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PHARMACEUTICAL ORGANIC CHEMISTRY II

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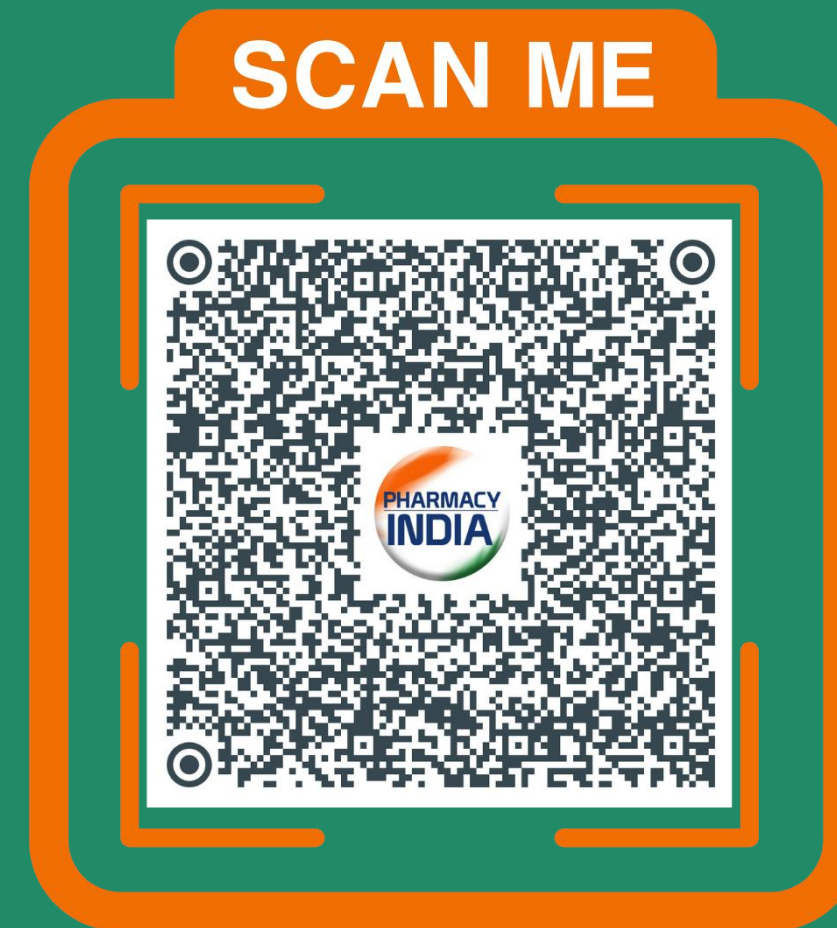
NOTES

CYCLOALKANES

INTRODUCTION

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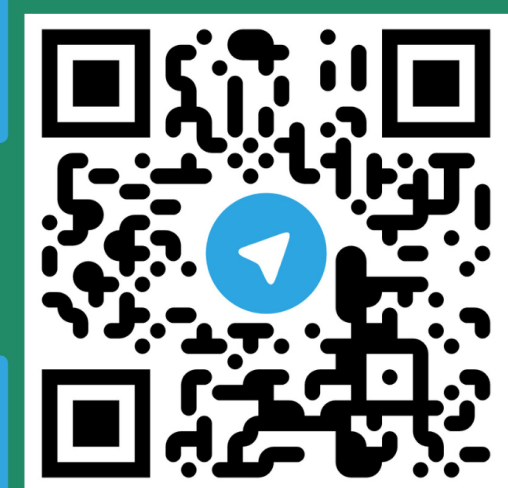
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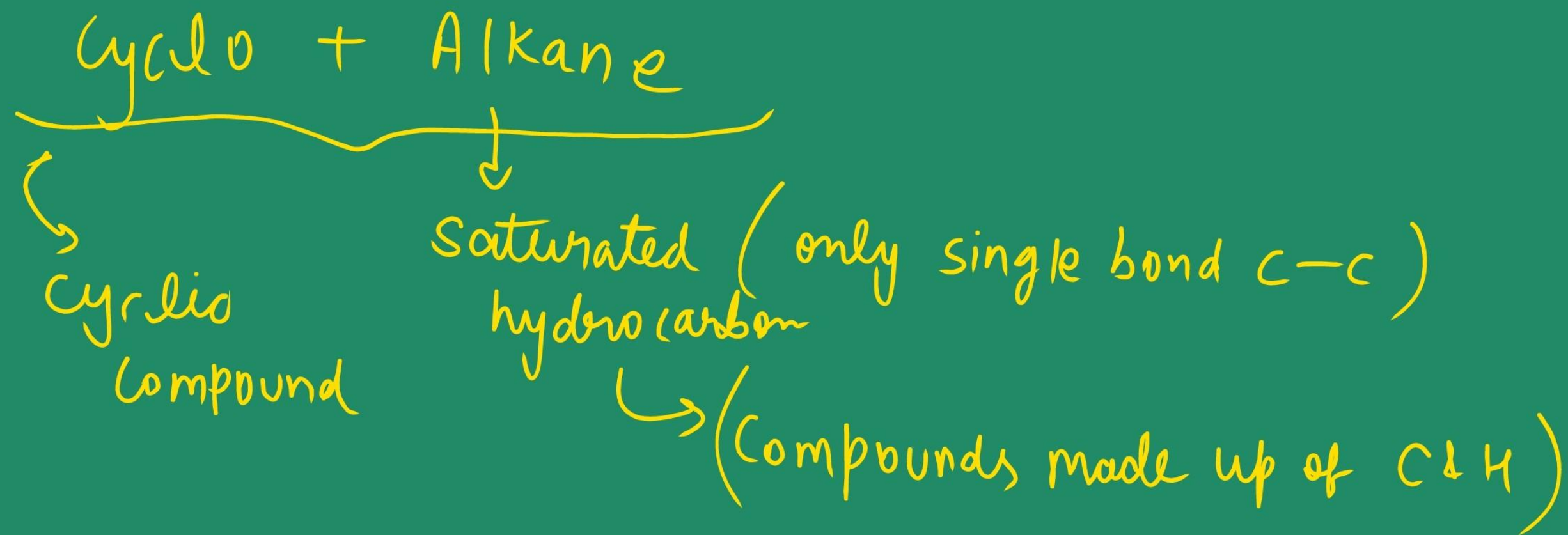
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TOPIC: Cycloalkanes

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Cyclo-alkanes



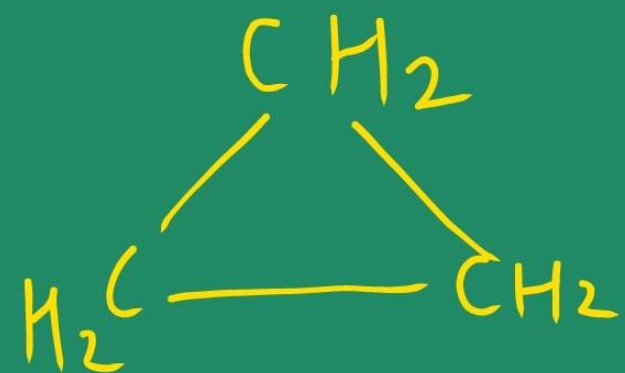
These are the simple hydrocarbons in which C-atom is joined together through a single bond.

[(C-C) : Saturated hydrocarbon]

These compounds are cyclic in nature i.e., cyclic hydrocarbons

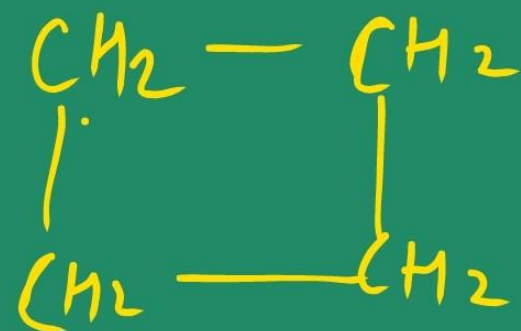
Hybridization: These compounds are sp^3 hybridized due to C-C.

IUPAC:- We will add cyclo as a Prefix in such compounds.

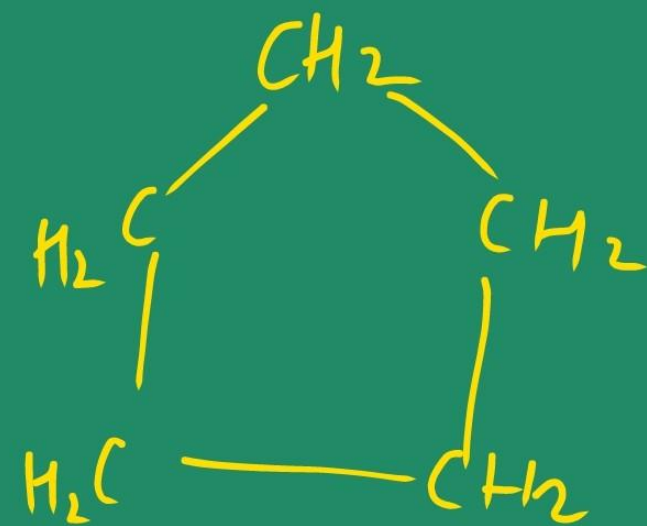


Cyclo Propane suffix
 Prefix Word Suffix
 Root

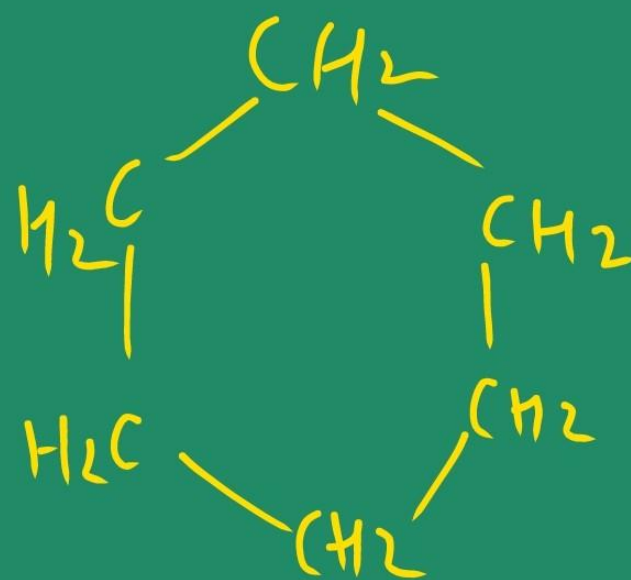
[Prefix + Word root + Suffix]



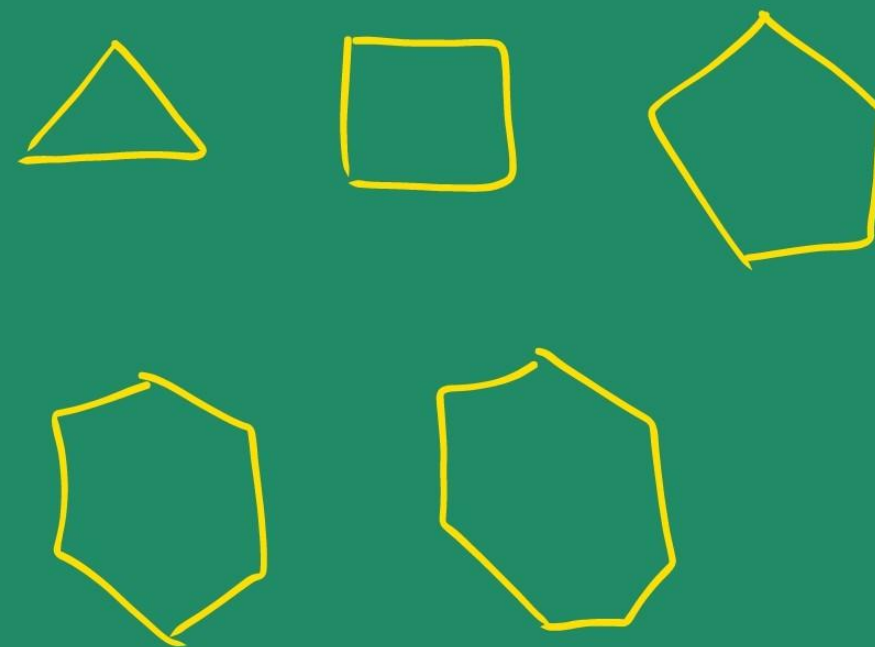
cyclobutane



cyclopentane



cyclohexane



Bond-line structure

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PHARMACEUTICAL ORGANIC CHEMISTRY II

CYCLOALKANES

- METHODS OF PREPARATION
- THEORIES
- PROPERTIES
- CHEMICAL REACTIONS

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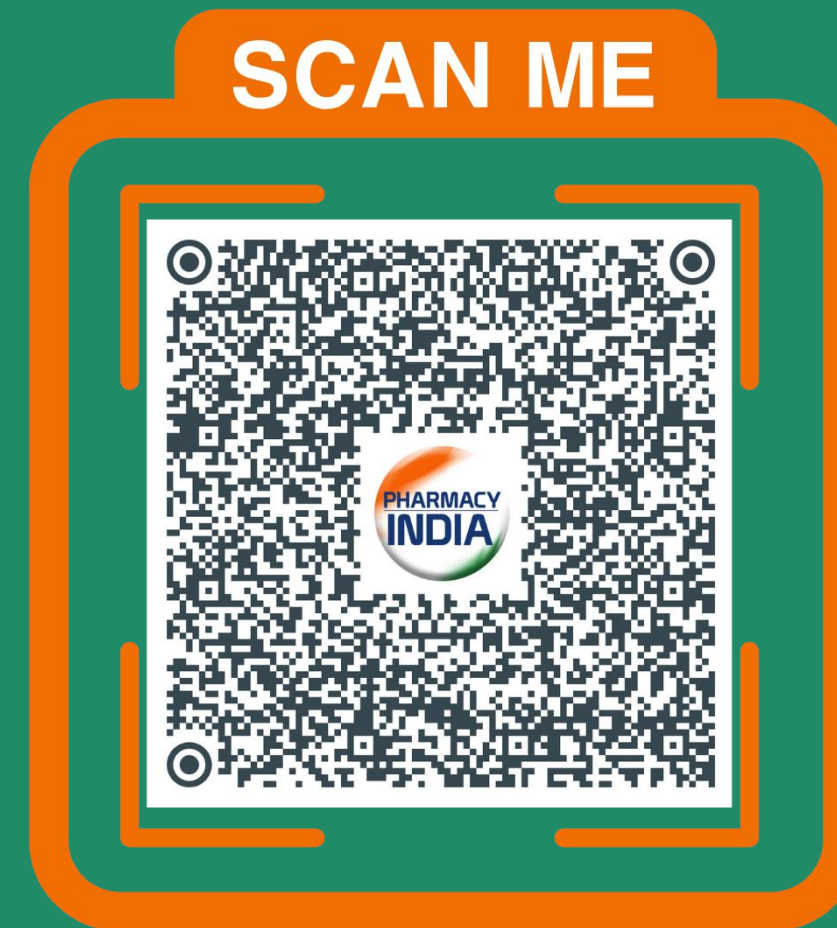
TOPIC: Cycloalkanes

→ Methods of Preparation

→ Physical

→ Chemical Rxns.

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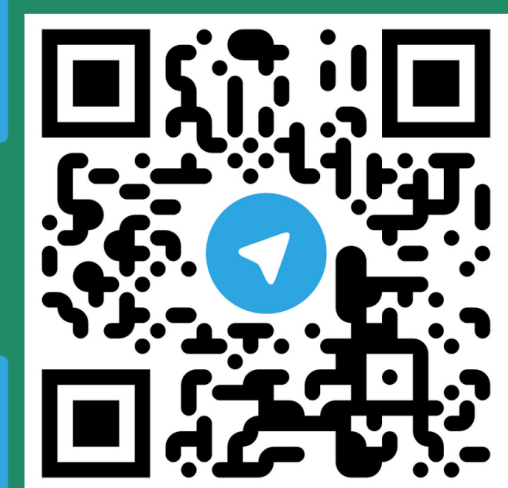
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Cycloalkane

There are the saturated cyclic hydrocarbons.

in which C-atoms are connected through a single bonds.

eg:-



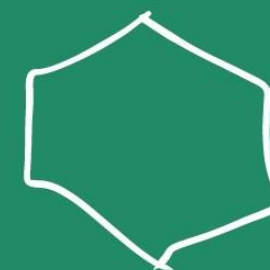
cyclopropane



cyclobutane



cyclopentane

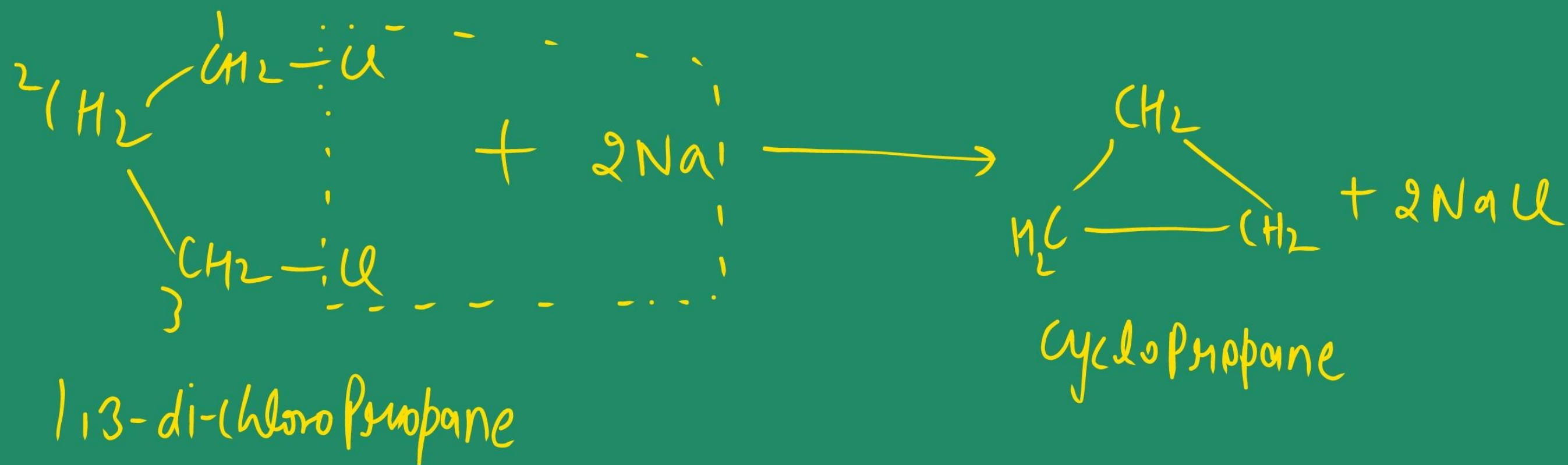


cyclohexane.

Methods of Preparation

1. From Di-halide

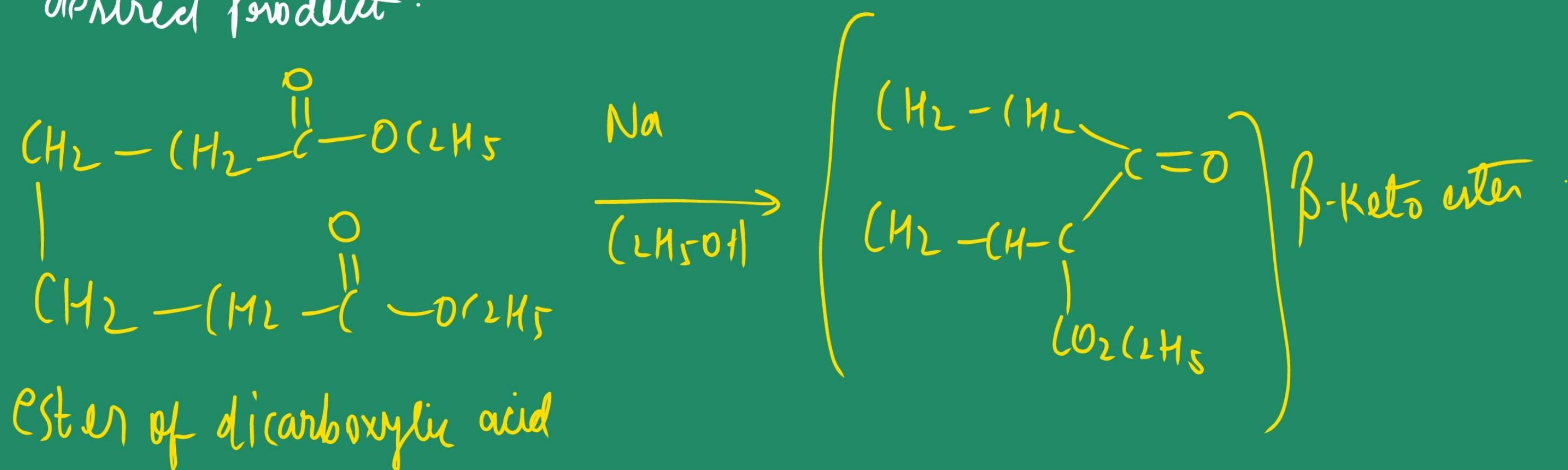
In this method, Terminal dihalides are reacted with active metals Na/Zn for the formation of cycloalkanes.

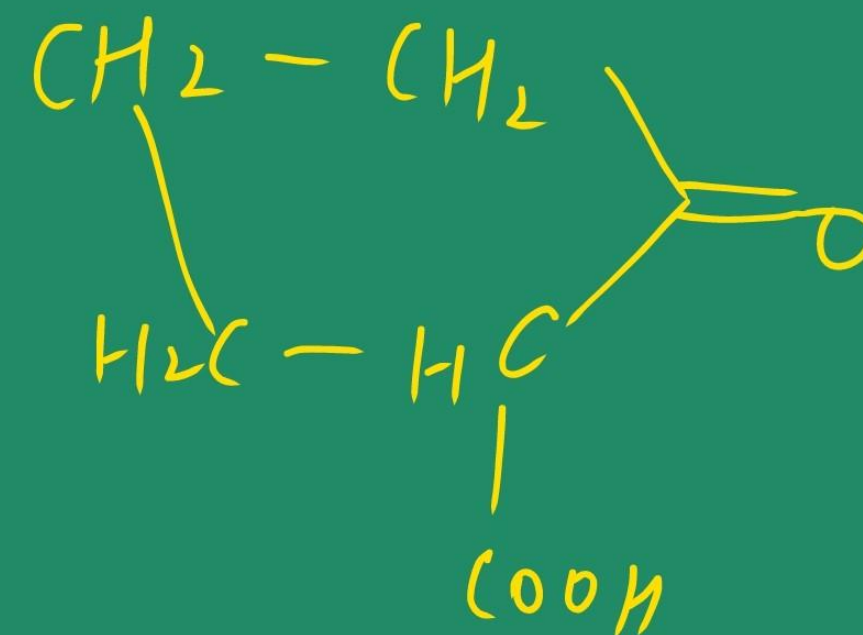
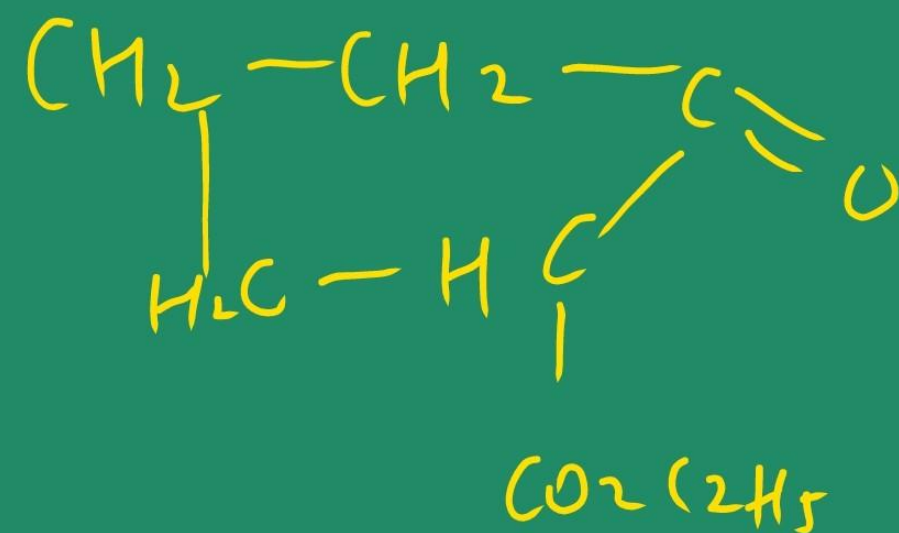


2. Dieckmann's Reaction

Ester of di-carboxylic acid are heated with an active metal (Na), β -Keto ester is formed.

Obtained β -Keto esters are further hydrolysed for the formation of desired product.



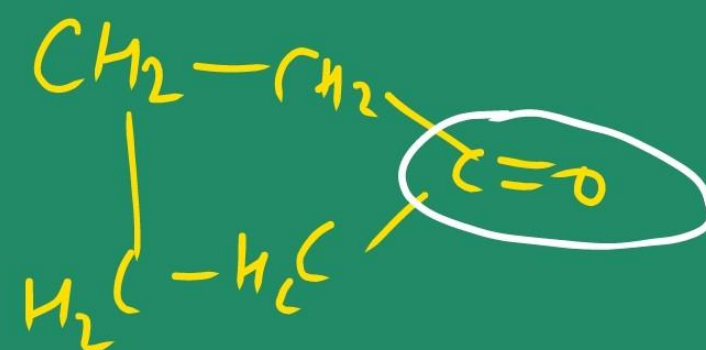


Clemensen

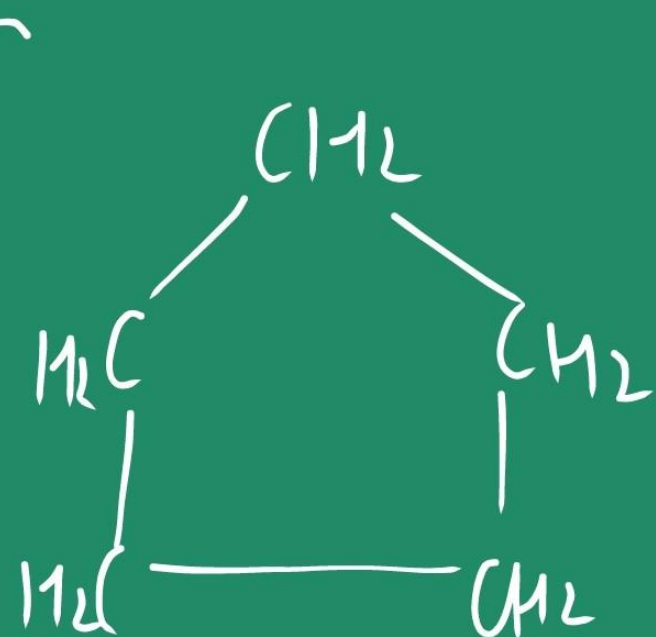
Reduction

Zn-Hg

(conc. HCl)



Cyclic
ketone

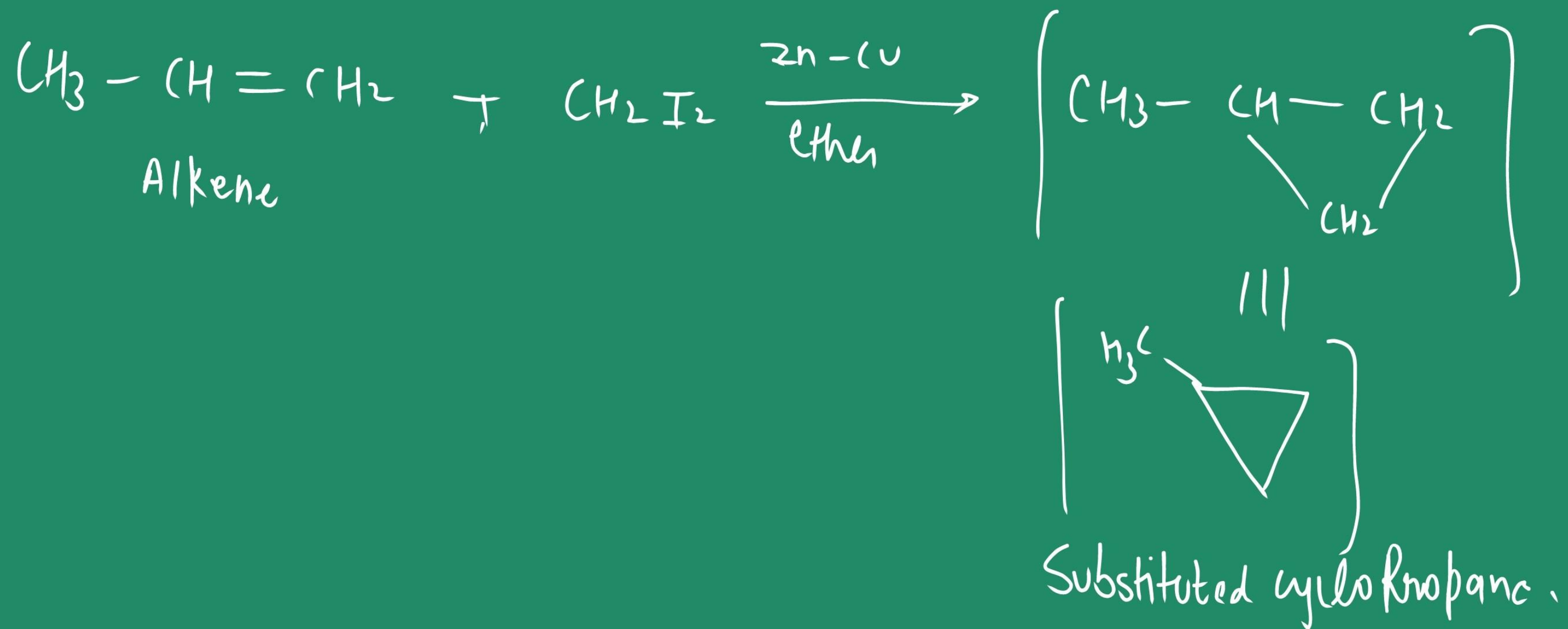


Cyclopentane



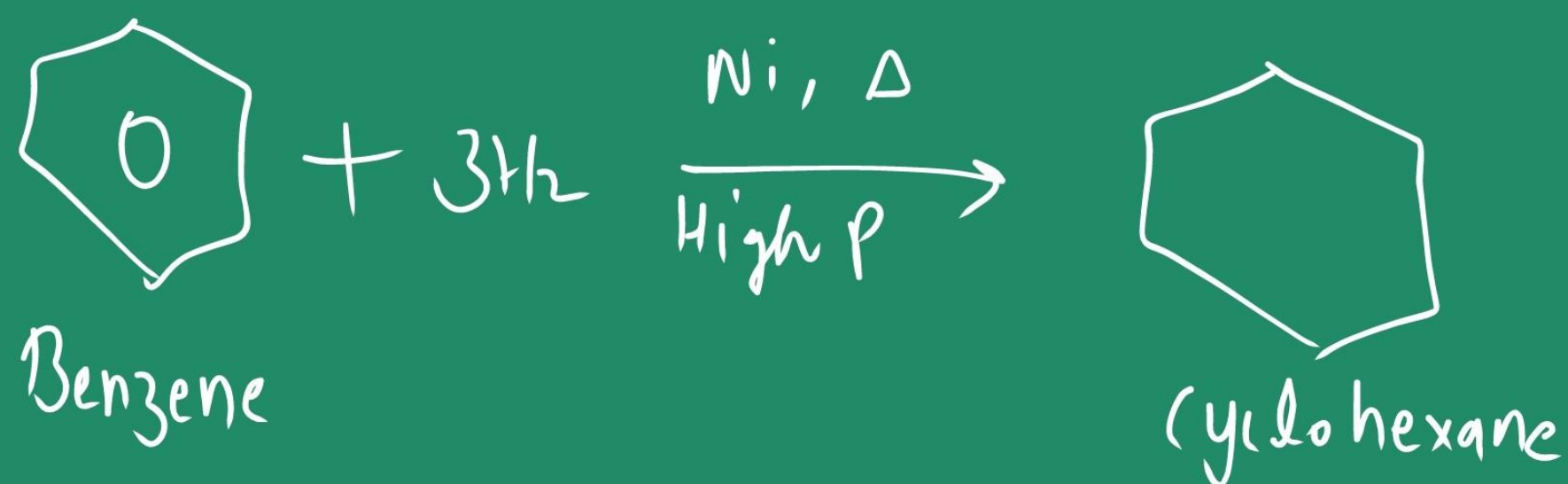
3. Simmon-Smith Reaction

In this reaction, Alkenes are reacted with CH_2I_2 in the presence of Zn-Cu .



4' From aromatic hydrocarbons

In this method, six-membered cycloalkane can be prepared by the catalytic reduction of Benzene & their derivatives.



Physical Properties

1. Cyclopropane & cyclobutane are generally gaseous in nature remaining are liquid.
2. Cycloalkanes are insoluble in water but they are completely soluble in organic solvents.
3. Melting Point & Boiling Point of any cycloalkane, gradually increases as their molecular weight increases.

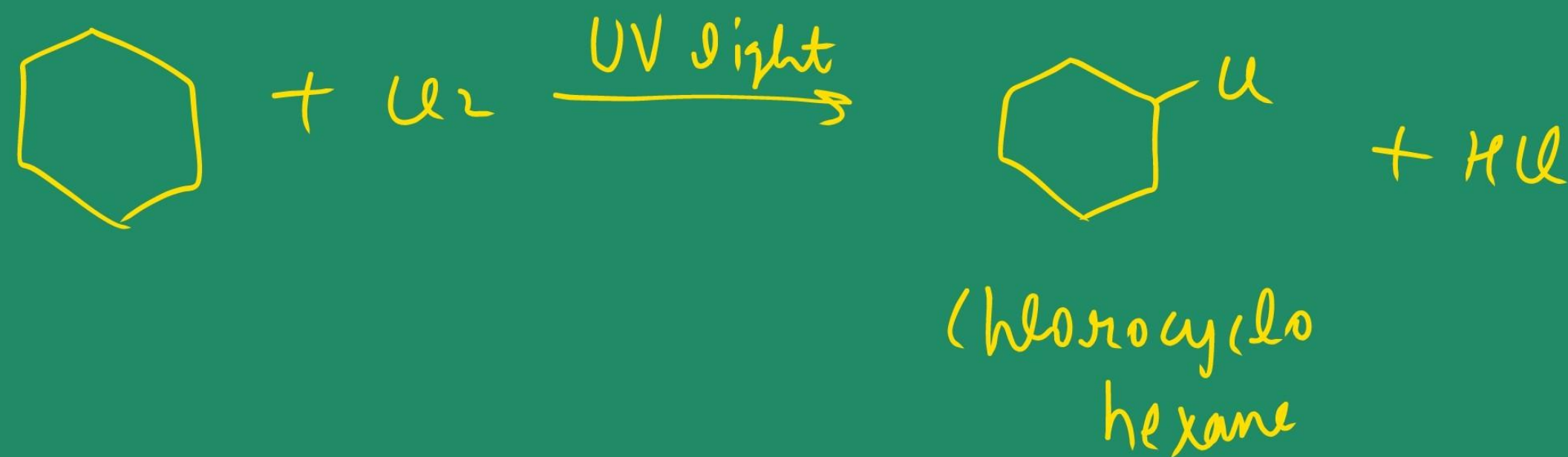
Chemical Reactions

Cycloalkanes generally shows two types of chemical reactions;

1. > Substitution reaction.
2. > Addition Reactions.

Substitution Reaction

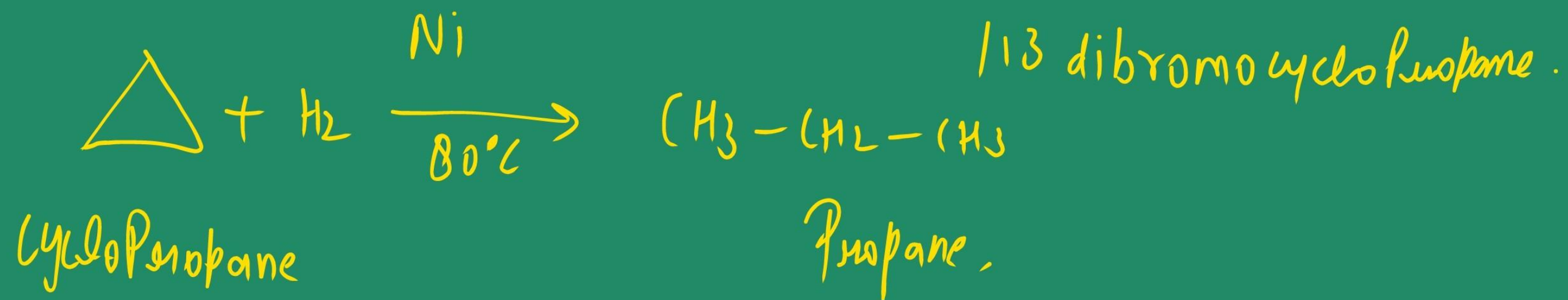
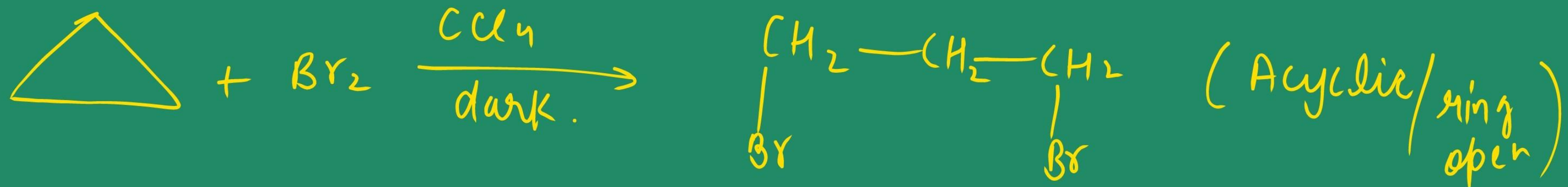
In this Particular reaction, one H-atom gets substituted or replaced.



Addition Reaction

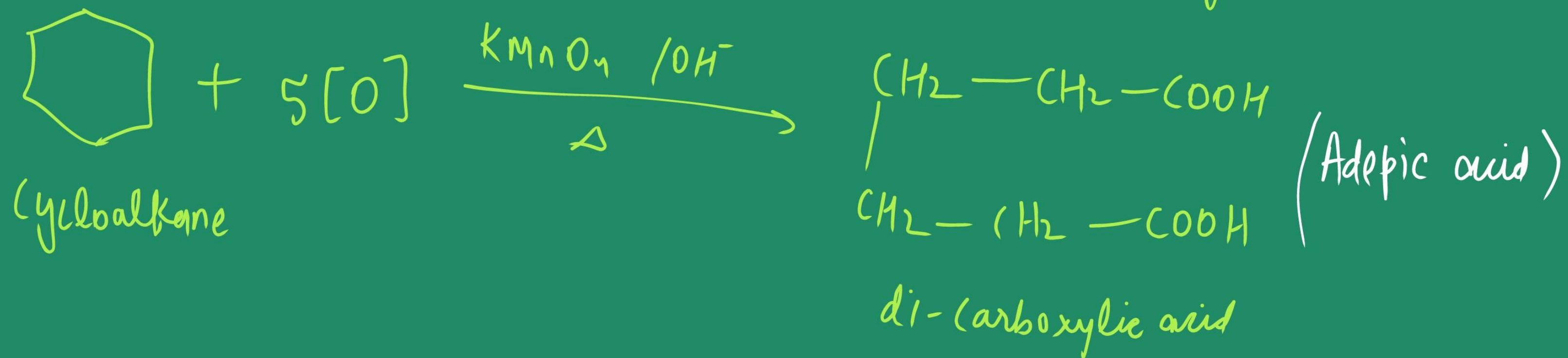
Such reactions are also known as 'Ring opening Reaction'.

~~But~~ Higher cycloalkanes never shows this ring-opening reactions.



Oxidation Reaction

Cycloalkanes may give oxidation reactions in the presence of oxidising agent (alk KMnO_4) to form di-carboxylic acid.



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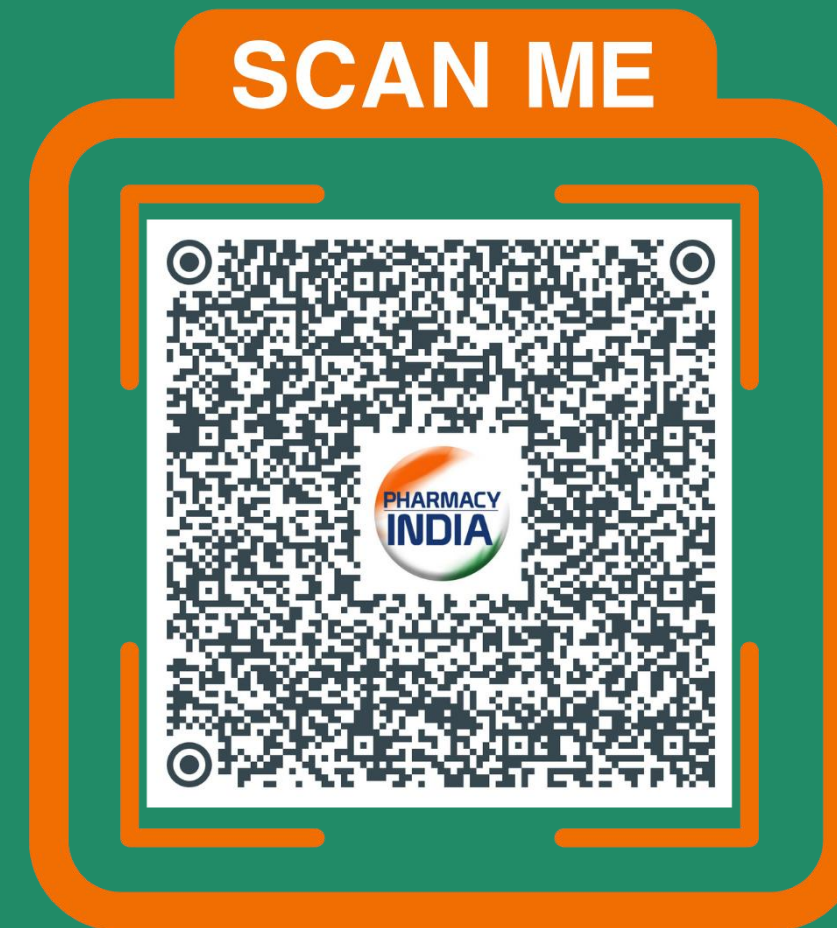
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CYCLOALKANES

**BAEYER'S STRAIN
THEORY**

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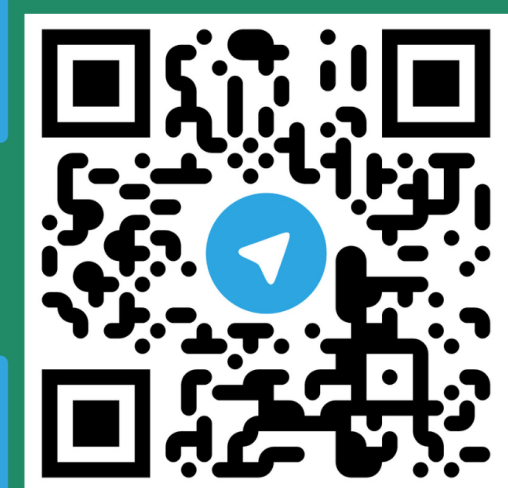
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TOPIC:- . Baeyer's strain Theory.

~~m note~~

Baeyer's Strain Theory

- Adolf Baeyer proposed this theory in 1885.
- This theory explains the stability of cycloalkanes on the basis of their **Bond Angle strains**.
- According to Adolf Baeyer, the stability of cyclic compound depends upon the deviation of bond angle from their ideal bond angle.

In the case of Alkanes,

The hybridization is sp^3

For the sp^3 -hybridization, the ideal Bond Angle is 109.5° or $109^\circ 28'$.

If the Bond angle of cycloalkane is deviated from its ideal Bond Angle (109.5°), molecule experiences angle strain. (Baeyer strain)

Examples

Cyclo Propane :



Hybⁿ $\rightarrow$ sp^3 (Alkane)

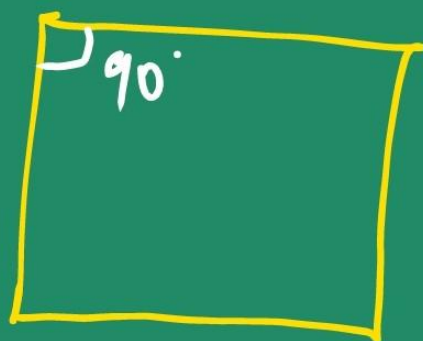
Ideal
Bond Angle $\rightarrow 109.5^\circ$

deviation $\rightarrow 109.5 - 60 \rightarrow 49.5^\circ$

Much Angle strain

least stable compound. (Highly strained Molecule)

2. cyclobutane



Alkane: Hybridization $\rightarrow sp^3$

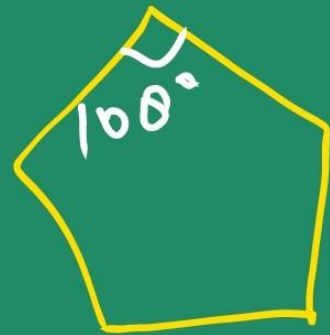
ideal Bond angle: $\rightarrow 109.5^\circ$

Deviation = $\boxed{11.5^\circ}$

Strained, less stable than larger rings

3.

Cyclopentane



it is also a cycloalkane, having sp^3 -hybrⁿ.

Bond Angle = $\sim 108^\circ$

Ideal Angle = 109.5°

It is an almost strain free ring.

$\therefore$

Very stable

4.

Cyclohexane



It is also a cycloalkane having sp^3 hybridization with an ideal Bond Angle of $\boxed{109.5^\circ}$

$$\text{Deviation} = 10.5^\circ$$

Baeyer Predicted a strain here.
But Experimentally, cyclohexane is a stable ring because it is non-Planar.
(Adopts chair conformation to attain the stability)

$$\left[\text{Angle strain} \propto \frac{1}{\text{Stability}} \right]$$

Thus,

Stability of cycloalkane Follows the order;

~~W.P.~~



Limitations

1. It is only applied to the lower cycloalkanes, it is not able to explain the effect of angle strain in large ring.
2. They do not give ring-opening reactions easily like cyclopropane.

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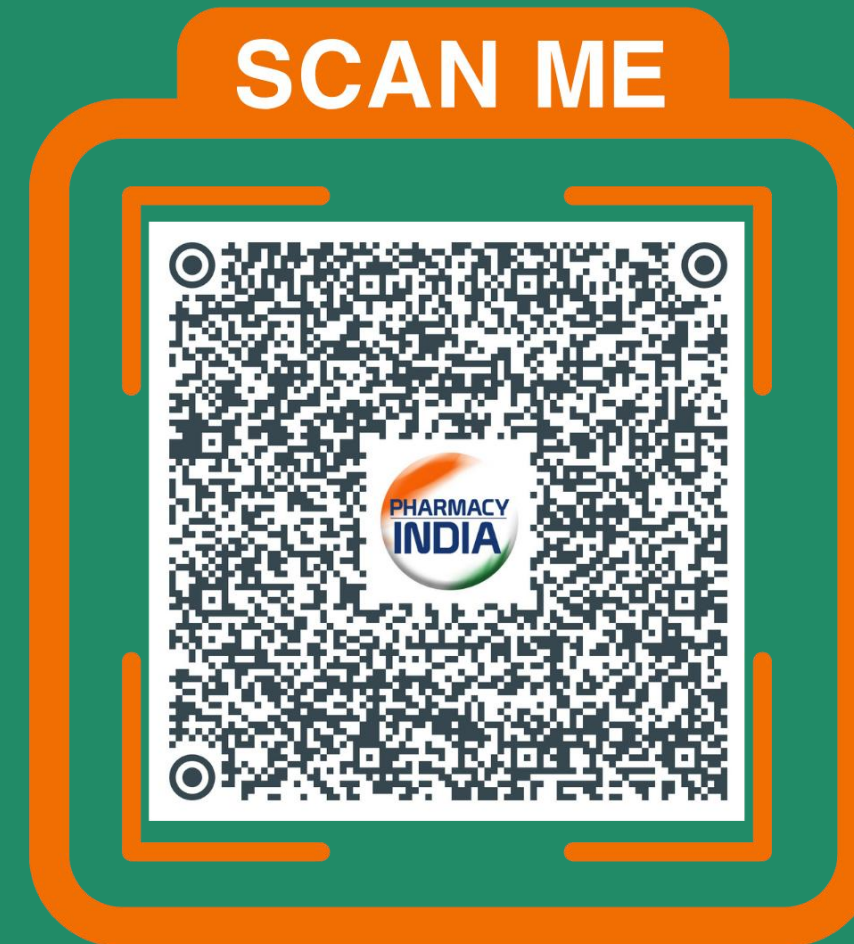
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CYCLOALKANES

**COULSON'S & MOFFIT'S
MODIFICATION THEORY**

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TOPIC:- Coulson's & Maffit's Modification
Theory.

Coulson & Moffitt's Theory

This theory is also known as Banana Bond theory.

It is based on the concept of maximum overlapping of orbitals.
it also explains the stability of cycloalkane.

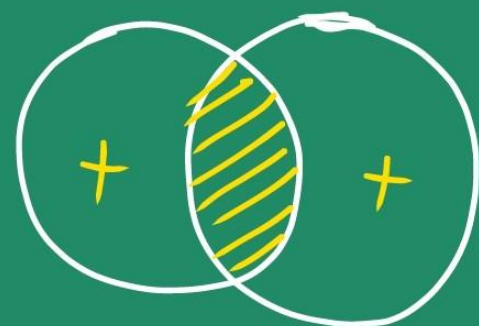
(Why cyclopropane is least stable).

It is based on the concept that, higher the overlapping of atomic orbitals,
Stronger will be the bond.

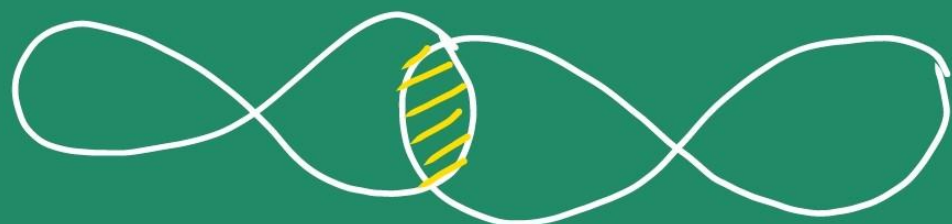
[Stability $\propto$ Bond strength]

eg.

Head-to-Head overlapping



σ -bond

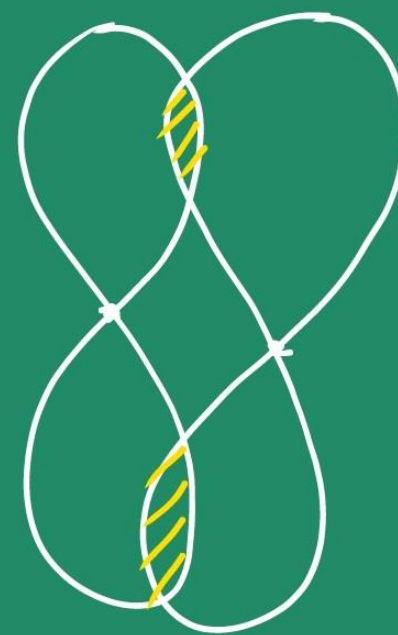


σ -bond

This is a Proper overlapping.

Thus, it is a strong bond

Partial/Lateral overlapping

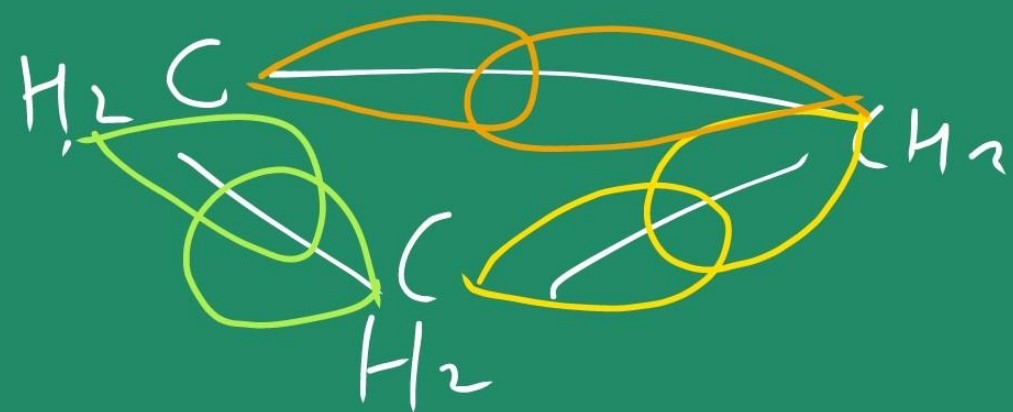


π -bonds.

→ There is Partial overlapping.

$\therefore$ Weaker bond.

A/c to this theory, the bond formation in cyclopropane can be observe as follows;



→ Due to the formation of Bent Bond in cyclopropane, the C-C bonds are weaker than normal bonds.

Bent Bond

Weaker Bond

(sp^3)

→ It is unstable & will give ring-opening reactions.

→ Here the Bond Angle is slightly decreased from

$109.5^\circ \rightarrow 104^\circ$

Due to this decrease in overlapping, bond becomes weaker.

Thus,

Cyclobutane is more stable than cyclopropane but it is less stable than higher membered cycloalkanes.

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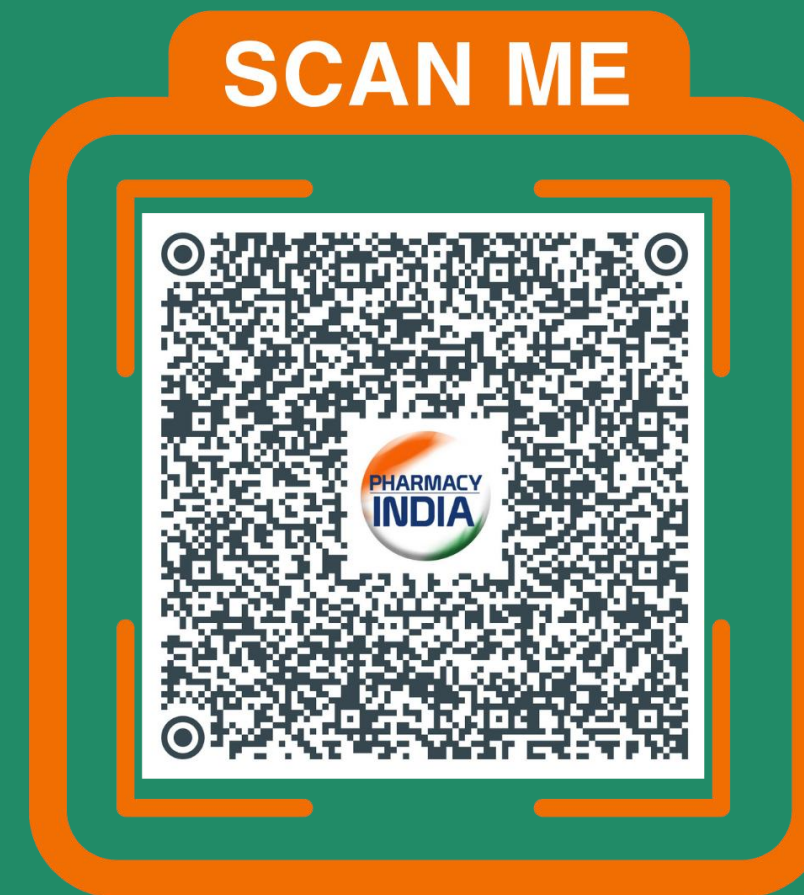
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CYCLOALKANES

**SACHSE MOHR
THEORY**

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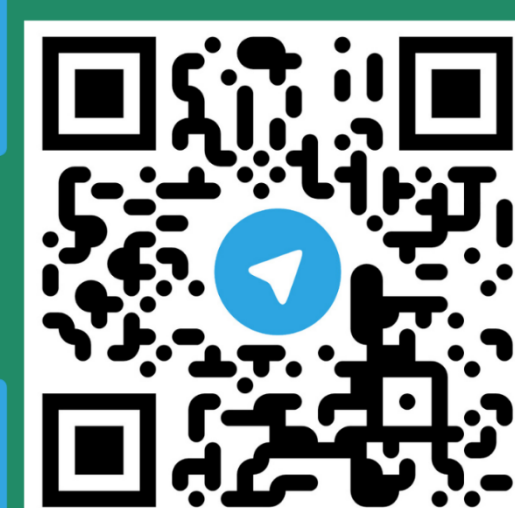
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TOPIC:- Sachse - Mohn
Theory

Sachse-Mohr

Theory

This is a theory of strain-less rings.

Sachse & Mohr, Proposed this theory in 1918.

it explains the stability of cyclohexane & other higher cycloalkanes.

A/c to this theory, cyclohexane is not in a plane i.e., co-planar.

They Proposed that higher membered cycloalkanes, they are free from the strain.

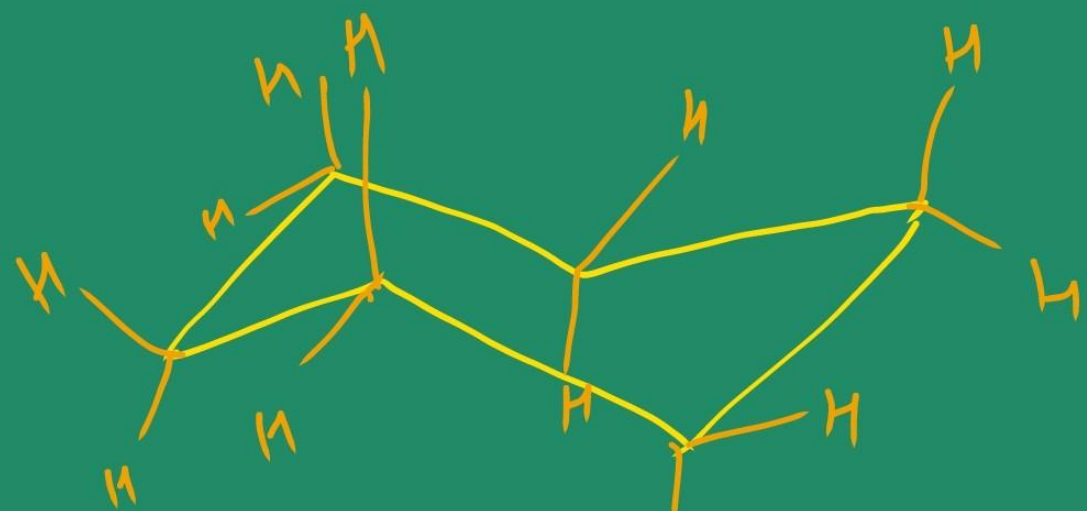
These are strain-free rings in which all the C-atoms are not forced to remain in one plane.

They exist in 'folded' and 'Puckered' conformation.

Which are completely strain-free conformers.

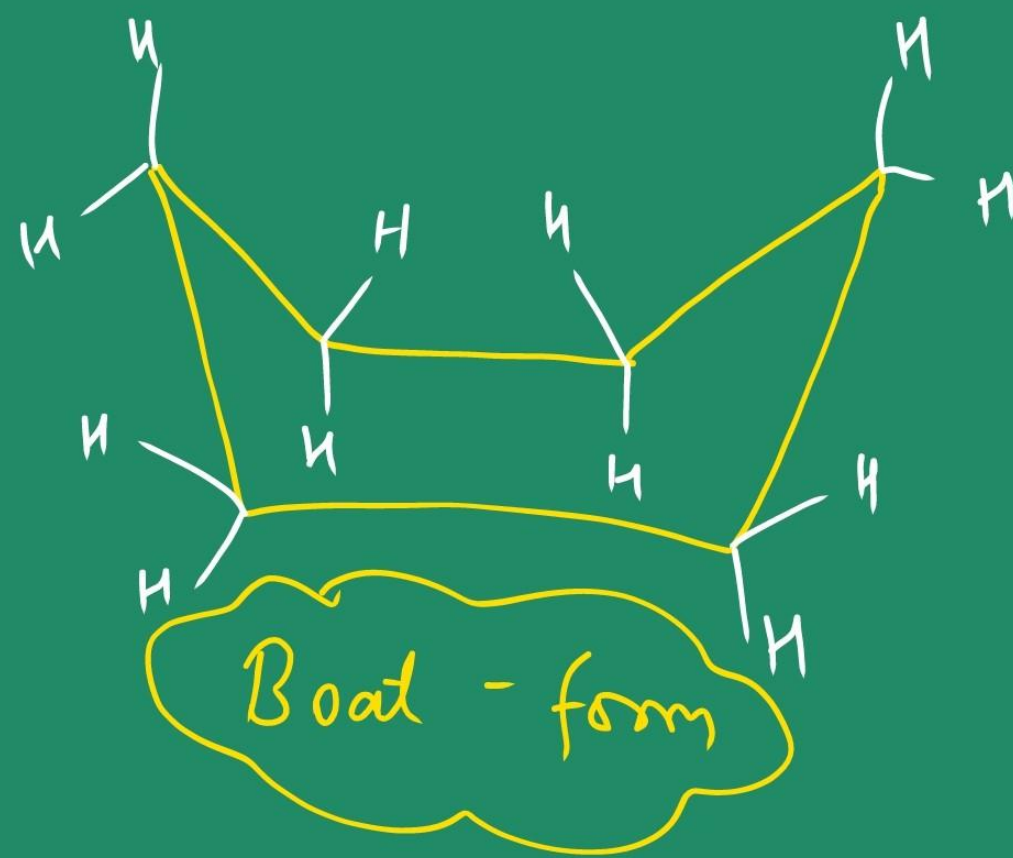
These are strainless conformations of higher cycloalkanes.

These conformations can be drawn as follows;



Cyclohexane

Chair-form



Boat-form

Cyclohexane

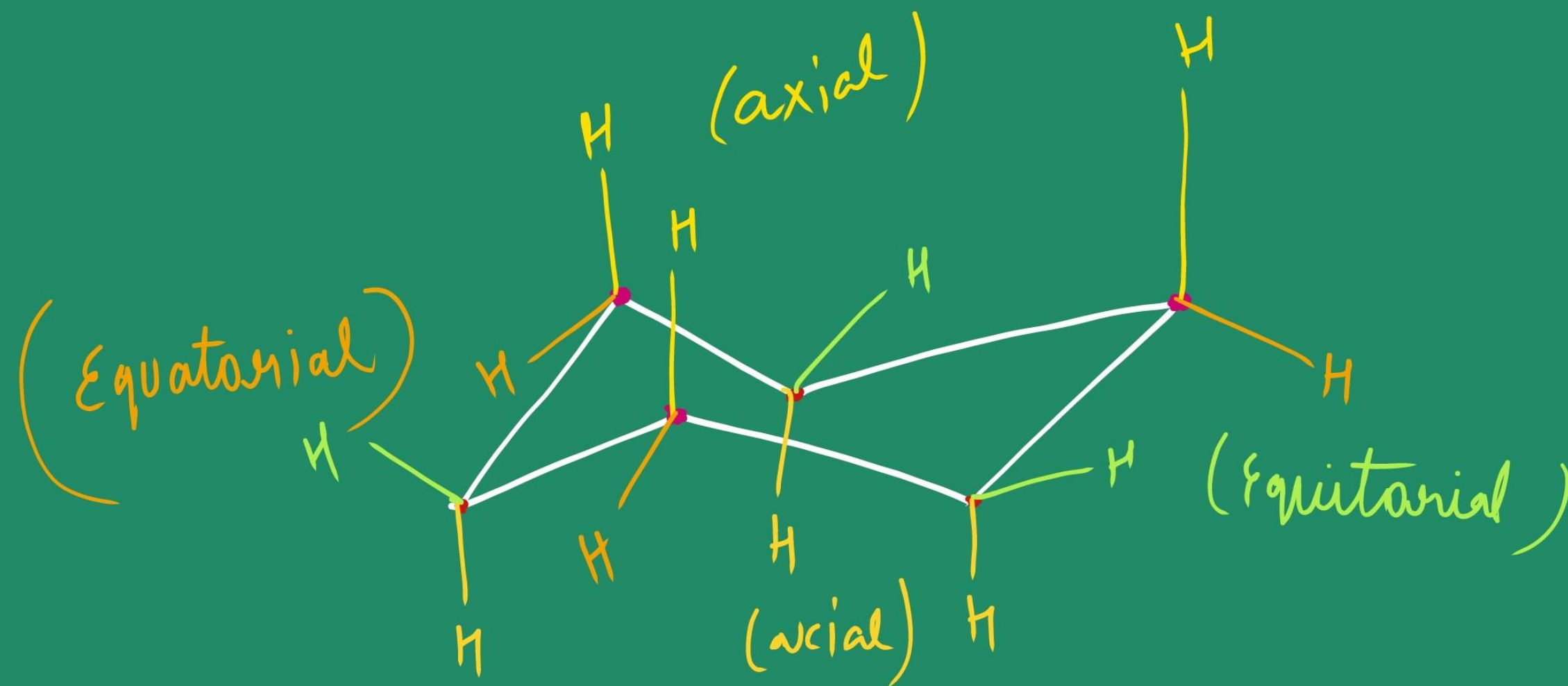
The above conformations are free from strain.

The chair conformation of cyclohexane is more stable than Boat conformation.

Two Positions are there in above conformation

1) Axial : Perpendicular ($\perp$) to the Plane.

2) Equatorial : Parallel ($\parallel$) to Plane.



- → Elevated Carbons
- → Depressed Carbons

Chair - Conformation

cyclohexane

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