



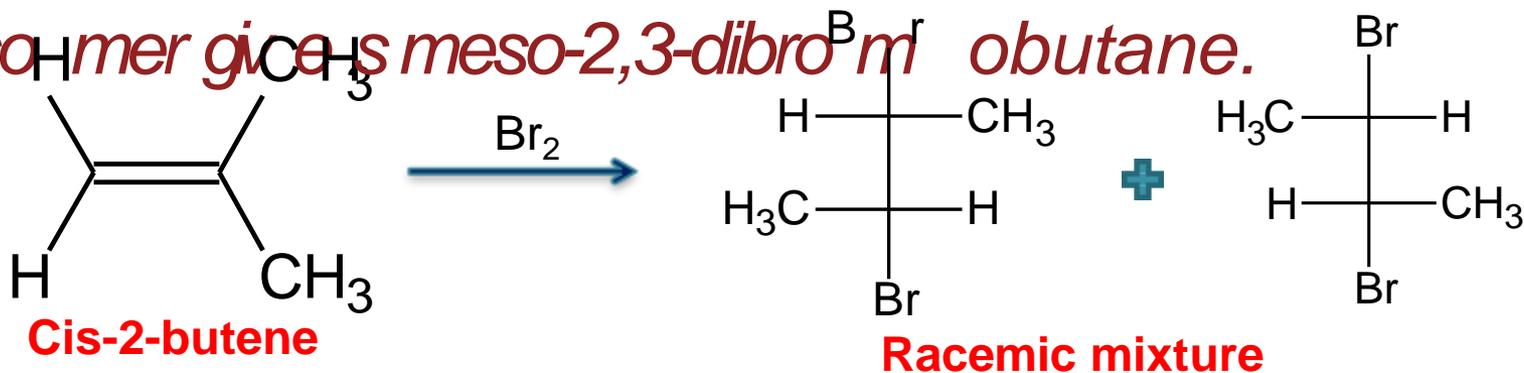
# **Stereospecific and stereoselective reactions**

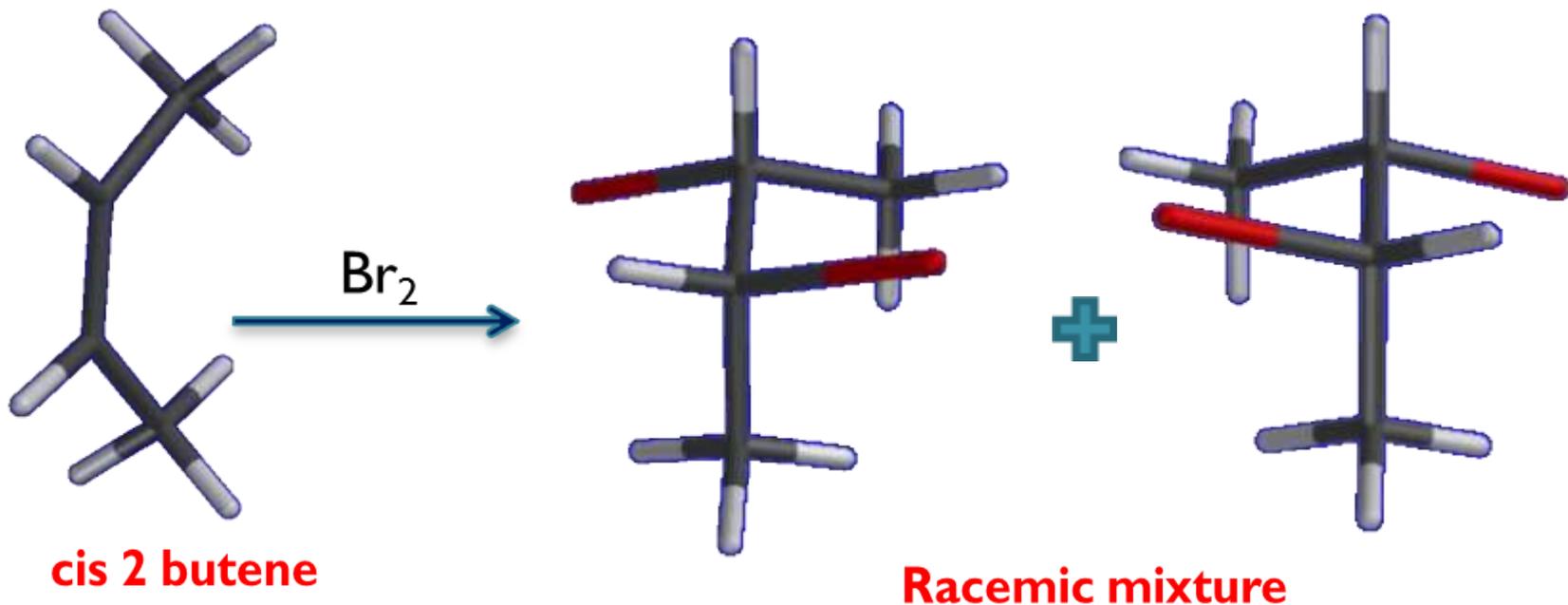
# INTRODUCTION

- **Stereochemistry** is the branch of chemistry concerned with the three-dimensional arrangement of atoms and molecules and the effect of this on physical and chemical properties.
- **Stereospecificity** is the property of a reaction mechanism that leads to different stereoisomeric reaction products from different stereoisomeric reactants.
- A **stereoselective process** is one in which one stereoisomer predominates over another when two or more may be formed.

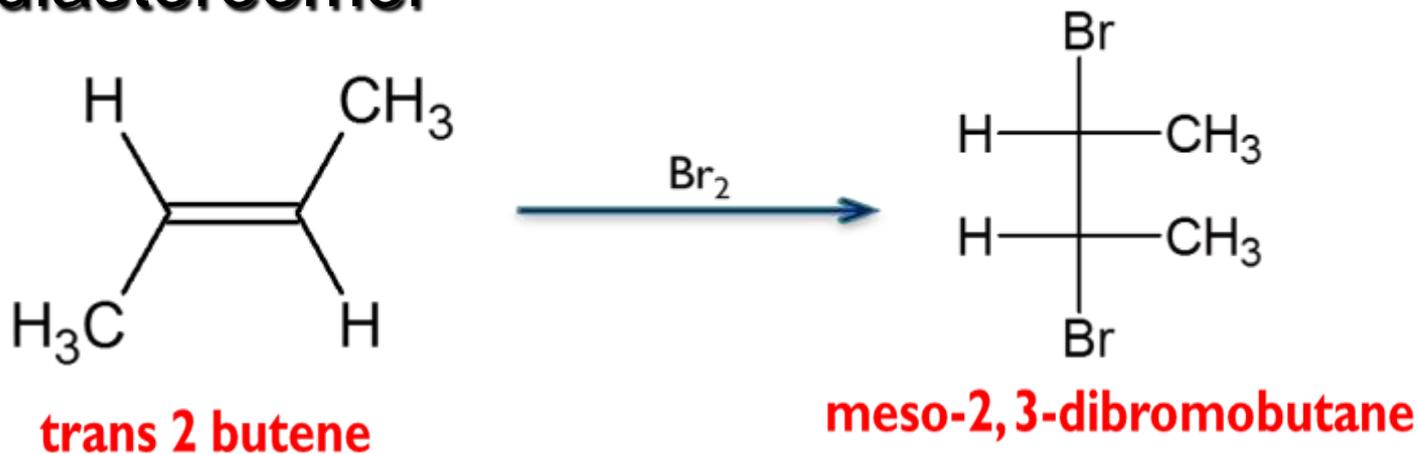
# STEREOSPECIFIC REACTIONS

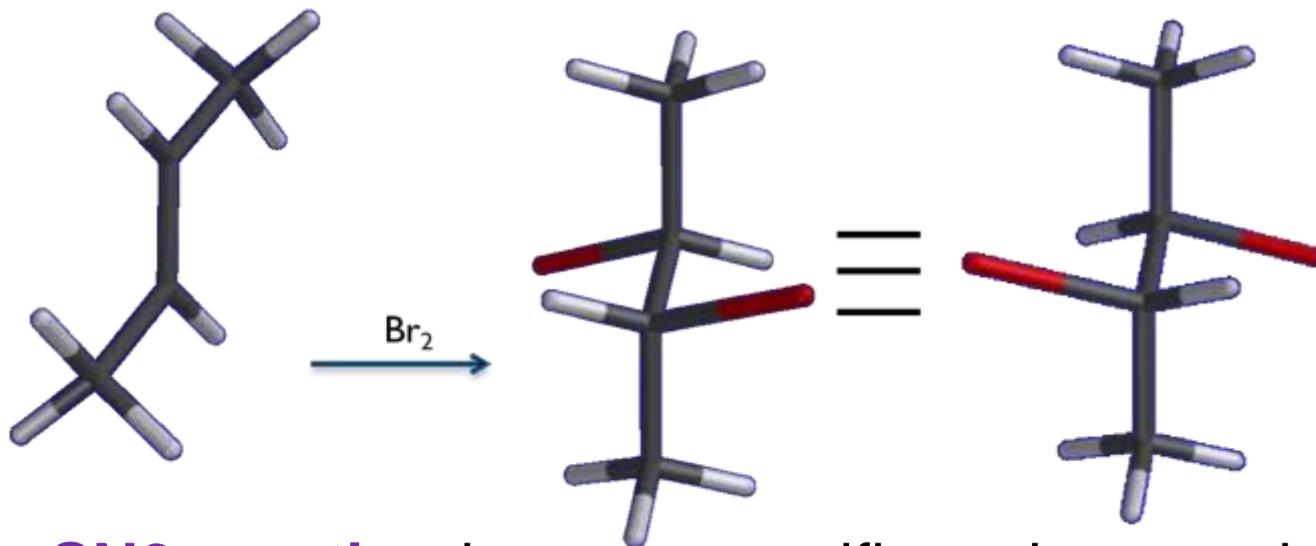
- A reaction in which a particular stereoisomer reacts to give one specific stereoisomer of the product.
- A **stereospecific reaction** gives a different stereoisomer of the product from each stereoisomer of the starting material.
- **For example:** *addition of bromine to cis-2-butene gives racemic 2,3-dibromobutane, while the trans isomer gives meso-2,3-dibromobutane.*





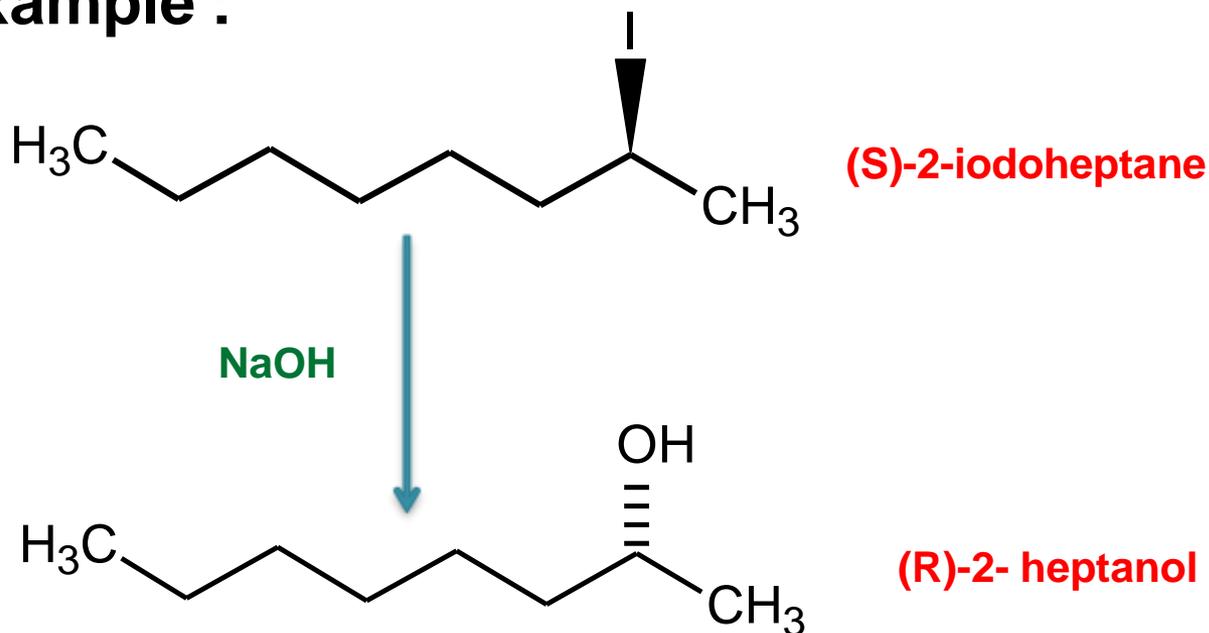
Anti addition to *trans*-2-butene gives meso diastereomer



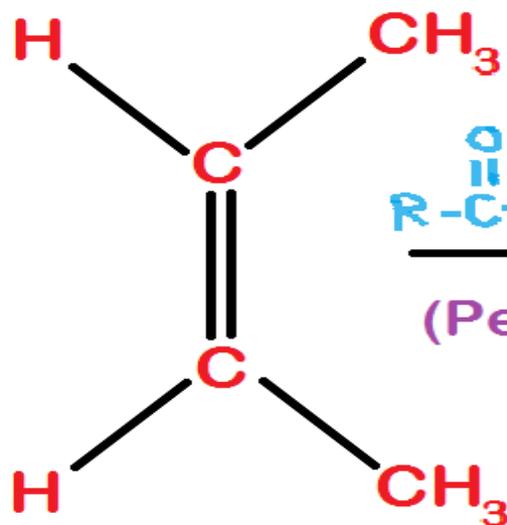
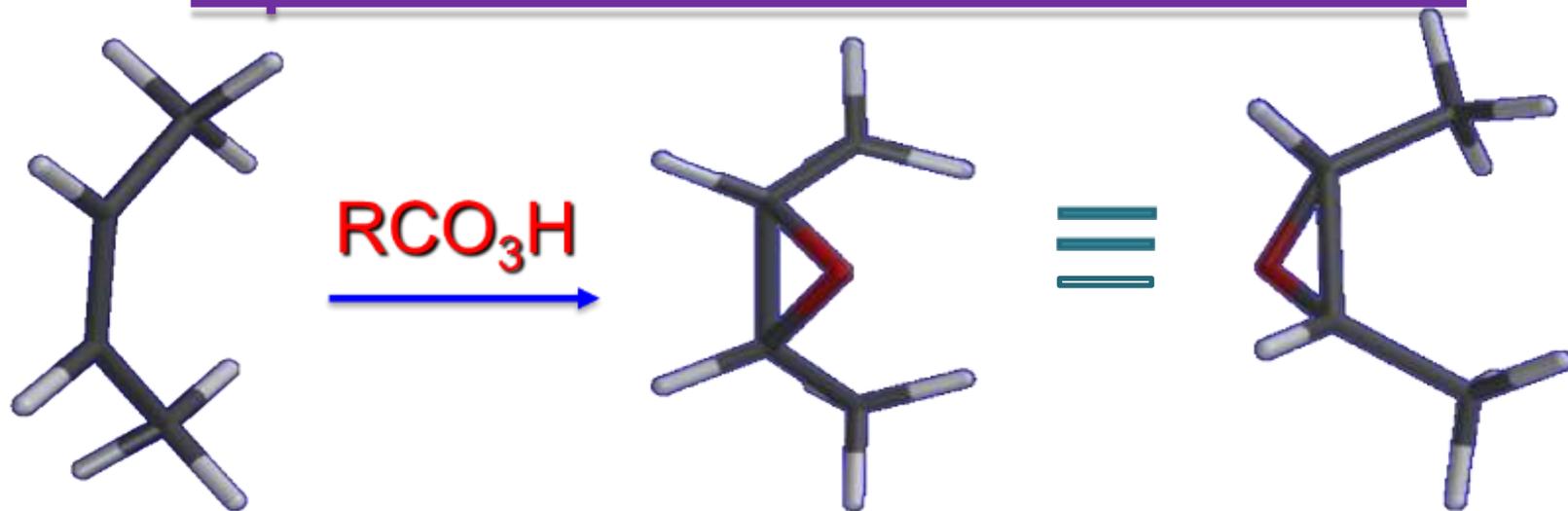


➤ **SN2 reaction** is stereospecific and proceeds with inversion of configuration at a chiral centre,

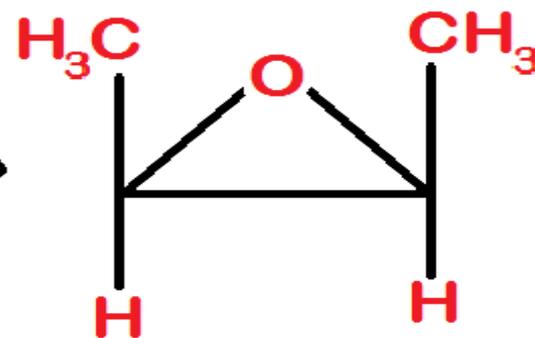
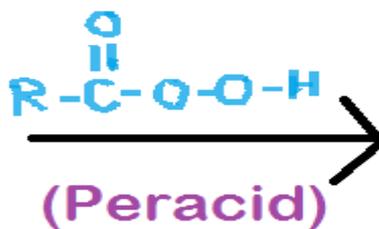
➤ **For example :**



# Epoxidation of cis-2-Butene



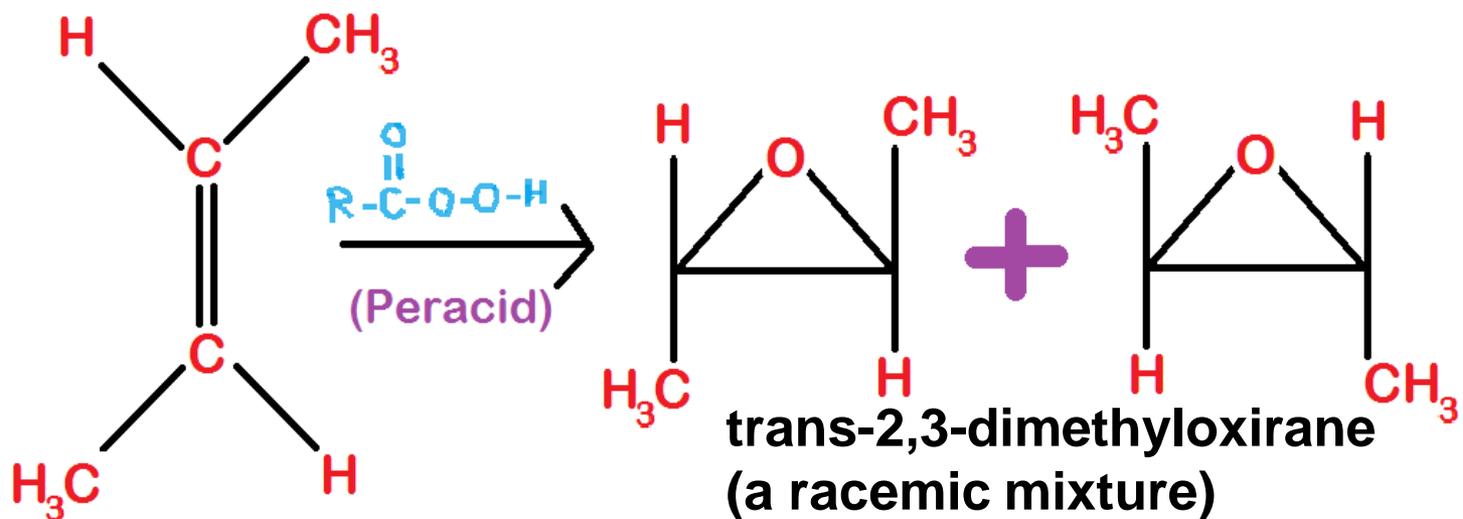
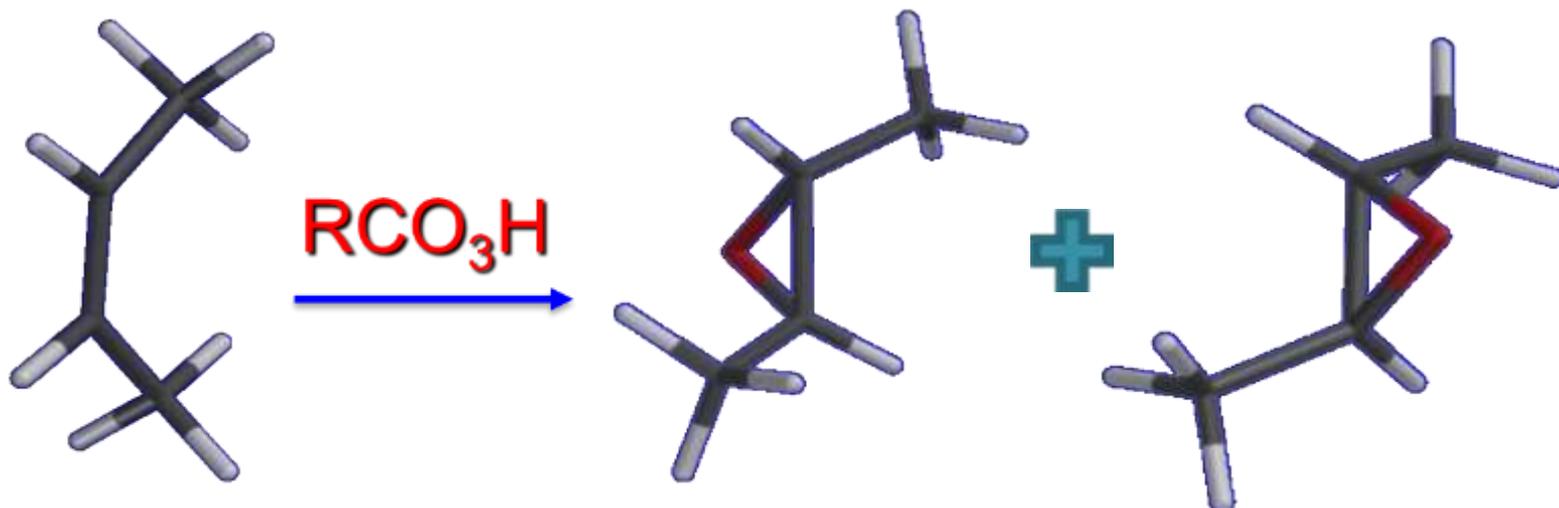
Cis-2-butene



Cis-2,3-dimethyloxirane  
(a meso compound)

syn addition to cis-2-butene gives meso diastereome

# Epoxidation of trans-2-Butene

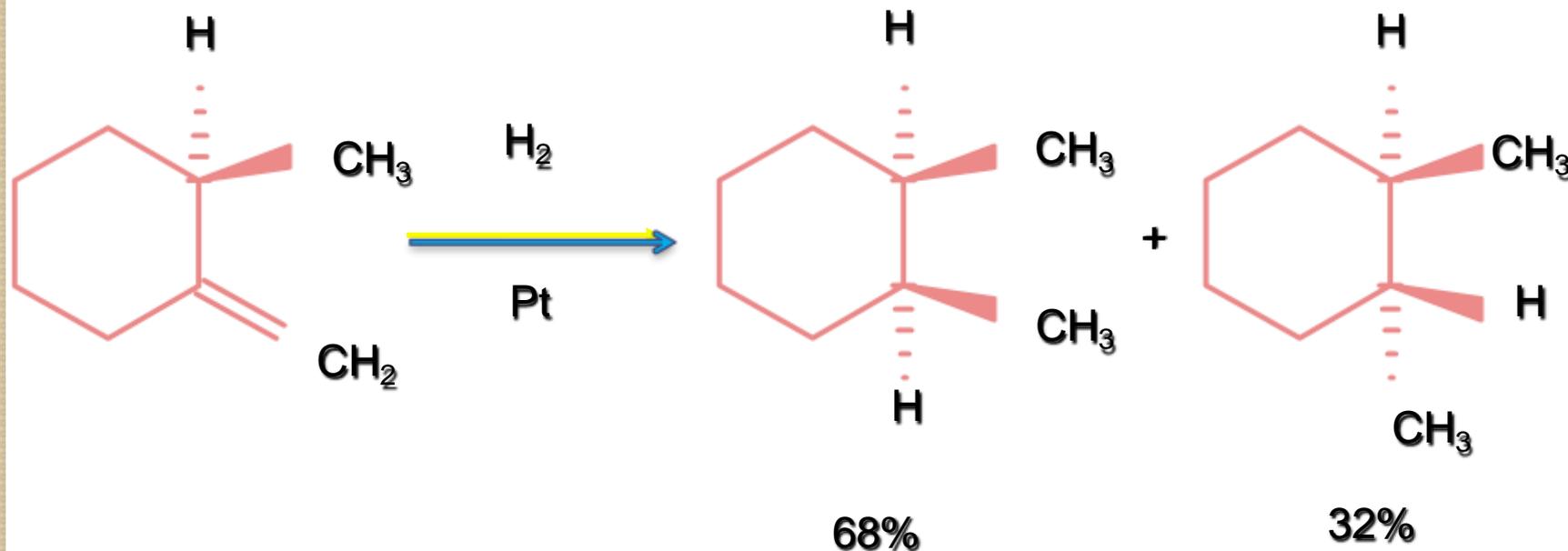


syn addition to *trans*-2-butene gives  
racemic mixture of chiral diastereomer

# STERESELECTIVE REACTION

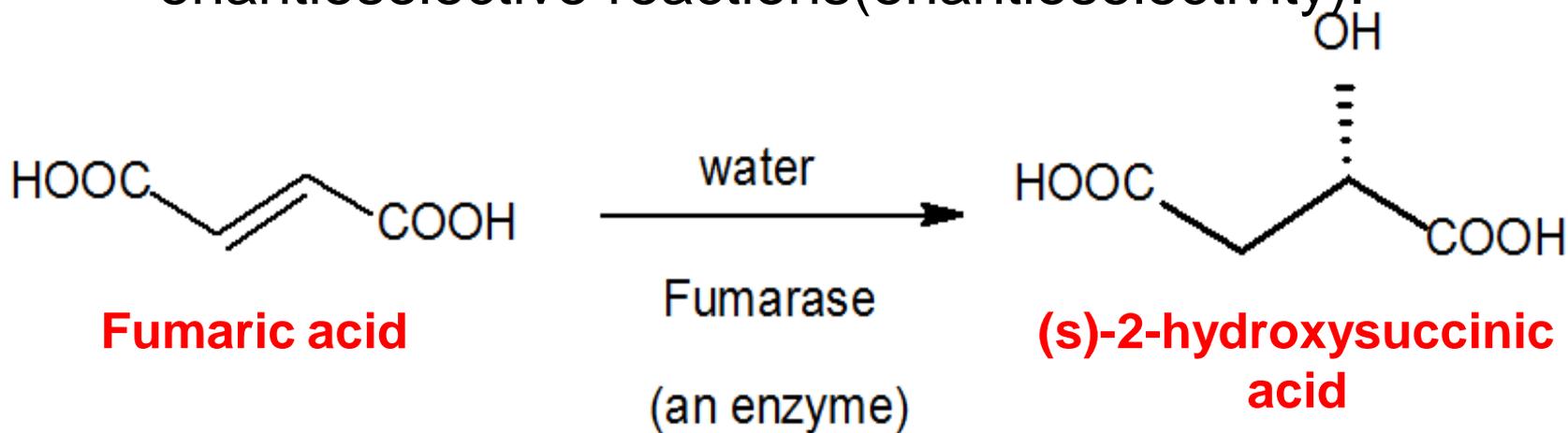
- In a stereoselectivity reaction one stereoisomer is formed (or destroyed) more rapidly than another thus resulting in predominance of the favoured stereoisomer in the mixture of products.
- The stereoselective requirement of the mechanism of a stereoselective reaction offers alternative paths so that the reaction may proceed either via the most favourable path (kinetic control) or via the path which gives the most stable stereoisomer as the major product (thermodynamic control).
- It is subdivided into **enantioselectivity** and **diastereoselectivity**.

A single starting material can give two or more stereoisomeric products, but gives one of them in greater amounts than any other.



# 1. ENANTIOSELECTIVITY

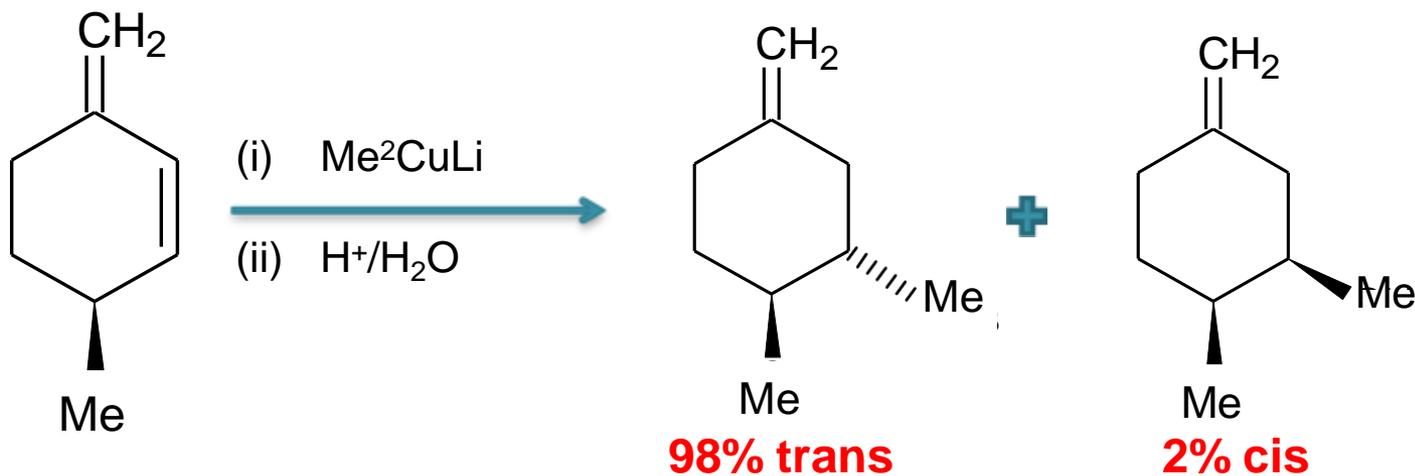
- It is defined as the formation of one of the two enantiomers predominantly or exclusively.
- Reactions which involve preferential attack by a reagent on one of the two enantiotopic group or faces are said to exhibit enantiotopic or enantiofacial selectivity, respectively.
- It is achieved by using chiral substrate, reagent, catalyst or solvent. The following is the example of enantioselective reactions(enantioselectivity).



## 2.

# DIASTEREOSELECTIVITY

- **Distereoselectivity** is most commonly achieved through the presence of steric hindrance.
- **For example:-** The conjugate addition of lithium dimethyl cuprate to 4-methylcyclohexenone is highly distereoselective because the approach of the bulky cuprate reagent occurs predominantly on the less sterically hindered face of the enone.
- Thus, the trans isomer is the major product.



# OPTICAL PURITY

- The "**optical purity**" is a comparison of the optical rotation of a pure sample of unknown stereochemistry versus the optical rotation of a sample of pure enantiomer.
- It is expressed as a percentage.
- If the sample only rotates plane-polarized light half as much as expected, the optical purity is 50%.
- An equal mixture of two enantiomers is called a racemic mixture or racemate.
- If two enantiomers rotate plane-polarized light in opposite directions, a racemate will not rotate light at all. The effects of the two enantiomers will cancel out.

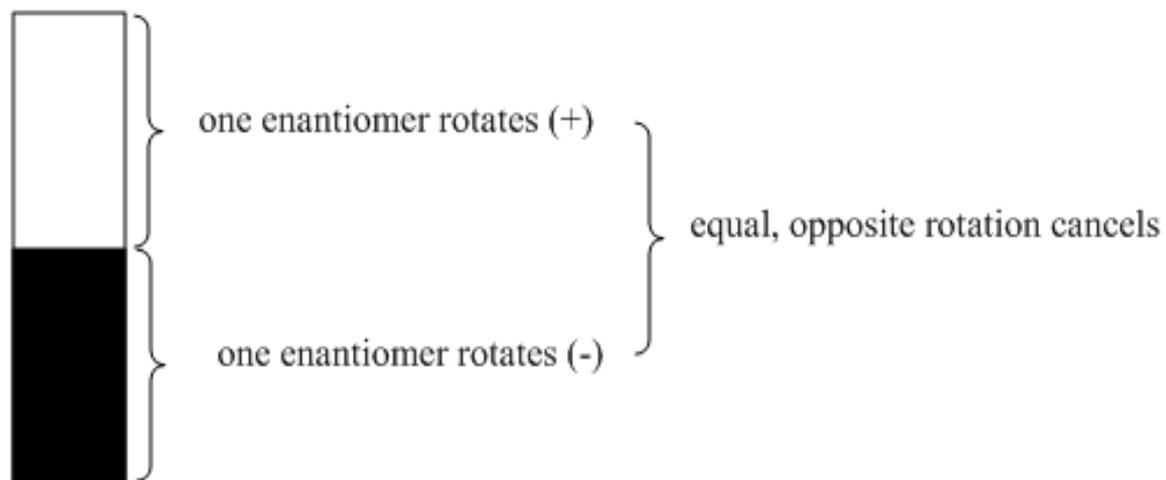


Figure: - Optical rotation canceled out in a racemic mixture.

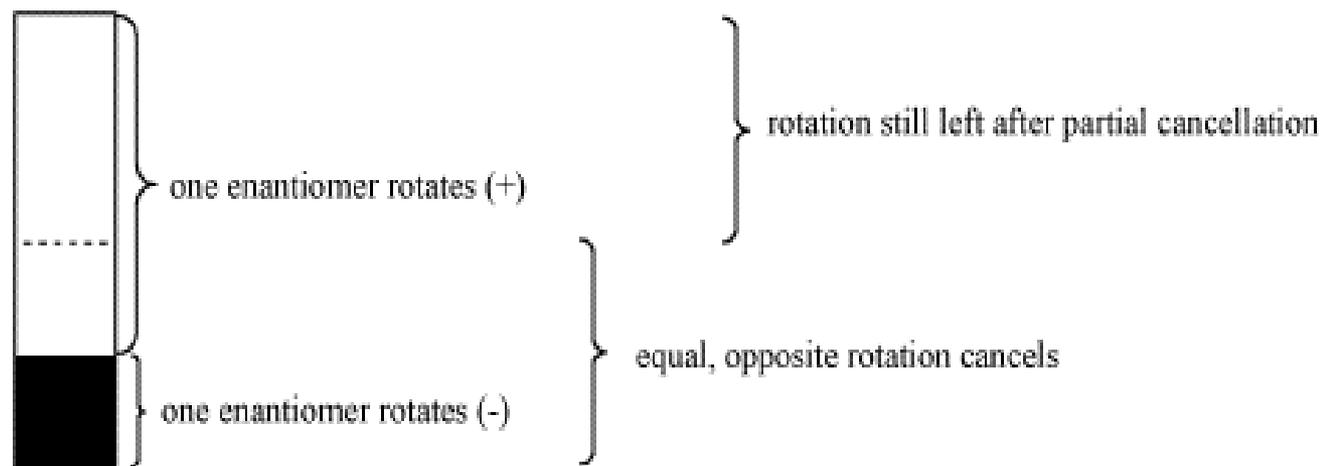


Figure :- Optical rotation only partially canceled in a non-racemic mixture of enantiomers.

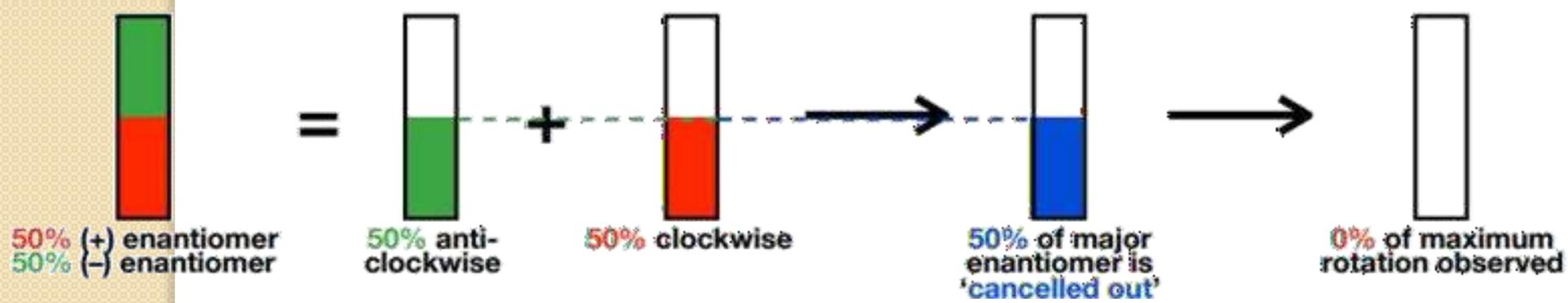
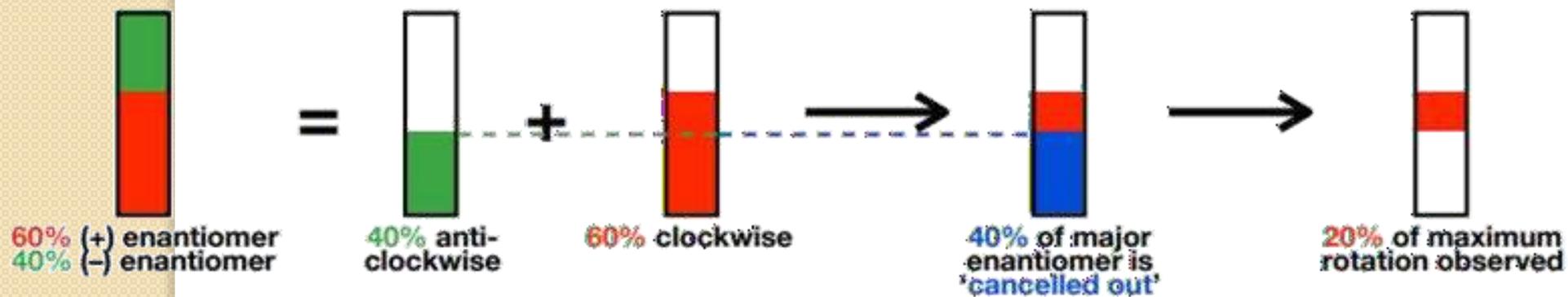
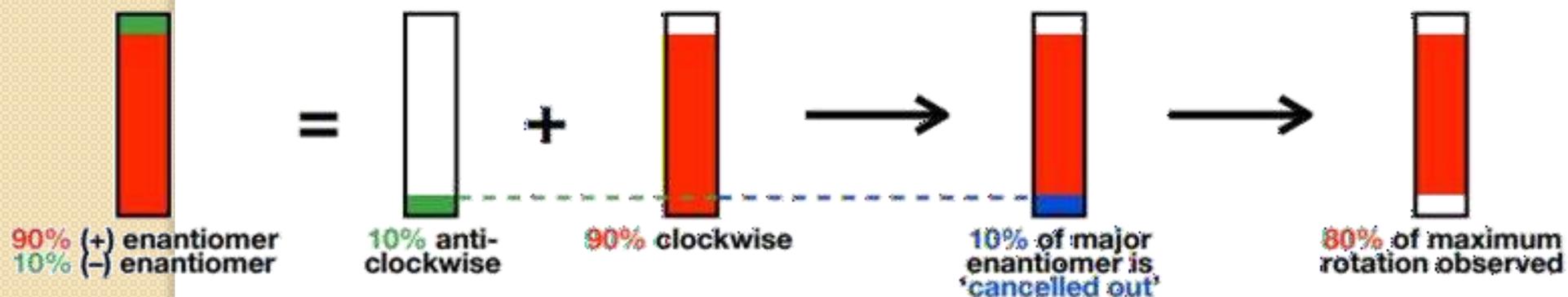
- If two enantiomers are present in an unequal ratio, only part of the optical rotation will be canceled out.
- By comparing the rotation of the sample to the rotation of a pure enantiomer, the enantiomeric purity can be determined.

## Formula of optical purity :-

$$\text{o.p.} = \frac{\text{observed rotation}}{\text{rotation of pure enantiomer}} \times 100 \%$$

# ENANTIOMERIC EXCESS

- **Enantiomeric excess (ee)** is a measurement of purity used for chiral substances.
- It reflects the degree to which a sample contains one enantiomer in greater amounts than the other.
- A racemic mixture has an **enantiomeric excess** of 0%, while a single completely pure enantiomer has an ee of 100%.
- A sample with 70% of one enantiomer and 30% of the other has an **enantiomeric excess** of 40% (70% – 30%).
- Enantiomeric excess is defined as the absolute difference between the mole fraction of each enantiomer:
- Enantiomeric excess is used as one of the indicators of



- Previous slide indicates that a polarimeter measures difference in the amount of each enantiomer
- **Racemate (racemic mixture)** - 1 to 1 mixture of enantiomers (50% of each)
- **Racemisation** - converting 1 enantiomer to a 1:1 mixture of enantiomers
- Optical rotation very unreliable so use new methods to measure amounts and use the value enantiomeric excess.

$$\text{Enantiomeric excess (\% ee)} = \frac{[R] - [S]}{[R] + [S]} = \%R - \%S$$

# REFERENCE

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- [chem.ucalgary.ca](http://chem.ucalgary.ca)