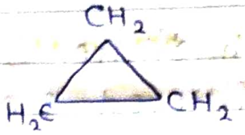
Unit - V

✦ Cycloalkanes ✦

Cyclopropane →

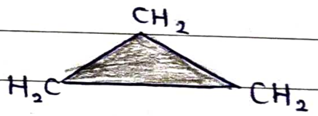
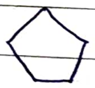
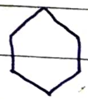
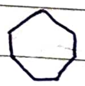
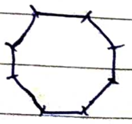


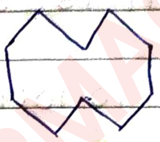
Definition →

Cycloalkanes are also called as alicyclic compounds.

These are cyclic hydrocarbons in which Carbons of the molecules are arranged in the form of ring.

Cycloalkanes are saturated in which carbon atoms in the rings are single bonded to the other atoms
(No double or triple bonds)

Cycloalkane	Mol. formula	Structure
① Cyclopropane	C_3H_6	
② Cyclobutane	C_4H_8	
③ Cyclopentane	C_5H_{10}	
④ Cyclohexane	C_6H_{12}	
⑤ Cycloheptane	C_7H_{14}	
⑥ Cyclo octane	C_8H_{16}	

⑦ Cyclononane	C_9H_{18}	
⑧ cyclodecane	$C_{10}H_{20}$	

* Classification of cycloalkane →

① Depending upon the size of ring
② Depending upon the number of rings.

① Depending upon the size of rings →

It means how many carbon atoms are present in that cycloalkanes.
It is subclassified into 4 types :-

ⓐ Small Rings → (C_3 - C_4)
e.g...
cyclopropane and cyclobutane.

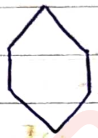
ⓑ Common Rings → (C_5 - C_6)
e.g...
cyclopentane and cyclohexane.

ⓒ Medium rings → (C_7 - C_{12})
e.g....
cycloheptane, cyclo octane, nonane, decane.

② Depending upon the no of rings →

It is subclassified into two types.

ⓐ Monocyclic →
e.g...
cyclohexane

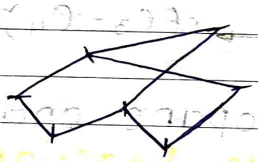


ⓑ Polycyclic →
More than 1 ring.

(i) Fused Polycyclic →
e.g..

Decaline.

(ii) Bridged polycyclic →
e.g...



Bicytoheptane

(iii) Spiranes →
e.g...

Spiro - octane.

* Methods of preparations of cycloalkanes.

There are 3 methods by which cycloalkanes are prepared :-

① From di-halides
② Dieckmann Reaction
③ Simmons - Smith reaction
④ From aromatic hydrocarbons.

① From Dihalides →

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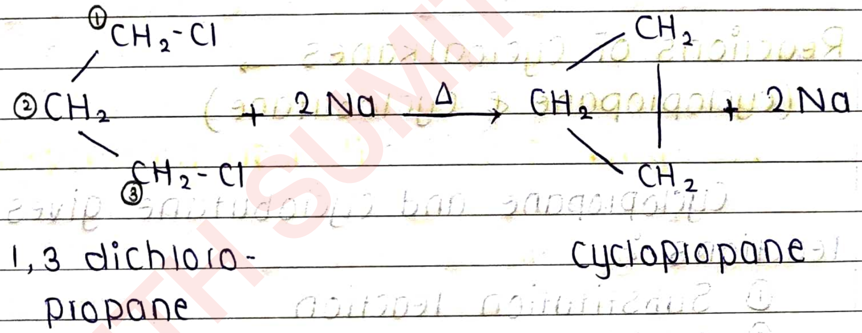
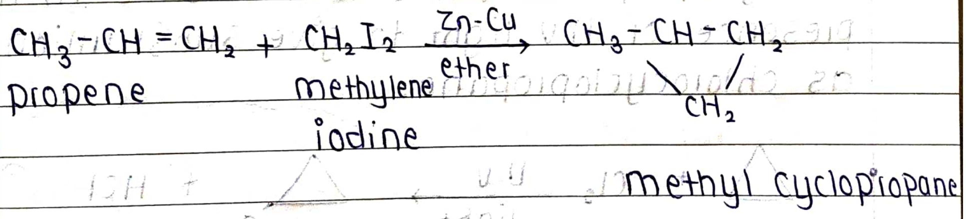


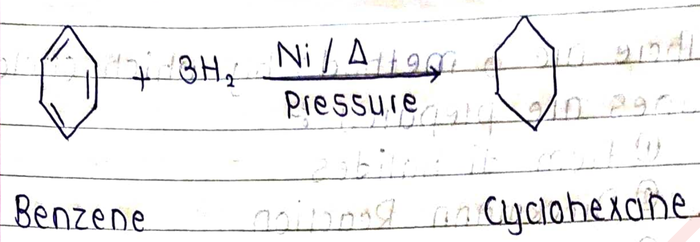
Cyclopropane is obtained from reaction between 1,3 dichloropropane and sodium metal.

③ Simmons Smith Reaction →



When alkanes are treated with methylene iodine in the presence of Zinc-Copper and ether, cyclopropane are formed.

④ From aromatic hydrocarbons →



Six membered cycloalkanes can be prepared by reduction of benzene in the presence of a catalyst.

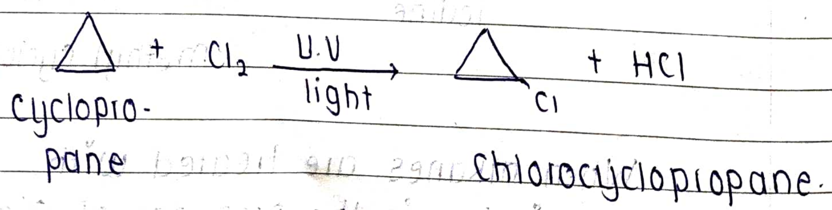
* Reactions of Cycloalkanes → (cyclopropane & cyclobutane)

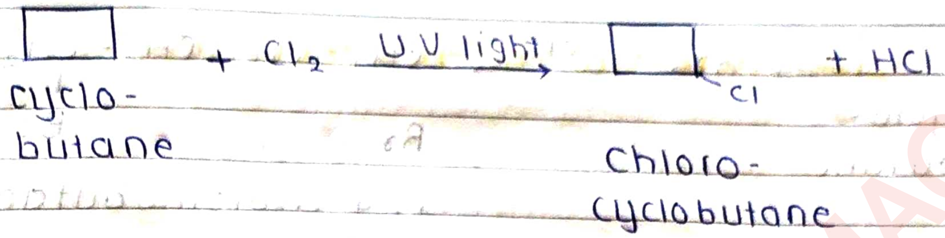
Cyclopropane and cyclobutane gives following reactions :-

① Substitution reaction
② Addition of hydrogen
③ Addition of Chlorin and bromine.
④ Addition of HBr and HI

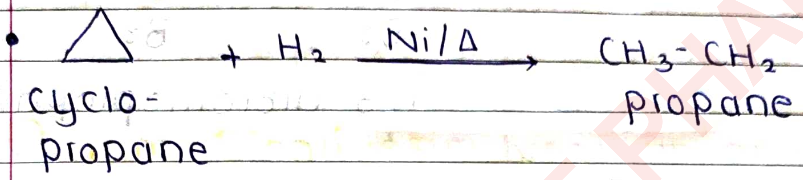
① Substitution Reaction →

Cyclopropane reacts with chlorine in the presence of U.V light to give substitution product as chlorocyclopropane.

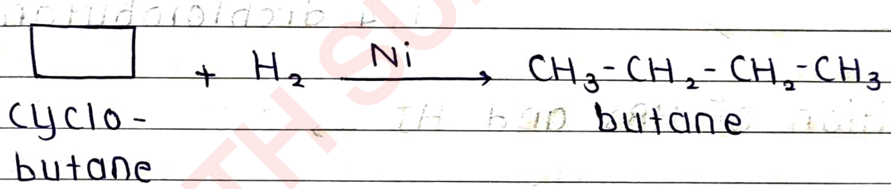




② Addition of hydrogen →

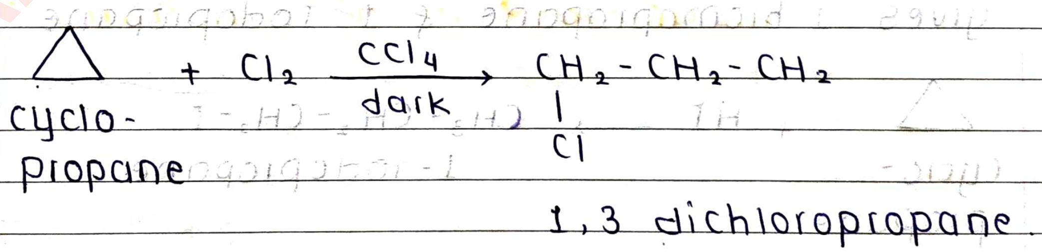


Cyclopropane reacts with hydrogen in presence of catalyst nickel.

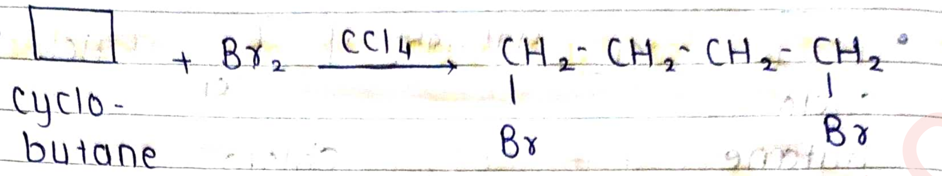


Cyclobutane reacts with hydrogen in the presence of catalyst nickel to give butane.

③ Addition of chlorin & Bromin →

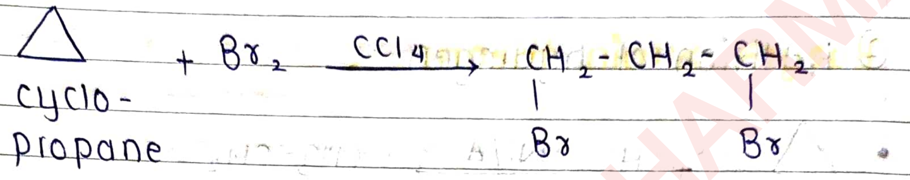


Cyclopropane reacts with chlorine in presence of CCl_4 in the dark to give 1,3 dichloropropane



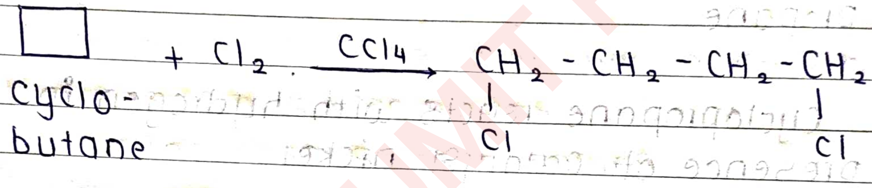
$$\text{cyclobutane} + Br_2 \xrightarrow{CCl_4} \underset{Br}{CH_2}-CH_2-CH_2-\underset{Br}{CH_2}$$

1, 4 dibromobutane.



$$\text{cyclopropane} + Br_2 \xrightarrow{CCl_4} \underset{Br}{CH_2}-CH_2-\underset{Br}{CH_2}$$

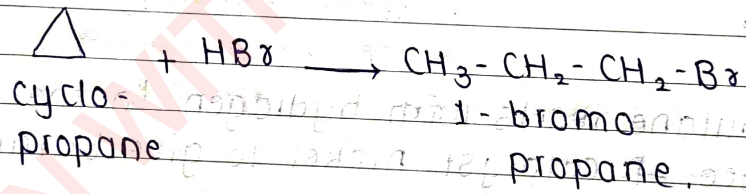
1, 3 dibromopropane



$$\text{cyclobutane} + Cl_2 \xrightarrow{CCl_4} \underset{Cl}{CH_2}-CH_2-CH_2-\underset{Cl}{CH_2}$$

1, 4 dichlorobutane.

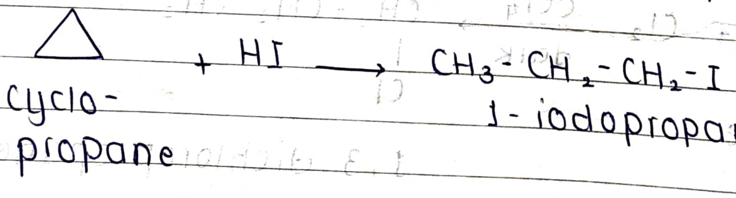
Imp ④ Addition of HBr and HI →



$$\text{cyclopropane} + HBr \longrightarrow CH_3-CH_2-CH_2-Br$$

1-bromo propane.

Cyclopropane reacts with con. HBr and HI to gives 1 bromopropane & 1 Iodopropane.



$$\text{cyclopropane} + HI \longrightarrow CH_3-CH_2-CH_2-I$$

1-iodopropane.

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Stability of cycloalkanes →

① Baeyrs Strain theory
② Sache - Mohrs theory of Strainless ring.

① Baeyrs Strain theory →

Cyclopropane and cyclobutane are comparitively less Stable due to the more Strain. In ring and thus break up and open to give additions reactions.

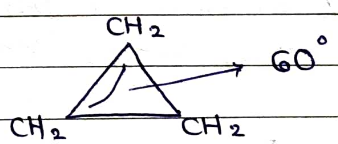
In 1885, Baeyrs proposed a Strain theory which explains reactivity and Stability of cycloalkanes.

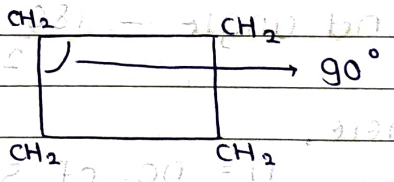
He proposed that, any deviation (change) of bond angle from ideal bond (109°28') will produced a Strain (force) in a molecule.

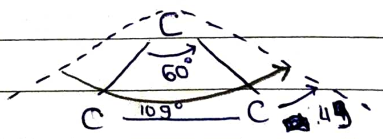
Higher the deviation, less is the Stability. If bond angles deviate from the ideal then ~~angles deviates from~~ produce a Strain in the molecule.

e.g...

cyclopropane or cyclobutane.







Angle Strain in cyclopropane.

In cyclopropane & cyclobutane the rings are planner with ring bond angle 60° & 90°. It shows that C-C is compressed from 109°.28 to 60° or 90° to fit the geometry of the ring.

The angle strain is maximum in cyclopropane and it is most unstable.

The angle strain in cyclobutane is less than the cyclopropane which shows that cyclobutane than cyclopropane.

While angle strain is minimum in case of cyclopentane & it is more stable.

The various bond angles of different cycloalkanes are as follows :-

cyclopentane = 108°
cyclohexane = 120°
cycloheptane = 12
cyclooctane = 135°

The bond angle in each angle cycloalkane is given by the formula.

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

Where,

n = no. of sides of cycloalkanes.

* Limitations of Baeyis strain theory →

① Baeyer was not able to explain the effect of angle strain in larger ring system.

② According to baeyer C.P should must stable than cyclohexane, but practically, it is reversed.

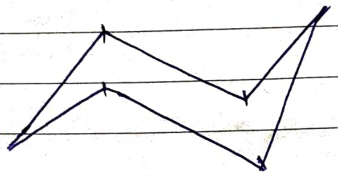
③ larger ring system are not possible accord. to baeyis they have -ve strain but they exist & much stable.

④ larger ring systems are not planner but contracted to eliminate angle strain.

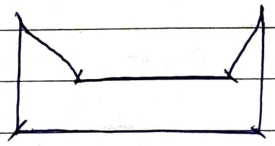
② Sache - Mohr's theory of Strainless ring →

Sache and mohr proposed the new theory that rings in cycloalkanes are absolutely free from, if all the rings carbons are not in the same plane.

Acc. to this theory, cyclohexane can exist in two non-polar strainless forms i,e. chair from and boat form as follows



Chair form



Boat form

The chair form of cyclohexane is more stable than boat form because the ratio of chair to boat confermation is 1000 : 1

The chair form of cyclohexane shows that the hydrogen atoms can be divided into two categories.

Six of the bonds to plane of the molecule and are called Axial hydrogen.

Other Six H are slightly above or below the planes of cyclohexane ring and are called equatorial hydrogens.

* Axial and equatorial hydrogen in chair form of cyclohexane.

Ha=6
He=6