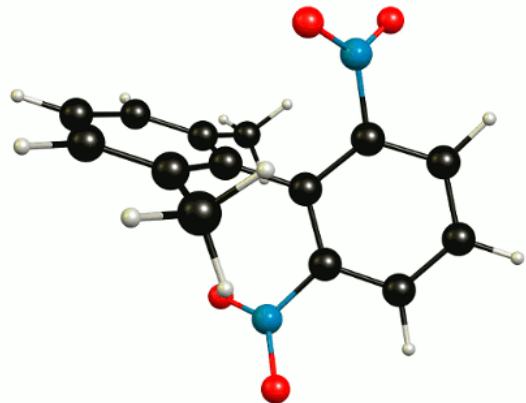


STEREOCHEMISTRY II B

Paper C5T

Indranil Chakraborty

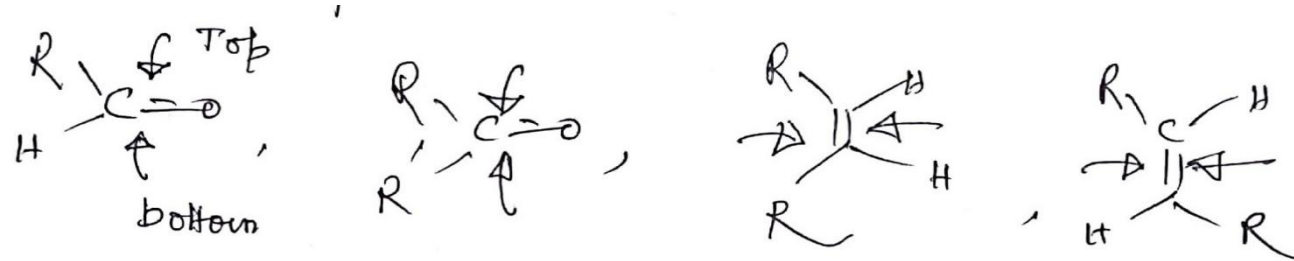


ITEMS TO BE COVERED

- Topicity of faces
- Re /Si and re/si descriptors
- Dihedral and Torsion angle
- Conformations of acyclic compounds
- KLYNE-PRELOG system of conformational terminology
- Conformational analysis/Potential energy diagrams of organic molecules

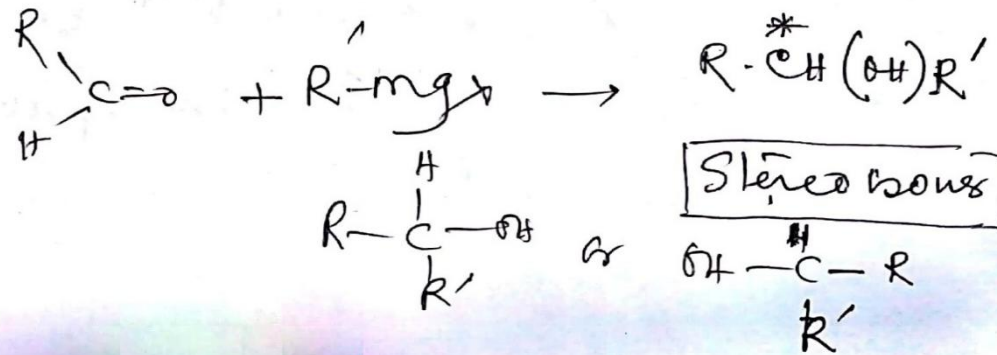
Topicity of faces

Prochiral faces: **Chiral stereoisomers are produced when reagents attack two faces separately**



Chiral stereoisomers are produced when reagents attack two faces separately.

E.g.

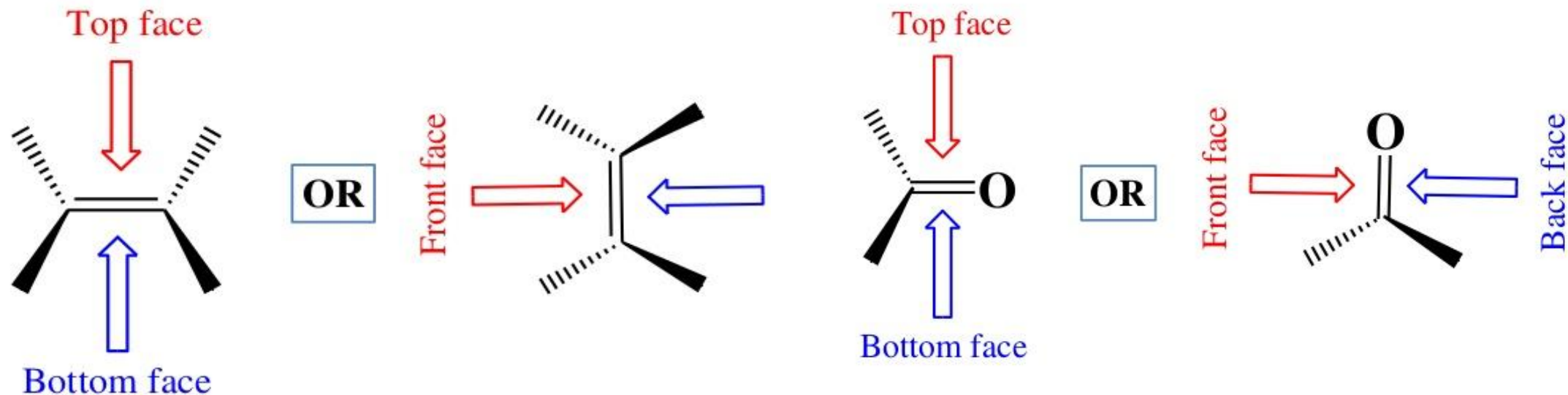


HOMOTOPIC FACES

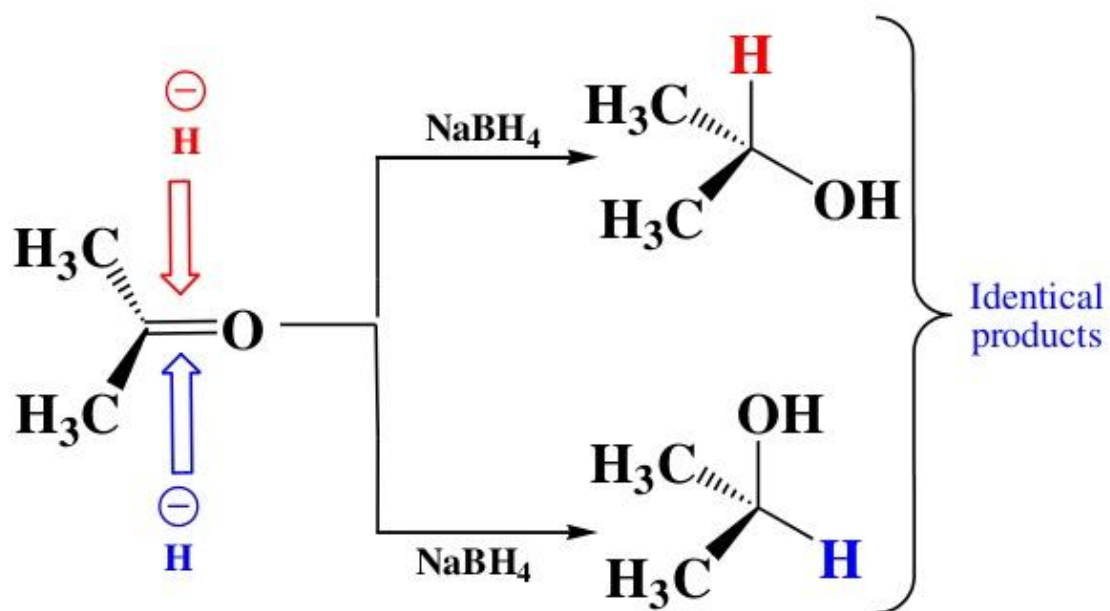
Criterion I: Addition of same reagents to either faces generate the same compound

1. (b) Homo topic faces

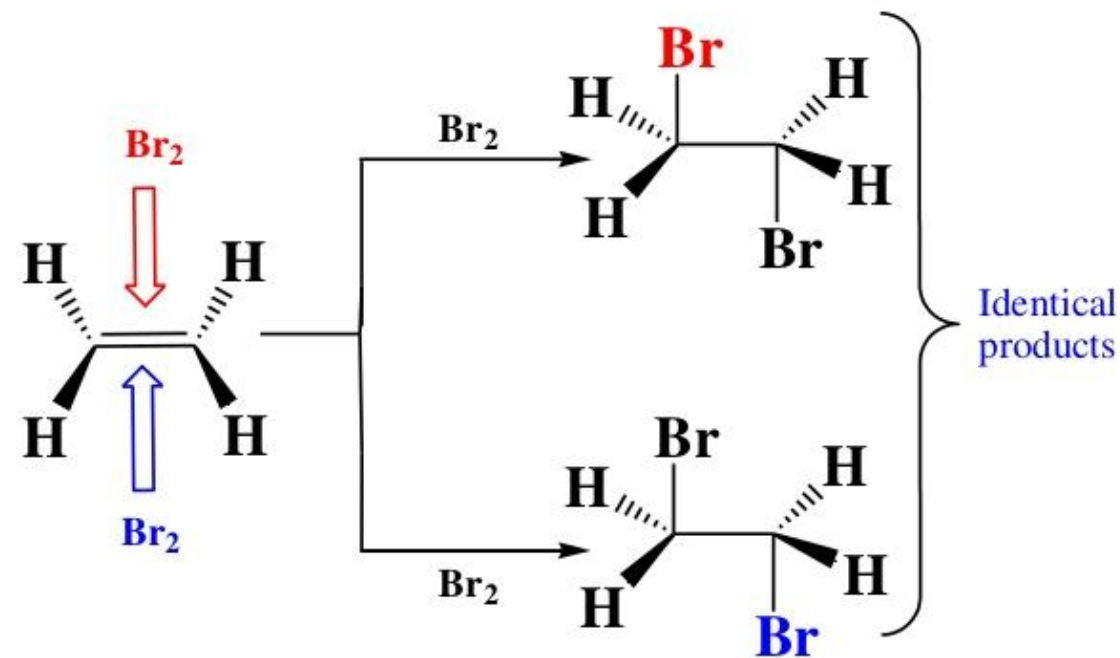
Two faces of a pi system or a double bond are homotopic if addition to either face gives same or identical product.



Same reagent attacking both faces separately



Two products are homomers. Hence, acetone has homotopic face

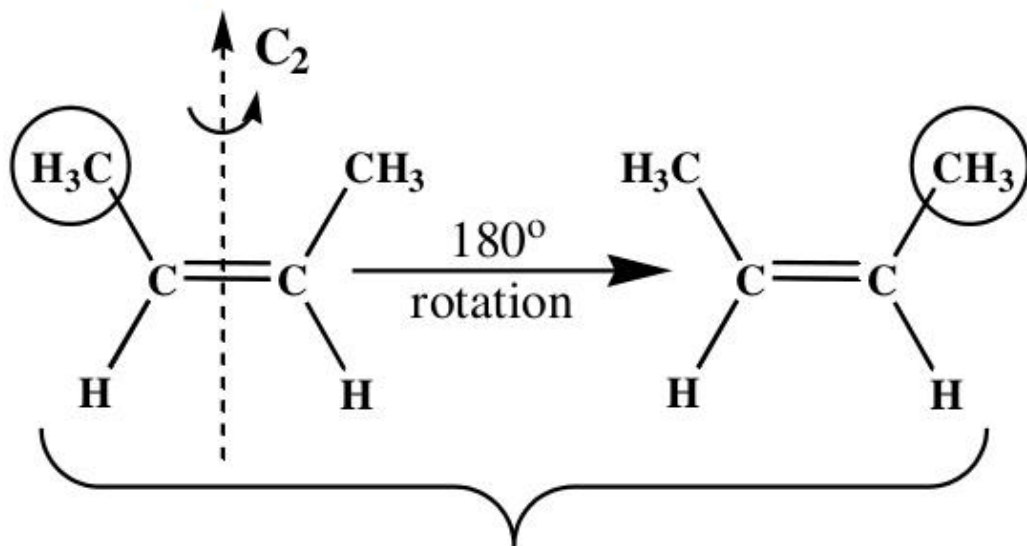


Hence, ethylene has homotopic face

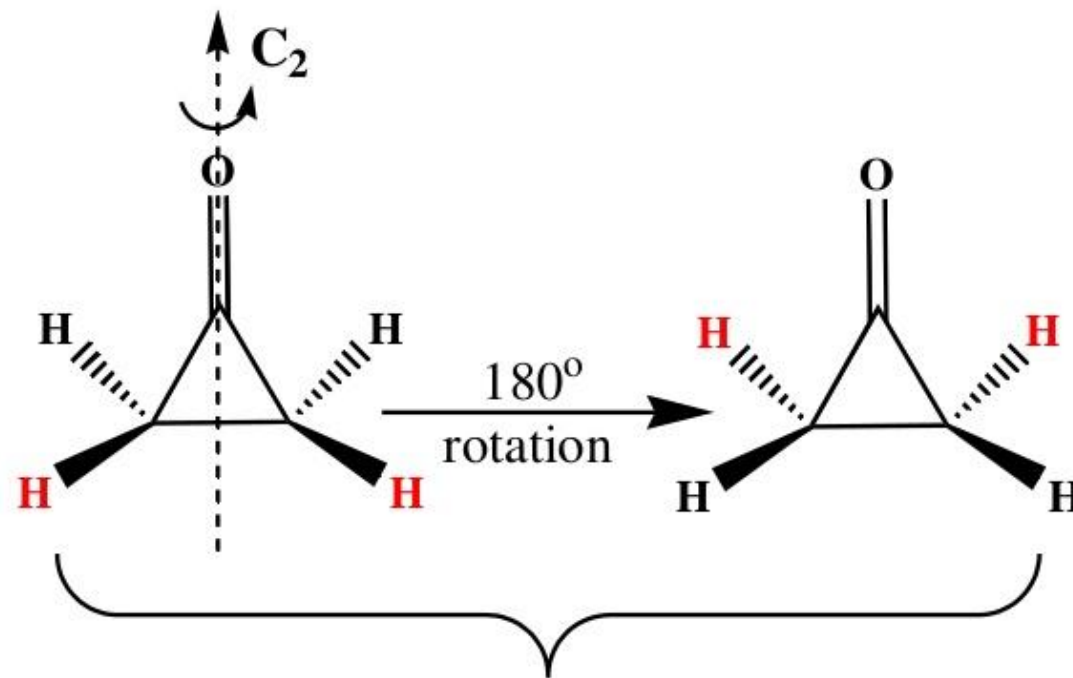
Criterion II: The two faces should be exchangeable by C_n ($n = \text{Even}$)

2. (b) Homo topic faces

Two faces of pi system are homotopic if they can interchange face result in same structure by rotation around C_2 axis.



They are identical and hence it has homotopic face



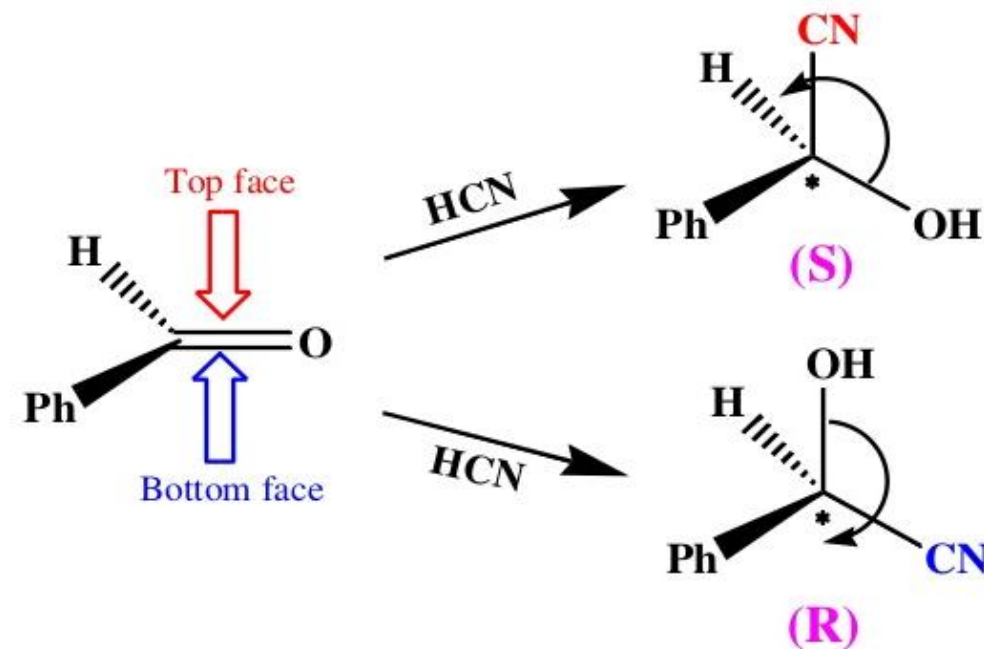
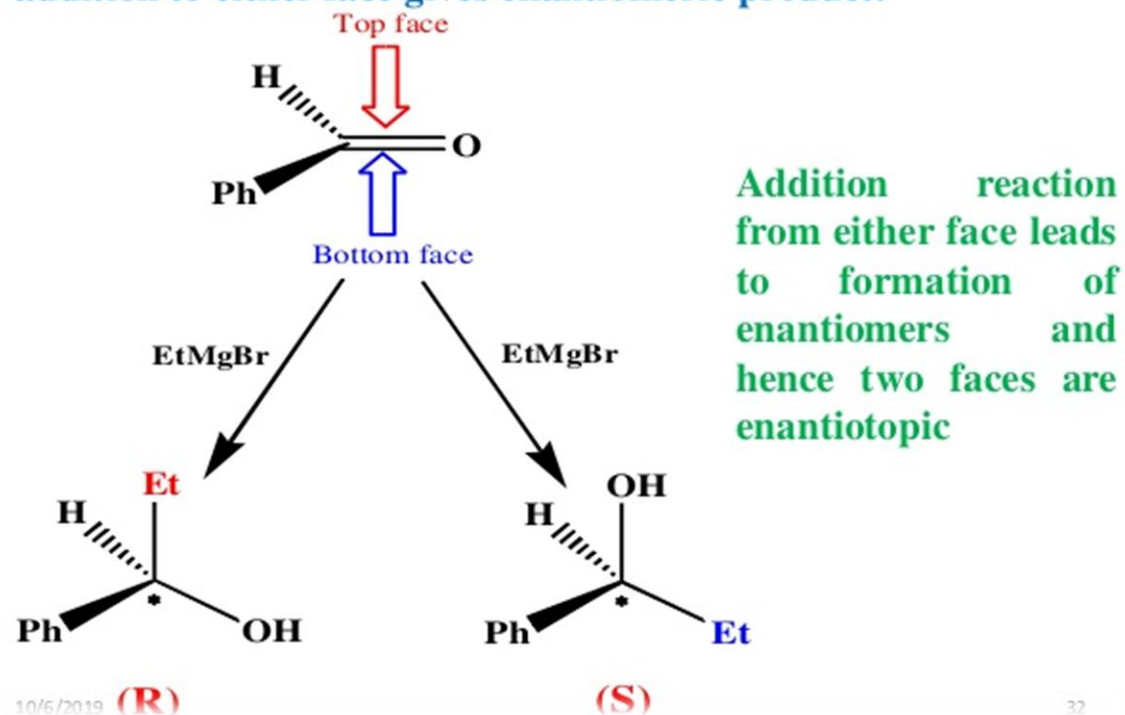
They are identical and hence it has homotopic face

Enantiotopic faces

Criterion I: Addition of same reagents to either faces generate a pair of enantiomers

(b) Enantiotopic faces

Two faces of a pi system or a double bond are enantiotopic if addition to either face gives enantiomeric product.

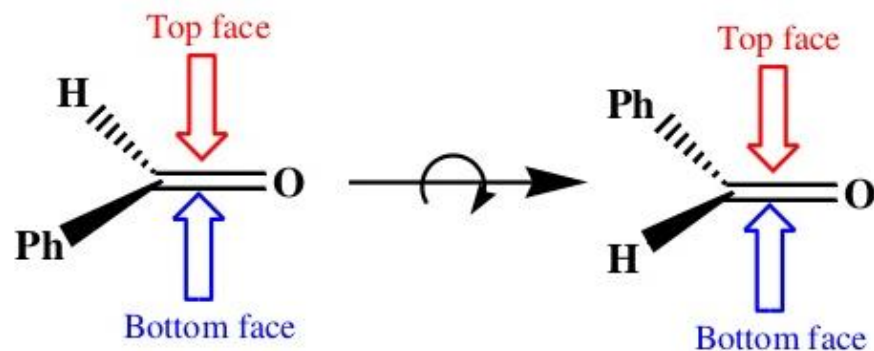


Addition reaction from either face leads to formation of enantiomers and hence two faces are enantiotopic

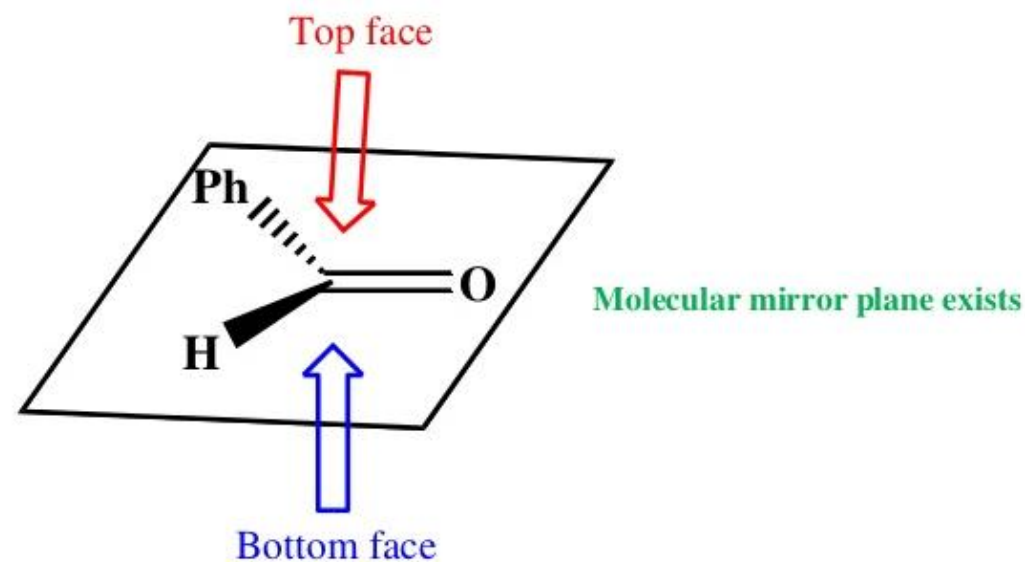
Criterion II: The two faces should be exchangeable by Sigma, S_n or i

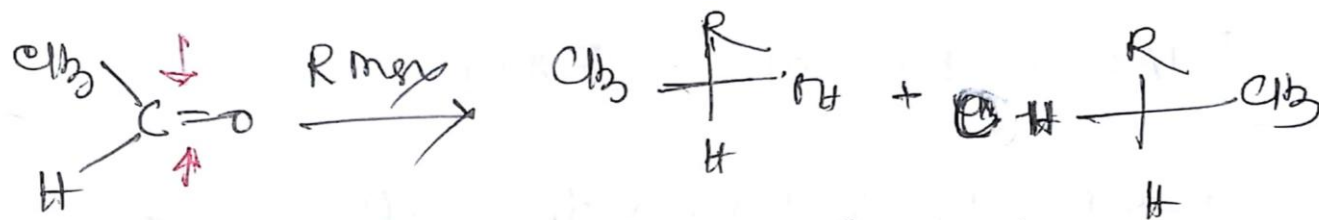
(b) Enantiotopic faces

Two faces are enantiotopic if they can interchange through plane of symmetry or center of inversion or S_n axis.



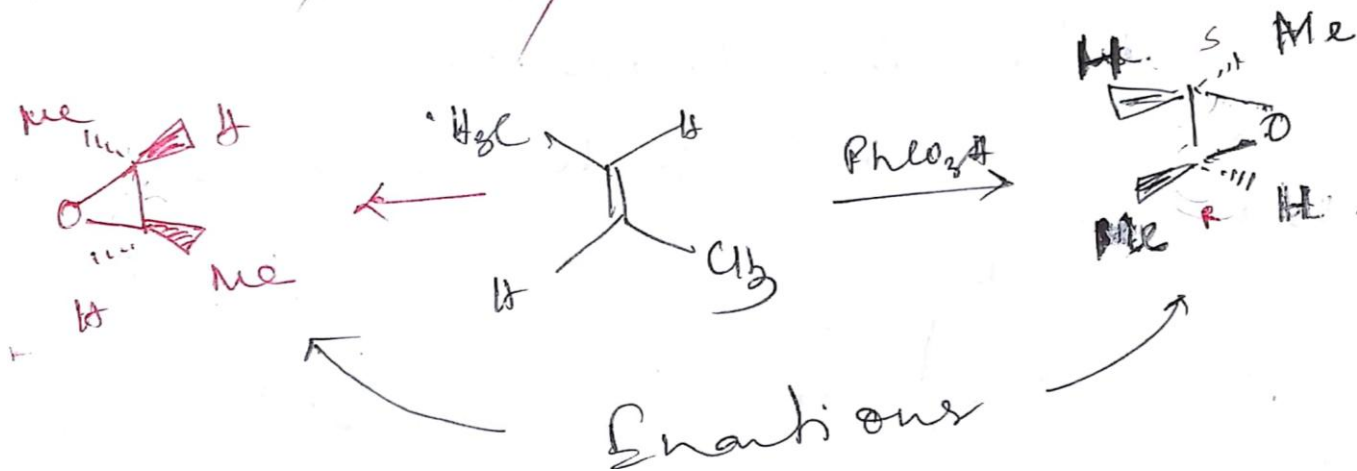
Structure is not same upon rotation hence mirror plane exists.





Face exchange by σ

Enantiomers.



Behaviour of ligands towards NMR

NMR Spectroscopy of Homotopic Hydrogen

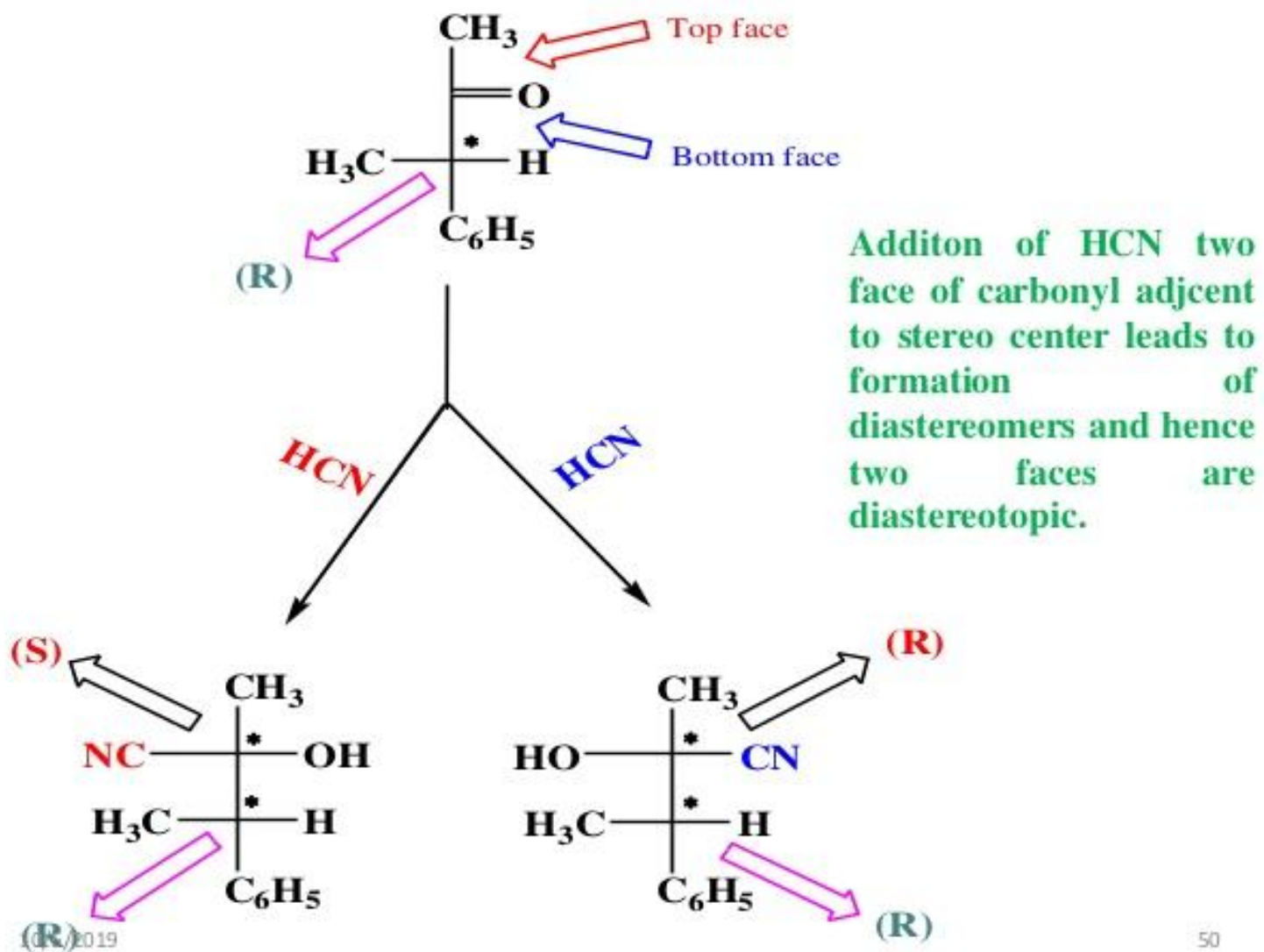
If the hydrogen atoms in the molecule are homotopic, then they are chemically equivalent. Hence they will resonate at same chemical shift values.

NMR Spectroscopy of Enantiotopic Hydrogen

If the hydrogen atoms in the molecule are enantiotopic, then they are chemically equivalent. Hence they will resonate at same chemical shift values.

NMR Spectroscopy of Diastereotopic Hydrogen

If the hydrogen atoms in the molecule are diastereotopic, then they are chemically and magnetically non equivalent. Hence they will resonate at different chemical shift values.



50

SUMMARY of the Faces

Between homotopic groups and faces no differentiation is possible either by enzyme or by NMR or by human being because they are homomers or identical.

Between enantiotopic groups and faces differentiation is possible either by enzyme or by NMR in chiral reagent or catalyst.

Topicity	Substitution-addition criteria	Symmetry criteria	Reactivity
Homotopic groups and faces	Homomers / Identical	C_n or C_2	No differentiation possible

Topicity	Substitution-addition criteria	Symmetry criteria	Reactivity
Enantiotopic groups and faces	Enantiomers	σ_h or S_n	Differentiation possible

Between diastereotopic groups and faces differentiation is possible either by enzyme or by reagent or by NMR.

Topicity	Substitution-addition criteria	Symmetry criteria	Reactivity
Diastereotopic groups and faces	Diastereomers	Not applicable	Differentiation possible

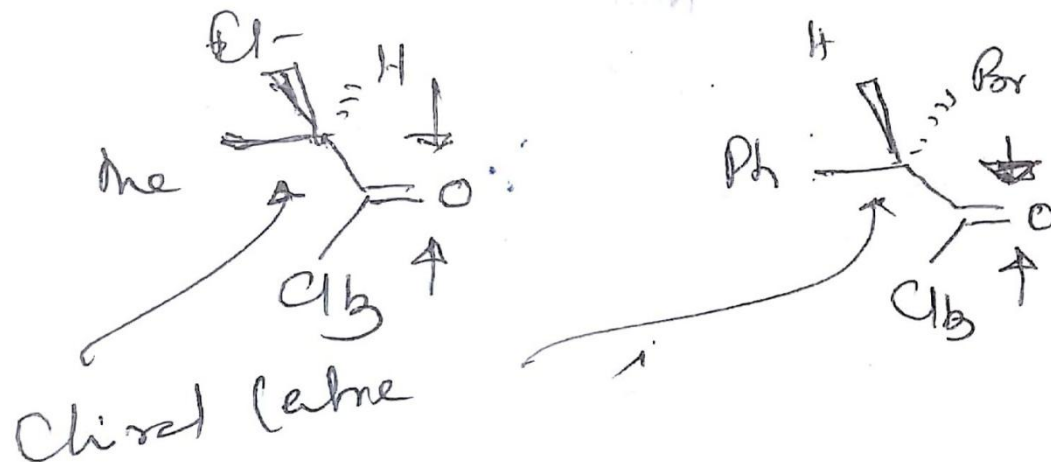
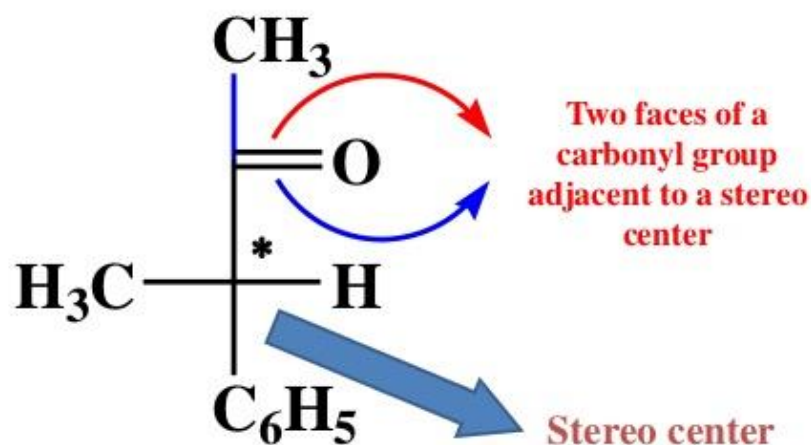
Diastereotopic faces

Criterion I: Reagents added to either sides of the faces lead to diastereomers

Criterion II: Faces are not exchanged by any symmetry elements

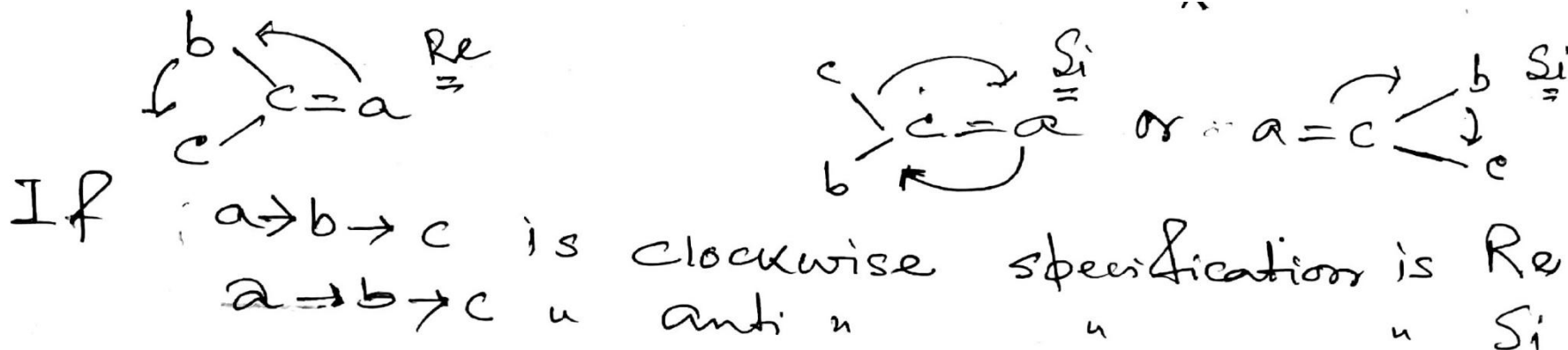
(b) Diastereotopic faces

Two faces of a carbonyl group adjacent to a stereo center on addition reaction leads to diastereomers and possess diastereotopic face.

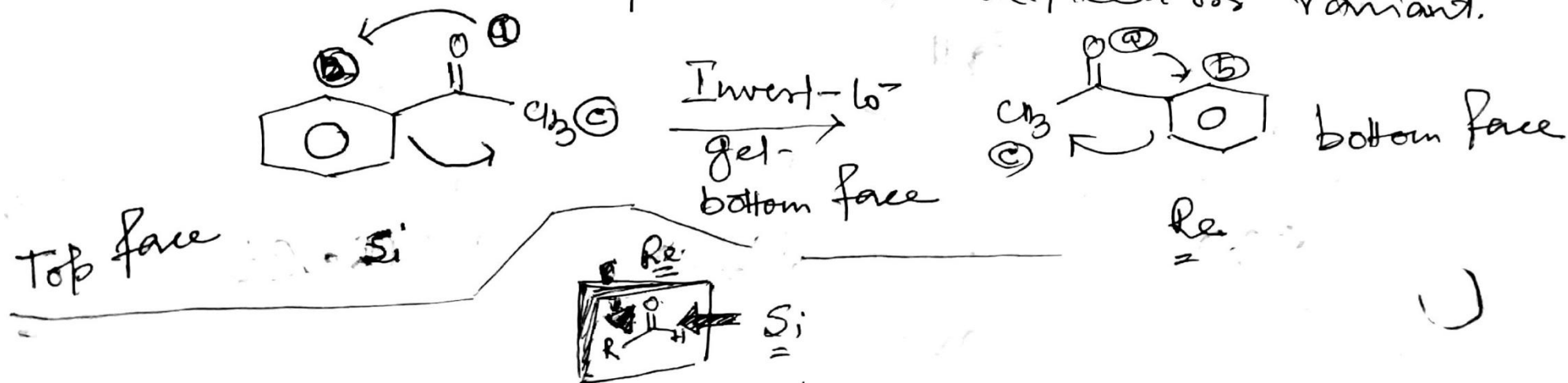


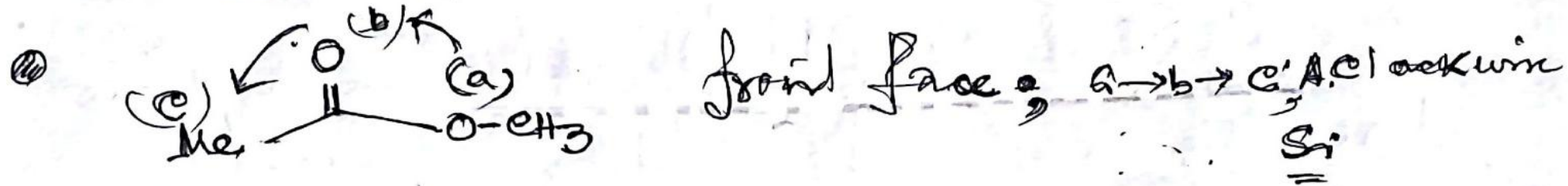
Re/Si notations for stereo heterotopic faces

a-b-c Clockwise- Re :: a-b-c Anticlockwise- Si



* Re and Si faces are reflections variant.

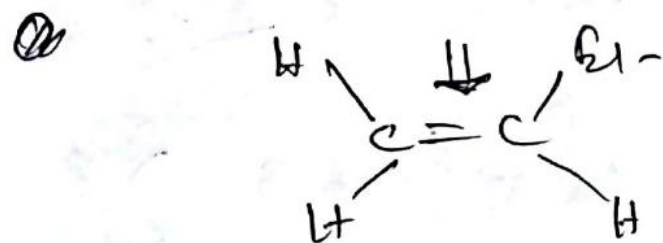




Methyl acetate-

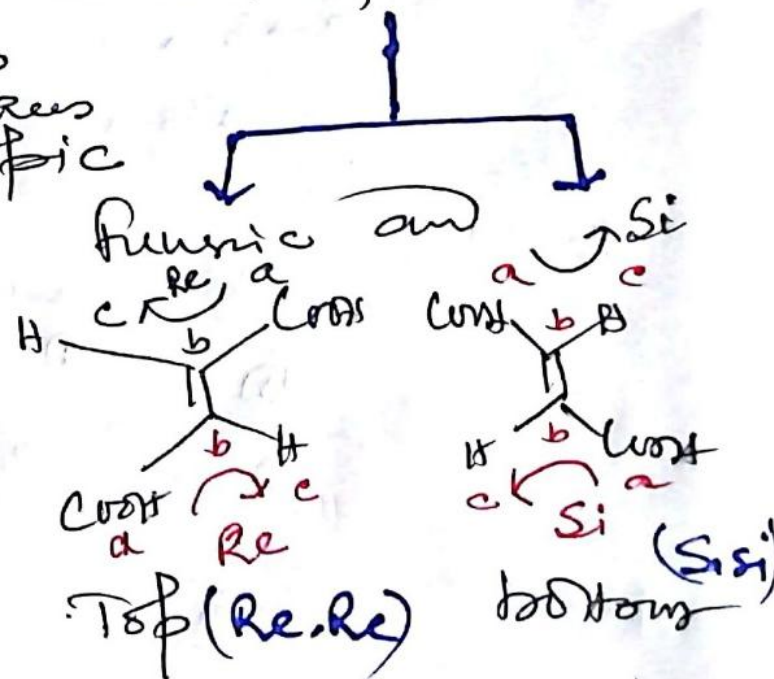
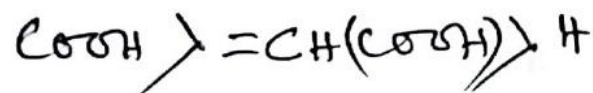
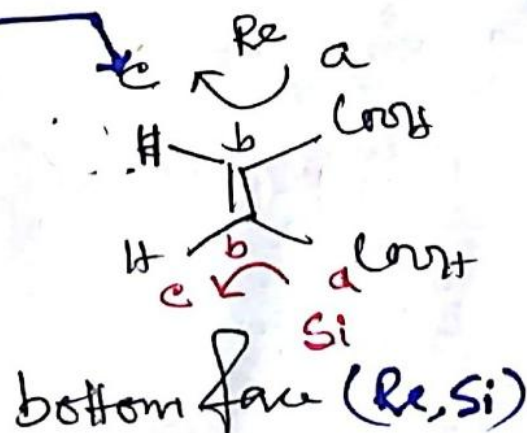
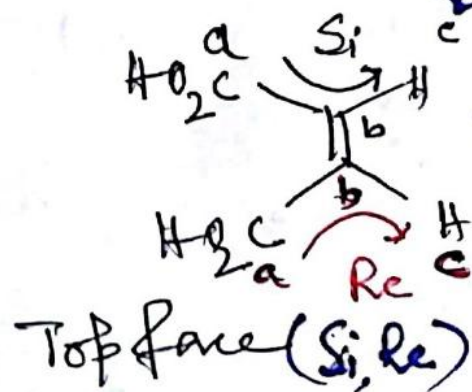


Top & bottom faces are enantiotopic



Maleic acid

Top & bottom faces are homotopic



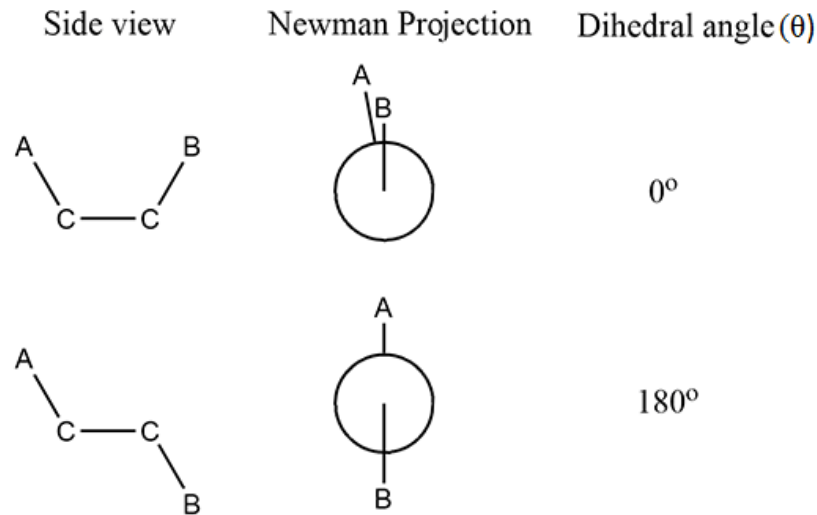
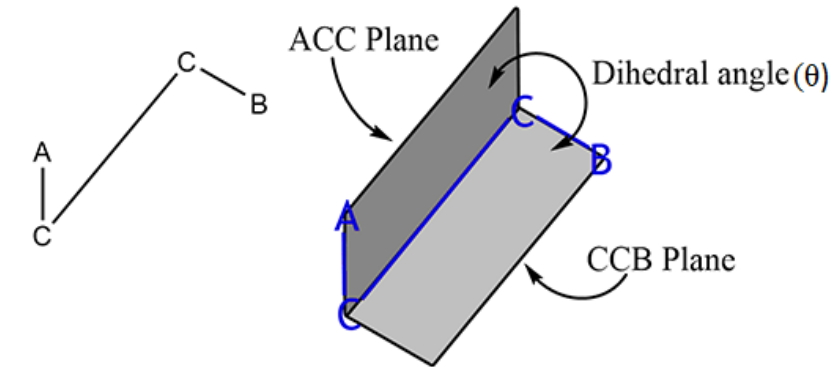
Conformations of acyclic compounds

Generally configurational isomers separated by energy gap of >100 KJ/mole are isolable at room temp

Conformational isomers have energy gap < 60 KJ/mole

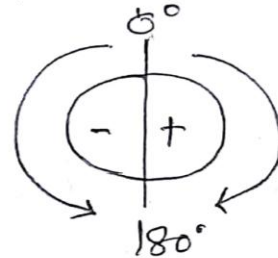
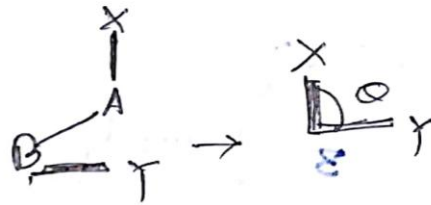
Dihedral angle

The angle generated by two intersecting planes, such as ACC and CCB



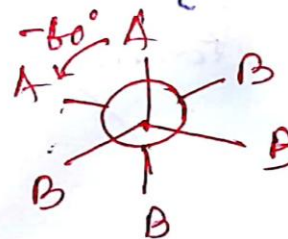
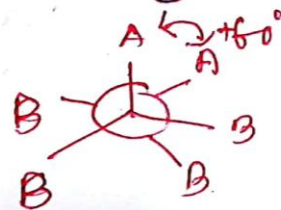
Torsional angle

Torsion angle: In $X-A-B-Y$ systems, neither X or Y are colinear with either A or B , the angle between $X-A$ and $B-Y$ is known as TORSION ANGLE.



Torsion angle has direction
i.e. +ve (from 0° to 180°)
clockwise
-ve (0° to -180°)
anticlockwise.

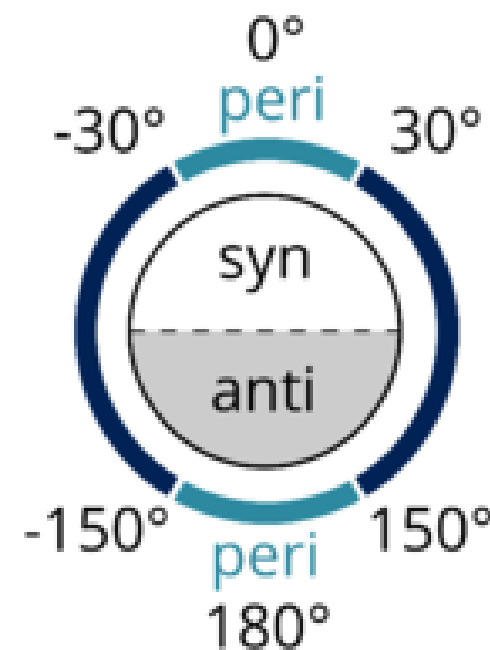
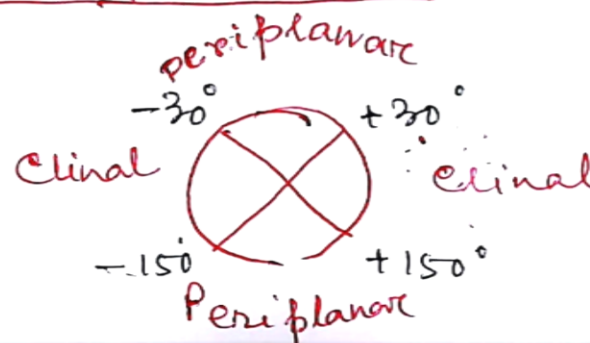
Starting from front Carbons to back Carbons in
Kewman proj.



(10)

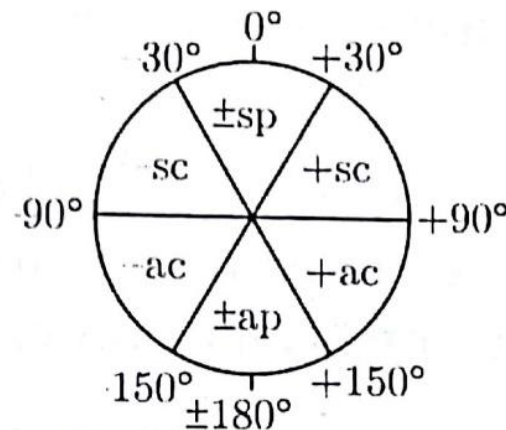
Klyne Prelog system

- ① Instead of mentioning exact torsion angle a range of torsion angle is mentioned.
- ② Torsion angles can't be exactly determined.
- ③ Divided the circle (in Newman proj formula) into two halves in three different ways.

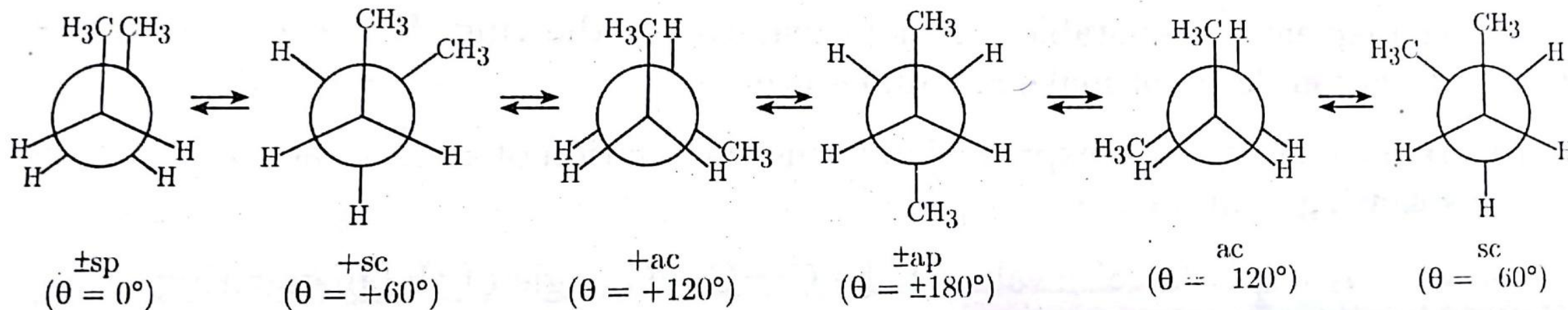


The terminologies

- (i) **\pm syn-periplanar (\pm sp)** : When the torsion angle between the two reference groups is $0^\circ \pm 30^\circ$, the conformation is designated as \pm syn-periplanar (\pm sp).
- (ii) **+syn-clinal (+sc)** : When the torsion angle between the two reference groups is $+60^\circ \pm 30^\circ$, the conformation is designated as +syn-clinal (+sc).
- (iii) **+anti-clinal (+ac)** : When the torsion angle between the two reference groups is $+120^\circ \pm 30^\circ$, the conformation is designated as +anti-clinal (+ac).
- (iv) **\pm anti-periplanar (\pm ap)** : When the torsion angle between the two reference groups is $180^\circ \pm 30^\circ$, the conformation is designated as \pm anti-periplanar (\pm ap).
- (v) **-anti-clinal (-ac)** : When the torsion angle between the two reference groups is $-120^\circ \pm 30^\circ$, the conformation is designated as -anti-clinal (-ac).
- (vi) **-syn-clinal (-sc)** : When the torsion angle between the two reference groups is $-60^\circ \pm 30^\circ$, the conformation is designated as -syn-clinal (-sc).

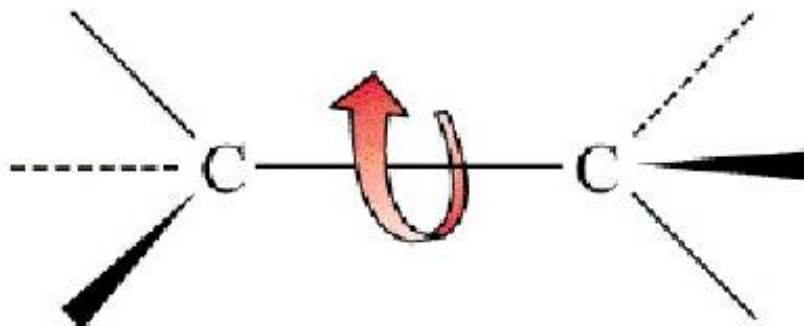


The different conformations of butane, for example, may be designated as follows :



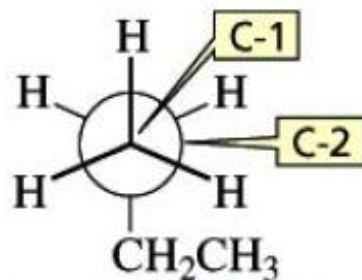
Conformations of Alkanes: Rotation about C-C Single Bonds

- Different spatial arrangements of atoms that result from rotation about carbon-carbon single bonds are known as **conformations**
- Different conformations also are called **conformational isomers** or **conformers**

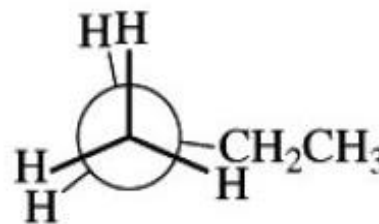


Conformations of Alkanes: Rotation About C-C Single Bonds

- When ethane molecules rotate about the carbon-carbon bond there are two extremes:
 - **staggered conformation**
 - **eclipsed conformation**

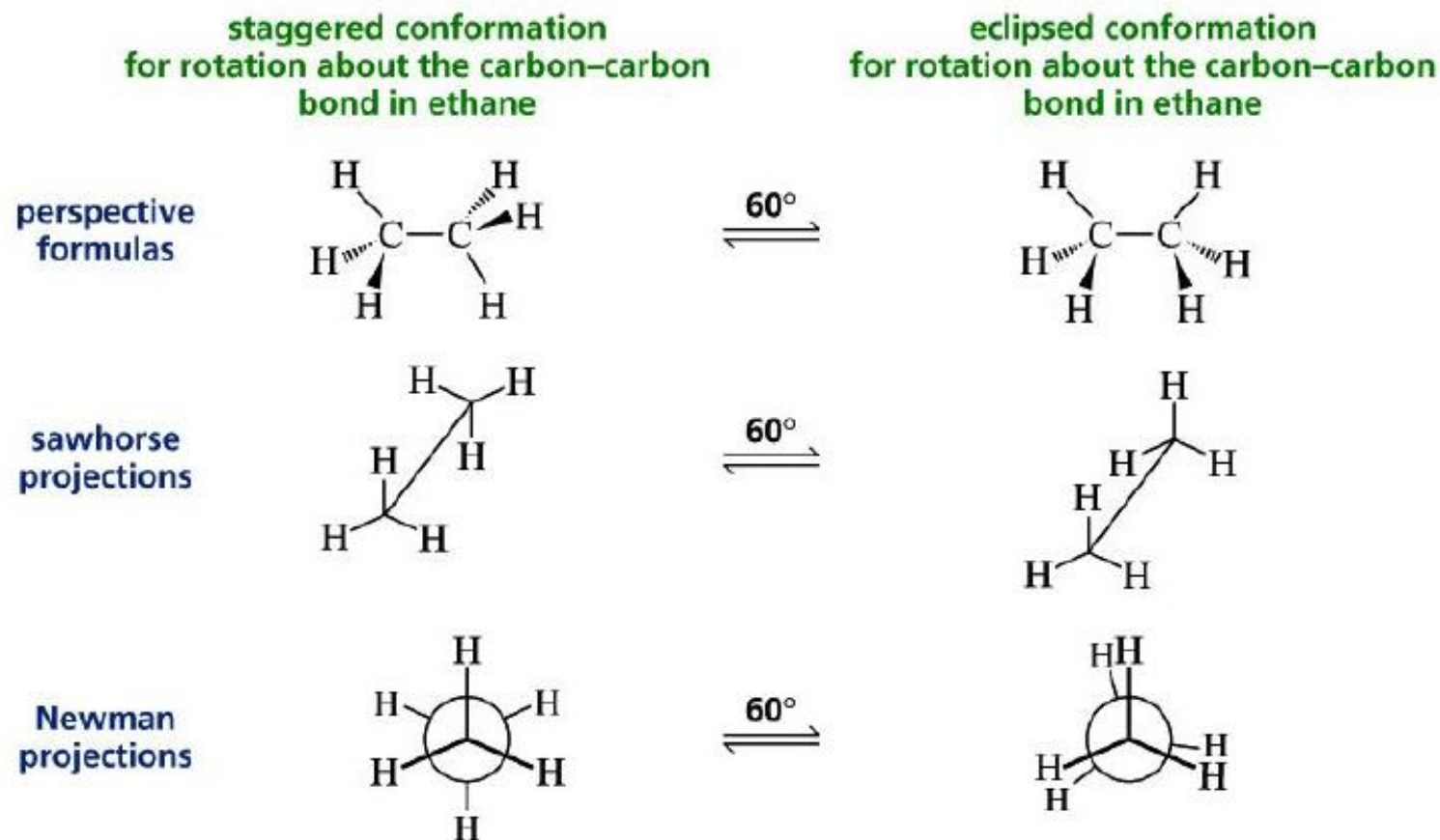


staggered conformation for rotation
about the C-1—C-2 bond in butane

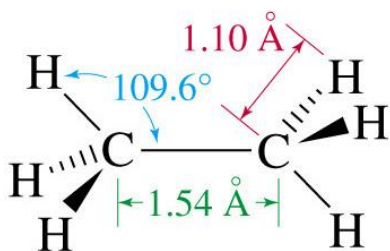


eclipsed conformation for rotation
about the C-1—C-2 bond in butane

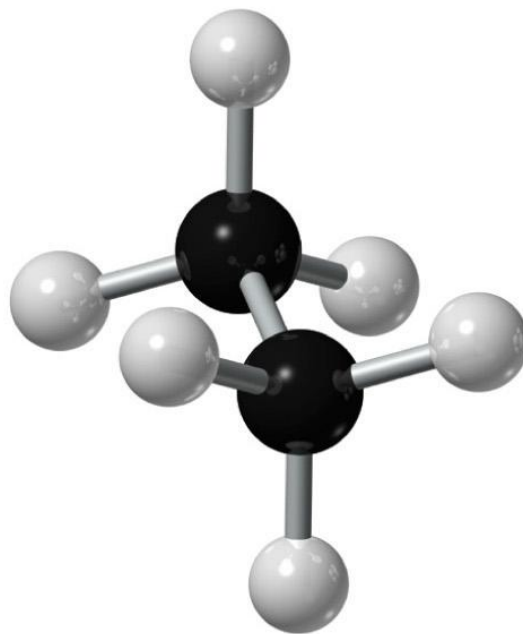
Conformations of Alkanes: Rotation About C-C Single Bonds



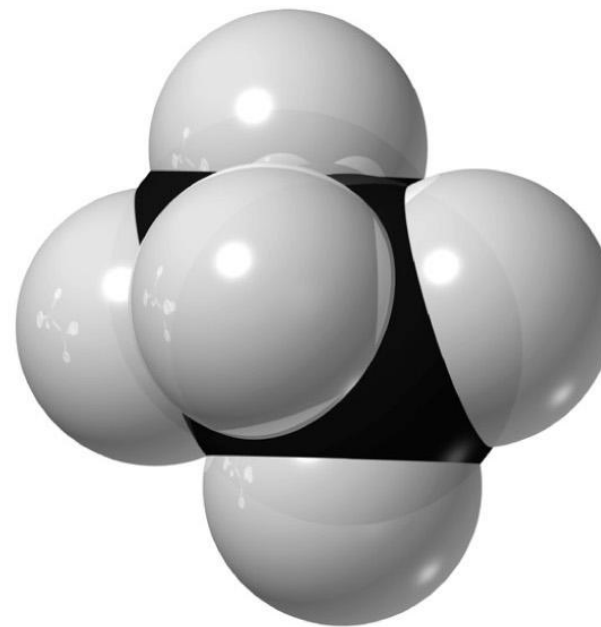
Views of Ethane



ethane

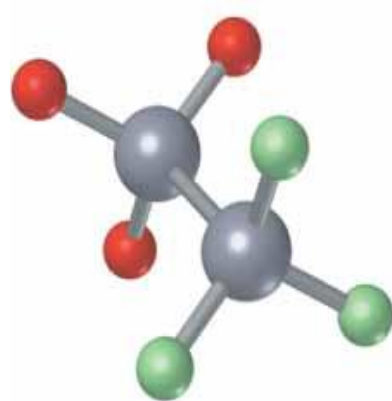


ethane

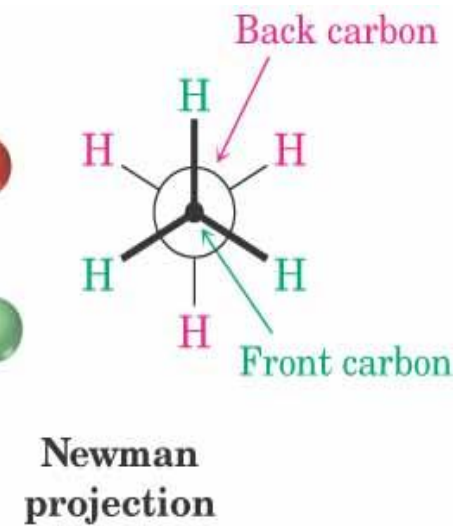
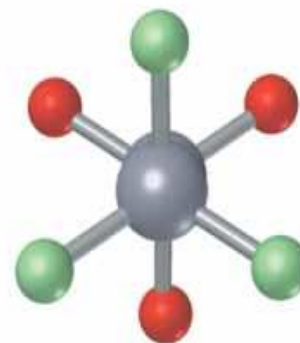
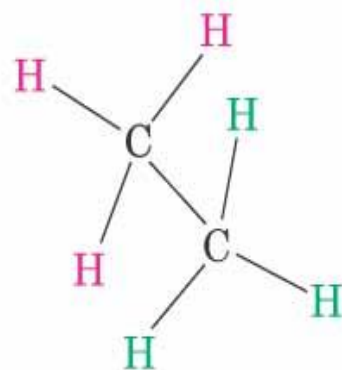


ethane

The Newman Projection

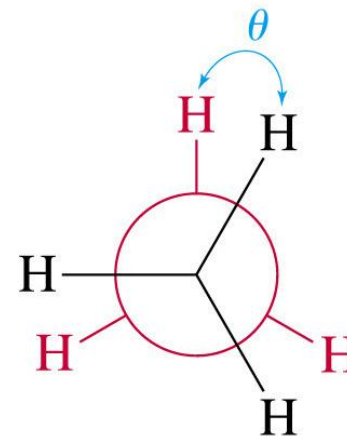
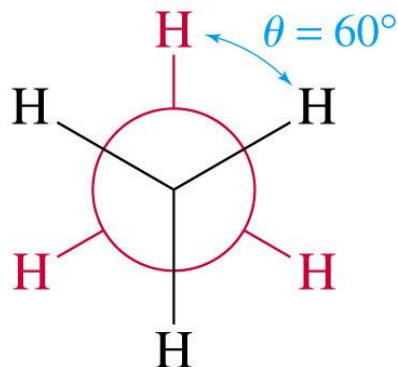
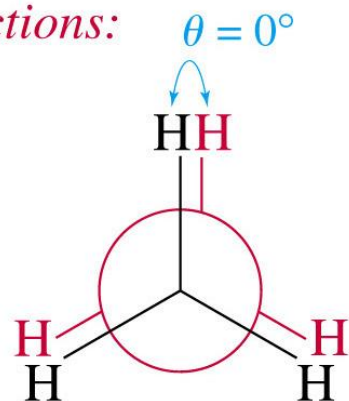


**Sawhorse
representation**

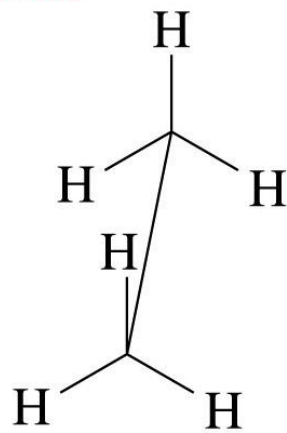


Rotational Conformations of Ethane

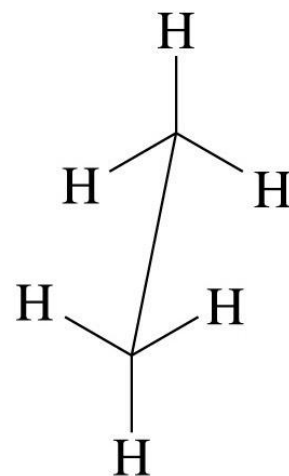
Newman projections:



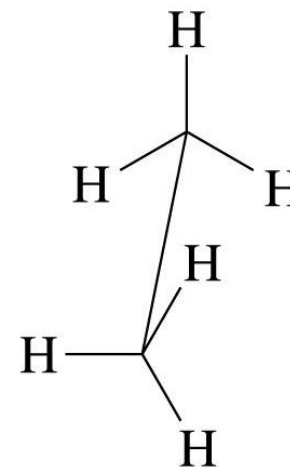
Sawhorse structures:



eclipsed, $\theta = 0^\circ$



staggered, $\theta = 60^\circ$

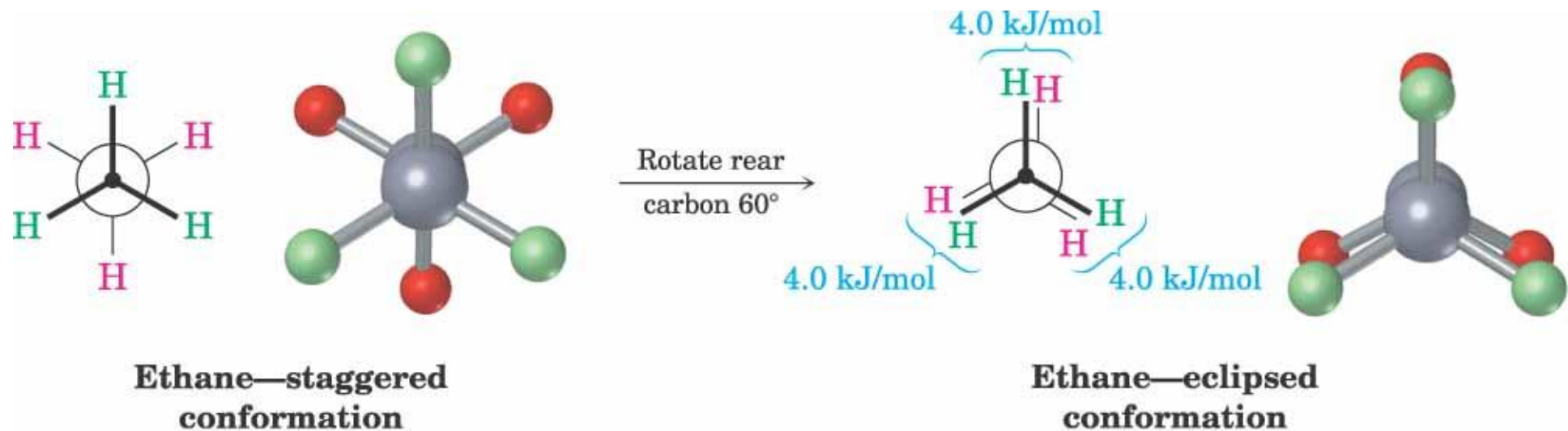


skew, $\theta = \text{anything else}$

Definitions

- **Conformations** - Different spatial arrangements that a molecule can adopt due to rotation about sigma bonds.
- **Staggered** - A low energy conformation where the bonds on adjacent atoms bisect each other (60° dihedral angle), maximizing the separation.
- **Eclipsed** - A high energy conformation where the bonds on adjacent atoms are aligned with each other (0° dihedral angle).

60° Rotation Causes Torsional or Eclipsing Strain



Types of Strain

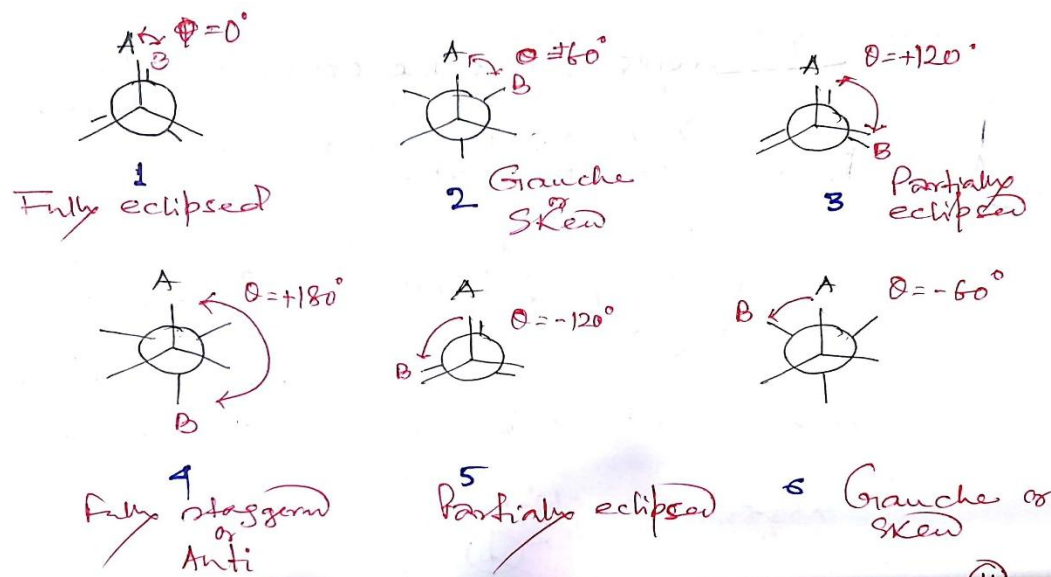
- **Steric** - Destabilization due to the repulsion between the electron clouds of atoms or groups. Groups try to occupy some common space.
- **Torsional** - Destabilization due to the repulsion between pairs of bonds caused by the electrostatic repulsion of the electrons in the bonds. Groups are eclipsed.
- **Angle** - Destabilisation due to distortion of a bond angle from its optimum value caused by the electrostatic repulsion of the electrons in the bonds. e.g. cyclopropane

Definitions

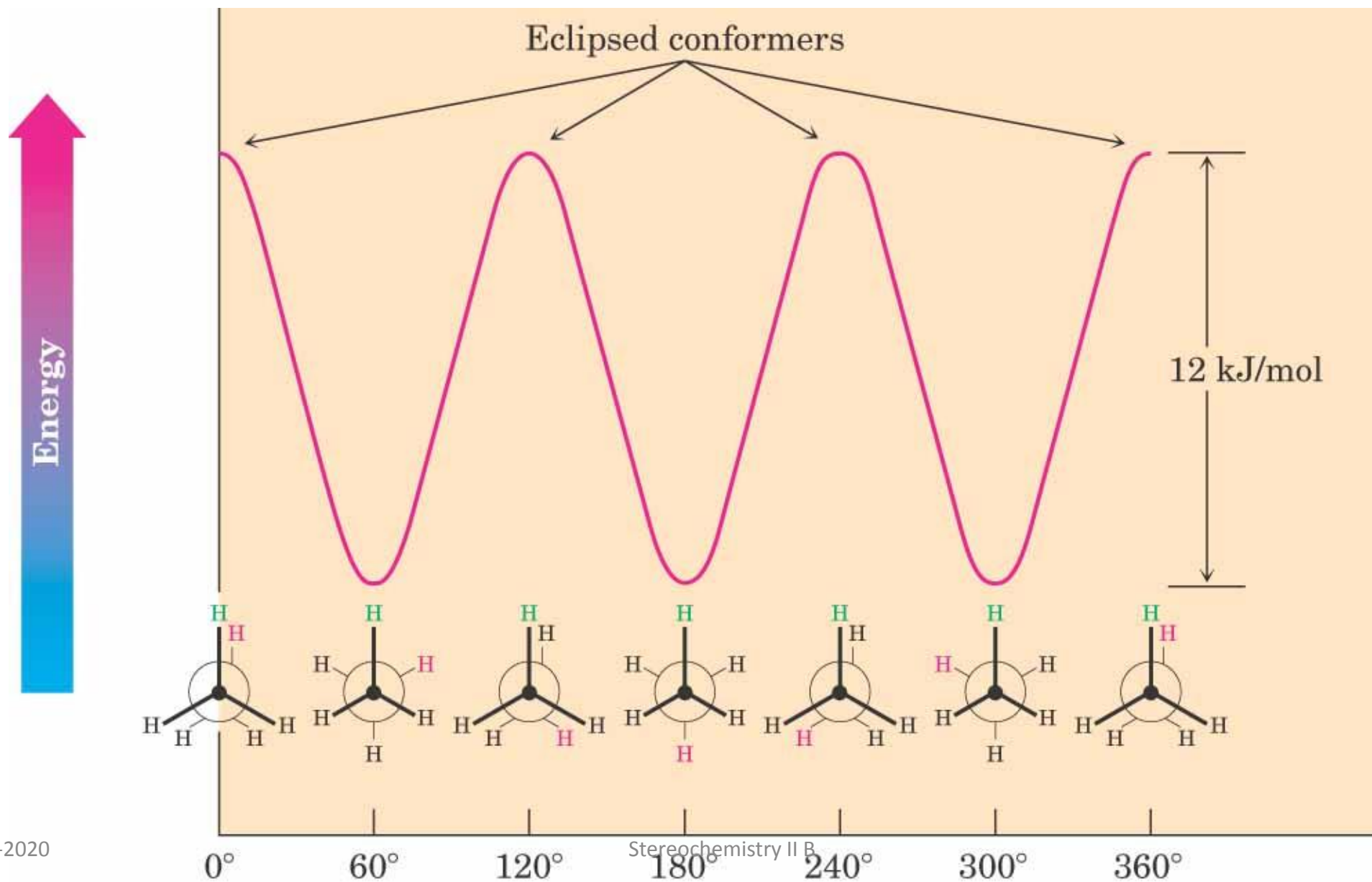
- **Anti/Fully staggered** - Two substituents attached to adjacent atoms when their bonds are at 180° with respect to each other.
- **Syn/ Eclipsed** - Two substituents attached to adjacent atoms when their bonds are at 0° with respect to each other
- **Gauche/Skew** - Two substituents attached to adjacent atoms when their bonds are at 60° with respect to each other.

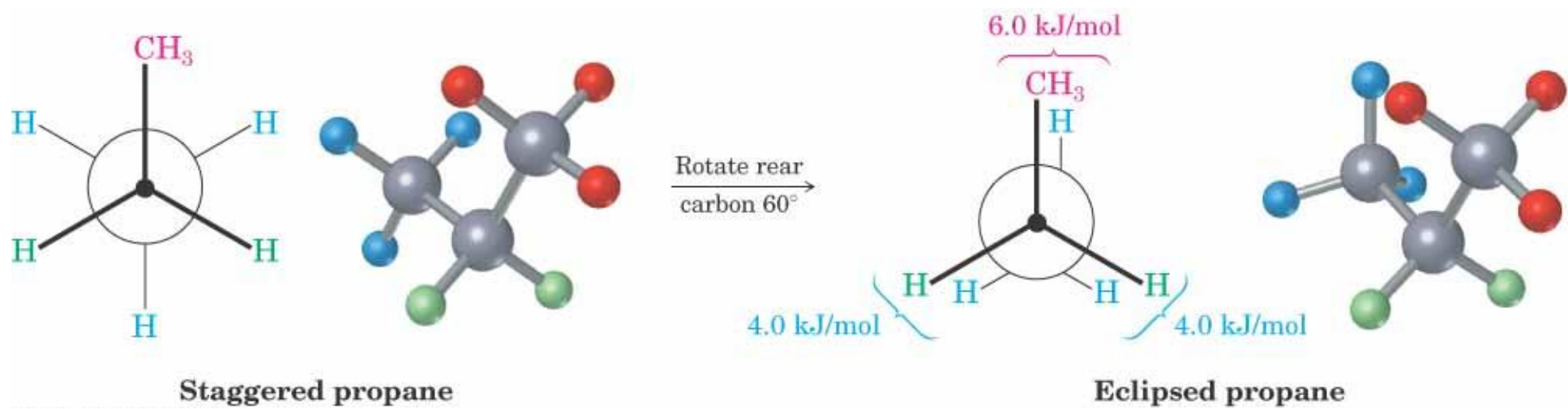
Different conformations

- **Anti/Fully staggered** - Two substituents attached to adjacent atoms when their bonds are at 180° with respect to each other.
- **Syn/ Eclipsed** - Two substituents attached to adjacent atoms when their bonds are at 0° with respect to each other
- **Gauche/Skew** - Two substituents attached to adjacent atoms when their bonds are at 60° with respect to each other.

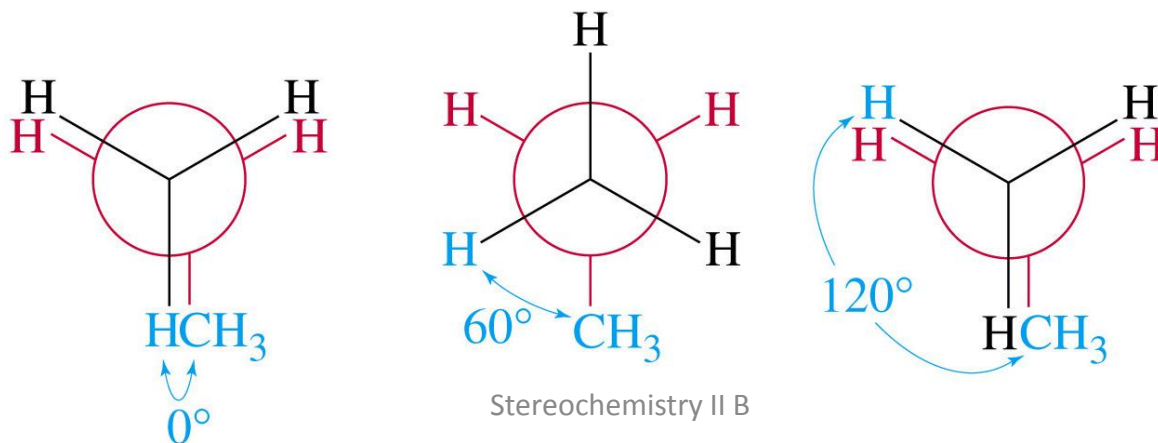
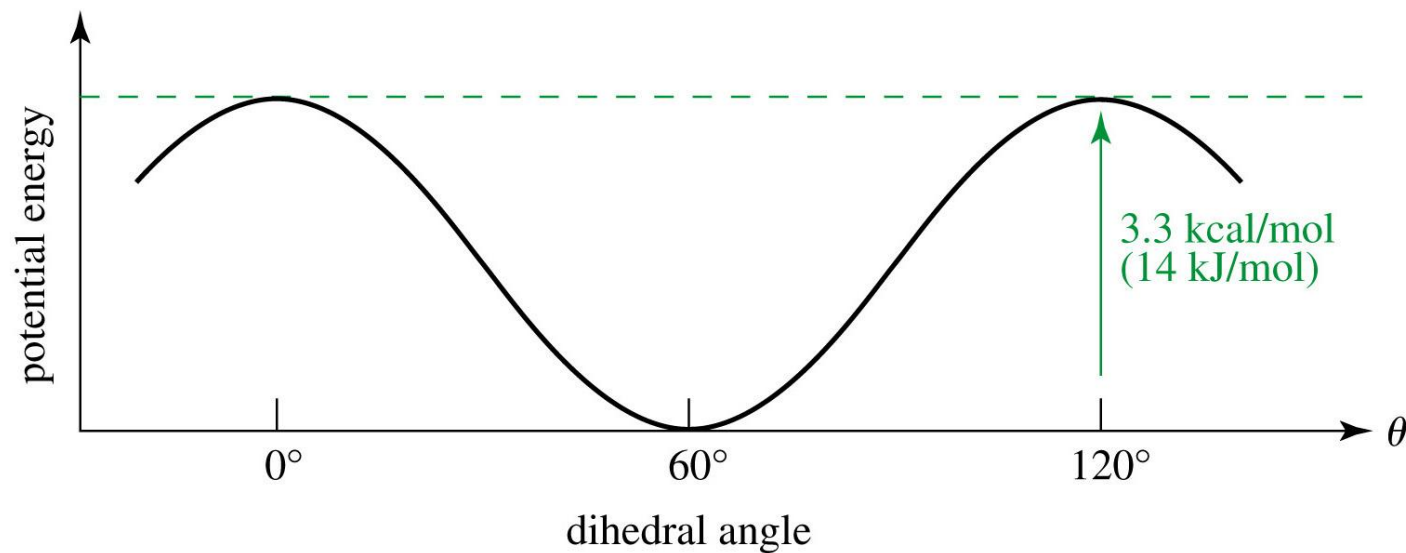


Potential Energy Diagram

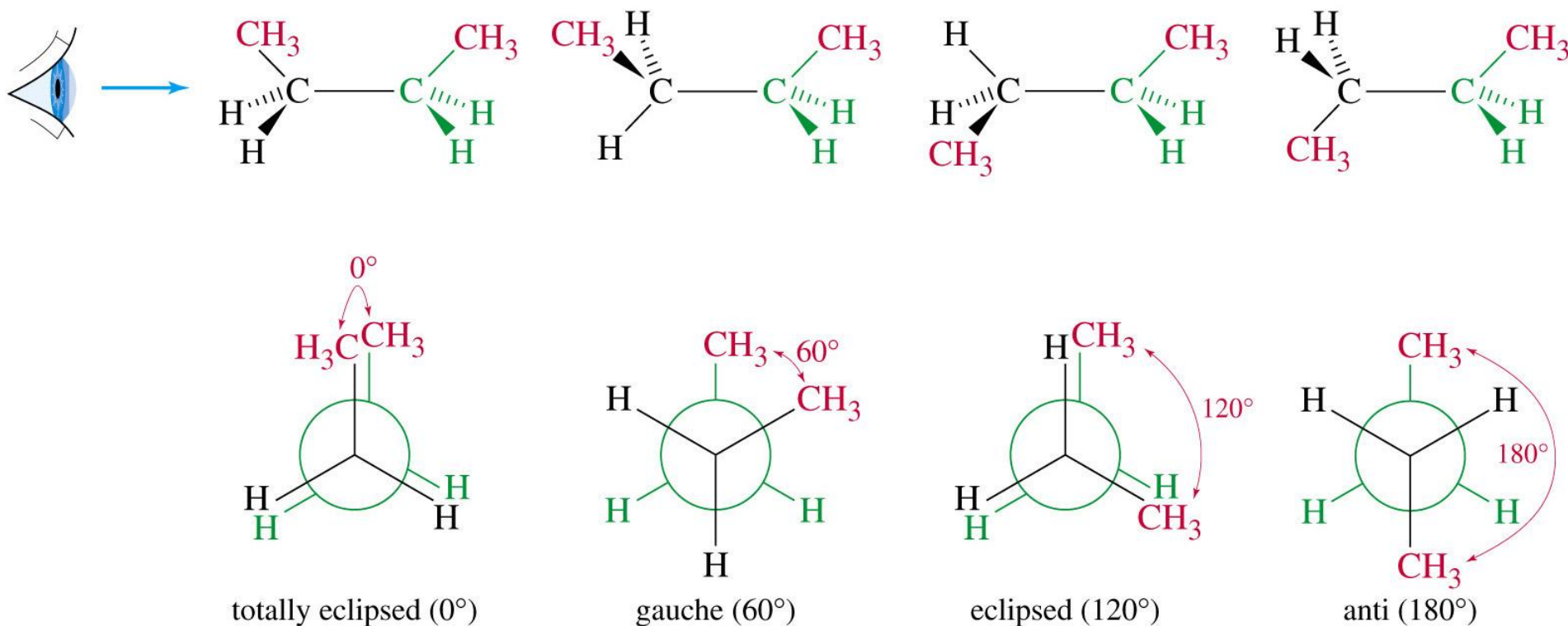




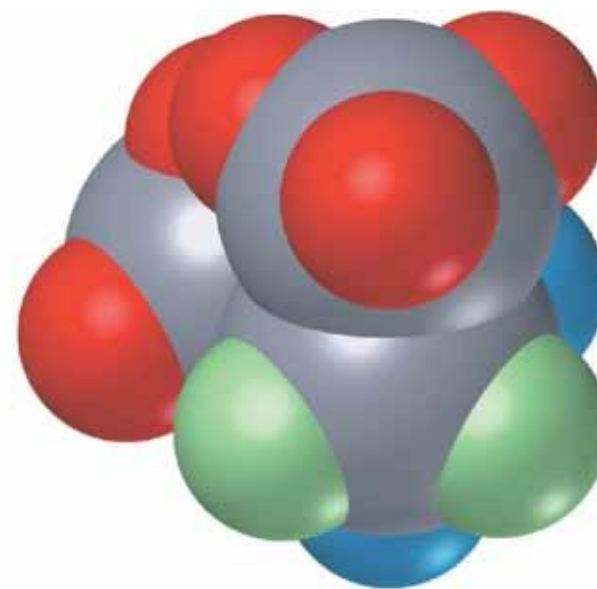
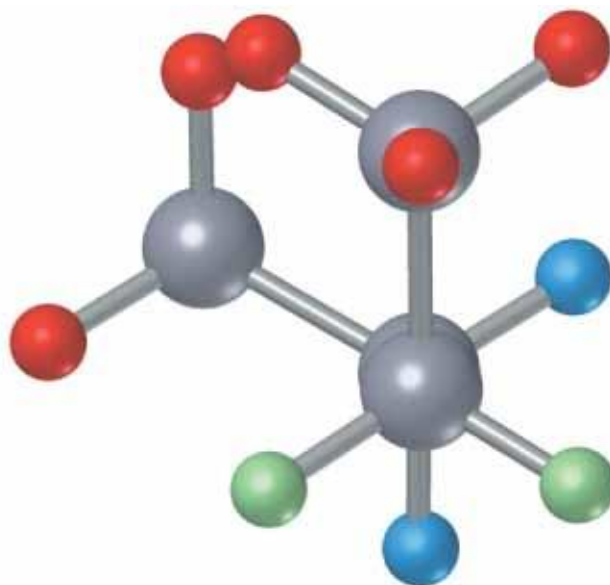
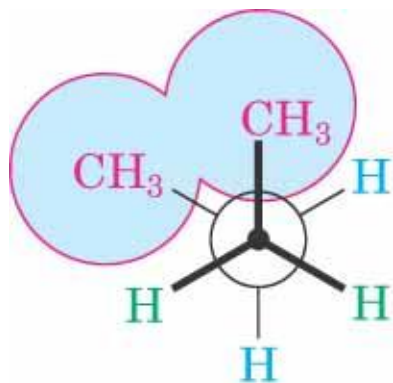
Propane Conformations: Larger Barrier to Rotation



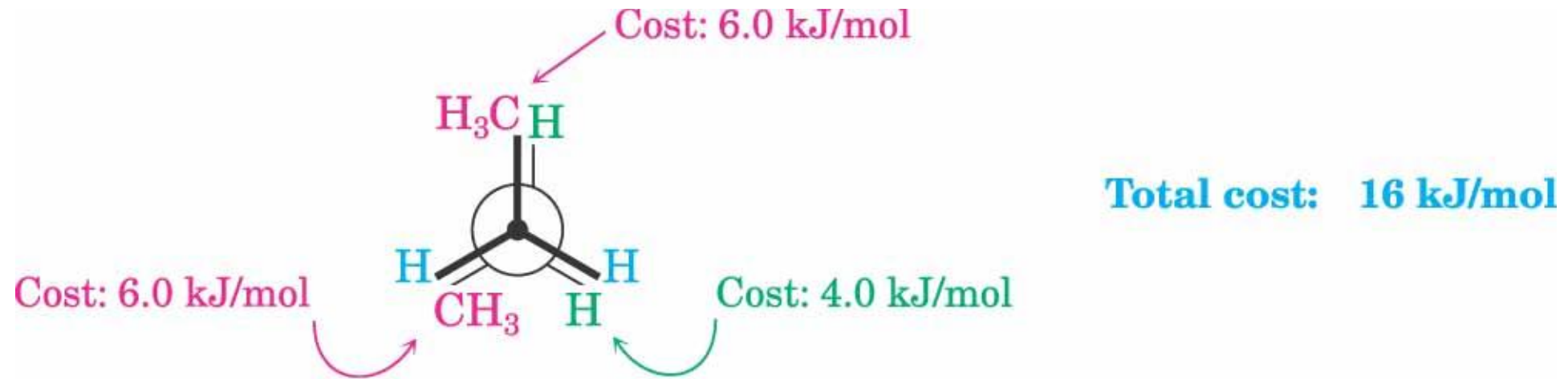
Butane Conformations (C_2-C_3)



Gauche Interaction in Butane



2 Different Eclipsed Conformations

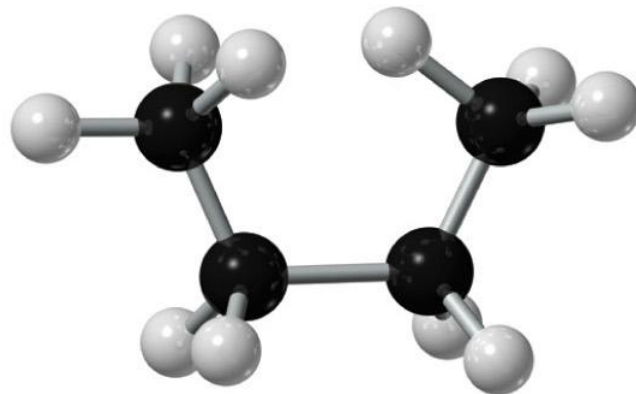
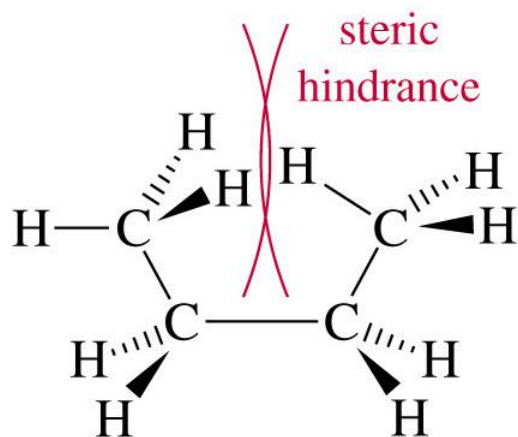


Strain Energy can be Quantified

TABLE 4.1 Energy Costs for Interactions in Alkane Conformers

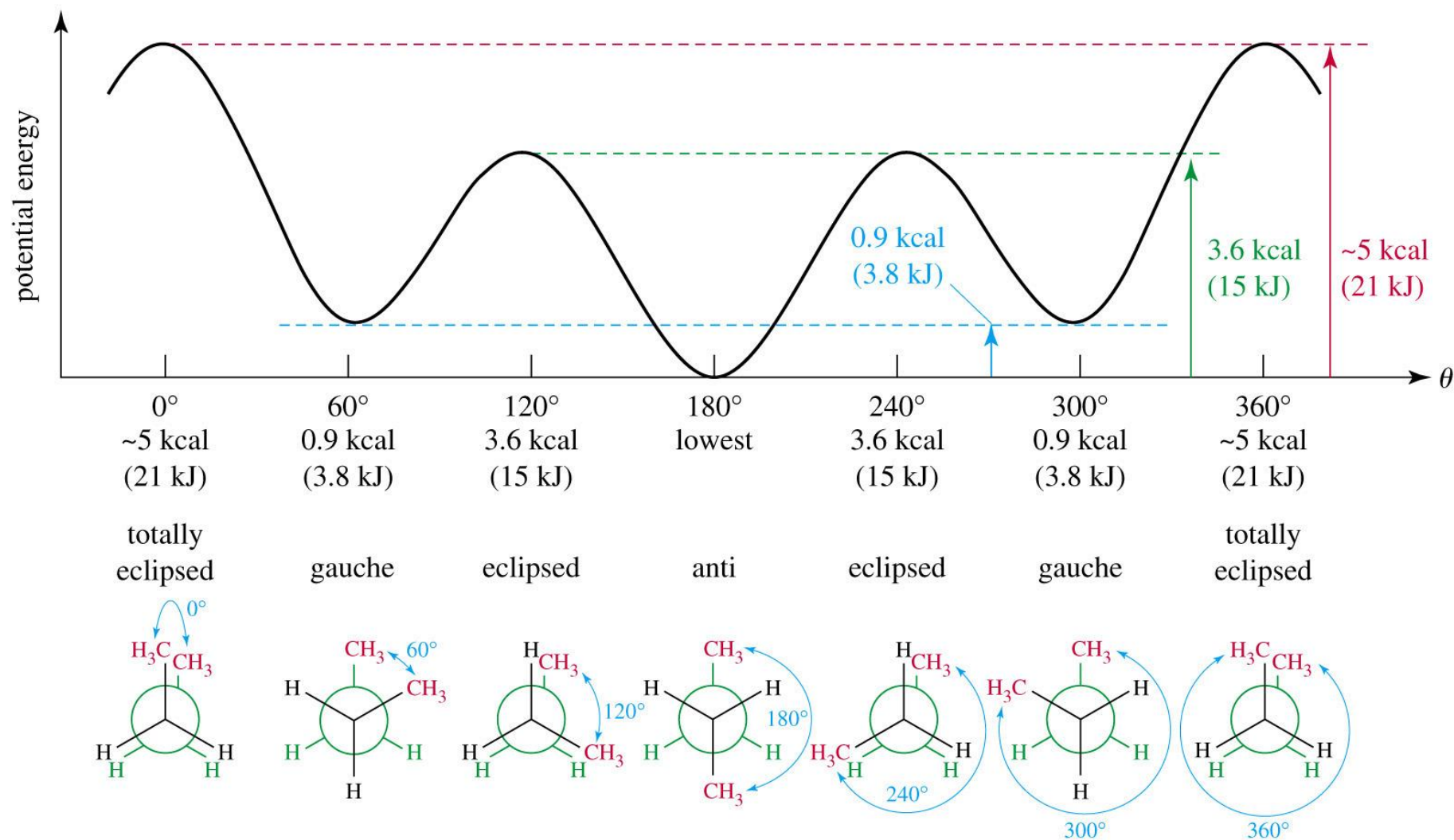
Interaction	Cause	Energy cost	
		(kJ/mol)	(kcal/mol)
H \leftrightarrow H eclipsed	Torsional strain	4.0	1.0
H \leftrightarrow CH ₃ eclipsed	Mostly torsional strain	6.0	1.4
CH ₃ \leftrightarrow CH ₃ eclipsed	Torsional plus steric strain	11	2.6
CH ₃ \leftrightarrow CH ₃ gauche	Steric strain	3.8	0.9

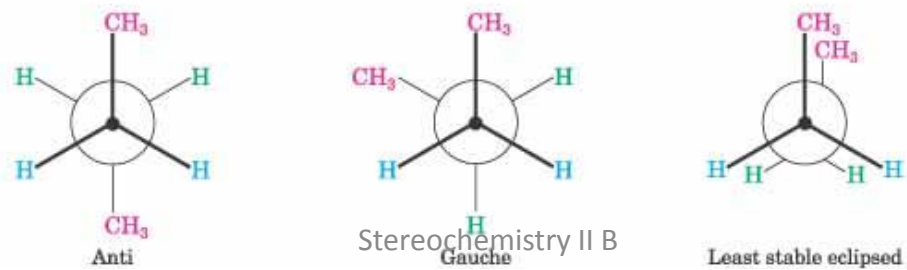
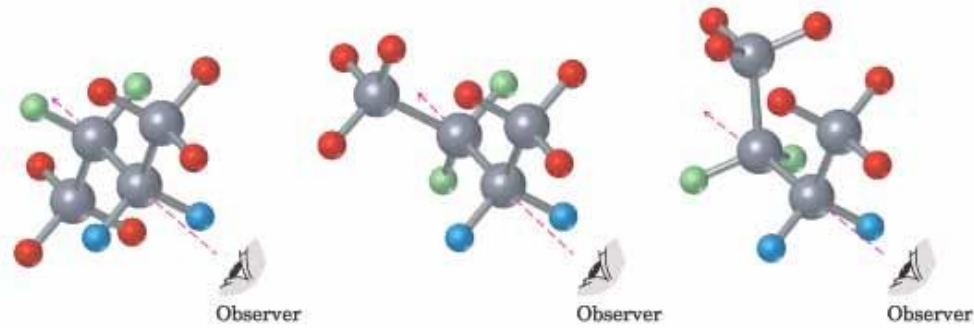
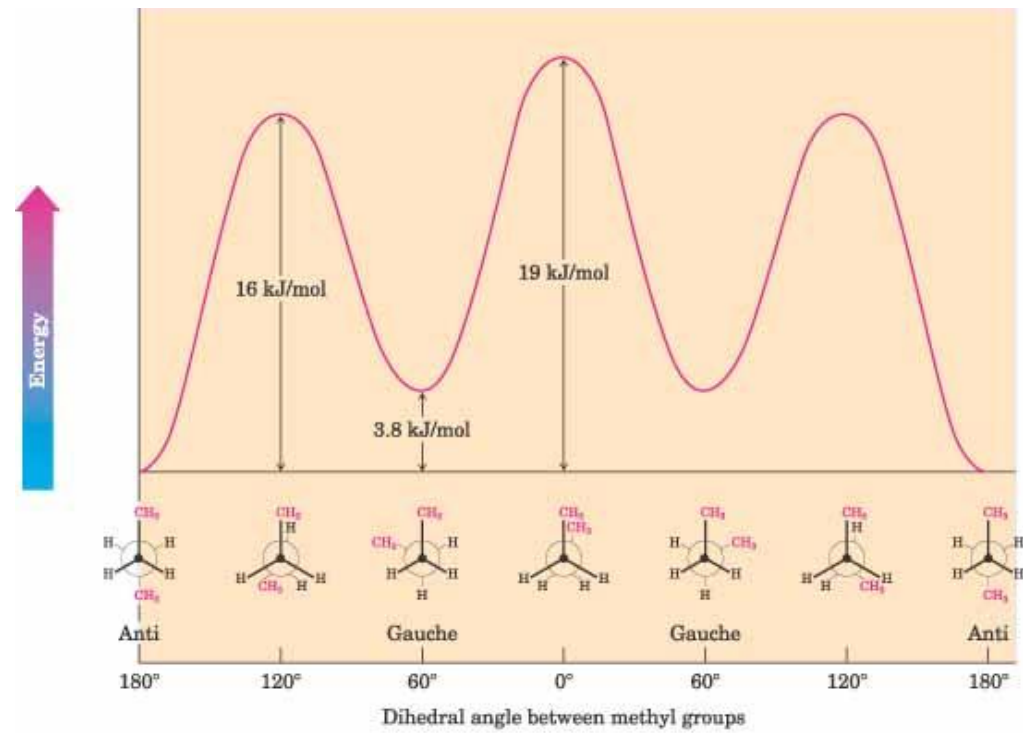
Butane has Steric and Torsional Strain When Eclipsed



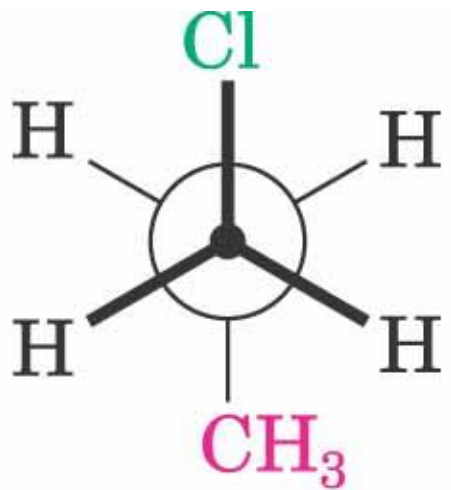
Totally eclipsed conformation of butane

PE Diagram for Butane ([link](#))

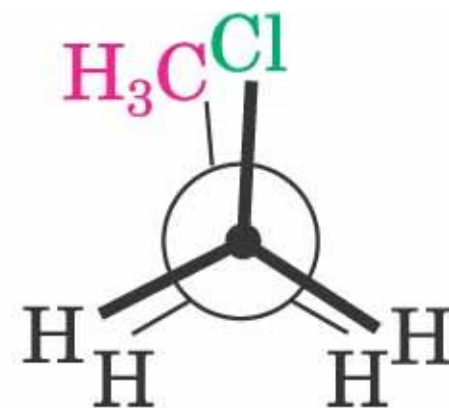




1-Chloropropane



Most stable (staggered)



Least stable (eclipsed)