Introduction

- Cycloalkanes or cycloparaffins are saturated hydrocarbons in which the carbon atoms are joined by single covalent bonds to form a ring.

- The unsubstituted cycloalkanes form homologous series with the general formula C_nH_{2n}

NOMENCLATURE

- The name of an unsubstiuted cycloalkane is obtained by attaching the prefix *cyclo.* to the name of the corresponding normal alkane having the same number of carbon atoms as in the ring.

- Substituent's on the ring are named, and their positions are indicated by numbers. The ring is numbered so that the carbons bearing the substituent's will have lowest possible numbers.

Nomenclature of Cycloalkanes

1. find the parent. Simply count the number of carbon atoms in the ring. If the number is larger than the number in the substituent, then it is named as a cycloalkane.
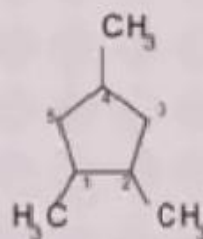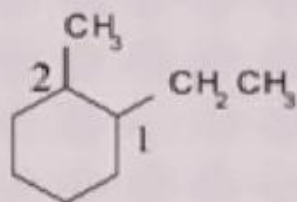
Methylcyclopentane   Cyclobutylpentane

2. Number the Substituents. C-1 always has a substituent attached. Number so that the second substituent has the lowest number possible, etc, .
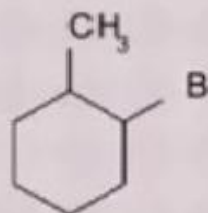
CH_3

H_3C CH_3

a. if two or more alkyl groups have potentially the same number, **number alphabetically.**

CH$_3$
2
CH$_2$ CH$_3$
1

1-ethyl-2-methylcyclohexane

Not 1-methyl-2-ethylcyclohexane

b. Treat other substituents exactly like other alkyl groups.

CH$_3$
B

1-Bromo-2-methylcyclohexane

Reactions:-

Just because unstability and due to holding the character of angle strain they (lower cycloalkane like cyclopropane and cyclobutane) are more suseptible to ring opening reactions.

Halogenation – Photo-halogenation

Catalytic-halogenation

Catalytic Hydrogenation
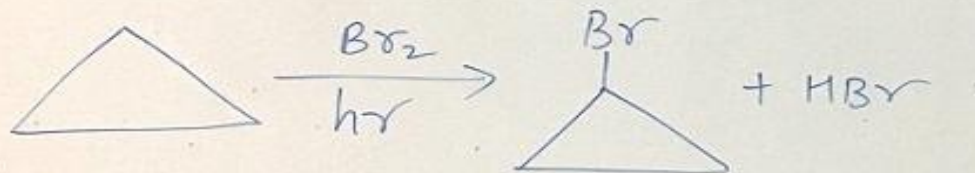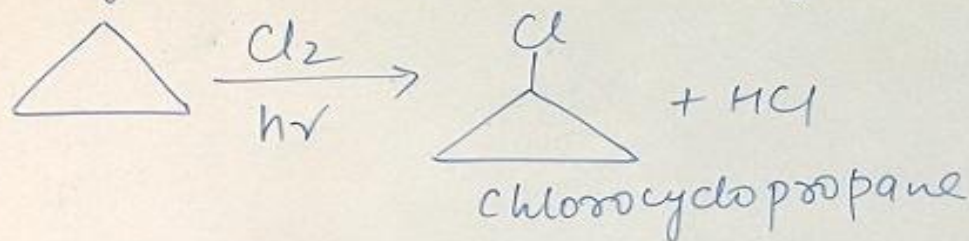
Effect of Heat
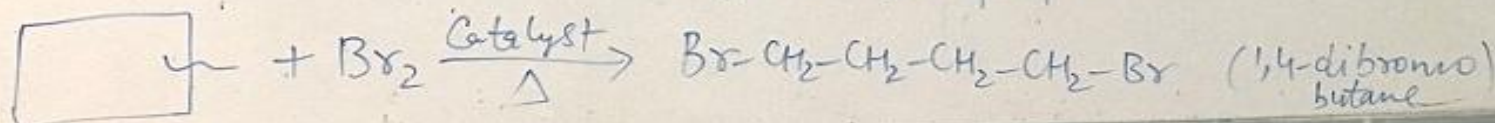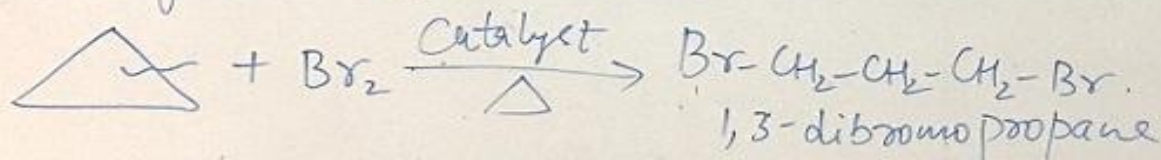
Reaction with hydrogen halides

Halogenation – Photo-halogenation Catalytic-halogenation

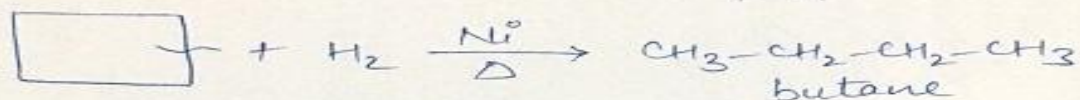Reaction of cyclopropane and cyclobutane :-

① Halogenation (photohalogenation)

chlorocyclopropane
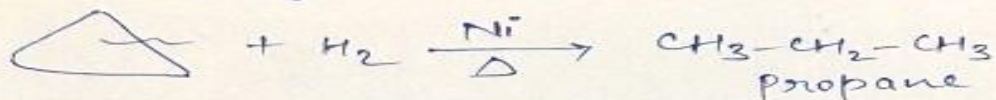

by Catalytic Halogenation :-

$$\triangle + Br_2 \xrightarrow[\triangle]{Catalyst} Br-CH_2-CH_2-CH_2-Br$$

1,3-dibromopropane

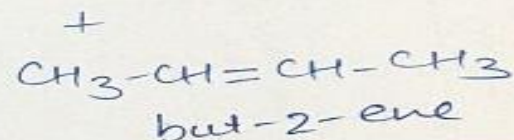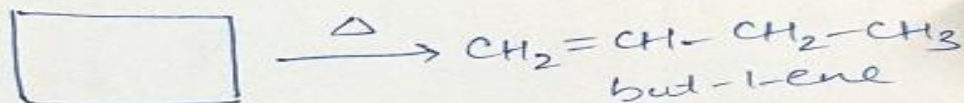$$\square + Br_2 \xrightarrow[\triangle]{Catalyst} Br-CH_2-CH_2-CH_2-CH_2-Br \quad (1,4\text{-dibromo}) butane$$

Catalytic Hydrogenation
Effect of Heat

Catalytic Hydrogenation :–

$$\triangle + H_2 \xrightarrow[\triangle]{Ni} CH_3-CH_2-CH_3$$
propane

$$\square + H_2 \xrightarrow[\triangle]{Ni^o} CH_3-CH_2-CH_2-CH_3$$
butane

(3) **Heat Effect :–**

$$\triangle \xrightarrow{\triangle} CH_3-CH=CH_2$$
propene

$$\square \xrightarrow{\triangle} CH_2=CH-CH_2-CH_3$$
but-1-ene

$$+$$

$$CH_3-CH=CH-CH_3$$
but-2-ene

e.g. propane

$CH_3-CH_2-CH_3$

$\updownarrow$

$CH_3-CH=CH_2$
$\boxed{\overset{|}{H} \quad \overset{|}{H}}$

butane

$CH_3-CH_2-CH_2-CH_3$

$\updownarrow$

$CH_2-CH=CH-CH_2$
$\overset{|}{H} \quad \overset{|}{H} \quad \overset{|}{H} \quad \overset{|}{H}$
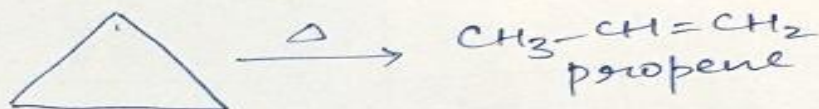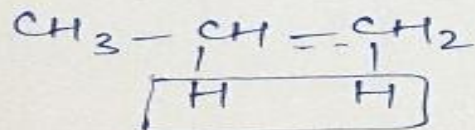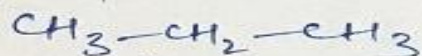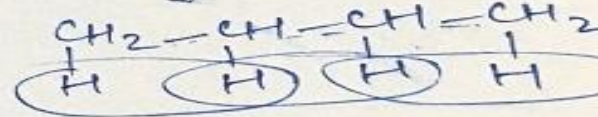
Reaction with hydrogen halides

④ Reaction with Hydrogen Halides :-

△ $\xrightarrow{\text{HI}}$ $CH_3-CH_2-CH_2-I$
Iodopropane

△ $\xrightarrow{\text{HBr}}$ $CH_3-CH_2-CH_2-Br$
Bromopropane

▭ $\xrightarrow{\text{HI}}$ $CH_3-CH_2-CH_2-CH_2-I$
Iodobutane

▭ $\xrightarrow{\text{HBr}}$ $CH_3-CH_2-CH_2-CH_2-Br$
Bromobutane
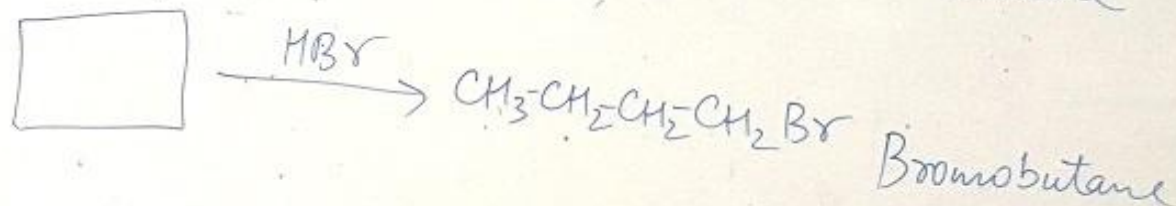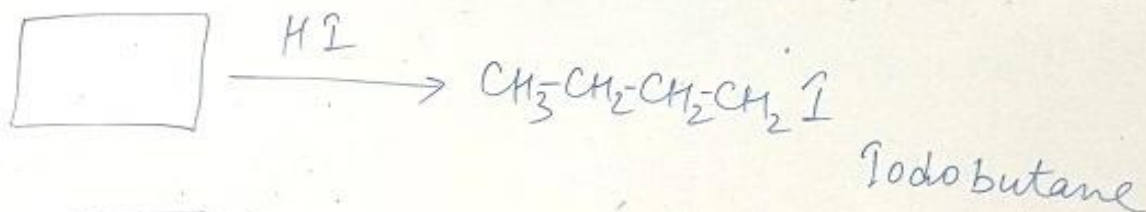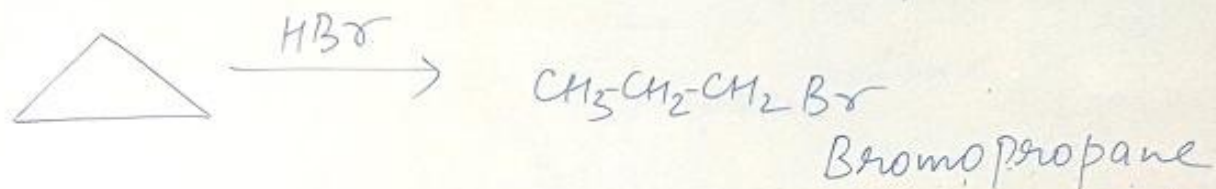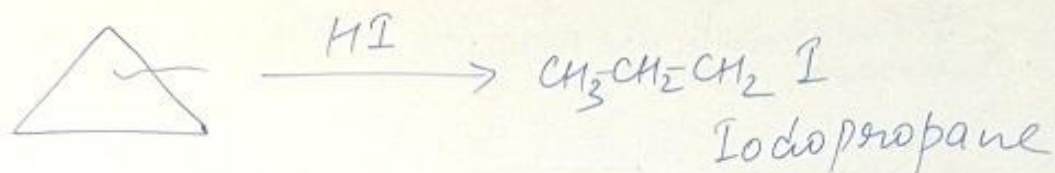
Preparation of Cycloalknes

1. **From Dihalogen Compounds:** Suitable dihalogen compounds on treatment with sodium or zinc give corresponding cycloalkanes.

- This reaction is an extension of *Wurtz Reaction and may be regarded as an* **Internal** Wurtz Reaction

Preparation of Cycloalknes

- **From Dihalogen Compounds**

$$H_2C \begin{array}{c} CH_2Br \\ \\ CH_2Br \end{array} + 2Na \xrightarrow{Ethanol} H_2C \begin{array}{c} CH_2 \\ \\ CH_2 \end{array} + 2NaBr$$

$$\begin{array}{c} H_2C-CH_2Br \\ | \\ H_2C-CH_2Br \end{array} + Zn \xrightarrow{Ethanol} \begin{array}{c} H_2C-CH_2 \\ | \quad\quad | \\ H_2C-CH_2 \end{array} + ZnBr_2$$
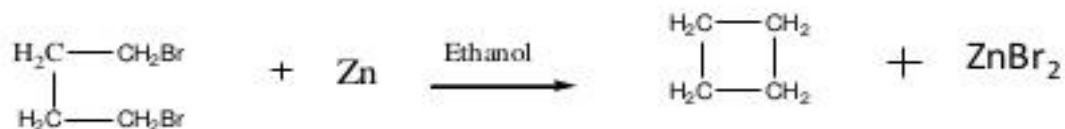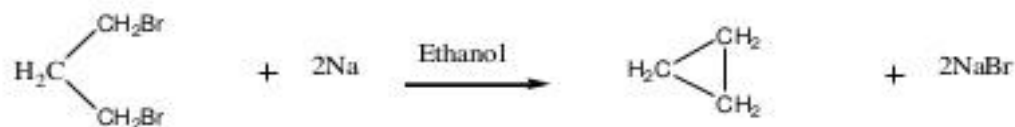
Preparation of Cycloalknes

2. From Calcium or Barium salts of Dicarboxylic acid:

- When the calcium or barium salt of adipic, pimelic, or suberic acid is heated, a cyclic ketone is formed.

- Cyclic ketones may be readily converted into the corresponding cycloalkanes by means of the *Clemmensen reduction*

Calcium adipate

Cyclopentanone

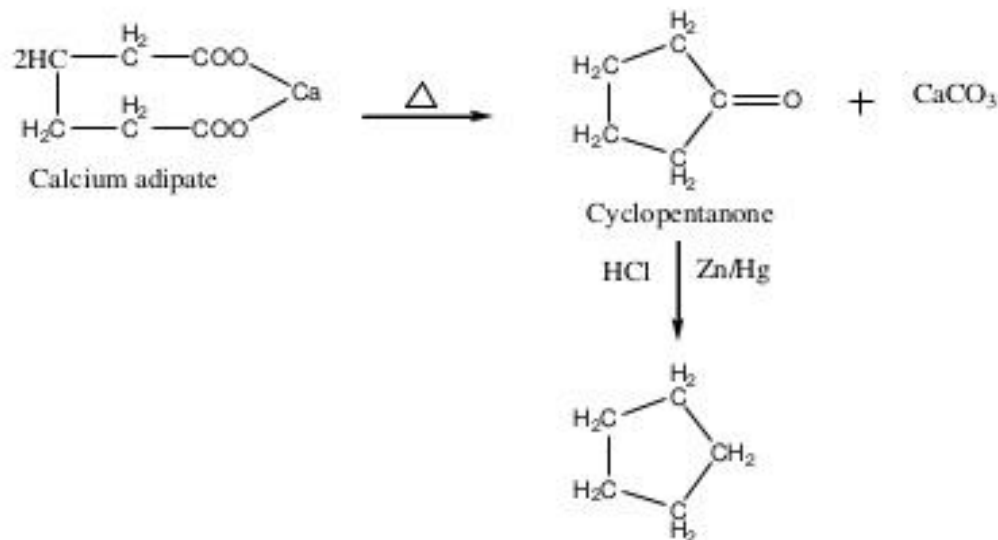# Preparation of Cycloalknes

3. From Esters of Dicarboxylic acids:

- The diester of adipic, pimelic, or suberic acid when treated with sodium undergoes intermolecular acetoaectic ester condensation and β-ketoester is formed.

- The β-ketoesters on hydrolysis give corresponding cyclic ketones.

- Cyclic ketones on reduction yield the corresponding cycloalkanes.

Preparation of Cycloalknes

- 3. From Esters of Dicarboxylic acids:
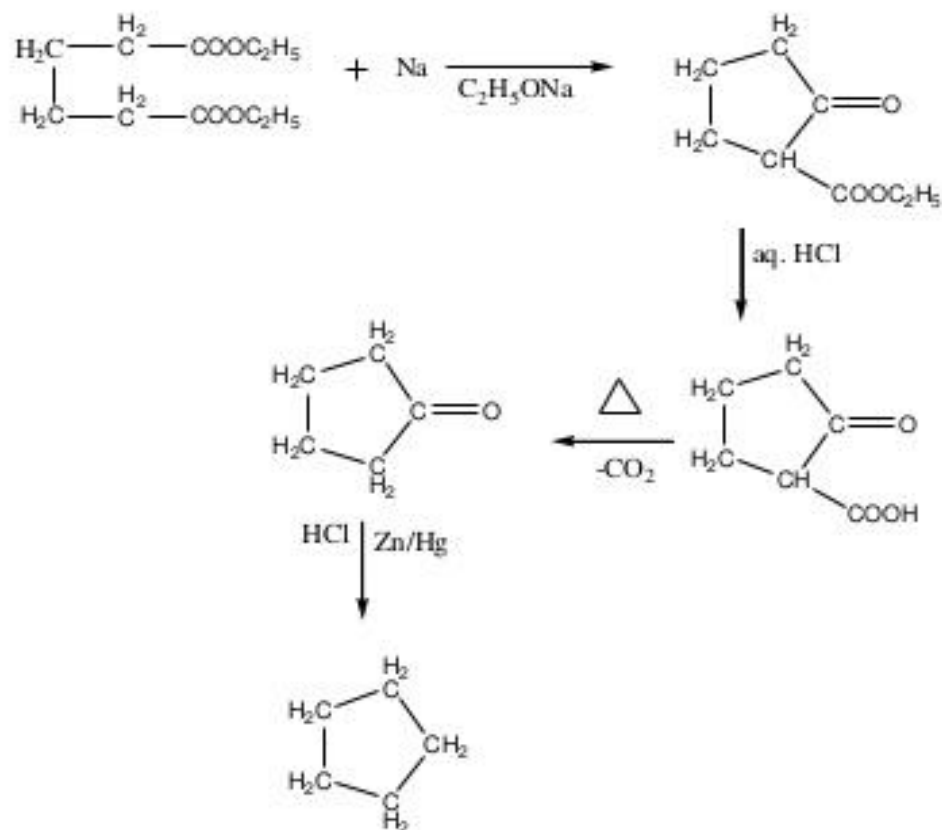
Preparation of Cycloalknes

4. From Aromatic Compounds: Benzene may be catalytically hydrogenated at elevated temperature and pressure to yield cyclohexane.
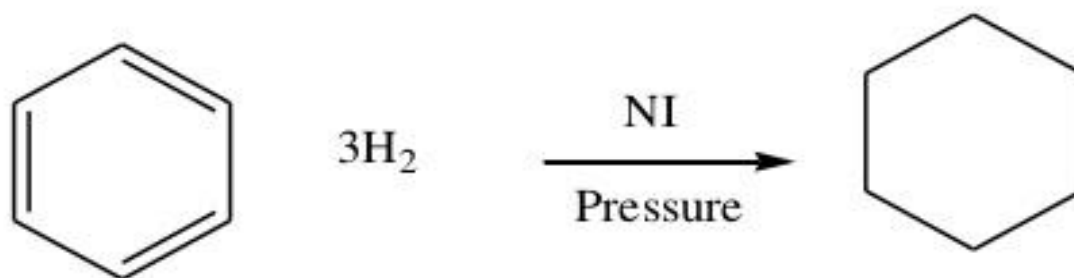
PHYSICAL PROPERTIES

(1) Cyclopropane and cyclobutane are gases at ordinary temperatures; the remaining cycloalkanes are liquids. Their melting points and boiling points show a gradual rise with the increase in molecular weight.

(2) They are all lighter than water; the series has a limiting density of less than 09.

(3) They are insoluble in water but are soluble in organic solvents such as ethers and alcohols

Reactions of cycloalkanes.

1. **Addition of Cl$_2$ and Br$_2$:** Cyclopropane reacts with Cl$_2$, and Br$_2$ *at room temperature* and in the absence of diffused sunlight to produce 1,3-dichlorocyclopropane and 1,3-dibromocyclopropane respective
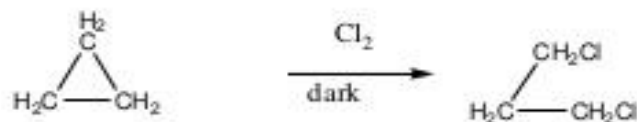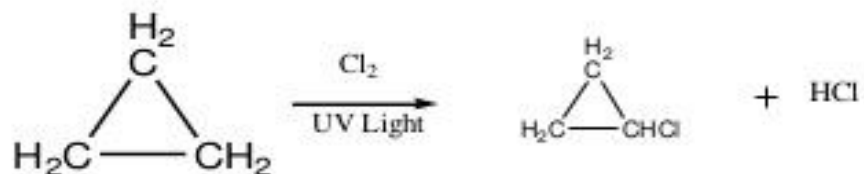
Reactions of cycloalkanes.

2. Addition of HBr and HI:

Cyclopropane reacts with HBr and HI to give 1-bromopropane and 1-iodopropane.
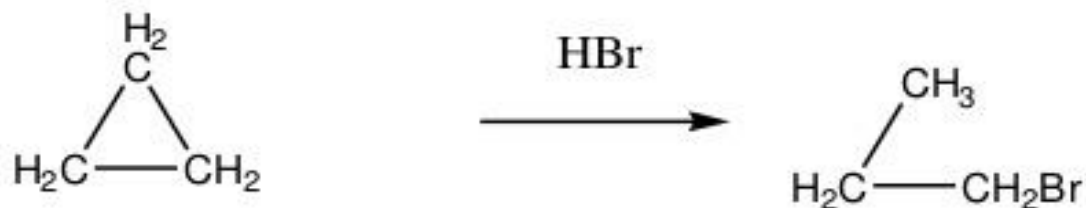
Reactions of cycloalkanes.

3. Addition of Hydrogen; Catalytic Redaction.

- Cyclopropane and cyclobutane react with hydrogen in the presence of a nickel catalyst to produce propane and n-butane respectively.
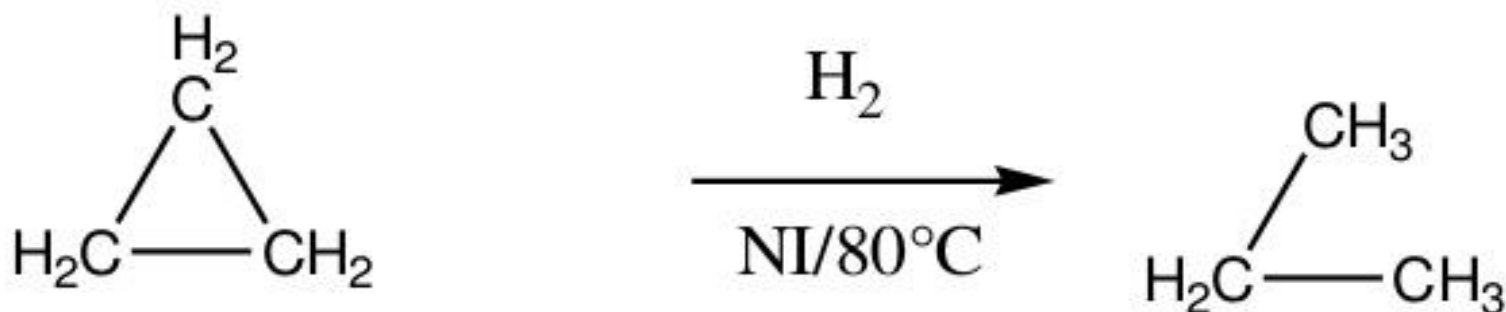
BAEYER'S STRAIN THEORY

Baeyer's theory is based upon some assumptions that are helpful to understand instability of cycloalkane ring systems.

All ring systems are planar. Deviation from normal tetrahedral angles results in to instable cycloalkanes.

The large ring systems involve negative strain hence do not exists.

Adolf Baeyer (1885). Proposed a theory to explain the relative stability of the first few cycloalkanes on the fact that the normal angle between any pair of bonds of carbon atom is 109^0 28' (or 109.5^0) in tetrahedral geometry (methane molecule).

The H-C-H bond angle in Tetrahedron
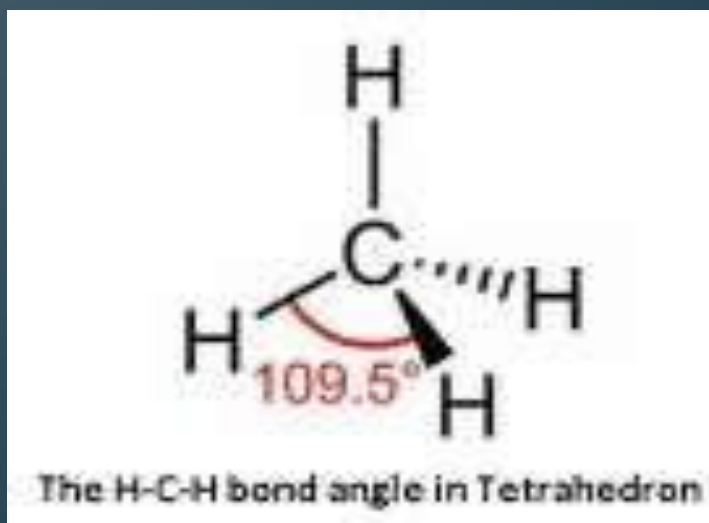
Baeyer postulated that any deviation of bond angles from the normal tetrahedral value would impose a condition of internal strain on the ring. This is called Angle Strain, which determined the stability of the ring.

Baeyer proposed that the optimum overlap of atomic orbitals is achieved for bond angel of 109.5^0 (for carbon atom, in a molecule if it is $\mathbf{sp^3}$ hybridized and orbital overlap is maximum).

In short, it is ideal bond angle for alkane compounds that produces maximum bond strength and stable molecule.
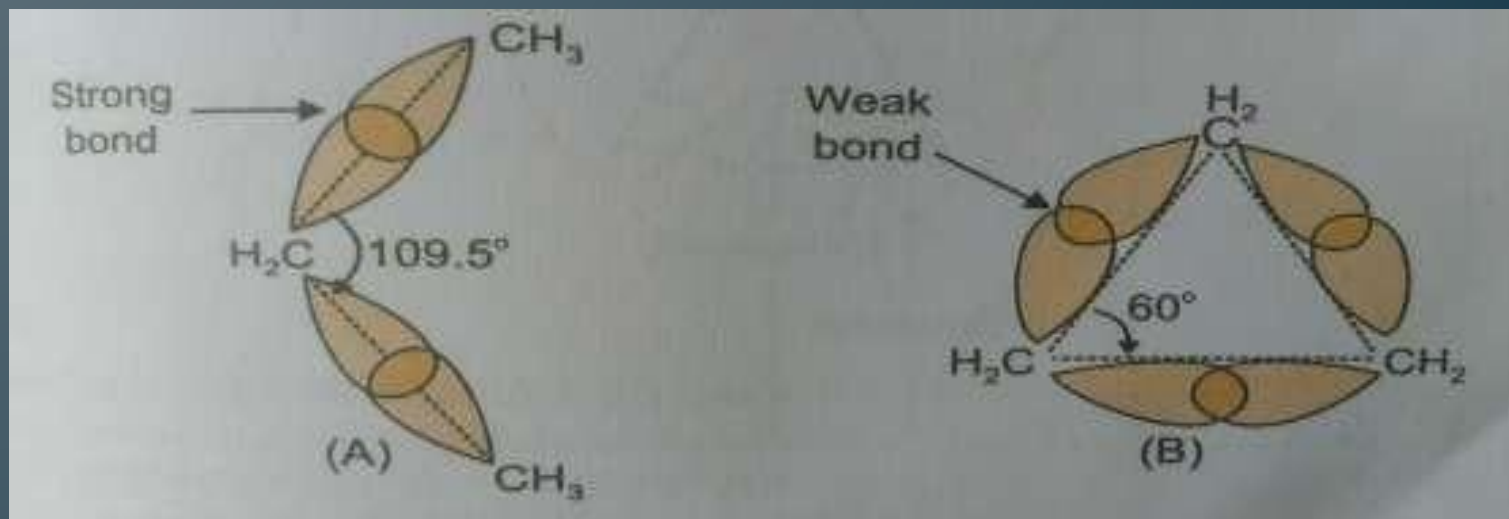
Fig.1: Orbital overlap between (A) Propane (B) Cyclopropane. Maximum overlap occurs in propane

- If bond angles deviate from the ideal then the ring produce strain. Higher strain produces higher instability, increased reactivity and increases heat of combustion. In simple higher the deviation lesser the instability.

- According to Baeyer, the relative order of stability for some common cycloalkanes is as under

  Cyclopentane > Cyclobutane > Cyclopropane

Ring Strain in Cycloalkanes based on heats of Combustion

The relative stabilites of cycloalkanes are determined by measuring their heats of combustion.

$$[-CH_2-]_n + 3/2nO_2 \rightarrow nCO_2 + nH_2O + Heat$$

The more heat per CH_2, the less stable the alkane.

Ring Size	Heat per CH_2 kcal/mol	Ring Strain per CH_2, kcal/mol	Total Ring Strain, kcal/mol
Long-Chain Alkane	157.4	0.0	0.0
3	166.6	9.2	27.6
4	164.0	6.6	26.4
5	158.7	1.3	6.5
6	157.4	0.0	0.0
7	158.3	0.9	6.3
8	158,6	1.2	9.6

Cyclopropane also possesses torsional strain because of eclipsed bonds.

Torsional strain: The Bonds to adjacent carbon atoms always try to assume staggered arrangement, any deviation from this causes strain called Torsinal strain.
In Cyclopropanes all the hydrogens are in eclipsed arrangement.

Stereo View
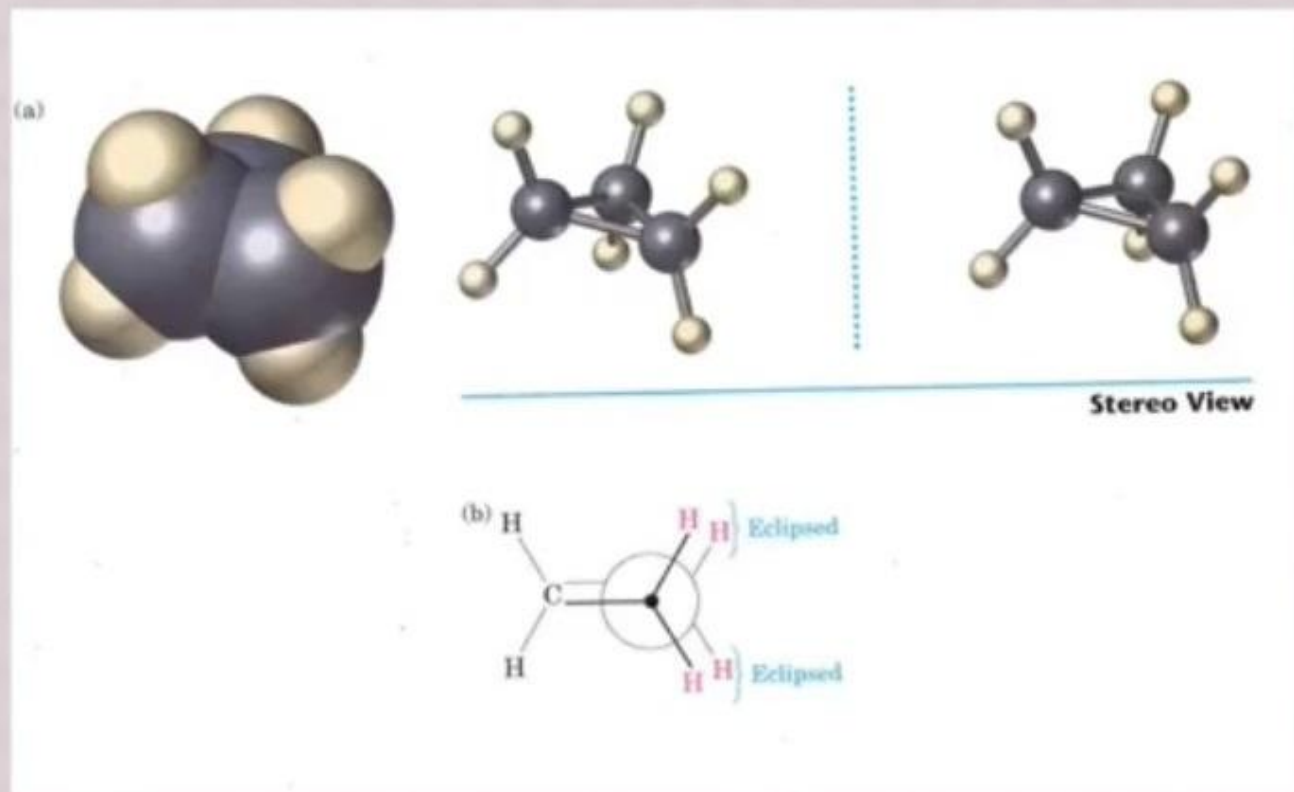
Deviation
$109.5° - 60° = 49.5°$
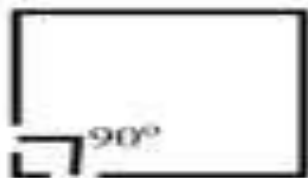
Deviation
$109.5° - 90° = 19.5°$

Deviation
$109.5° - 108° = 1.5°$

All carbon atoms are SP3 hybridized. Expected bond angle = 109.5°

Table 1: Angale strain of first few cycloalkanes

Compound	Bond angle	Deviation	Angle strain
Cyclopropane	60^0	49.5^0	24.75^0
Cyclobutane	90^0	19.5^0	9.75^0
Cyclopentane	108^0	1.5^0	0.75^0
Cyclohexane	120^0	10.5^0	-5.27^0

Angle Strain in Cyclopropane

$$\frac{109.5° - 60°}{2} = 24.75°$$
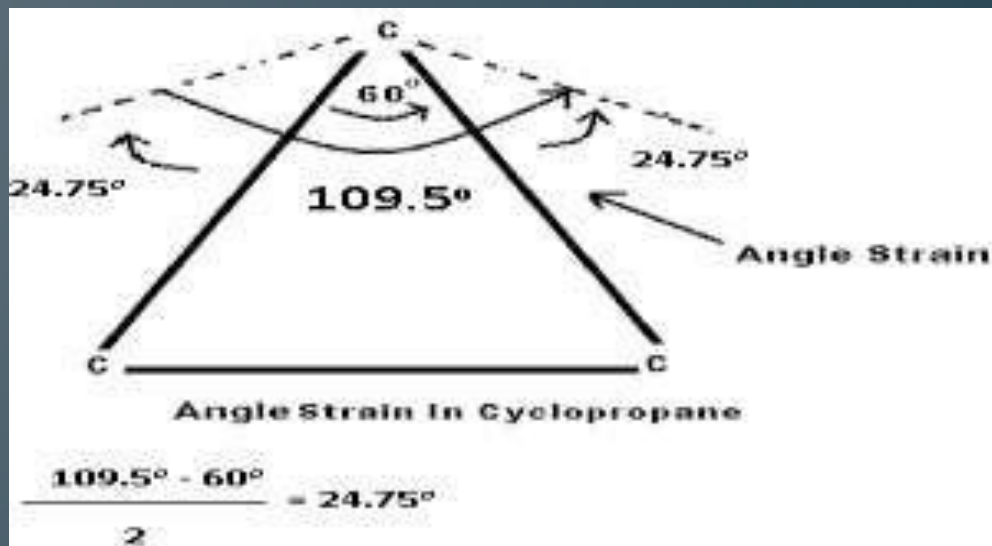
Limitations of Baeyer's angle strain theory

- Baeyer was not able to explain the effect of angle strain in larger ring systems.
- According to Baeyer Cyclopentane should be much stable than cyclohexane but practically it is reversed.
- Larger ring systems are not possible according to Baeyer as they have negative strain but they exist and much stable.
- Larger ring systems are not planar but wrinkled (puckered) to eliminate angle strain.

Coulson-Moffitt Model or Concept of Maximum Overlap of Carbon Orbitals (Bent bond/Banana bond Theory)

A **bent bond**, also known as a **banana bond**, is a type of covalent chemical bond with geometry somewhat indicative of a banana.

The term itself is a general representation of electron density or configuration resembling a similar "**bent**" structure within small ring molecules, such as cyclopropane (C_3H_6) or as a representation of double or triple bonds within a compound that is an alternative to the sigma and pi bond model.

Types of overlaps

Sigma Bond: good overlap strong bond

poor overlap weak bond : Bent bond

Bent bonds in cyclopropane

banana bonds

Atomic orbital overlap in cyclopropane
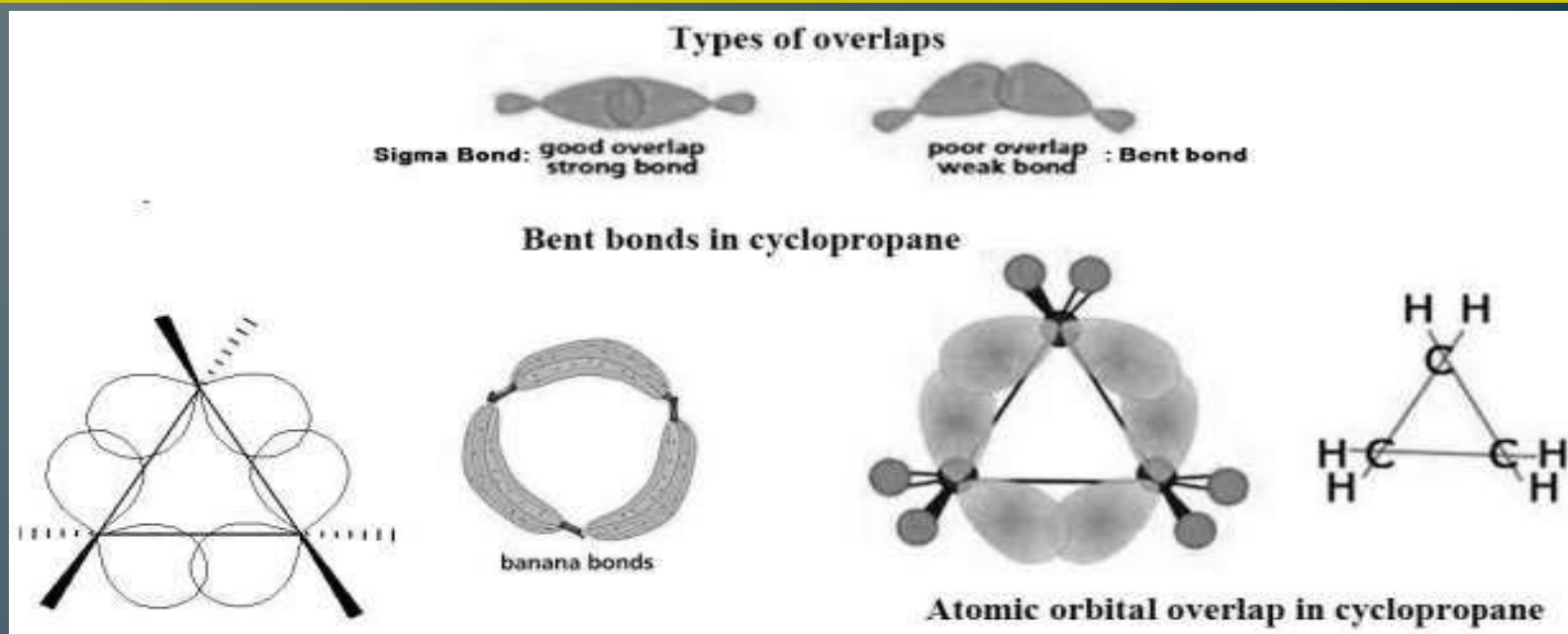
Note that sigma bond (strong bond) involves end-on-overlap and pi bond involves side-long overlap. Bent bond is intermediate between sigma and pi bonding. The overlap being neither end-on nor side-long. This makes the overlap less efficient than sigma overlap and the cyclopropane C-C bonds weaker than normal C-C sigma bonds

Coulson-Moffits proposed that the smallest carbon valency angle which can be 104^0. Therefore, suggested that in cyclopropane only a partial overlap of the sp3 hybrid orbitals occurs, so C-C-C bond angle is decreased slightly from 109.5^0 to 104^0 and the H-C-H angle increased to 120^0 compare to normal tetrahedral angle.

- This decrease in overlap results in weakening of the bond and therefore partially explains the instability of cyclopropane.

- In case of cyclobutane, also has bent bonds but the decrease in overlap is less than in the case of cyclopropane.

- Cyclobutane is, therefore more stable (not participate in ring-opening reactions) and less reactive than cyclopropane.

# Sachse-Mohr Theory (Theory of Strainless Rings)

Sachse Mohr's theory proposed that higher member ring can become free from strain if all the ring carbons are not forced into one plane. They exhibit in two non-planar 'folded' or 'puckered' conformations both of which are completely free from strain. These are strainless as the carbon atoms lie in different planes and the normal valency angle (109.5^0) is retained.

These are called the **'Chair' Form or the 'Z' Form** and the **'Boat' Form or the 'C' Form** because of their shapes.
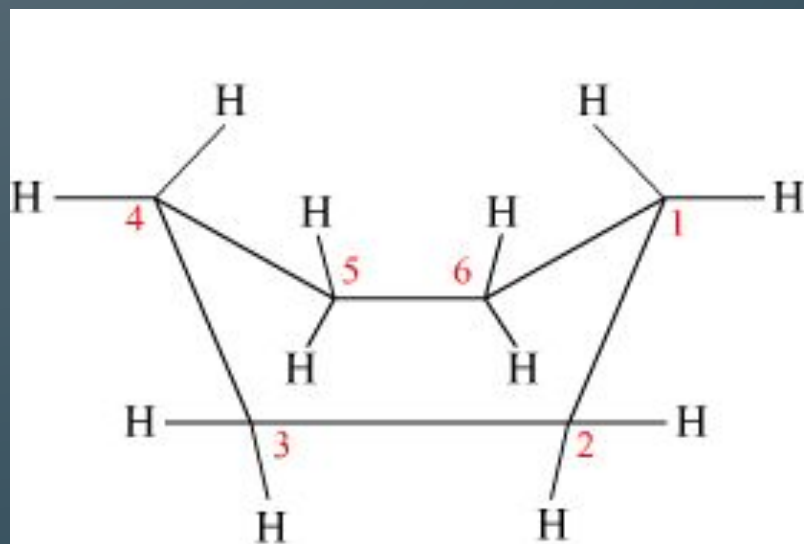
Boat conformation of cyclohexane
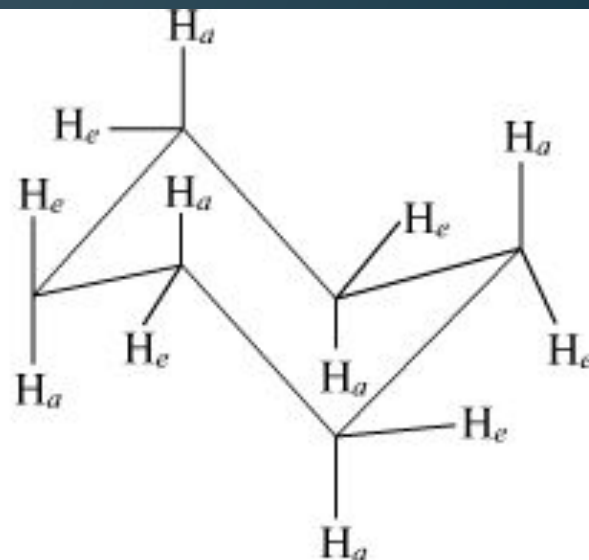
Chair conformation of cyclohexane
Six axial (*a*) and six equatorial (*e*) hydrogen atoms.

CYCLOHEXANE IS FREE OF RING STRAIN- SACHE-MOHR THEORY

All carbon atoms are non planar. Exist in puckered condition Cyclohexane present in either boat or chain form.

2. All Bonds are staggered and therefore no torsional strain.

3. All bond angles are near 109.5^0 so no angle strain.

Cyclohexane – the most stable conformation of cyclohexane is the chair.

Chair conformation showing only carbon atoms
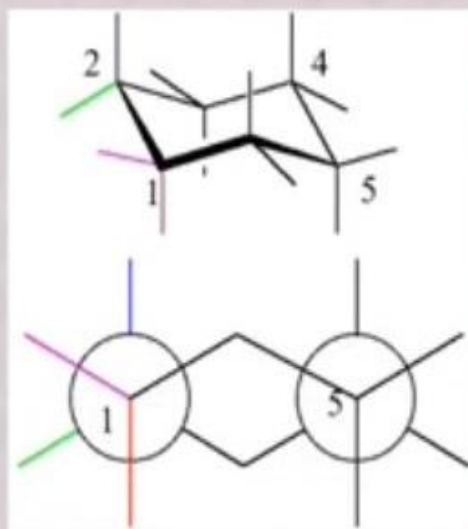
Chair conformations showing positions of hydrogens

Newman projection shows that all bonds are staggered. Bond angles are about 109.5°

The chair conformation is the most stable conformation of cyclohexane.

In chair cyclohexane there are two types of positions, axial and equatorial. The axial positions point perpendicular to the plane of the ring, whereas the equatorial positions are around the plane of the ring. Mohr (1918) further elaborated this theory and applied it to compounds with the two rings fused together.

STABILITY OF CYCLOHEXANES - BAEYER STRAIN THEORY

- All ring systems are **planar. Deviation from normal tetrahedral angles results in to unstable cycloalkanes.**
- The large ring systems involve **negative strain hence do not exists.**
- The bond angles in cyclohexane and higher cycloalkanes (cycloheptane, cyclooctane, cyclononane.........) are not larger than **109.5° because the carbon** rings of those compounds are not planar (flat) but they are puckered (Wrinkled).
- The ring of cyclopropane is triangle. All the three angles are of 60 ° in place of **109.5°c(normal bond angle for carbon atom) to adjust them into triangle ring system.**
- In same manner, cyclobutane is square and the bond angles are of 90o in place of
- **109.5° (normal bond angle for carbon atom) to adjust them into square ring system.**
- The deviation for cyclopropane and cyclobutane ring systems then normal tetrahedral angle will **produce strain in ring. The ring strain will make them unstable as** compare to molecules having tetrahedral bond angle.
- So, cyclopropane and cyclobutane will easily undergo **ring opening reactions to** form more stable open chain compounds.

STABILITY OF CYCLOHEXANES - BAEYER STRAIN THEORY

The bond angle in cyclopropane is 60°.

- The normal tetrahedral bond angle value is 109.5°.
- That is why, deviation = (normal tetrahedral bond angle) – (actual bond angle)
- Deviation = 109.5° – 60 = 49.5°.

The bond angle in cyclobutane is 90°.

- The normal tetrahedral bond angle value is 109.5°.
- That is why, deviation = (normal tetrahedral bond angle) – (actual bond angle)
- Deviation = 109° 5' – 90 = 19.5°.
- Deviation for cyclopropane is 49.5°
- Deviation for cyclobutane is 19.5°.
- The deviation is higher for cyclopropane than cyclobutane therefore cyclopropane is more prone to undergo ring opening reactions.
- As a result of this, the strain is more in cyclopropane as compare to cyclobutane.
- It will make **cyclopropane less stable than cyclobutane. So, cyclopropane easily undergoes** ring opening reaction as compare to cyclobutane.

Coulson-Moffitt Model

Both are considers that cyclopropane ring from sp3 hybridized CH2 groups.

All sp2 hybridized are pointed 22° outward from imaginary the line connecting the nuclei, resulting in about 20% less effective overlap than the C-C bond of ethane.

For this reason, the bonds are often referred to as bent.

This bending is considered for angle strain.

SACHE-MOHR THEORY OF STRAINLESS RING

- Sachse theory(1890)
- The carbon atom of cyclohexane and higher alkanes are not planar but asume strain free puckered configuration, in which each carbon retains its normal valency angle of 109.5°
- Saches constructed two models of cyclohexane called as boat and chair forms.
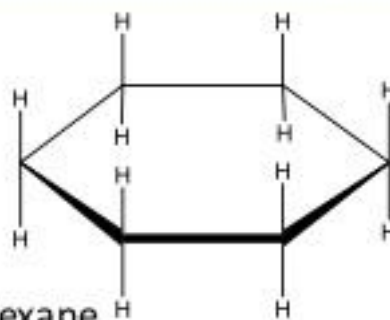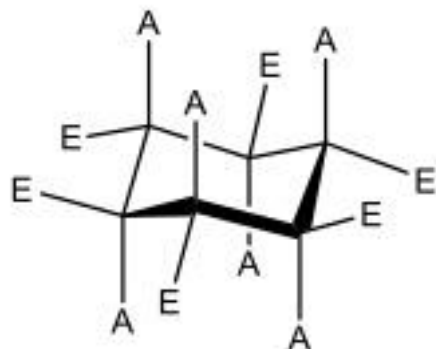

Chair

Twist-boat

Boat

SACHE-MOHR THEORY OF STRAINLESS RING

- Mohr theory(1931)

- Mohr suggested the possibility of existance of two forms which are readily undergo interconversion by rotation of single bonds involving negligible distortion of tetra hedral angles. Only 5kcal/mole energy is needed for their interconversion.

- The two confirmational isomers are indynamic equilibrium and have not been individualy isolated.

- On the basis of therotical and experimental evidence , it has been found chair confirmation is more stable than boat form.

Conformations of Cyclohexane

cyclohexane

Chair conformation of cyclohexane

Boat conformation of cyclohexane