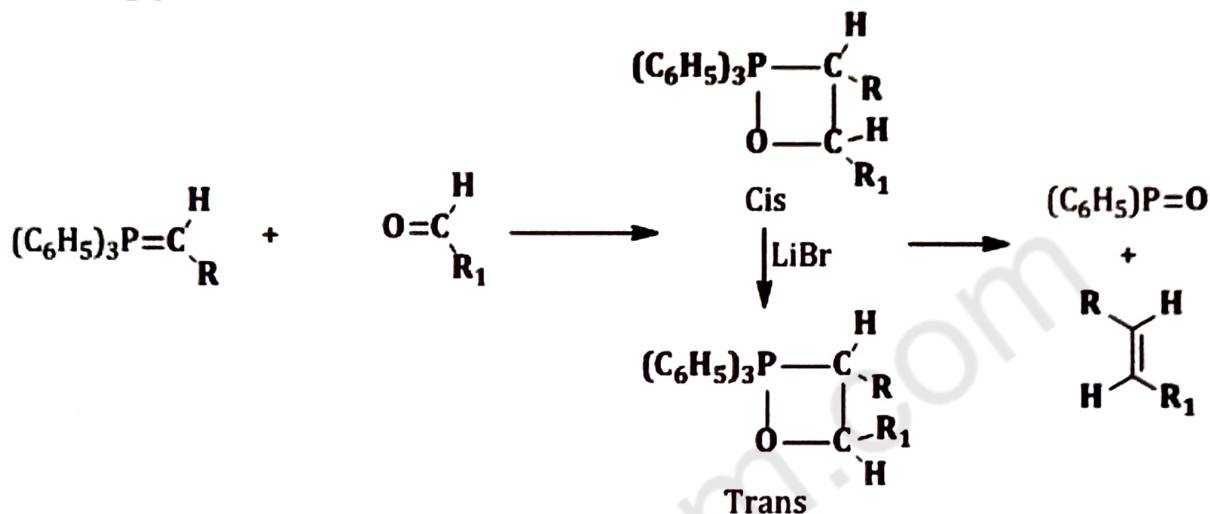
### (a) Absolute method

- (i) Functional groups in a cyclic compound **located cis to each other** can be converted **into cyclic lactones, anhydrides, or amides**. e.g., maleic acid containing **two -COOH groups cis to each other** forms anhydride easily. Hence, it can be identified as **cis-(maleic acid)**.

(ii) Through chemical reaction not affecting the configuration of the double bond



- The stereo selective reaction helps to predict the configuration of the resulting product.



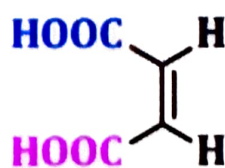
## ❖ PHYSICAL METHODS

### (a) Physical parameter

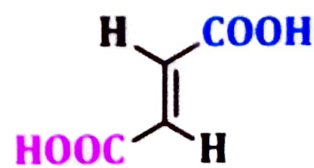
- The parameters like **boiling point, melting point, density, and refractive index** are **not very reliable** for the prediction of the configuration of the isomers.
- Dipole moment is variable for cis and trans isomer**, sometimes **higher for trans** and at **times for cis isomer**.
- Similarly, the **trans isomer** has greater symmetry than **the cis**.
- Therefore, trans has usually a **higher melting point**.

### (b) Acid strength

- The acid strength is strongly dependent on the **configuration of the compound** eg. pKa of cis and trans isomer of crotonic acid are:



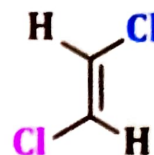
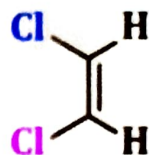
Maleic acid  
(PKa = 4.44)



Fumaric acid  
(PKa = 4.70)

### (c) Infra red and raman spectra

- Cis isomer **shows no IR absorption** but shows **raman absorption** at  $1577\text{ cm}^{-1}$ , while **trans isomer** shows strong **IR absorption** at  $1590\text{ cm}^{-1}$  but shows **no raman absorption**.



### (d) UV-visible Spectra

- Cis isomer has **two bulky groups on the same side**.
- Hence, internally the molecule is **extremely crowded** and thus has less **resonance energy** and is **less stable than trans isomer**

### (e) NMR Spectra

- NMR spectra are also capable of giving information about the **position and configuration of atoms** (environment) in the molecule.
- NMR spectra can **differentiate chemically unlike protons**.

### (f) X-ray and electron diffraction

- Single crystal X-ray diffraction is the **main source of information** on the geometrical structure of the molecules including **bond distances, bond angles, conformations of flexible molecules** as well as **intermolecular contacts**.

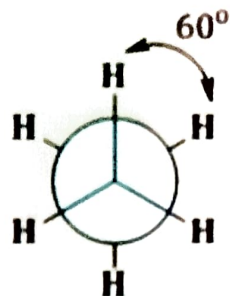
## □ CONFORMATIONAL ISOMERISM IN ETHANE, n-BUTANE AND CYCLOHEXANE

- In alkanes, the **distribution of electrons** in a **sigma molecular orbital** is symmetrical around the **internuclear axis of the C-C bond**.
- Thus, it permits the **possibility of free rotation** about the C-C single bond.
- Due to this rotation, **different spatial arrangements** of carbon atoms in space are observed which **can change into one another**.
- Such **spatial arrangement of carbon and hydrogen** atoms which can be **converted into one another by rotation** around a **C-C single bond** is called **conformation or conformer or rotamer**.

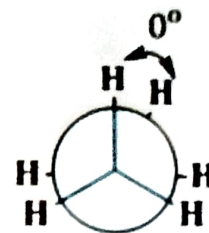
## ❖ CONFORMERS OF ETHANE

(i) Staggered conformation

(ii) Eclipsed conformation



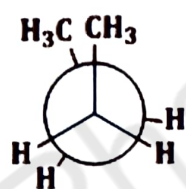
Staggered  
confirmation



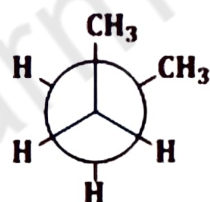
Eclipsed  
confirmation

- Angle between the C - H bonds of **1st and 2nd carbons** is  $60^\circ$ , the **staggered conformation is the most stable** conformation of ethane.
- In **eclipsed form**, the angle is  $0^\circ$  between **two C - H bonds** leading to **repulsion** in their electron cloud which raises the energy and **decreases the stability of the molecule**.
- The **eclipsed conformation of ethane is less stable** than the **staggered conformation**.
- In **eclipsed conformation**, the **bulky substituents of the molecule** are brought **closer leading to repulsion amongst** them.

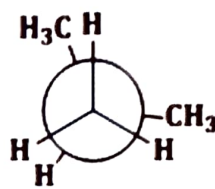
## ❖ CONFORMERS OF n-Butane



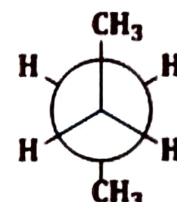
Fully eclipsed  
 $\theta = 0^\circ$



Gauche  
 $\theta = 60^\circ$

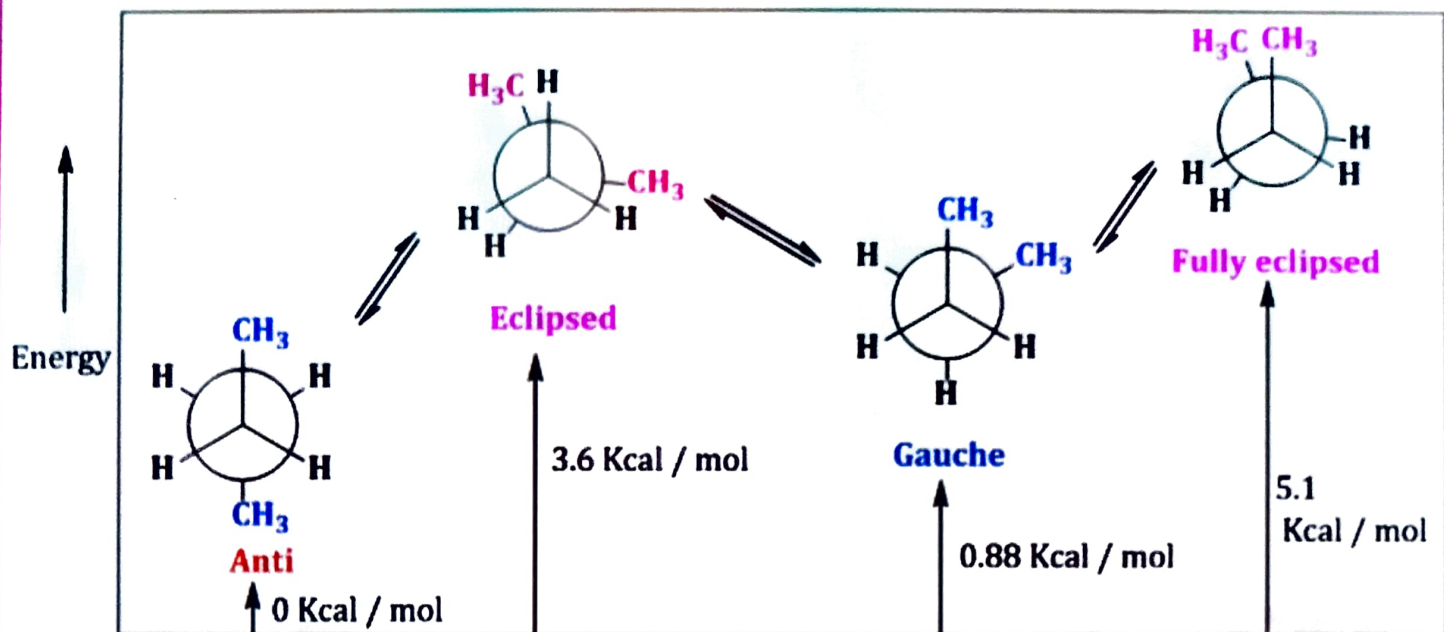


Eclipsed  
 $\theta = 120^\circ$



Anti  
 $\theta = 180^\circ$

- Generally, Butane has four conformation isomers which are **fully eclipsed, gauche, eclipsed, and anti butane** conformational isomers.
- If we rotate the **front methyl group by  $60^\circ$**  or when the dihedral angle is  $60^\circ$  then there is a **formation of gauche or staggered conformation**.
- If we make the **dihedral angle as  $120^\circ$**  then this form of isomer is also known as **eclipsed conformation**
- On rotating the isomer at **an angle of  $180^\circ$**  the **two methyl groups are** found to lie exactly opposite to each other. This conformation is known as **staggered conformation** or anti conformation.



### ❖ CONFORMERS OF Cyclohexane

- In cyclohexane all carbon atoms are  $sp^3$  hybridized with a **bond angle of  $109^\circ$** .
- Cyclohexane molecular formula  $C_6H_{12}$ , consisting of a **ring of six carbon atoms** that is flammable and is considered to be a volatile liquid
- Common cyclohexane conformations such as the **chair form, boat form, twist boat form, and half chair conformations**.



Chair form  
E = 0 KCal / mol

Twisted boat  
E = 5.5 KCal / mol

Boat form  
E = 6.5 KCal / mol

Half chair form  
E = 10 KCal / mol

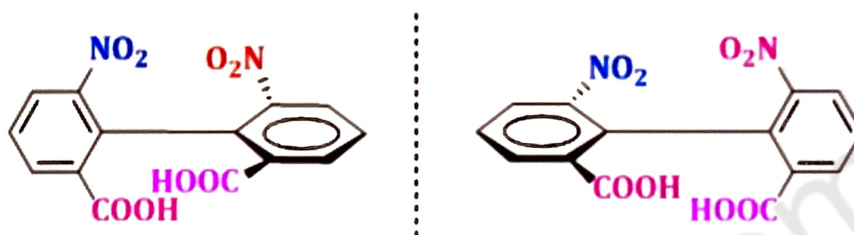
- Stability of Cyclohexane Conformers is: **Half Chair < Boat Form < Twist Boat Form < Chair Form**.

### ❑ ATROPISOMERISM

- **Atropisomerism** is derived from the Greek terms: "**a**" which means "not," and **tropos**, which means "turn."



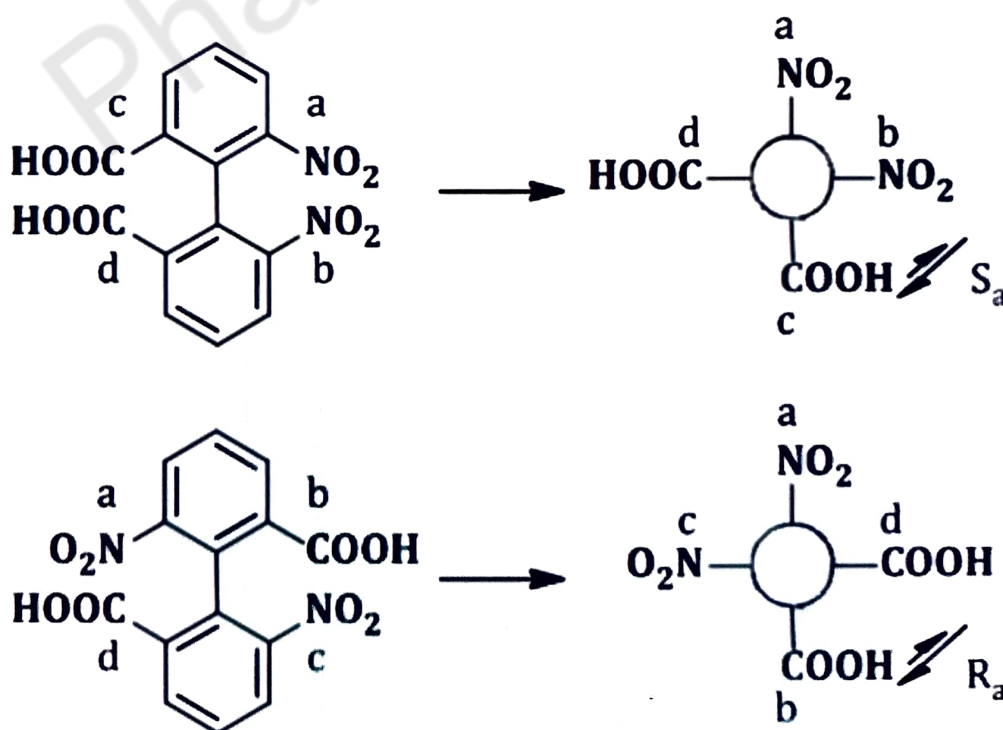
- Atropisomerism is also known as **axial chirality**, and the chirality is an axis rather than a centre or a plane.
- Atropisomers are stereoisomers arising because of **hindered rotation about a single bond**, where energy differences **due to steric strain** or other contributors
- ❖ Two necessary preconditions for axial chirality are:
  - a) A rotationally **stable axis**
  - b) Presence of **different substituents** on **both sides of the axis**



Enantiomers of the 6,6'-dinitrobiphenyl-2,2'-dicarboxylic acid

## Nomenclature

- All **four groups** are ranked with overall **priority given** to the groups on the **front atom of the Newman projection**.
- The **two configurations** are termed as **R<sub>a</sub>** and **S<sub>a</sub>** in analogy to the conventional R/S.



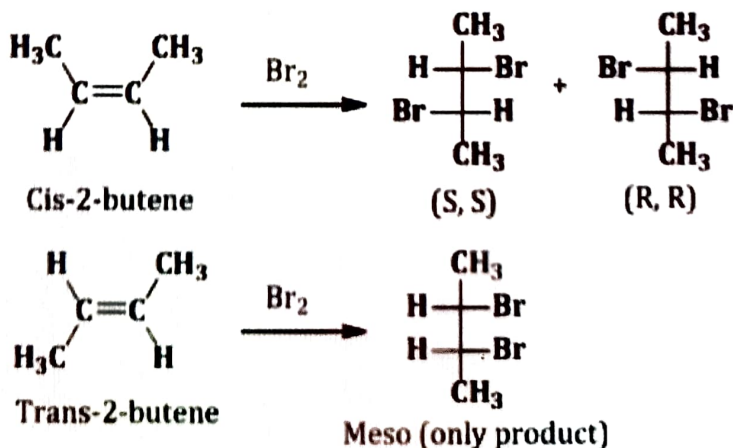
## ❑ CONDITIONS FOR OPTICAL ACTIVITY

- The planes of the **two aryl groups** must be **non-planar**.
- It is achieved by **placing bulky groups** in the **ortho positions**.
- **Ortho substituents increase** the restricted rotation by their steric repulsion.
- **Mono ortho substituted biaryl compounds** do not show atropisomerism at room temperature.
- In addition to **the substituents at ortho position**, the bulky groups adjacent to the **ortho substituents increase stability** and isolatability of atropisomers.
- Heteroaromatic system **provides chirality** even though their ortho substituents are same.

## ❑ STEREOSELECTIVE AND STEREOSPECIFIC REACTION

### ❖ Stereospecific Reactions

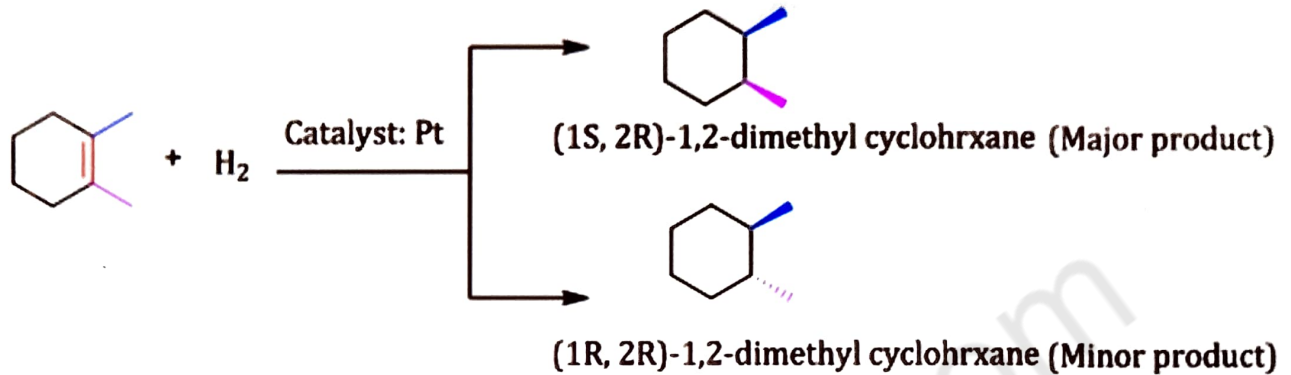
- When the **stereochemistry of the reactant** completely **determines the stereochemistry** of the **product in a stereospecific reaction**, there is no other alternative.
- Only a **single stereoisomer** is produced in a **given reaction rather than a mixture**
- For example, **bromination reaction of 2-butane**, two geometric isomers (cis and trans) of 2-butene gives **three stereoisomeric products** where **cis-2-butene gives (S, S) and (R, R) 2,3-dibromobutane** while **trans-2-butene gives meso-2,3-dibromo butane**.



- ✓ In above case, **bromination of cis-2-butene**, the stereochemistry of products is governed by **cis-2-butene**. Here it is stereospecific reaction

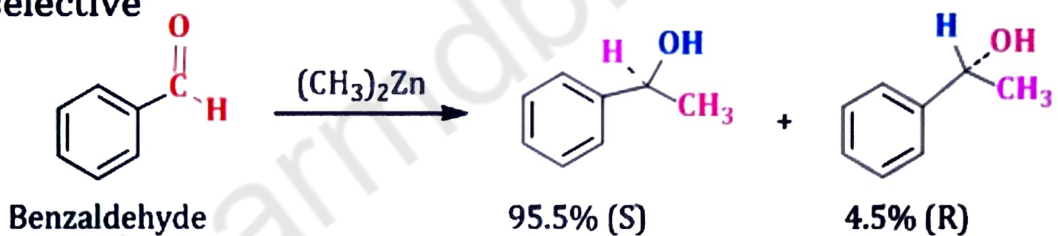
## ❖ Stereoselective Reactions

- Stereoselective reaction is a reaction where **one stereoisomer of a product** is formed **preferentially over another**
- A stereoselective reaction can **produce multiple product**



## ❖ Enantioselective reaction

- Enantioselective reactions **produce only enantiomers** and are therefore stereoselective



## ❖ Diastereoselective reaction

- Diastereoselective reactions **produce only diastereomers**

