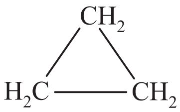
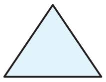
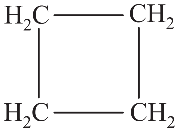
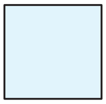
CYCLOALKANES AND CYCLOALKENES Section - 4

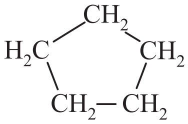
These are closed chain hydrocarbons having C_nH_{2n} as general formula. These are isomeric to alkenes.

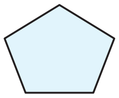
Cyclo propane or C_3H_6 or 

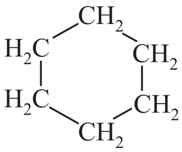
or 

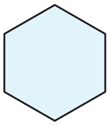
Cyclo butane or C_4H_8 or 

or 

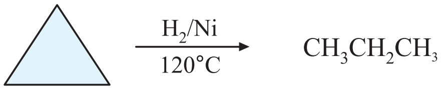
Cyclo pentane or C_5H_{10} or 

or 

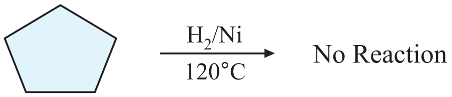
Cyclo hexane or C_6H_{12} or 

or 

The bond angles in lower members, i.e., in cyclopropane and cyclobutane are quite different from normal tetrahedral bond angle of 109.5°. Hence these are unstable as compared to higher member such as cyclopentane and cyclohexane which have bond angles nearer to tetrahedral bond angles. The two small cycloalkanes are said to have a ring strain due to bond deformation. This is referred to as Baeyer strain theory. Due to this strain, cyclopropane and cyclobutane are highly reactive and tend to open their rings.

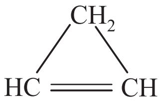


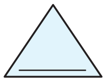
Cyclo propane

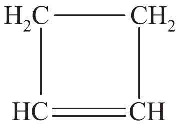


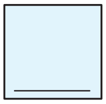
Cyclo pentane

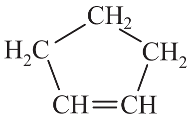
Cycloalkenes : These are isomeric to alkynes and alkadienes. Some important cycloalkenes are :

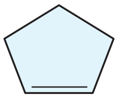
Cyclo propene or C_3H_4 or 

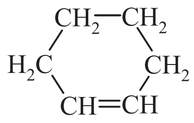
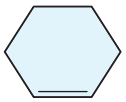
or 

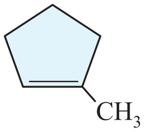
Cyclo butene or C_4H_6 or 

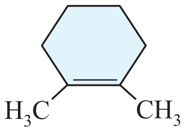
or 

Cyclo pentene or C_5H_8 or 

or 

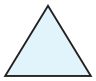
Cyclo hexene or C_6H_{10} or  or 

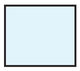
1-Methyl cyclopentene 

1, 2-Dimethyl cyclohexene 

Preparation of cycloalkanes and cycloalkenes :

1. Dehalogenation of isolated dibromides :

$BrCH_2 — CH_2 — CH_2Br \xrightarrow[\text{heat}]{\text{2 Na or Zn}}$  + 2NaBr ($ZnBr_2$)

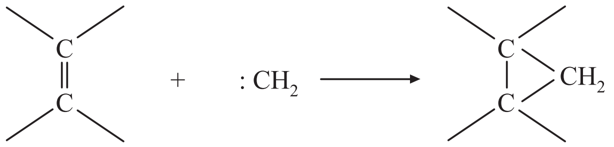
$BrCH_2 — CH_2 — CH_2 — CH_2Br \xrightarrow[\text{heat}]{\text{2 Na or Zn}}$  + 2NaBr ($ZnBr_2$)

It is not a good method because of poor yield.

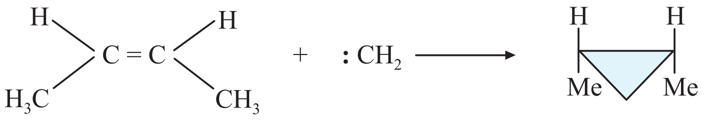
2. From diazomethane (CH_2N_2) :

Diazomethane on simple heating gives Carbene, $:CH_2$, which adds to the double bond of alkenes to give cyclopropane.

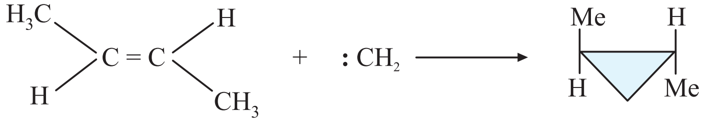
$$CH_2N_2 \xrightarrow{\Delta} :CH_2 + N_2$$



alkenes carbene cyclopropane and derivatives



cis-2-butene *cis*-1, 2-Dimethyl cyclopropane

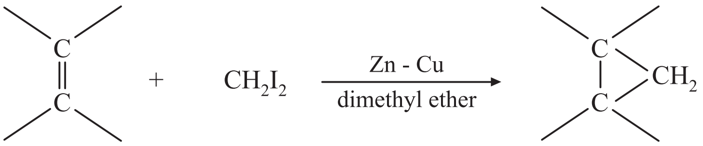


trans-2-butene *trans*-1, 2-Dimethyl cyclopropane

Note that the addition of $:CH_2$ (carbene) is stereospecific as 2-butene exist in *cis* and *trans* forms .

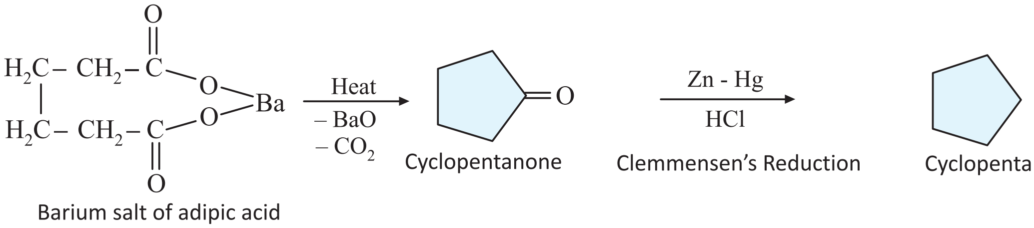
3. Simmon - Smith Reaction :

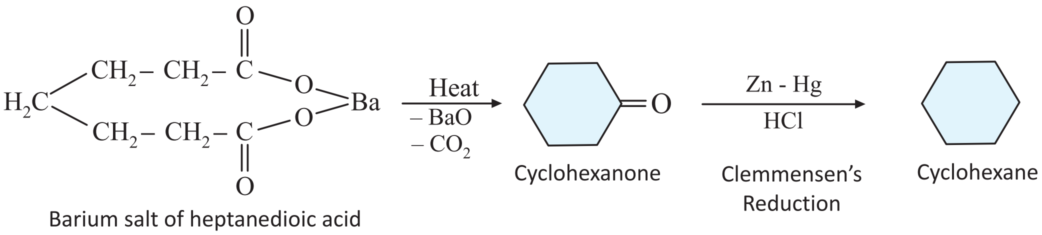
It is another method to form cyclopropane and its derivatives. Instead of diazomethane, di-iodomethane, CH_2I_2 with Zn - Cu alloy in diethyl ether is used. The rest of the reaction is same as above.



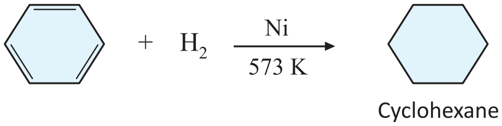
4. Heating calcium/barium salts of dicarboxylic acids :

By heating barium salts of dicarboxylic acids, cyclic ketones are formed, which on Clemmensen's reduction (Zn-Hg/HCl) give cyclopentane, cyclohexanes and other higher derivatives.



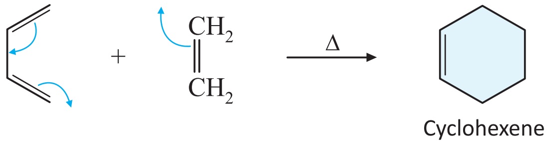


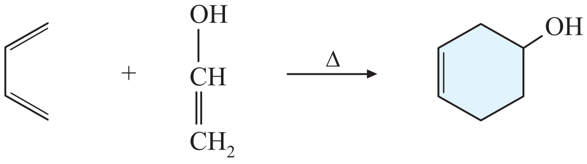
5. Hydrogenation of benzene :



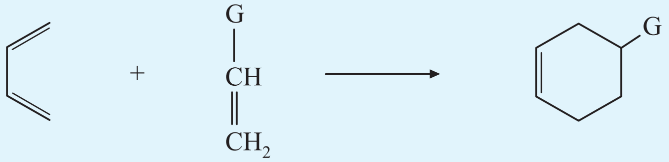
6. Diel - Alder Reaction :

It is an important reaction of conjugated dienes with double bonded compounds to form unsaturated cyclic compounds. Let us take 1, 3–Butadiene as conjugated diene and consider its reaction with some unsaturated compounds such as Ethene and Vinyl alcohol. The unsaturated compounds are called as dienophiles. This reaction proceed because of formation of six membered cyclic transition state.





Note : (i)

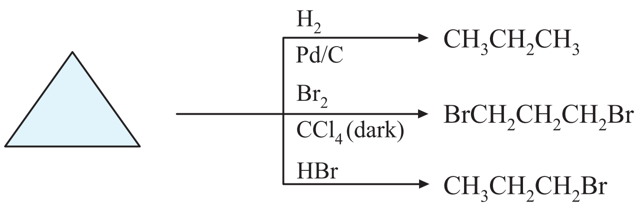


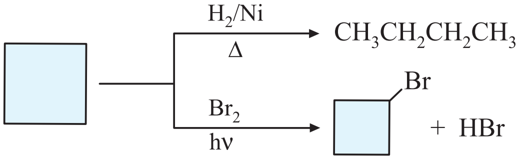
‘G’ is preferably an electron withdrawing group (electronegative in nature) such as $-OH$, $-NH_2$, $-CN$, $-NO_2$, etc.

(ii) Each of the product can be hydrogenated to give a saturated compound.

Reaction of cycloalkanes :

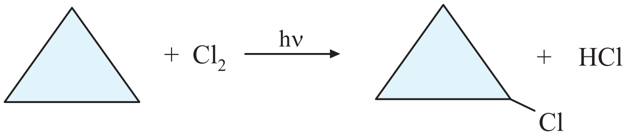
1. Ring opening :

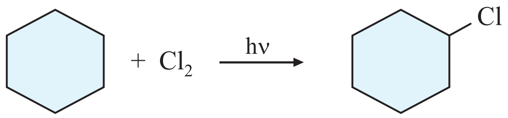




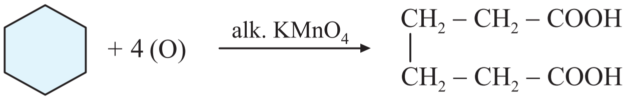
The ring of 5 carbons being stable does not open after reaction with hydrogen.

2. Chlorination :





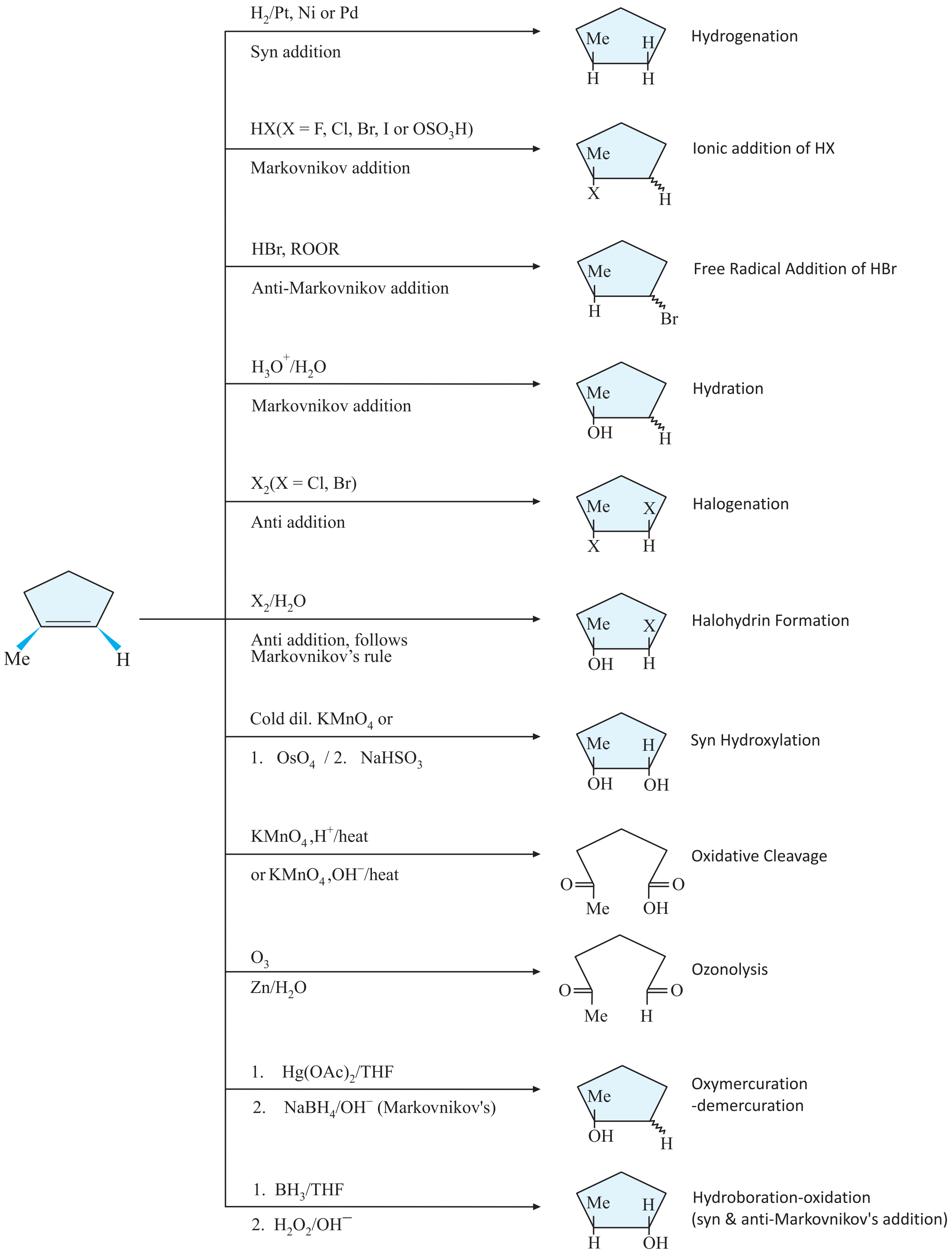
3. Oxidation :



Note : Cyclobutane is opened in the presence of hydrogen and Ni. At ordinary temperatures, cyclobutanes resists the action of halogens and hydrogen halides.

Reaction of Cycloalkenes :

The cycloalkenes show all the reactions of alkenes. (*Refer to the reactions of Alkenes*). For a quick review of the reactions, please go through the following page carefully. It shows all the typical reactions of alkenes taking 1-Methylcyclopentene as the substrate.


Me
H
H_2/Pt, Ni or Pd
Syn addition
Me H H H
Hydrogenation
HX(X = F, Cl, Br, I or OSO_3H)
Markovnikov addition
Me X H
Ionic addition of HX
HBr, ROOR
Anti-Markovnikov addition
Me H Br
Free Radical Addition of HBr
H_3O^+/H_2O
Markovnikov addition
Me OH H
Hydration
X_2(X = Cl, Br)
Anti addition
Me X X H
Halogenation
X_2/H_2O
Anti addition, follows Markovnikov's rule
Me X OH H
Halohydrin Formation
Cold dil. $KMnO_4$ or
1. OsO_4 / 2. $NaHSO_3$
Me H OH OH
Syn Hydroxylation
$KMnO_4, H^+$/heat
or $KMnO_4, OH^-$/heat
O Me OH O
Oxidative Cleavage
O_3
Zn/H_2O
O Me H O
Ozonolysis
1. $Hg(OAc)_2$/THF
2. $NaBH_4/OH^-$ (Markovnikov's)
Me OH H
Oxymercuration -demercuration
1. BH_3/THF
2. H_2O_2/OH^-
Me H H OH
Hydroboration-oxidation (syn & anti-Markovnikov's addition)

IN-CHAPTER EXERCISE-D

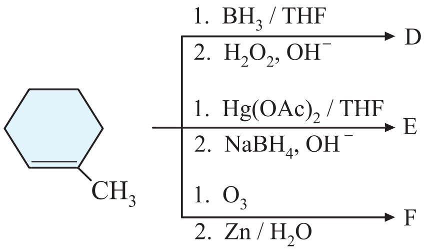
1. *Identify the products A, B, C ....*

(i) 1, 2-*Dimethyl cyclopentene* + $Br_2 \xrightarrow{CCl_4} A$

(ii) *Cyclobutene* + $Br_2 / H_2O \longrightarrow B$

(iii) *Cyclohexene* + $\underset{\text{Deuterium molecule}}{D_2} \xrightarrow{Pt} C$

(iv)



Choose the correct alternative. Only one choice is correct.

2. *The most reactive cycloalkane is :*

(A) *Cyclopropane* **(B)** *Cyclobutane*

(C) *Cyclopentane* **(D)** *Cyclohexane*

3. *Cyclopentene on treatment with alkaline* $KMnO_4$ *gives :*

(A) *Cyclopentanol*

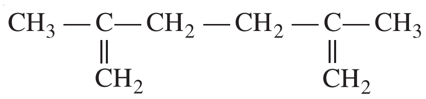
(B) *trans* 1, 2-*Cyclopentanediol*

(C) *cis* 1, 2-*Cyclopentanediol*

(D) 1 : 1 *mixture of cis and trans*-1, 2 *Cyclopentanediol*

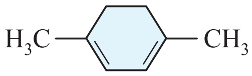
4. *An organic Compound on reaction with* O_3 *followed by Zn and* H_2O *gives* $CH_3COCH_2CH_2COCH_3$. *The structures is(are).*

I.

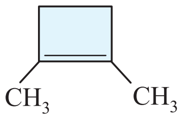


$$CH_3-\underset{\underset{CH_2}{\|}}{C}-CH_2-CH_2-\underset{\underset{CH_2}{\|}}{C}-CH_3$$

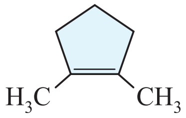
II.



III.



IV.



The correct choice is :

(A) I **(B)** II, III **(C)** I, II, III **(D)** I, III, IV