

STEREOCHEMISTRY II

PART II

SEM II

CBCS System



By

Dr. Mumu Chakraborty

Department of Chemistry

Government Girls' General Degree College

7, Mayur bhanj Road, Kolkata - 700023

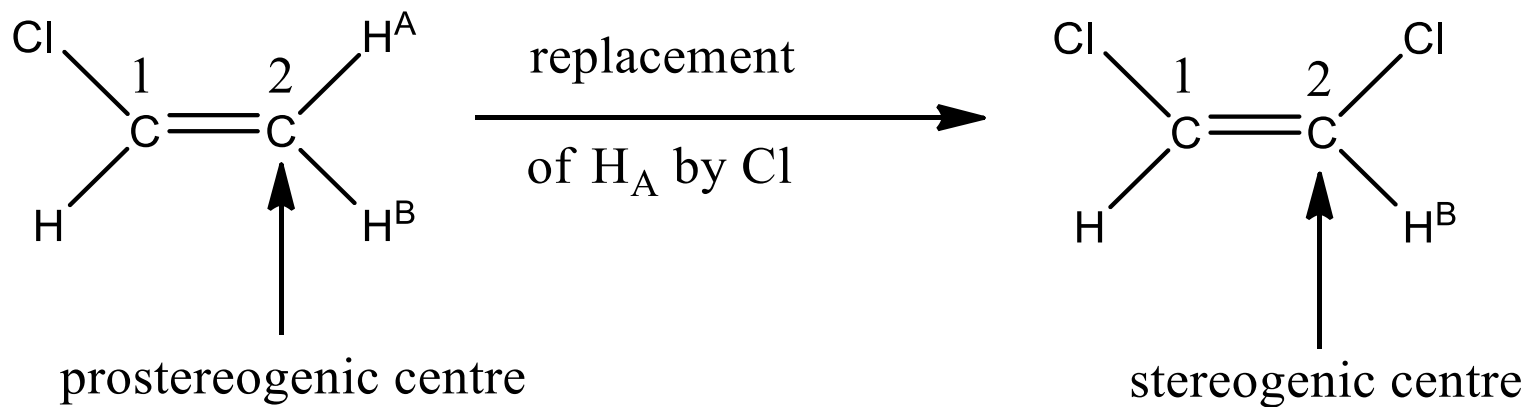
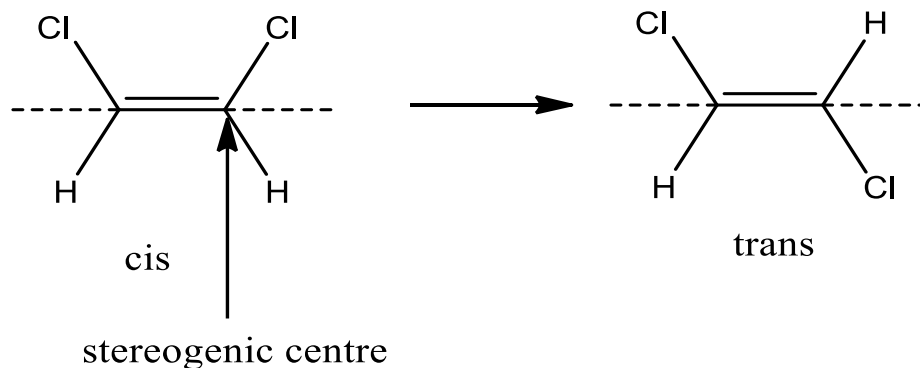


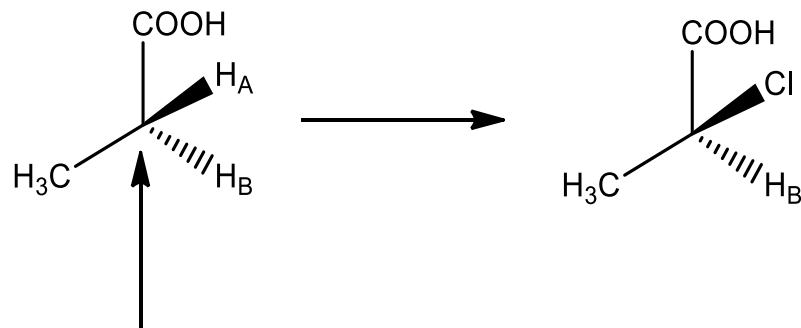
Concept of prostereoisomerism:

prostereogenic centre; concept of *(pro)n-chirality*:
topicity of ligands and faces (elementary idea);
pro-R/pro-S, pro-E/pro-Z and Re/Si
descriptors; *pro-r and pro-s descriptors of ligands*
on propseudoasymmetric centre.

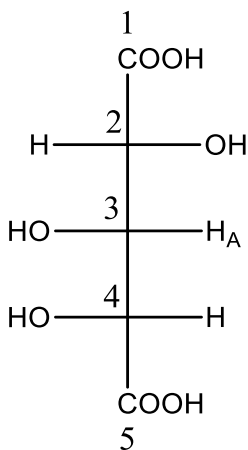
Prostereogenic centre:

Prostereogenic centre is defined as the centre bearing homomorphic atoms and groups which can be converted into a stereogenic centre by replacing one of the homomorphic atoms or groups by different substituents.



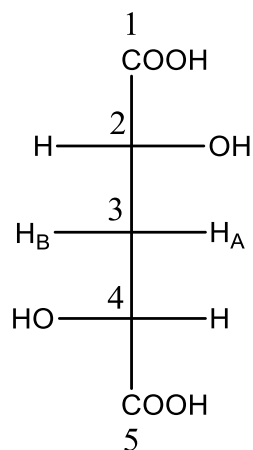


prostereogenic and prochiral centre



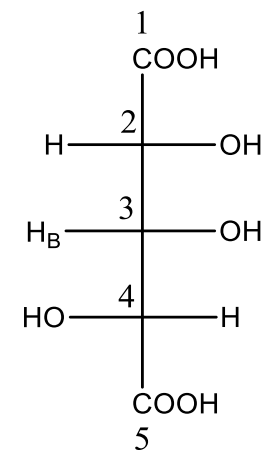
(III)

← replacement of
H_B by -OH group



(I)

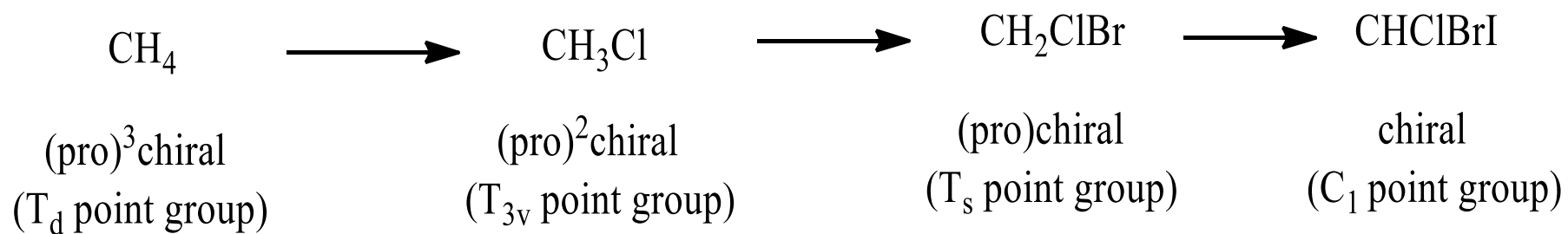
→ replacement of
H_A by -OH group



(II)

(II) and (III) are superimposable homomers by in-plane rotation of 180°. Therefore, C-3 is prochirotopic but not prostereogenic and hence, prostereogenic centre is not necessarily prochirotopic and *vice versa*.

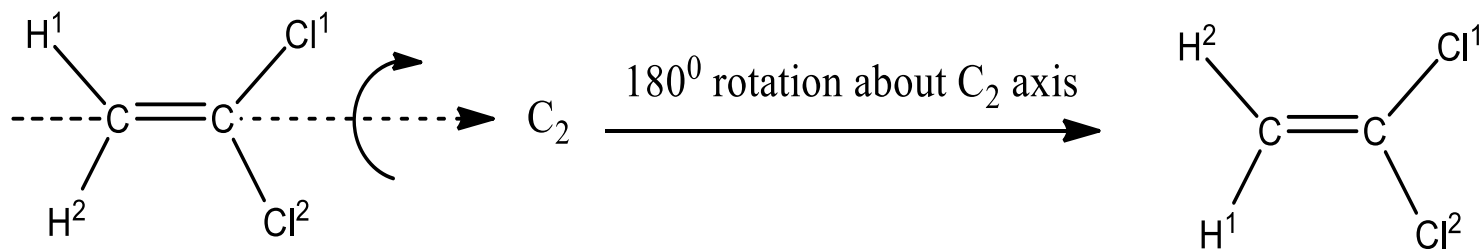
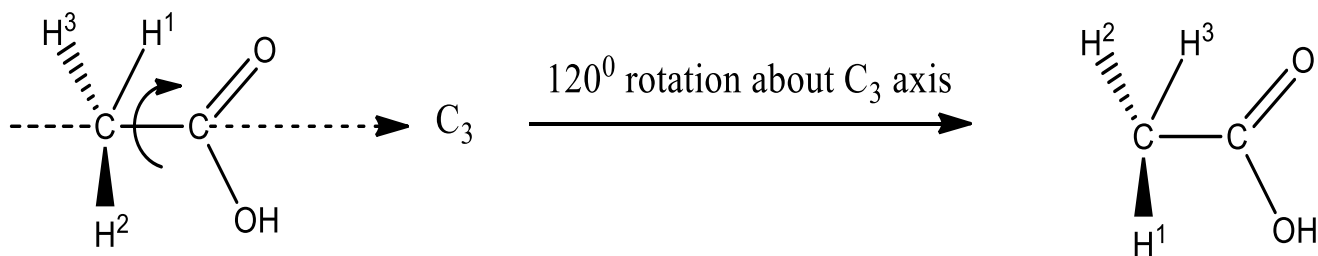
Concept of (pro)ⁿ – chirality :



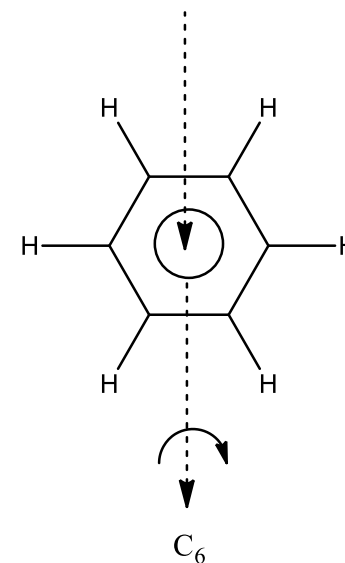
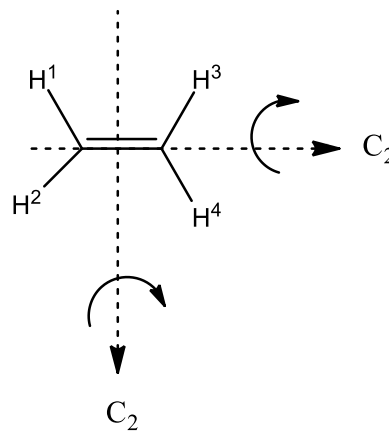
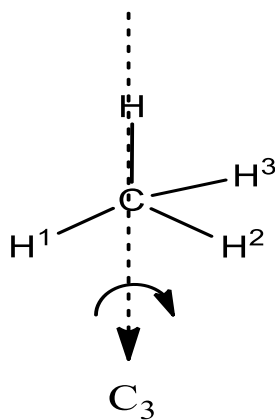
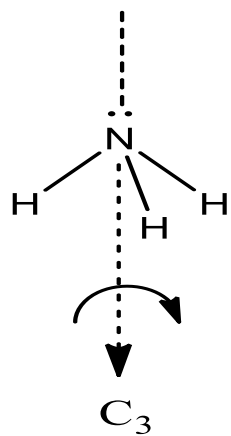
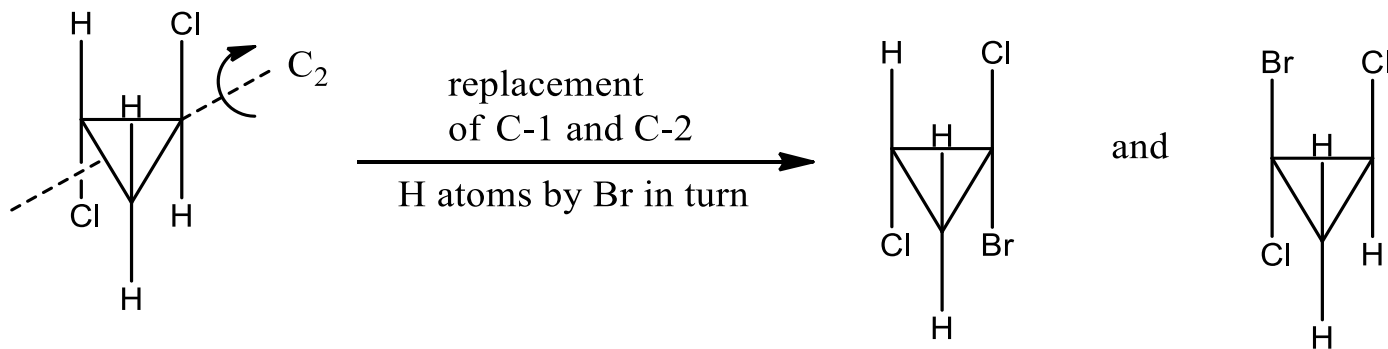
Topicity of ligands and faces :

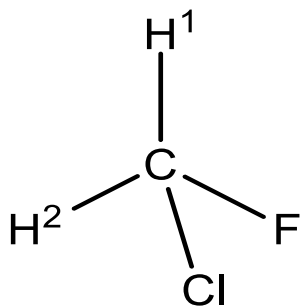
Homomorphic atoms or groups can be classified as homotopic, enantiotopic or diastereotopic.

Homotopic atoms or groups: Homotopic ligands in a molecule are those whose positions can be interchanged by rotation about proper axis of symmetry C_n ($n \geq 1$).



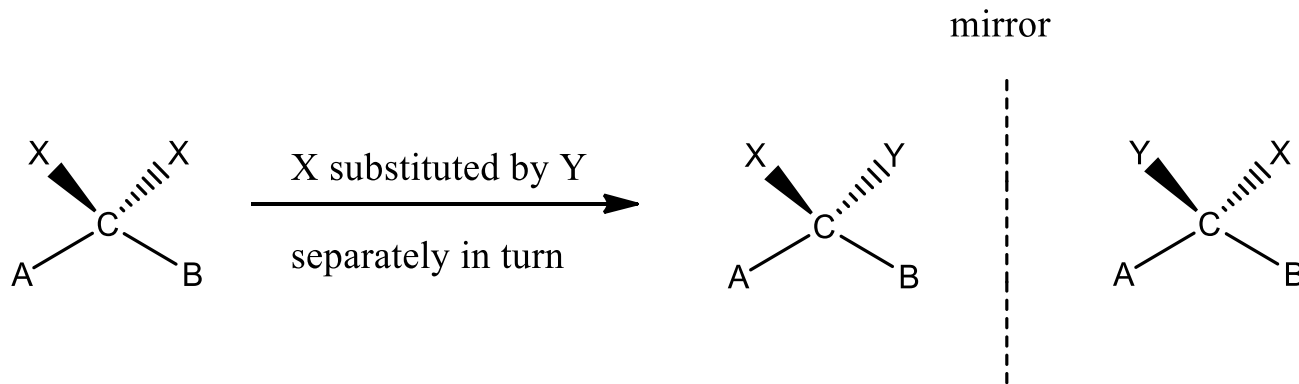
Replacement of each of the homotopic atoms or groups by similar ligands produces homomers.



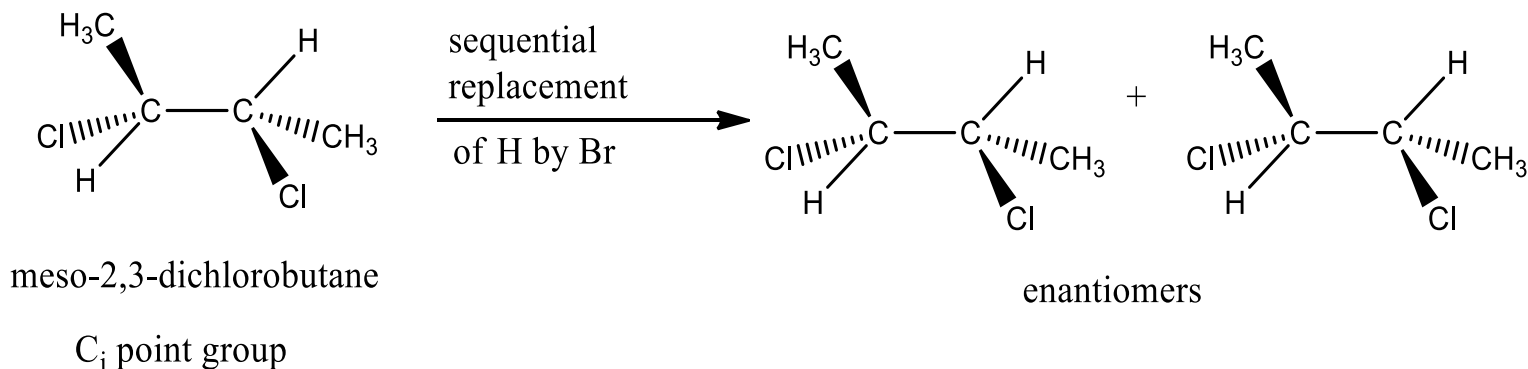


H¹ and H² are not homotopic because of the absence of C_n axis (n>1). Molecules belonging to symmetry point groups C₁, C_s, C_i and C_{αv} cannot have homotopic ligands.

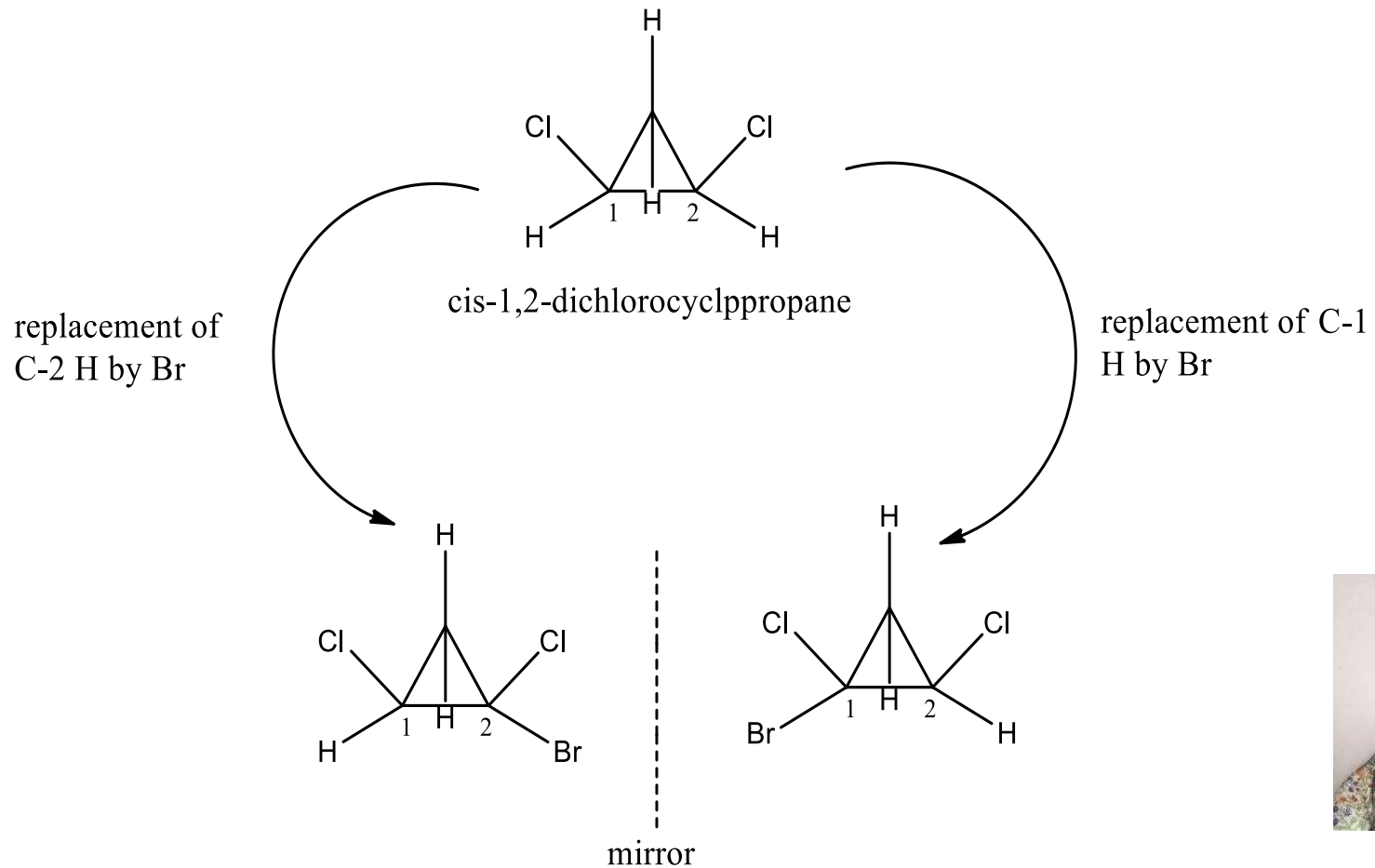
Enantiotopic atoms and groups:



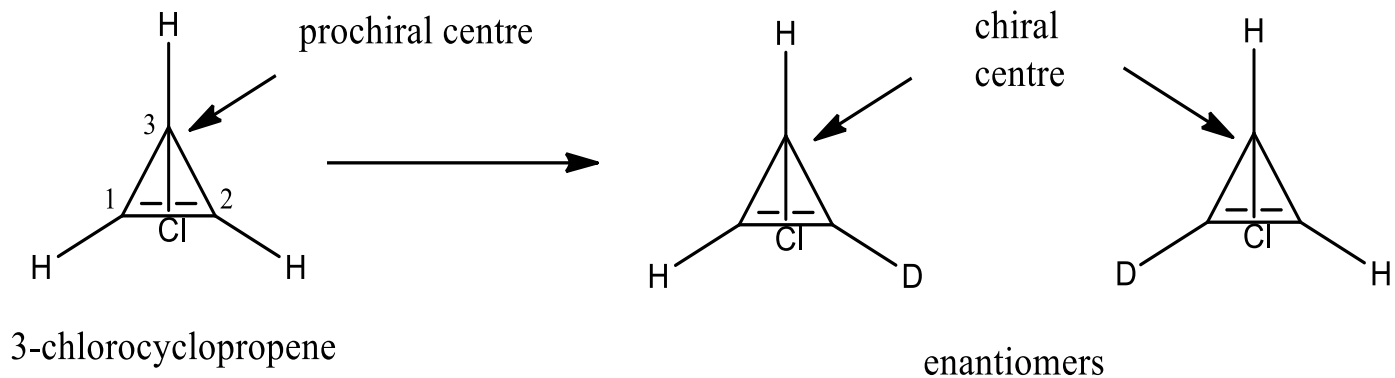
X,X are enantiotopic atoms or groups.
The molecule has a sigma plane (C_s)
plane which bisects A,B and the carbon atom



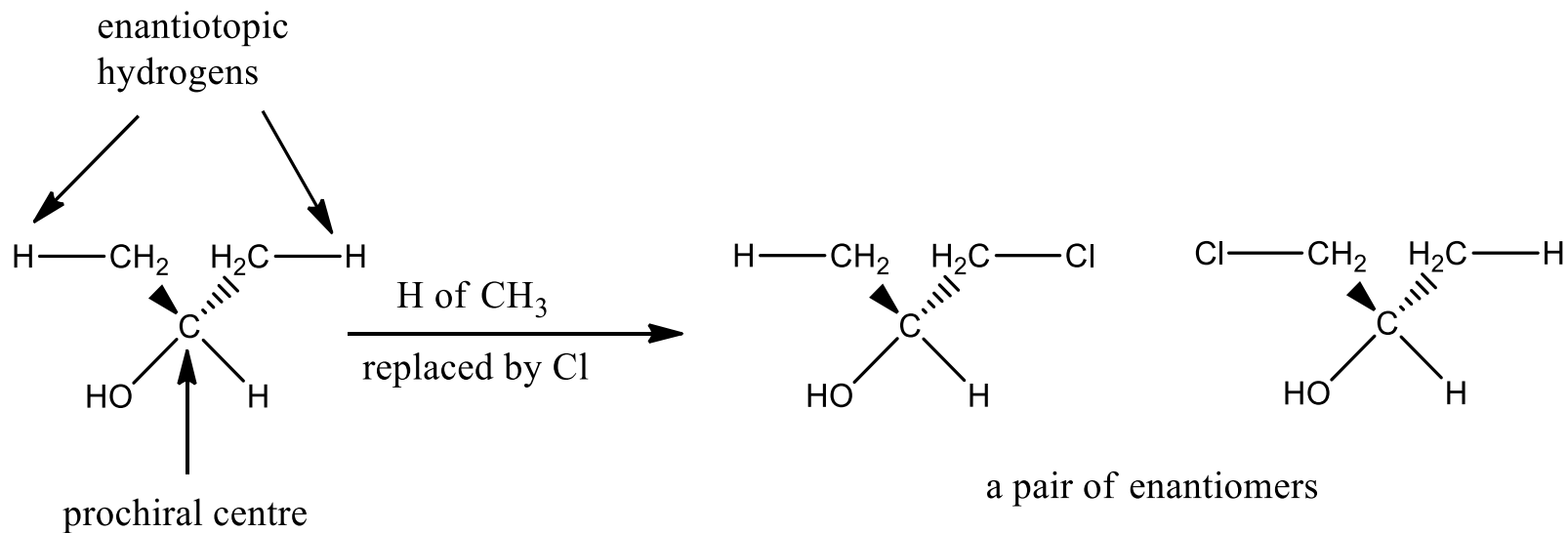
The two H atoms, two Cl atoms and two methyl groups are enantiotopic.



The two H atoms and the two Cl atoms at C-1 and C-2 are enantiotopic.

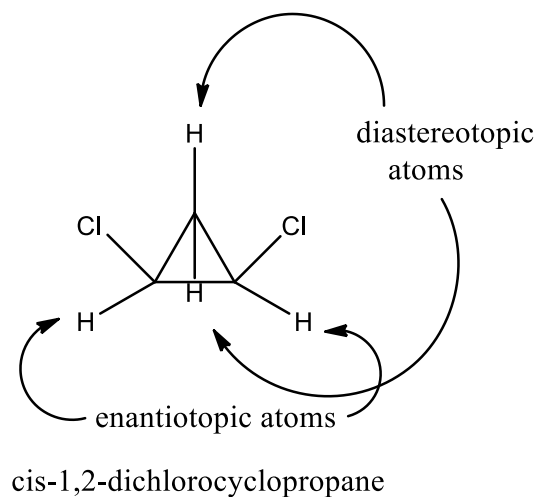
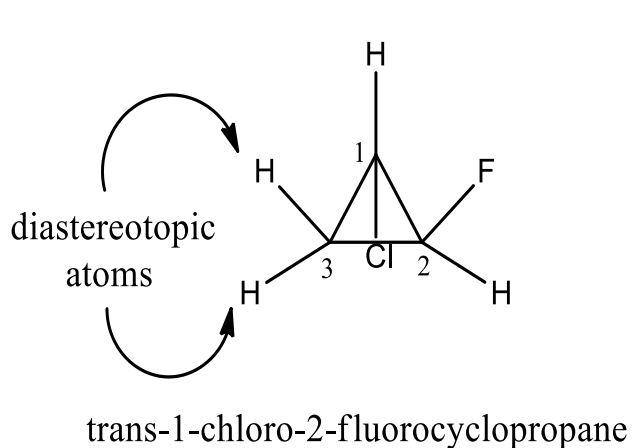
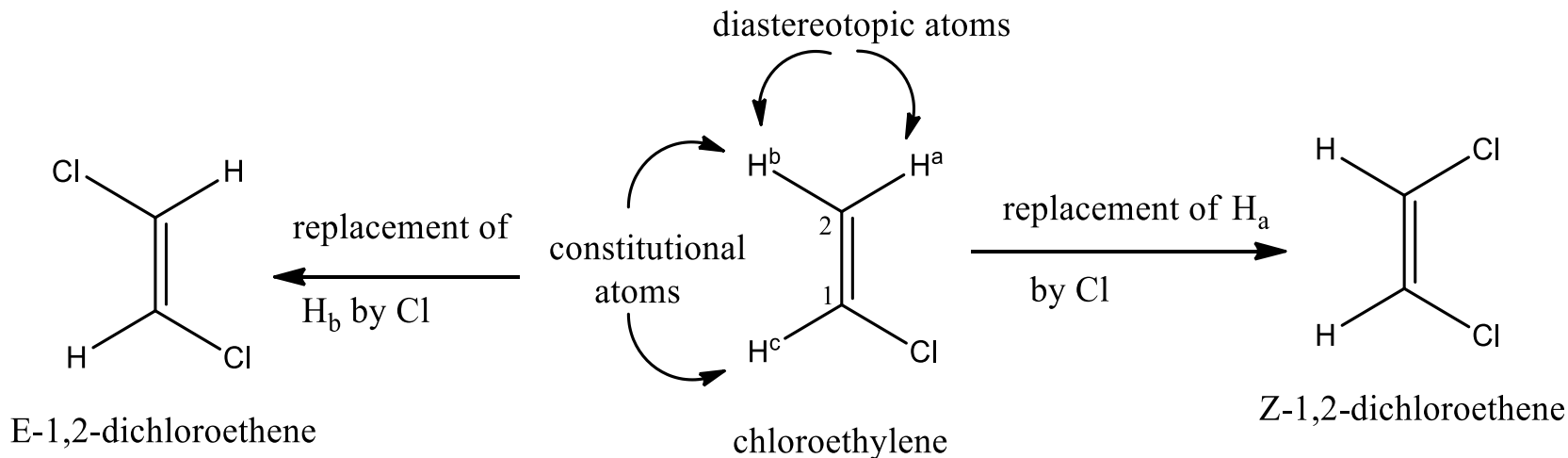


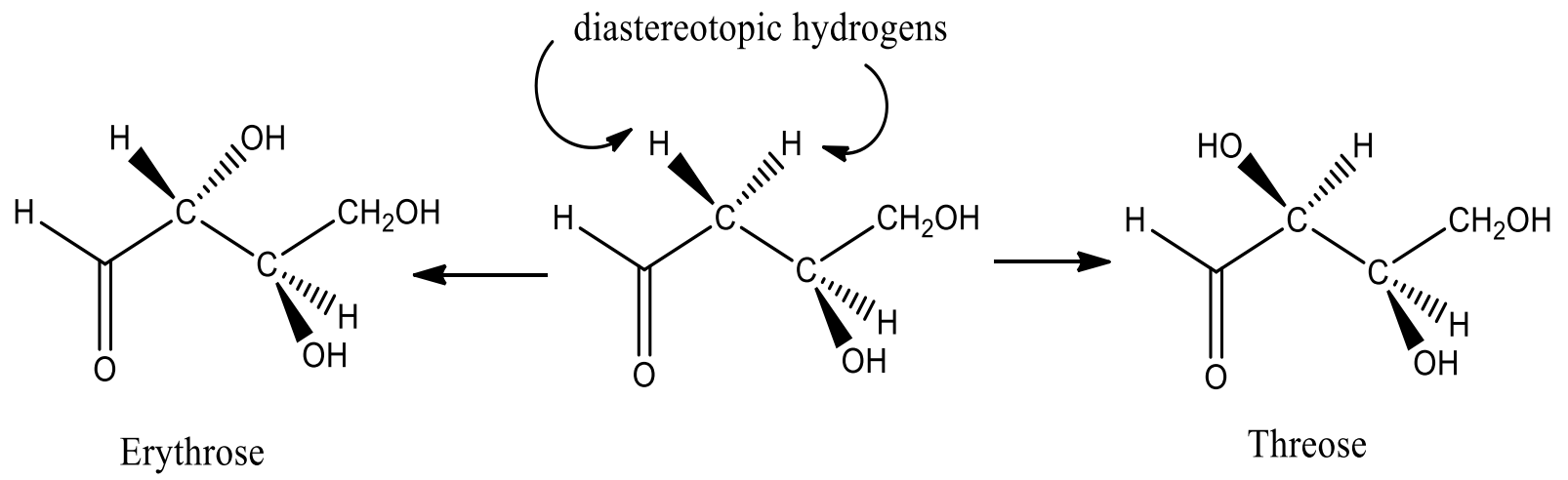
The two H atoms at C-1 and C-2 are enantiotopic.



Diastereotopic atoms and groups :

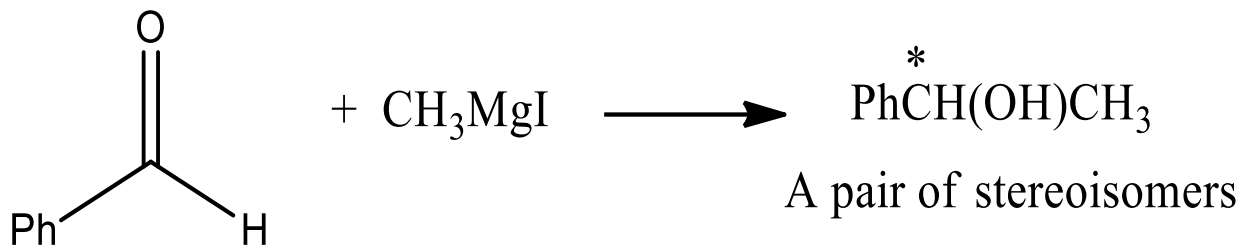
Two atoms or groups in a molecule are said to be diastereotopic if sequential replacements of these atoms or groups by two homomorphic ligands result in the formation of a pair of diastereoisomers.



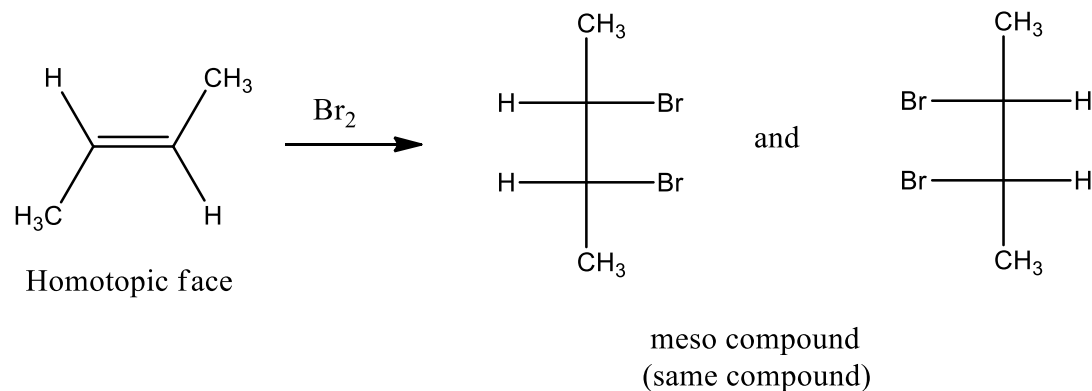
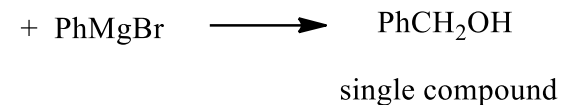
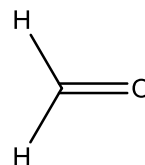
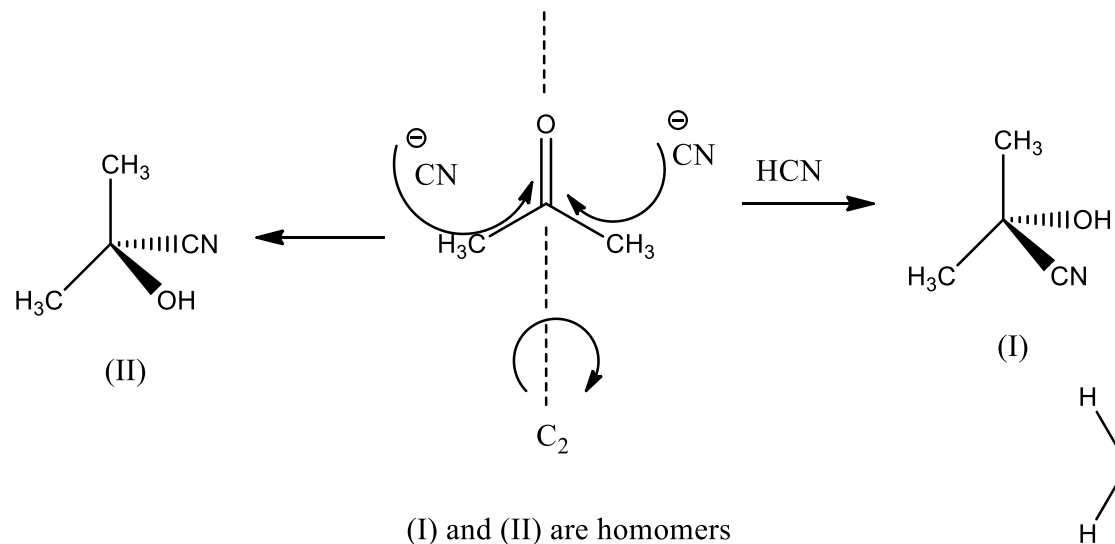


Prochiral faces :

Planar groups like $C=O$, $C=C$, etc, in certain molecules are said to present prochiral faces if chiral stereoisomers are produced by addition reaction at the two faces of the groups.



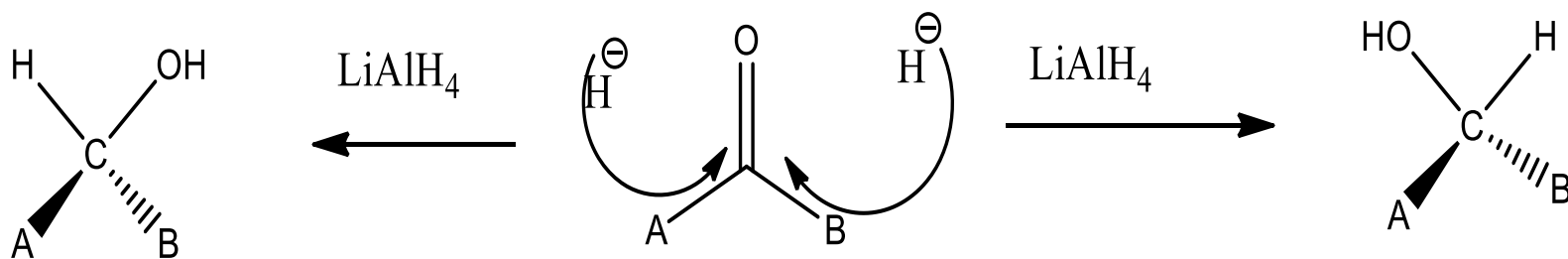
Homotopic Faces:



Symmetrical ketones like RCOR and HCHO have homotopic faces.

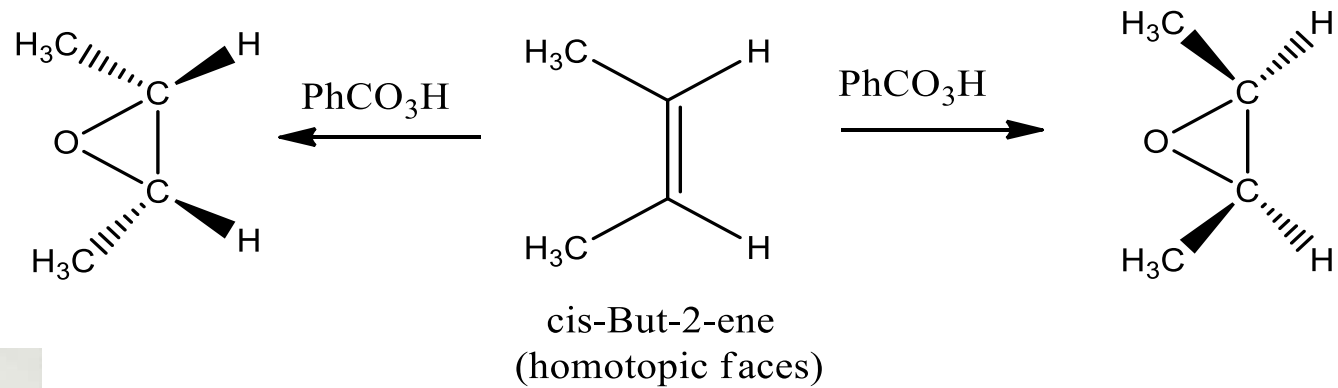
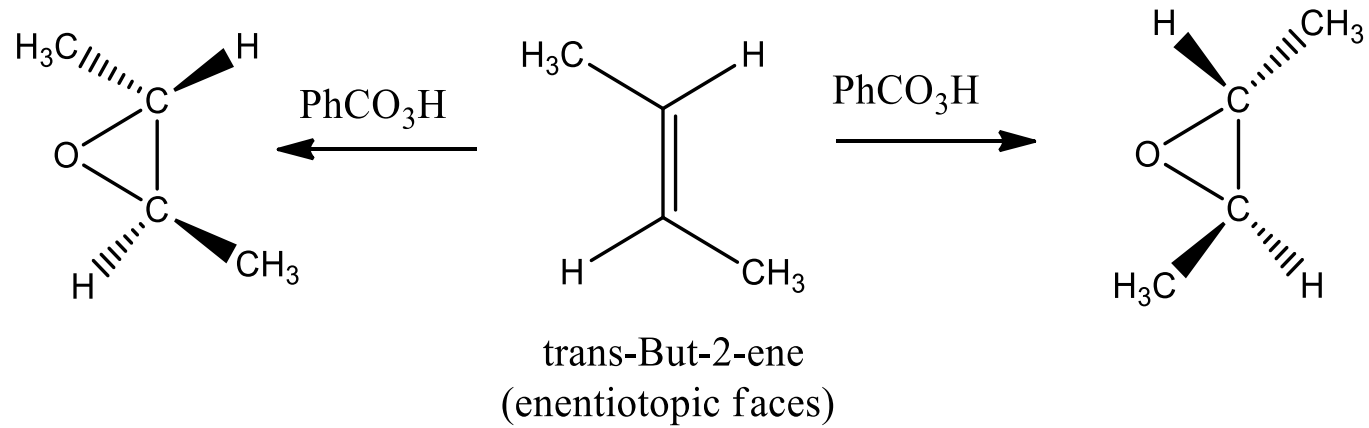
Enantiotopic faces:

A carbonyl compound of general structure A-CO-B has enantiotopic faces. Attack of reagent on one side of the bond yields one enantiomer, whereas attack on the opposite side leads to the other enantiomer.



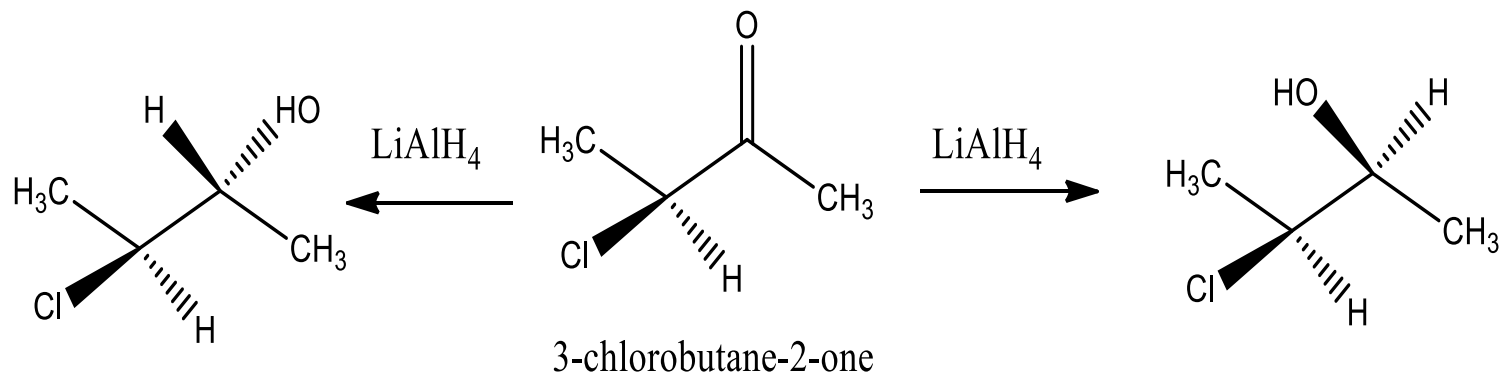
Two faces of CO are exchangeable
by bisecting the molecule by a
molecular plane

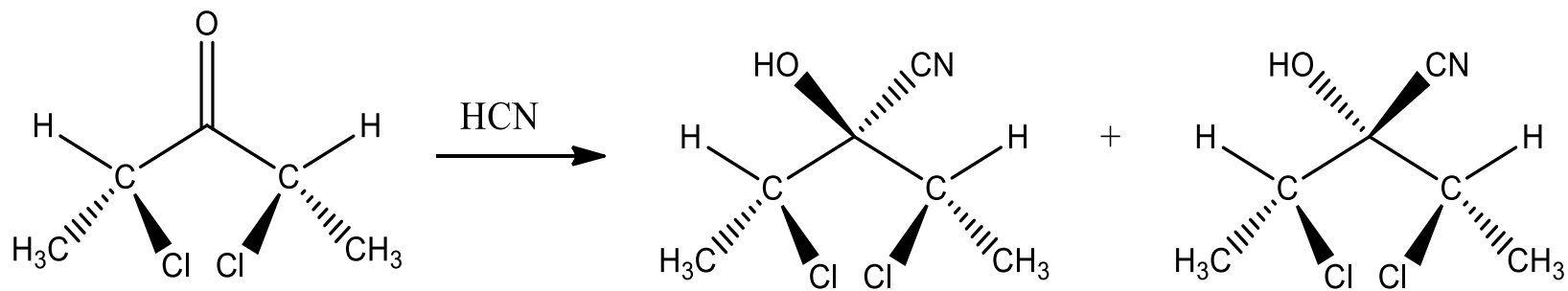




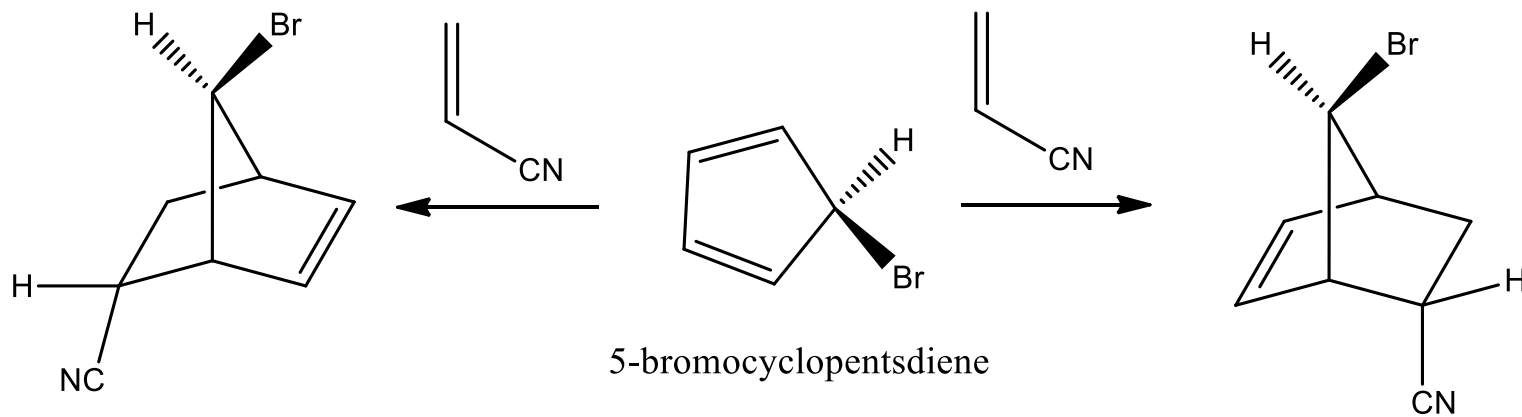
Diastereotopic faces:

Attack of a reagent on one side of the π -bond leads to one diastereoisomer, whereas attack on the opposite side leads to the other diastereoisomers. Diastereotopic face in a molecule is found to be attached to an adjacent chiral centre already present in the molecule.





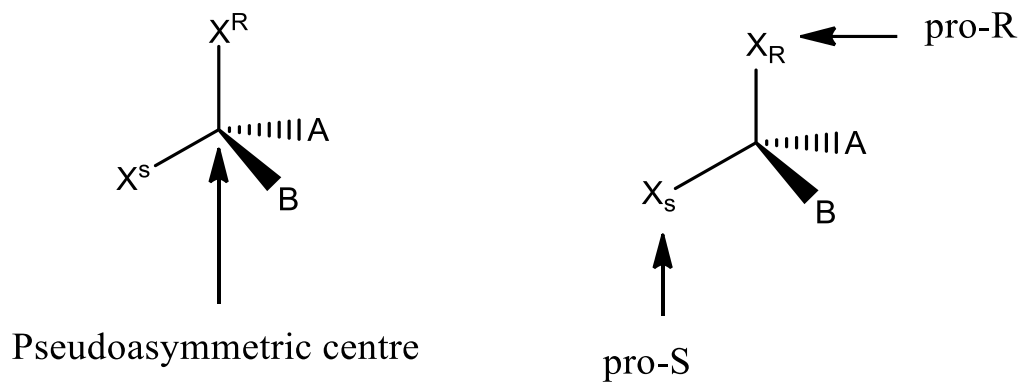
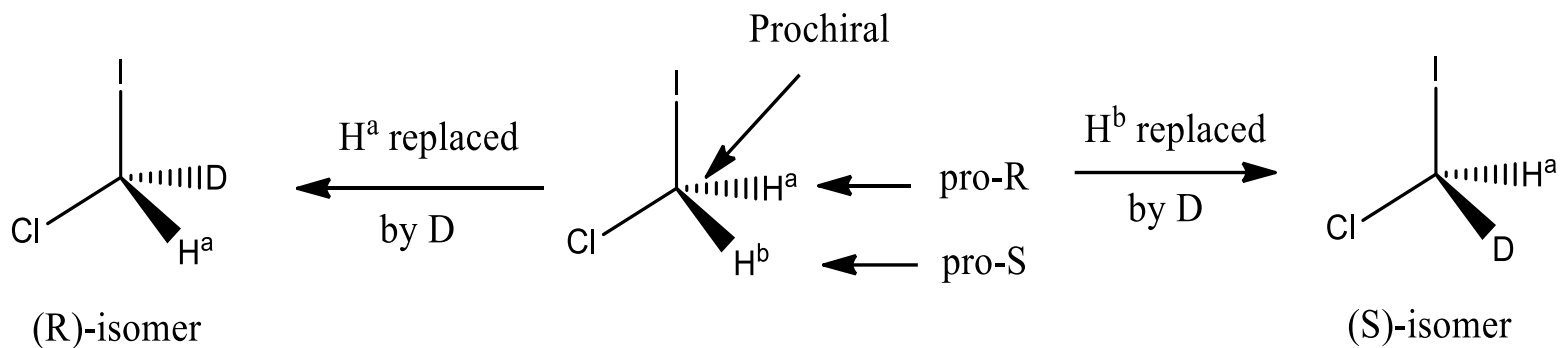
Diastereoisomers



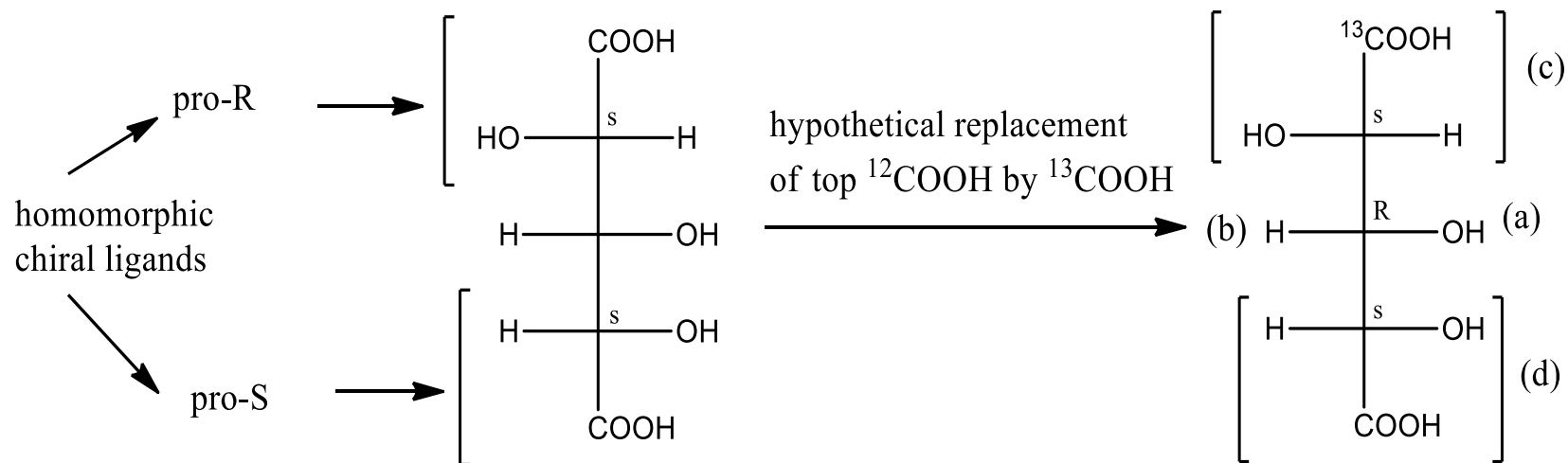
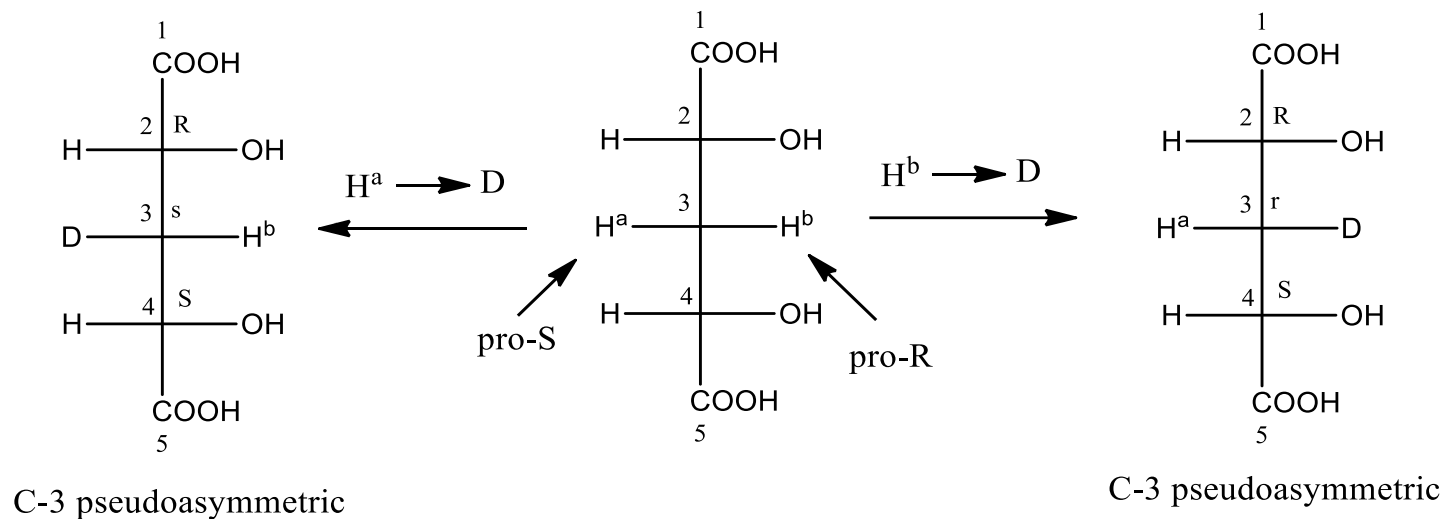
5-bromocyclopentadiene



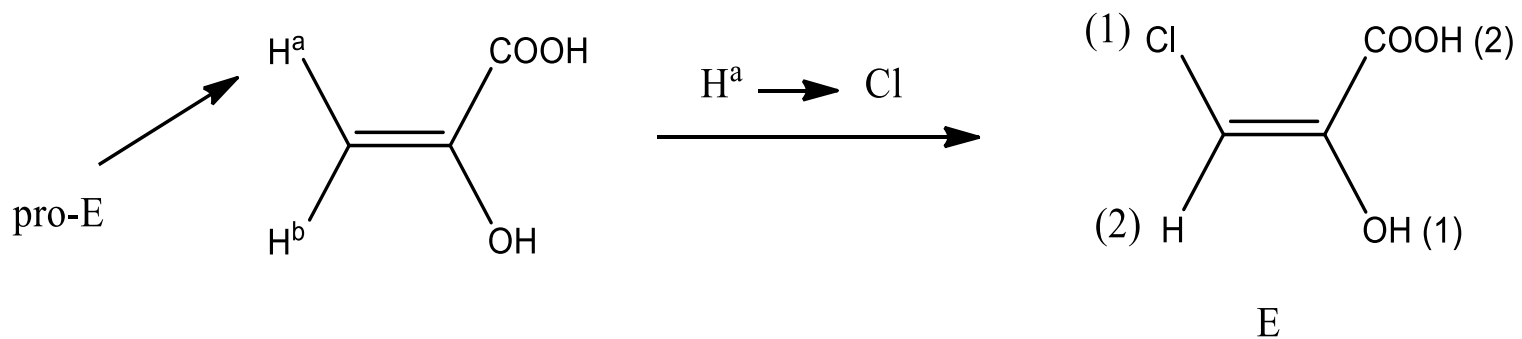
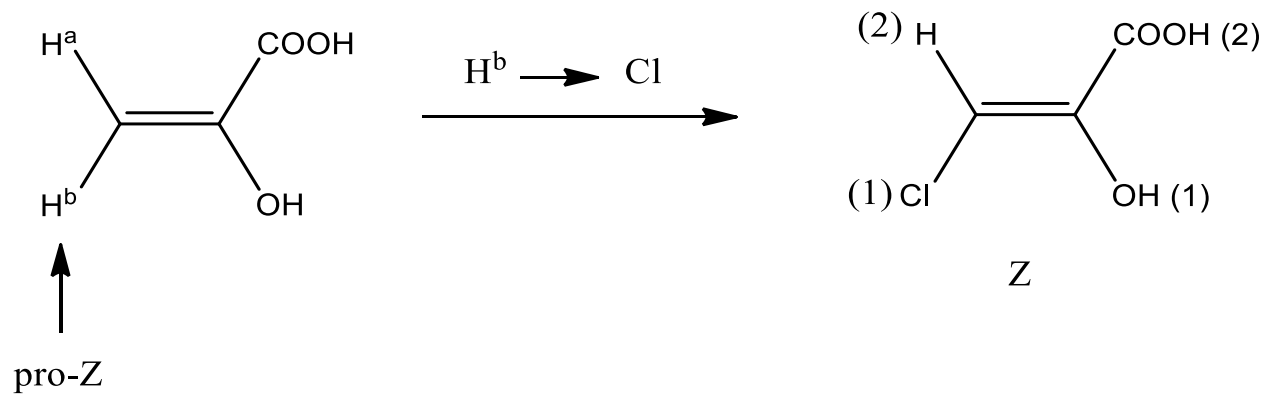
pro-R and pro-S designation:



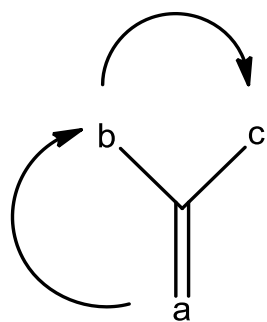
Pro-r and pro-s descriptors of ligands on propseudoasymmetric centre:



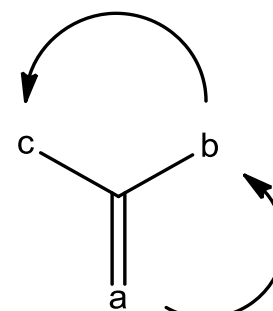
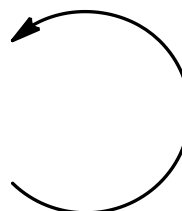
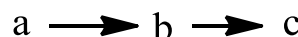
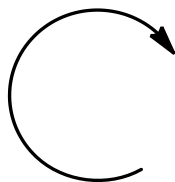
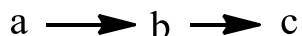
pro-E/pro-Z :



Re and Si designation of enantiotopic and diastereotopic faces:

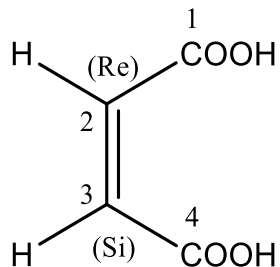


Re (rectus) face

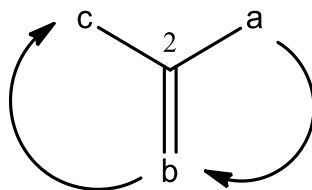


Si (sinister) face



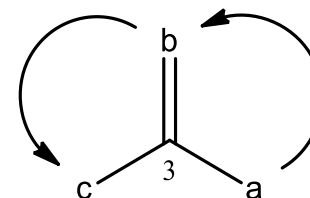


(Re,Si) - maleic acid
or cis-butenedioic acid

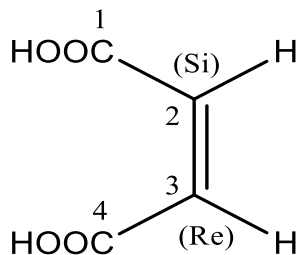


Re

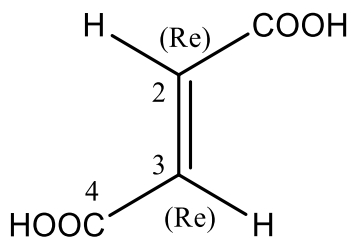
and



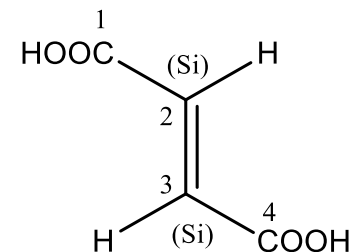
Si



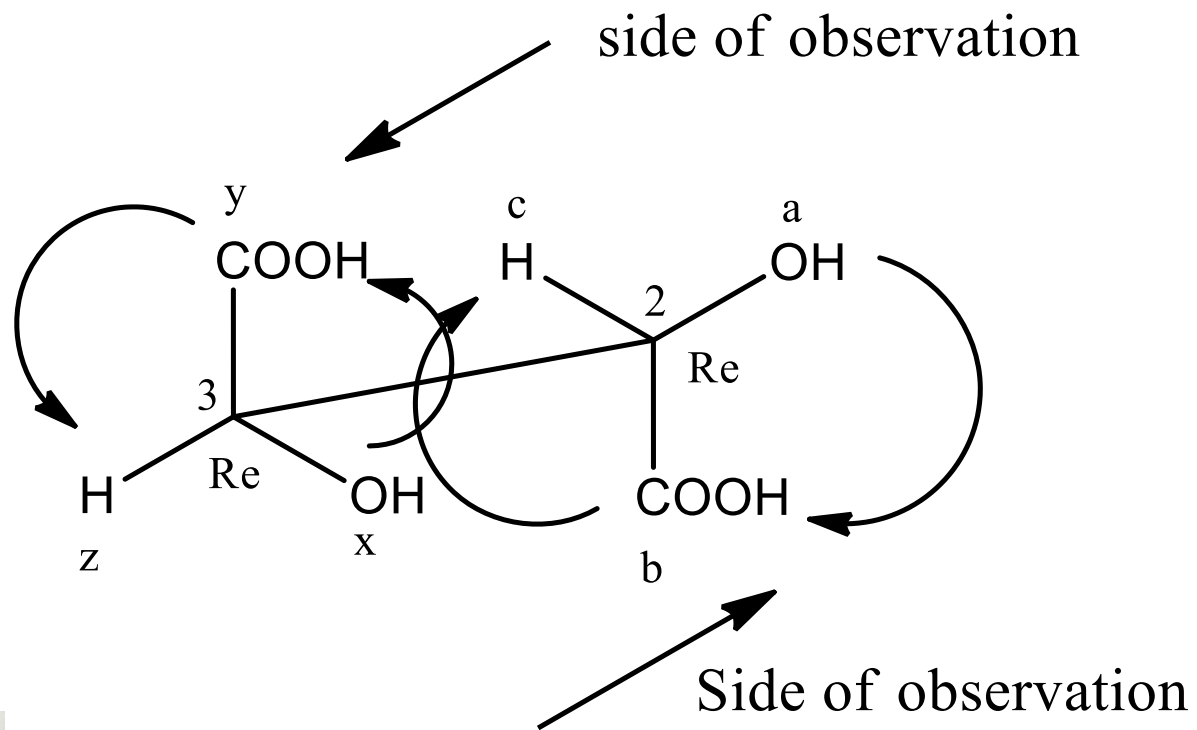
(Si,Re) - maleic acid
or cis-butenedioic acid



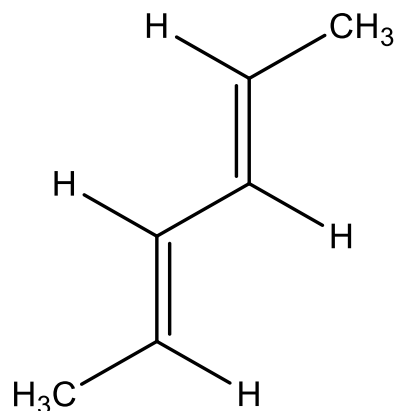
(Re,Re) - fumaric acid
or trans-butenedioic acid



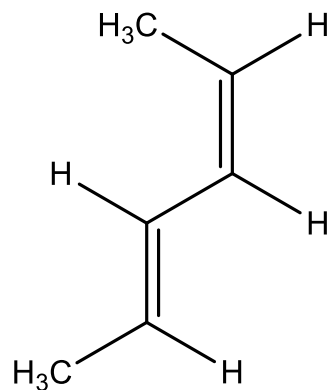
(Si,Si) - fumaric acid
or trans-butenedioic acid



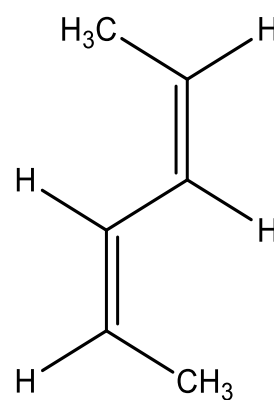
Conformation of conjugated systems (*s-cis* and *s-trans*):



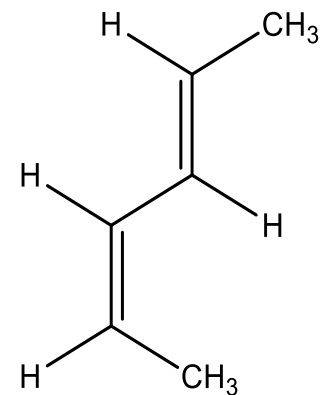
(2E,4E)-2,4-Hexadiene



(2Z,4E)-2,4-Hexadiene

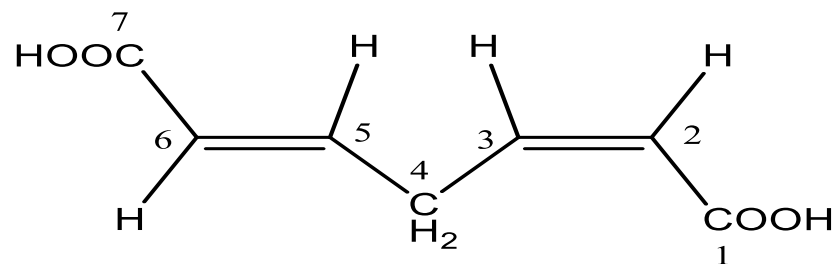


(2Z,4Z)-2,4-Hexadiene



(2Z,4E)-2,4-Hexadiene

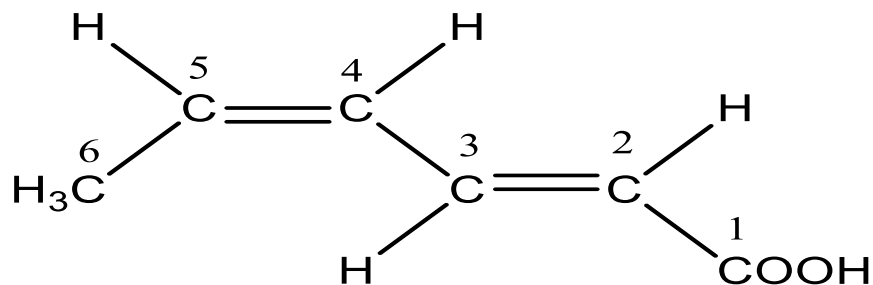




(2Z,5E)-hepta-2,5-dienedioic acid

(2E,5Z)-hepta-2,5-dienedioic acid

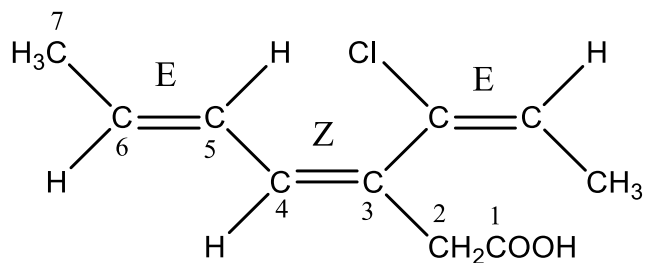
x



(2E,4Z)-hexa-2,4-dienoic acid

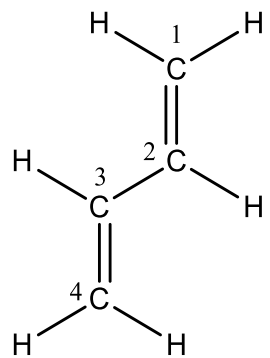
(4Z,2E)-hexa-2,4-dienoic acid

X

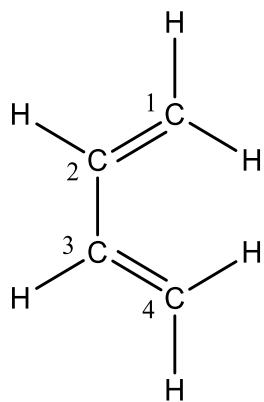
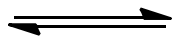


3-[(E)-1-chloropropenyl]-(3Z,5E)-hepta-3,5-dienoic acid

Buta-1,3-diene

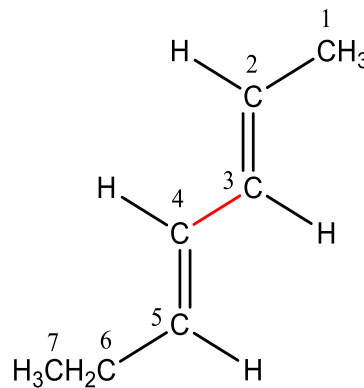


s-trans or s-transoid

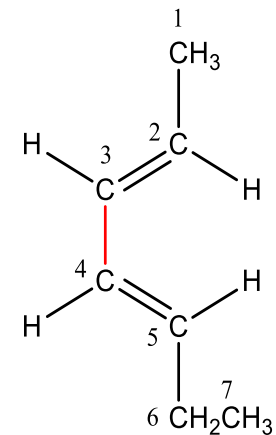
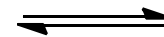


s-cis or s-cisoid

(2E,4E)-hepta-2,4-diene

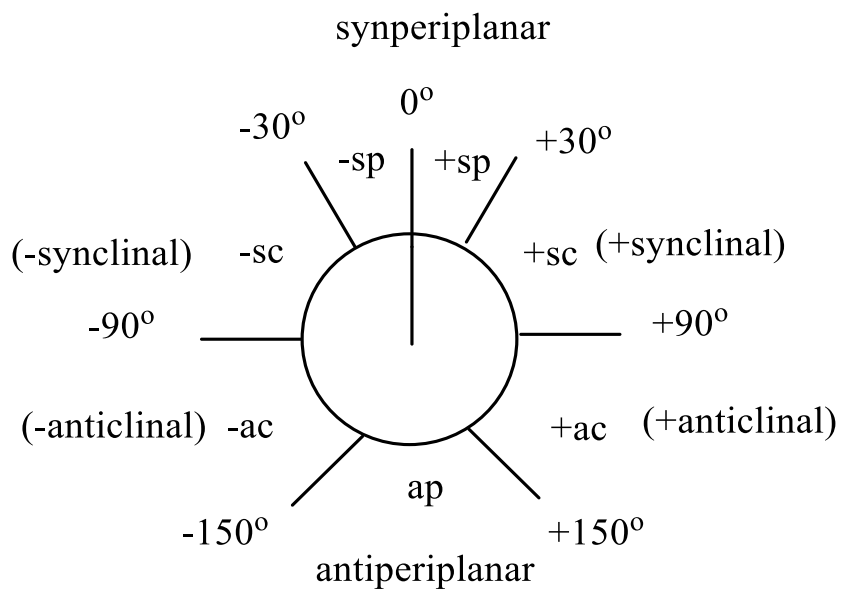
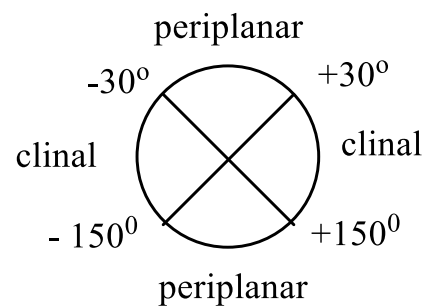
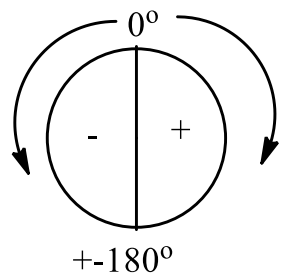
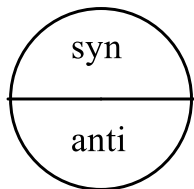


s-trans or s-transoid



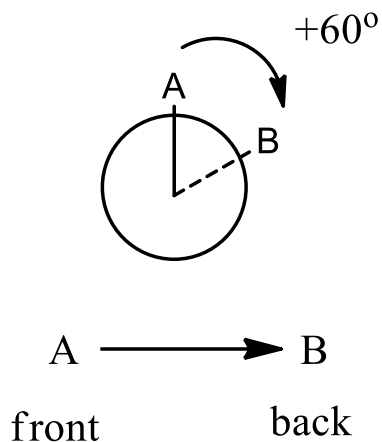
s-cis or s-cisoid

Klyne-Prelog terminology:

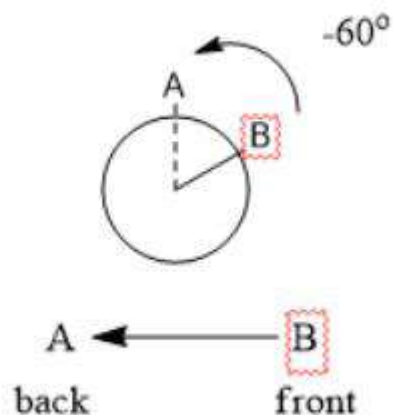




clockwise movement

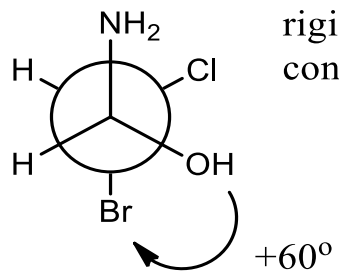
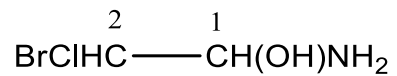


anticlockwise movement

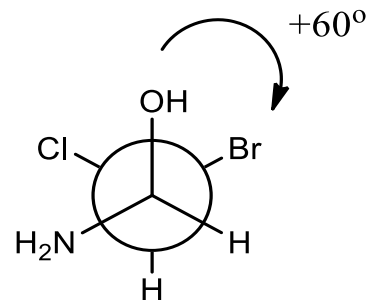


In Klyne-Prelog system, it is necessary to choose two reference groups, one from each set of substituents on adjacent carbons, to specify the particular conformation on the basis of torsion angle between the reference groups. This choice of reference groups is done on the basis of Cahn conformation selection rules.

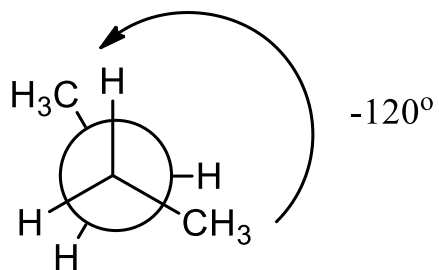
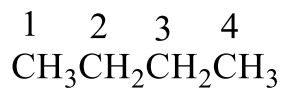
Cahn conformation selection rules:



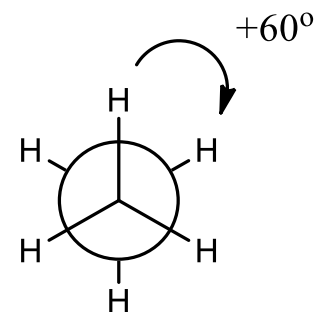
rigid rotation of the
conformation as a whole
≡



+sc-conformation

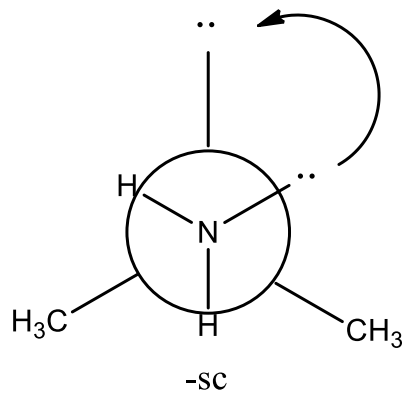
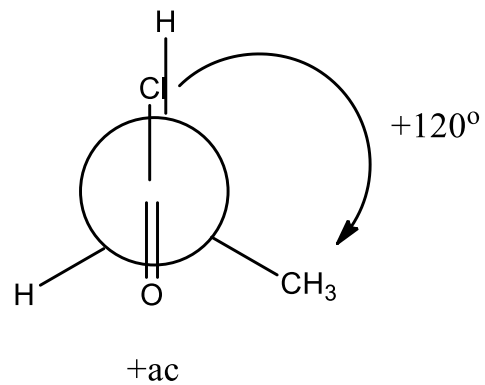
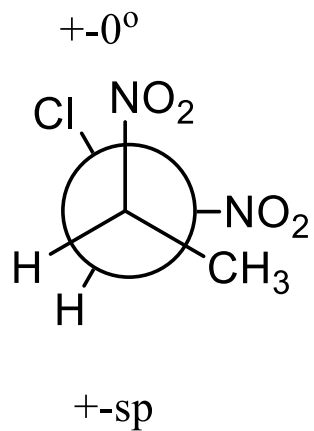


-ac-conformation



(+sc) conformation of ethane





a particular conformation of $(CH_3)_2\overset{\dots}{N}NH_2$



Conformation according to Klyne-Prelog method:

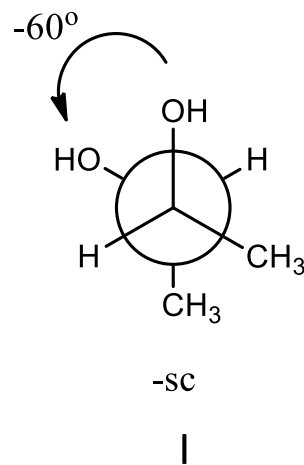
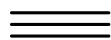
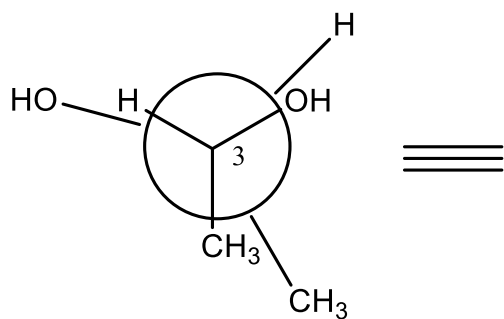
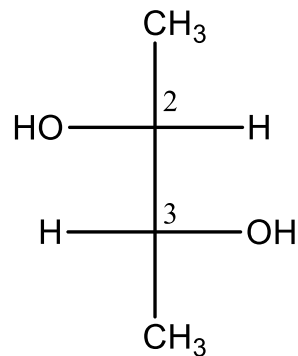
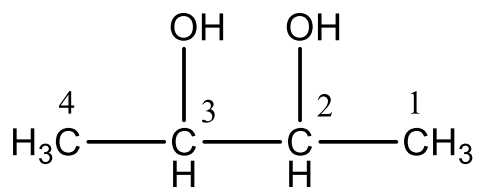
Torsion angle between the two reference groups	Designation	Symbol
0° to $+30^\circ$	synperiplanar	+ - sp
Greater than $+30^\circ$ upto $+90^\circ$	synclinal	+ - sc
Greater than $+90^\circ$ upto $+150^\circ$	anticlinal	+ - ac
Greater than $+150^\circ$ upto $+180^\circ$	antiperiplanar	+ - ap

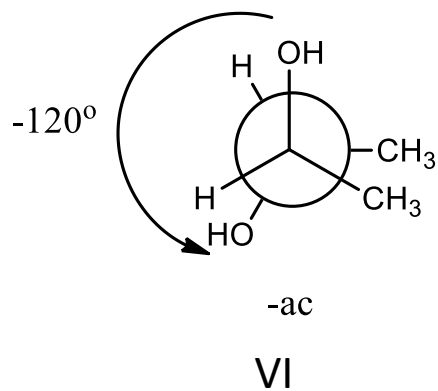
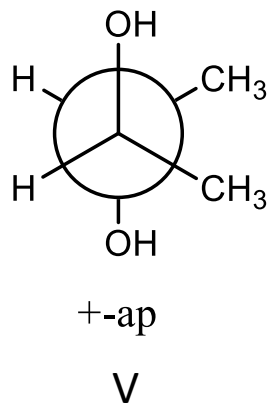
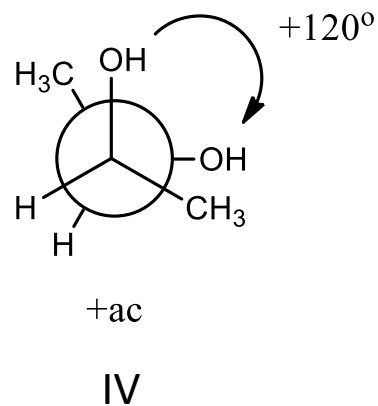
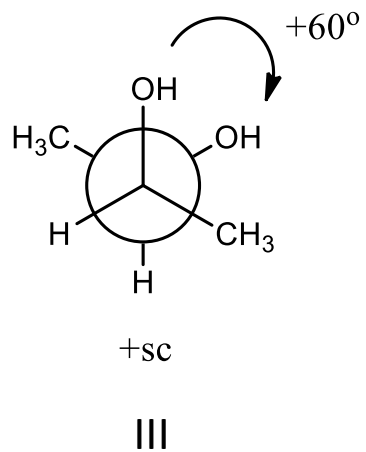
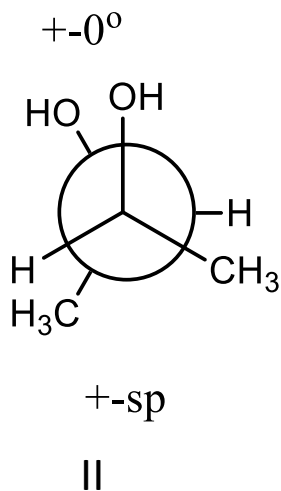
References:

- 1. Eliel, E. L. & Wilen, S. H. *Stereochemistry of Organic Compounds*, Wiley: London, 1994.**
- 2. Nasipuri, D. *Stereochemistry of Organic Compounds*, Wiley Eastern Limited.**
- 3. Subrata Sen Gupta. *Basic stereochemistry of organic molecules*. Second edition, 2007.**

C.U. SEM-2, 2019

2.b) Write down the (-)sc conformation of active butane-2,3,-diol. Propose the other conformers of it and indicate their relative stability. 3+2





Decreasing order of stability:
 $III > I > V > II > VI > IV$

