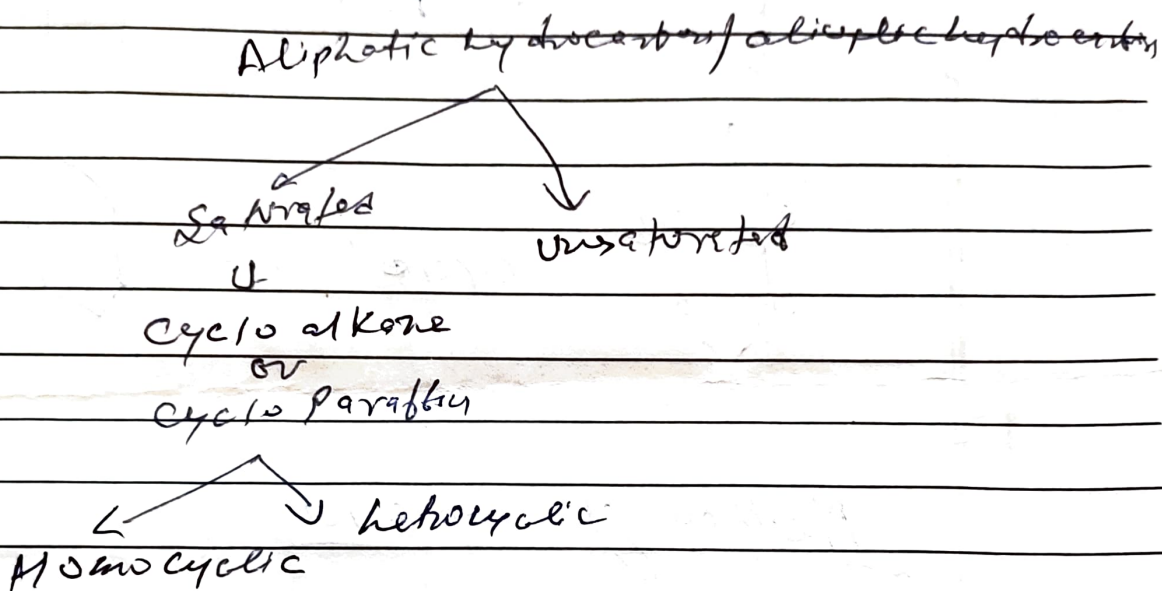


Cyclo Alkanes

Introduction

Carbon atoms which are attached to one another to form rings are called cyclic compounds.

Aliphatic cyclic compounds or cyclic aliphatic hydrocarbons are called alicyclic compounds.



Nomenclature :-

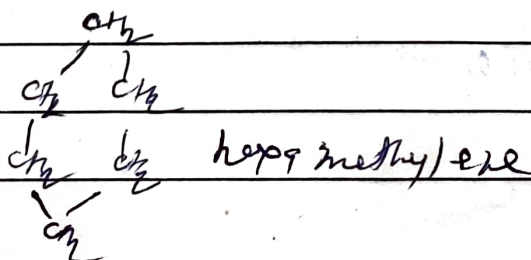
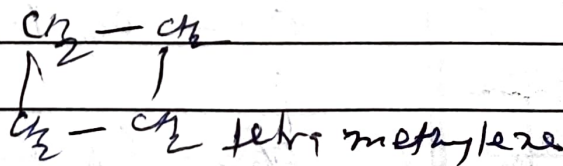
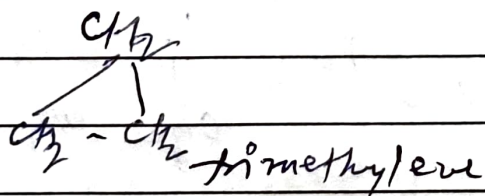
General formula - C_nH_{2n} or $(CH_2)_n$

$n = 3, 4, 5, 6,$

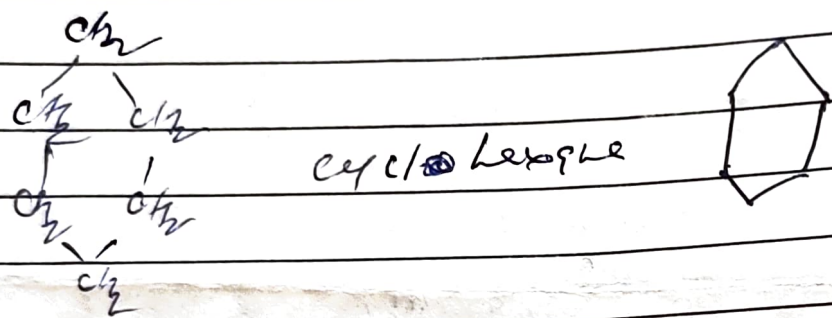
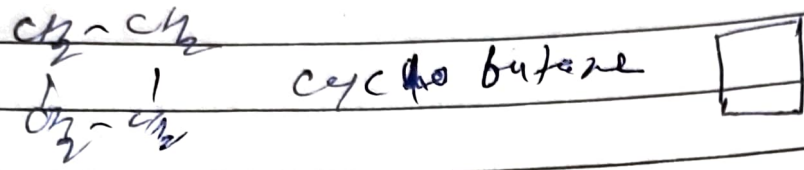
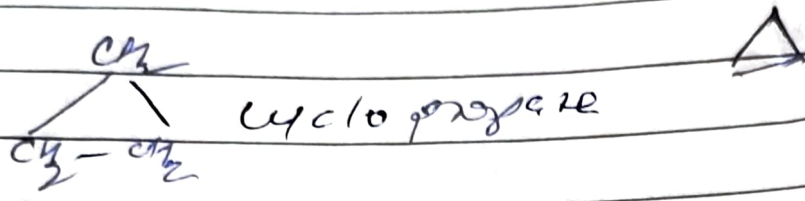
- methylene (CH_2) KPOD Polymethylene.

Common names

- prefix - tri, tetra, penta.

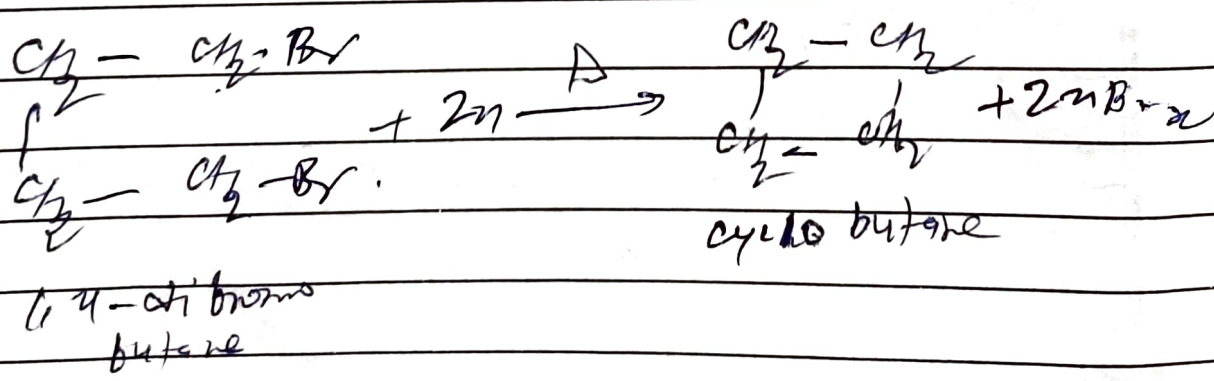
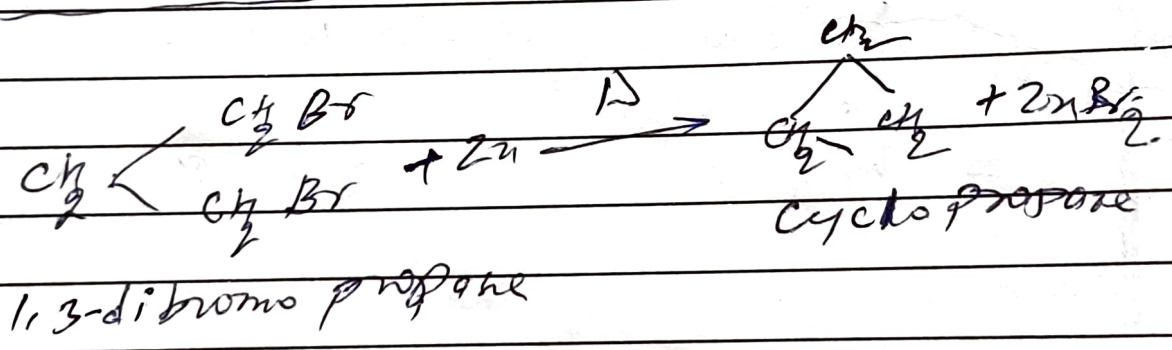


(b) IUPAC Prefix = cyclo and alkane having same numbers.



Method of Preparation

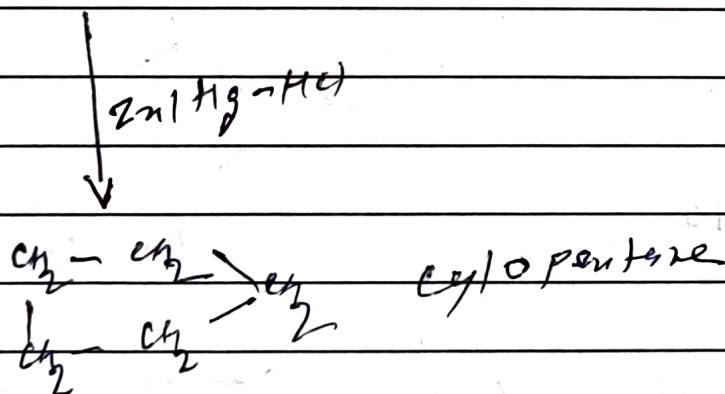
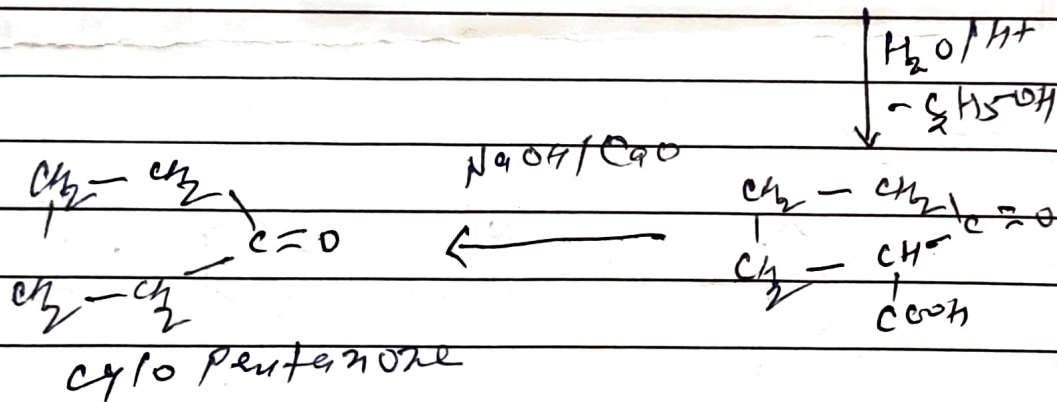
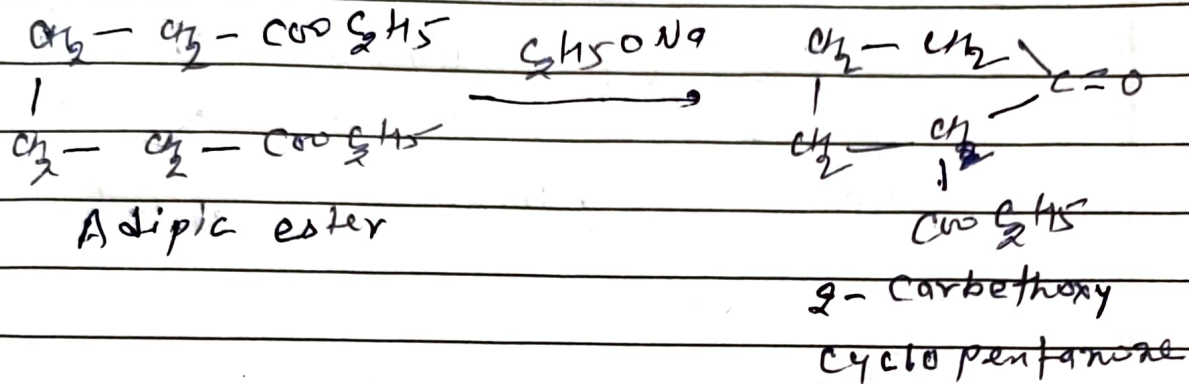
Preund Method



Limitations:-

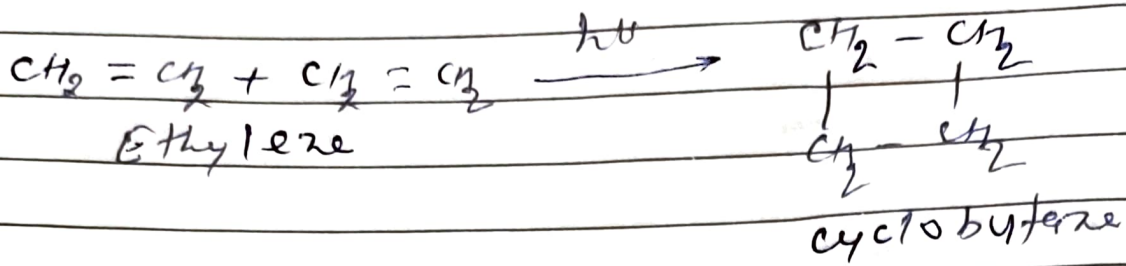
- ① If halide is present at 1,5 or 1,6 carbon then reaction forms open chain alkanes.
- ② This method gives only good yield of cyclopropane

② Dieckmann Condensation

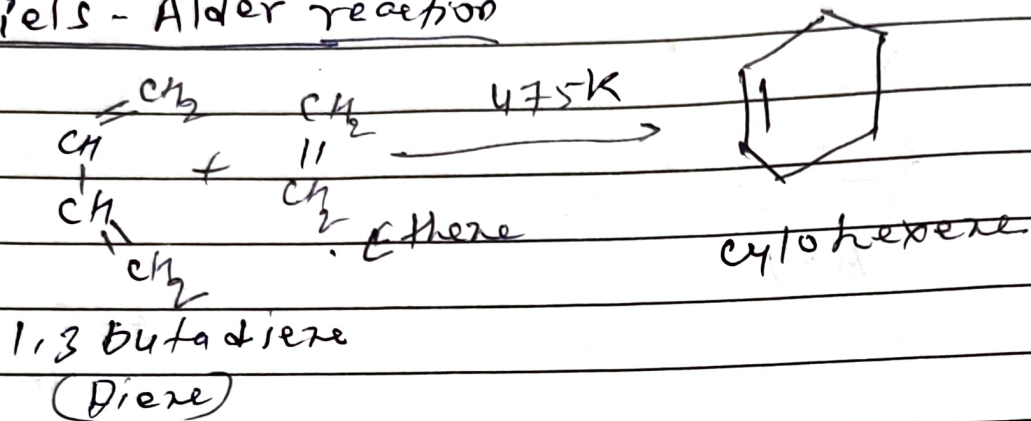


This method suitable for preparation of five or six-membered rings.

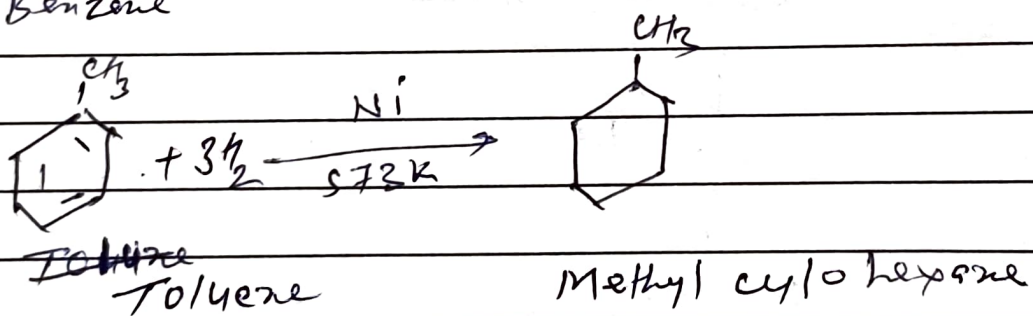
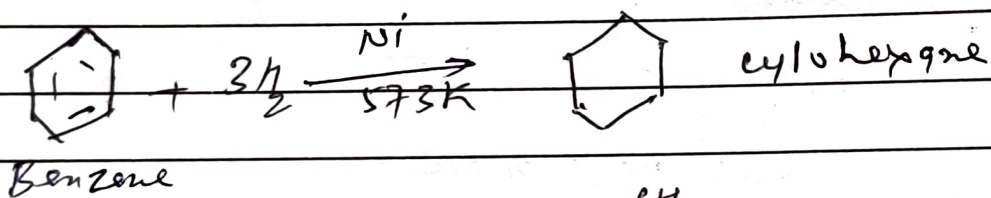
③ [2+2] cyclo addition reaction



④ Diels - Alder reaction

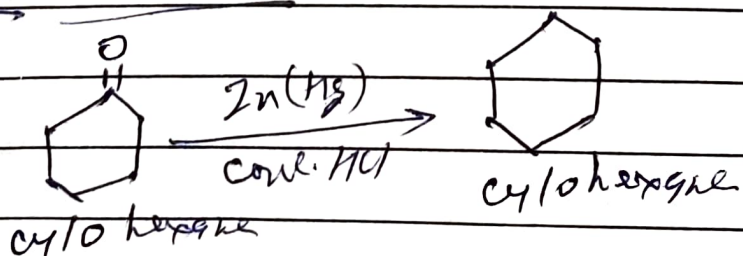


⑤ Hydrogenation of aromatic compounds

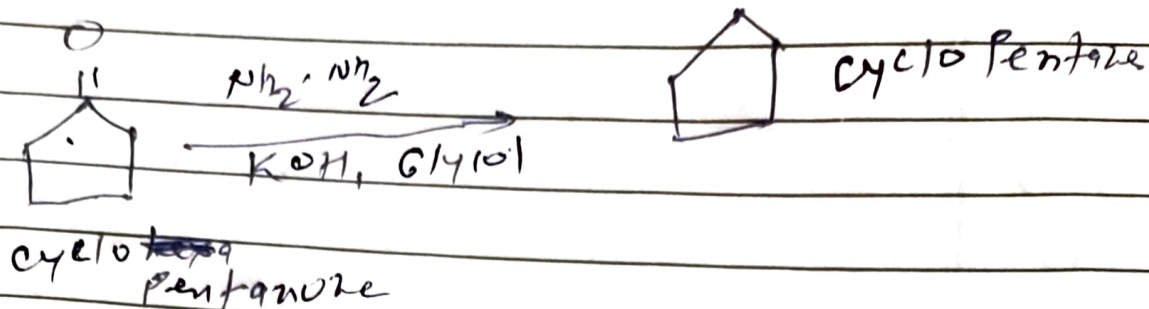


6. Reduction of cyclic carbonyl compounds

① Clemmensen's reduction



(b) Wolff-Kishner Reduction

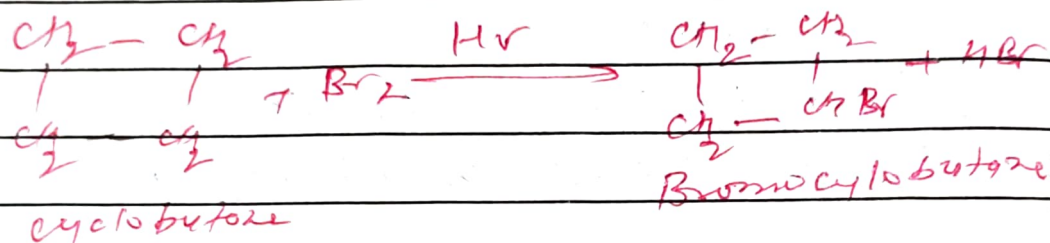
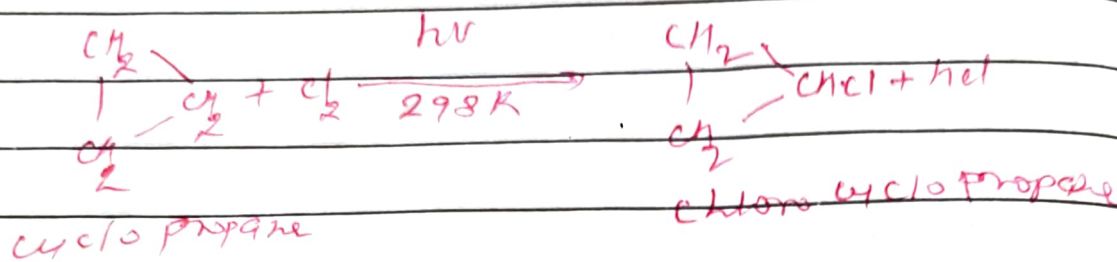


Physical Properties

- ① Cycloalkane higher m.p, B.P, and densities than alkane
- ② cyclopropane and cyclobutane are gases. while higher members are liquids.
- ③ Cycloalkanes are lighter than water and non-polar in nature.
- ④ they are insoluble in water and but soluble in non-polar solvents like acetone, etc.

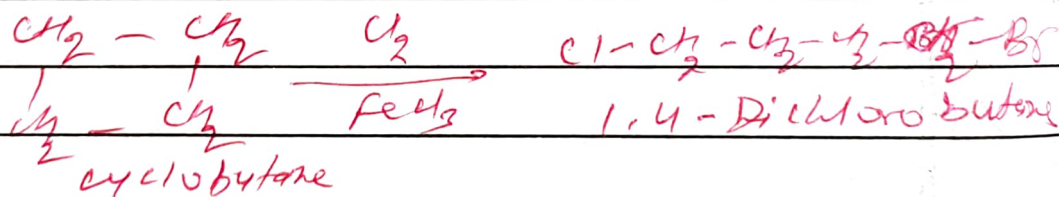
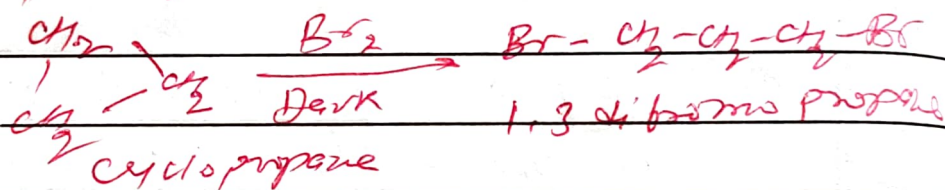
B. Chemical Properties

① Free Radical substitution reaction

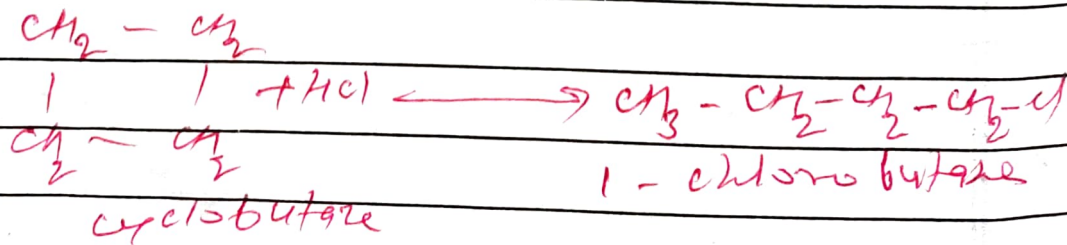
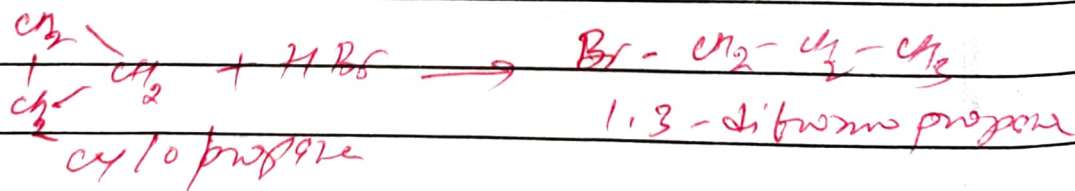


② Addition reaction

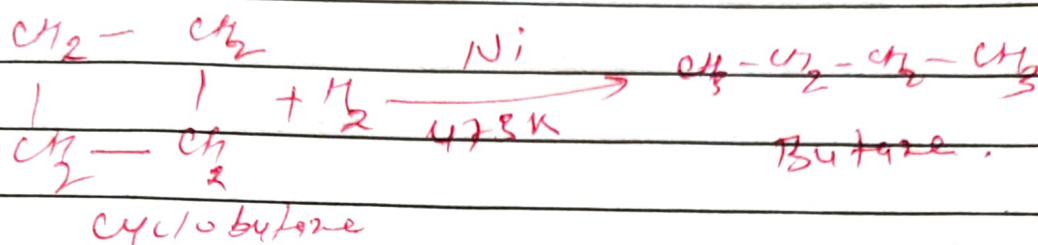
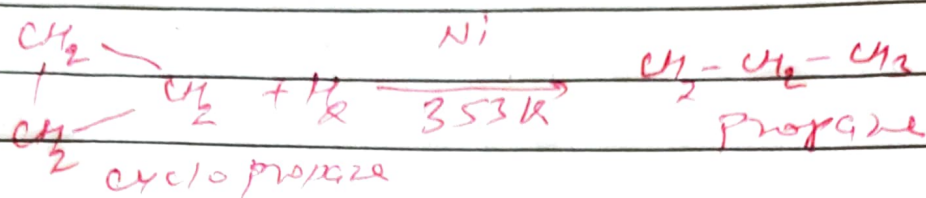
① Addition of halogens



② Addition of Halo acid



© Addition of Hydrogen :-



Bayer's strain theory [Relative stabilities of cycloalkanes]

- The difference in the relative stabilities of cycloalkanes was initially explained in terms of Bayer's strain theory.

The main postulates of this theory are:-

1. In cycloalkanes each carbon atom is sp^3 hybrid and bonded to other four carbon atoms. The angle between any pair of adjacent bonds should be tetrahedral (109.5°).
2. Due to cyclic nature, cycloalkanes are planar in nature.
3. Any distortion or deviation from the normal tetrahedral angle causes a strain in the ring and produce in stability of resultant molecule.

This strain is known as angle strain

$$\text{Angle strain} = \frac{1}{2} [109.5^\circ - \text{Bond angle in the planar ring}]$$

(4) The greater the deviation from the normal angle, greater will be angle strain and hence greater the reactivity of cycloalkane.

5. The more the stability of ring system the more easily it is formed or in other words the ease of formation of cycloalkane is directly related to stability of ring.

Stability of the ring & Angle strain

The angle strain of different cycloalkane are-

Compound	Number of Carbon atoms	Internal bond angle	Angle strain
Cyclopropane	3	60°	$\frac{1}{2} [109.5 - 60] = +24.44^\circ$
Cyclobutane	4	90°	$\frac{1}{2} [109.5 - 90] = +9.44^\circ$
Cyclopentane	5	108°	$\frac{1}{2} [109.5 - 108] = +0.44^\circ$
Cyclohexane	6	120°	$\frac{1}{2} [109.5 - 120] = -5.00^\circ$
Cycloheptane	7	128.26°	$\frac{1}{2} [109.5 - 128.26] = -9.33^\circ$
Cyclooctane	8	135°	$\frac{1}{2} [109.5 - 135] = -12.44^\circ$

The internal bond angle can be calculated as

$$\text{Bond angles} = \frac{180(n-2)}{n}$$

$n = \text{NO. of carbon atoms present in ring.}$

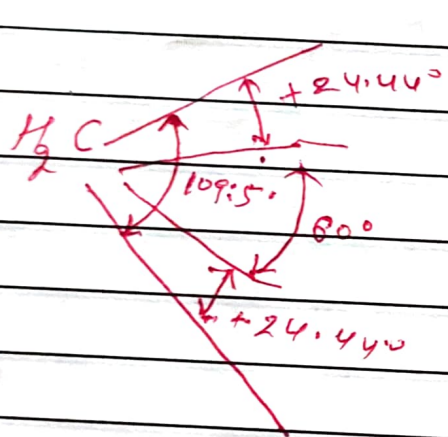
eg cyclo propane

$$\text{Bond angles} = \frac{180(3-2)}{3} = 60^\circ$$

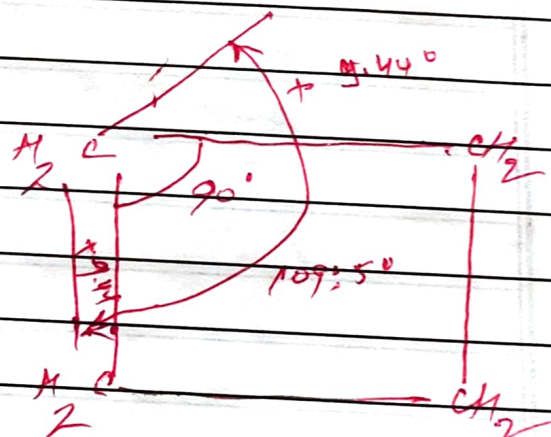
From the above table

→ cyclo propane has maximum angle strain so it is least stable.

→ cyclohexane has least angle strain, therefore it is more stable of all the cycloalkane.



cyclo propane



cyclo butane

Limitations of Baeyer's strain theory :-

1. In alkenes angle-strain is very large, therefore, it should be formed with difficulty. but actually in alkenes the double bond is formed easily by dehydration of alcohols, dehydrogenation of alkyl halides. So Baeyer's theory could not explain the formation of carbon-carbon double bond.
2. According to this theory, due to large angle strain cyclic rings the higher carbon atoms. ($n > 6, 7$) should not exist but actually these rings are found to be more stable than cyclopentane ring. Thus Baeyer's strain theory fails with higher rings containing six or more carbon atom and applicable only to three, four and five members.

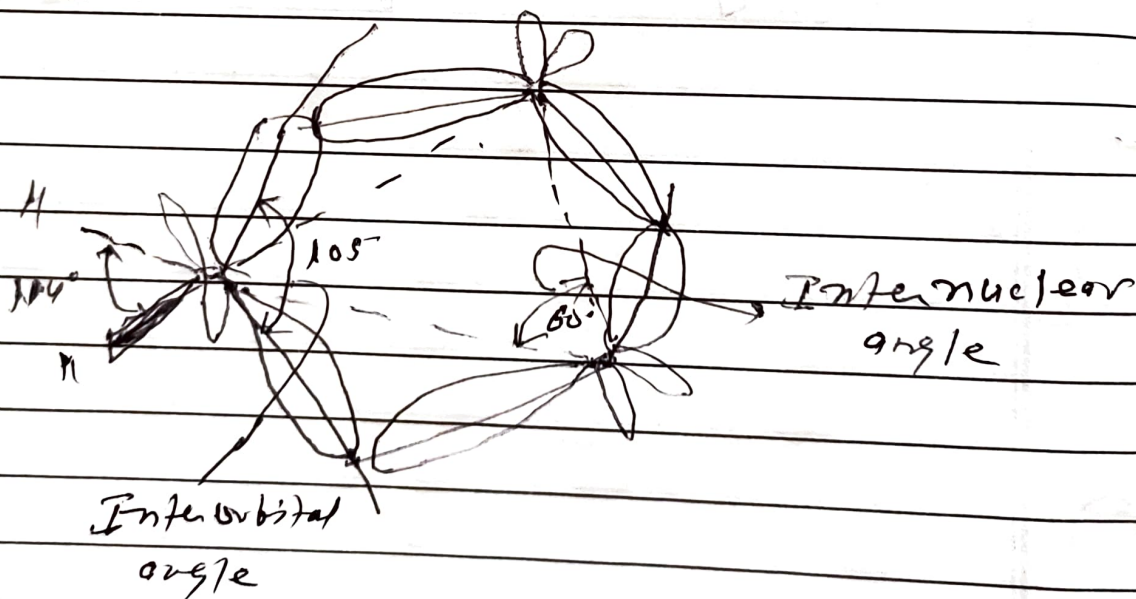
Coulson and Moffitt's Modification

- cyclopropane has a triangular planar structure with internal bond angle b/w carbon-carbon bond are 60° . The sp^3 hybrid orbitals of carbon atoms in cyclopropane can not undergo complete overlap with each other because this requires a considerable deviation from the tetrahedral angle of 109.5° .

Due to this there is a considerable amount of ring strain in cyclopropane.

In addition to angular strain, cyclopropane also suffers additional torsional strain.

This torsional strain is due to coplanar arrangement of carbon atoms which are leading to the eclipsed arrangement of C-H bonds.



Gen. Coulson - Moffitt Model

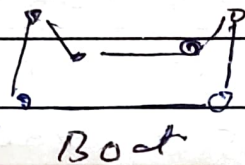
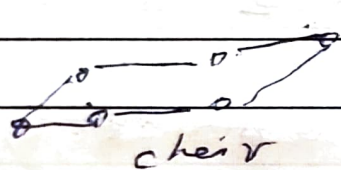
In cyclopropane re-hybridization occurs and bonding between the carbon centres exists in form of "bent" bond wherein carbon-carbon bonds are bent outwards so that interorbital angle is 105° which consequently reduce the level of bond strain.

So it is intermediate b/w sp^3 and π bonding. These bonds are also called as banana bonds. So that C-C bonds have more p-character than normal whereas C-H bonds have s-character. Thus it can be seen that ring strain weakens the C-C bonds of cyclopropane ring. Therefore cyclopropane is much more reactive than alkanes or other higher ring systems.

Sachse Mohr Theory / Theory of strainless rings.

- Sachse Mohr Theory propose the existence of two types of multiplanar or puckered strainless rings known as boat and chair forms and boat forms for cyclohexane.

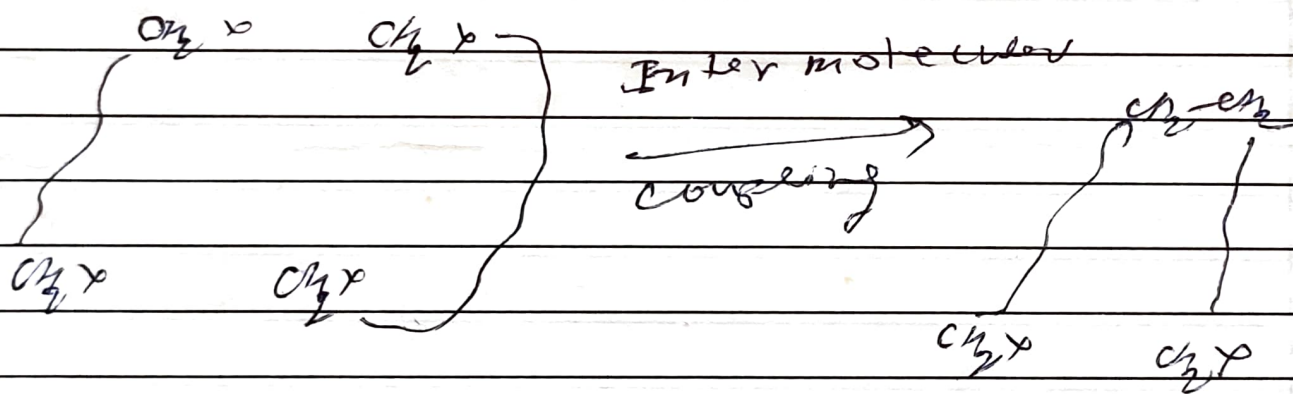
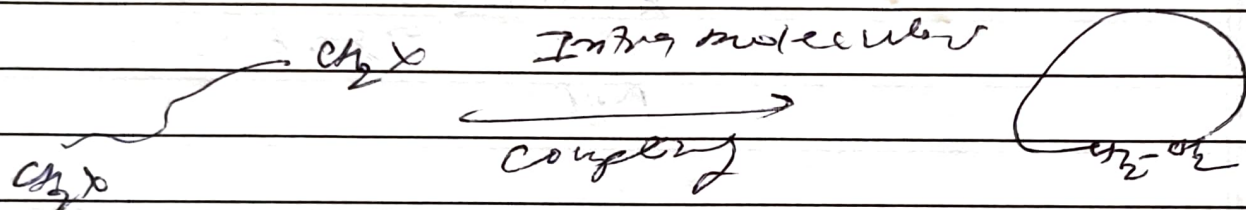
Both these forms are free angle strain and can be inter converted just by rotation around single bond.



It may be interesting to know that why bigger rings are difficult to synthesise even though there is no angle strain in them for the formation of ring the terminal ends of the chain must come closer so that the proper interaction between the groups present at two ends of chain could occur.

But in large sized rings, the terminal ends of open chain may also intersect with the terminal end of the other chain, such interaction inter molecular coupling leads to formation of different products. That's why bigger rings are difficult to synthesise.

However if the reaction is carried under dilute conditions, then collisions b/w the two different chains are minimised and inter molecular ring closure becomes more feasible than intra molecular ring closure.



① well come address by students

② Attendance of students.

③ College visit by faculty.

18/11/20
④ CDC → Dr. Sivaiah.

⑤ RCTH → Blast test, RT,

~~RT~~ RT

→ gift office

RT