






UNIT – 3 **CYCLOALKANES, CYCLOALKENES AND ALKADIENES:** - - [5]

Introduction: Carbocyclic or homocyclic compounds resembling aliphatic compounds in their properties are called alicyclic compounds or cycloalkanes. Cycloalkanes with one double bond are called cycloalkenes and aliphatic compounds with two double bonds are called alkadienes.

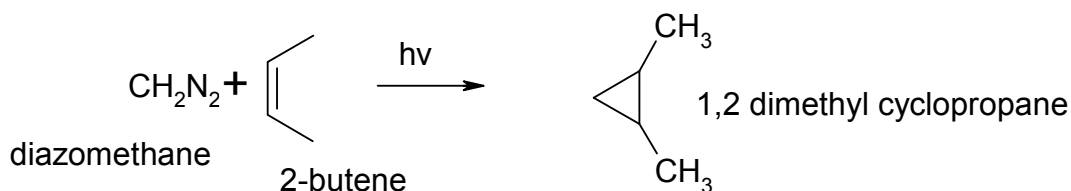
Cycloalkanes:

Nomenclature:

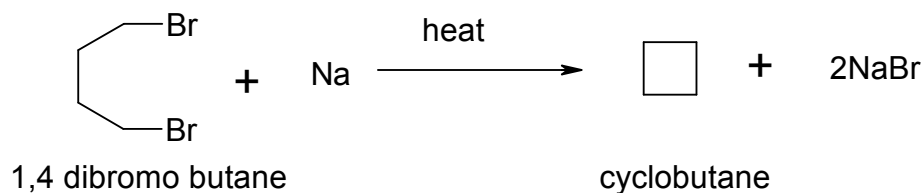
Structure					
Common	trimethylene	tetramethylene	Pentamethylene	hexamethylene	heptamethylene
IUPAC name:	cyclopropane	cyclobutane	cyclopentane	cyclohexane	cycloheptane

Methods of formation:

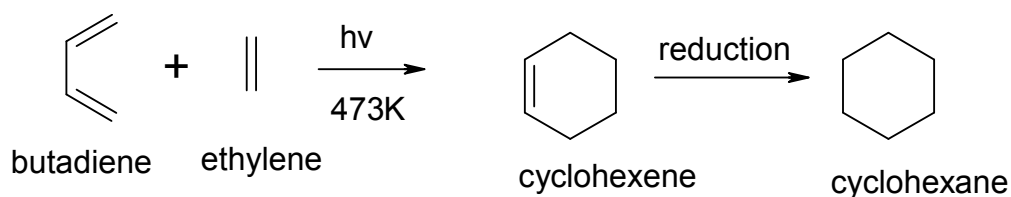
1. Addition of carbene to alkene: carbenes are highly reactive species which add to alkenes to give cyclopropane derivatives.



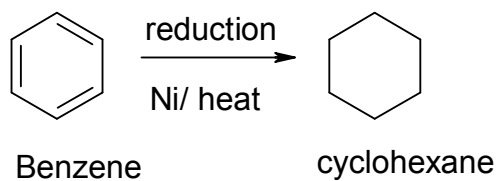
2. Action of metallic sodium on α, ω -dihaloalkane (Freund's method/ Internal Wurtz reaction)



3. By Diel's Alder Reaction:

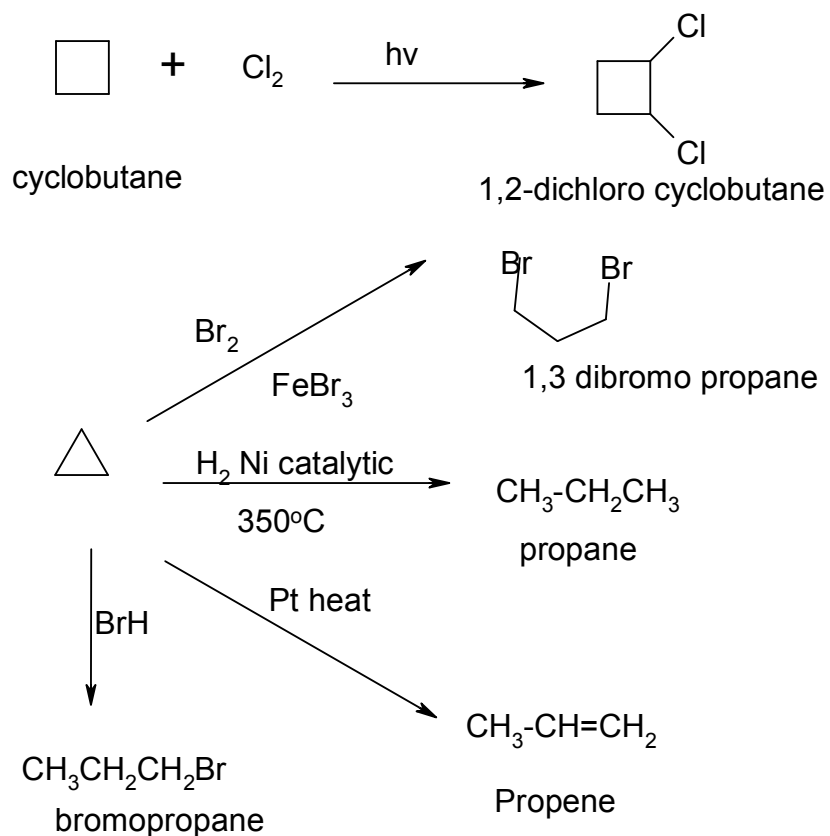


4. By reduction of aromatic compounds;



Chemical properties:





1. PhotoHalogenation



Cycloalkenes:

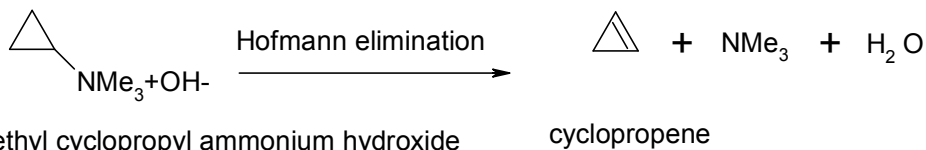
Alicyclic hydrocarbons containing one or more double bonds are called cycloalkenes.

Nomenclature: named as cycloalkenes with minimum possible numbers given to the position of double bonds.

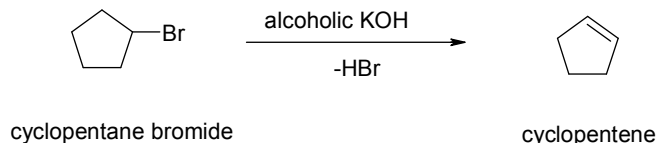
Structure				
IUPAC name:	Cyclopropene	cyclobutene	Cyclopenta 1,3 diene	Cyclohexa 1,4 diene

(2) Method of formation from cyclic compounds:

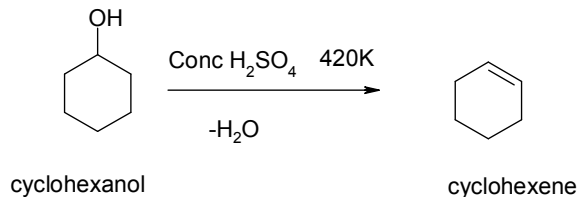
- Hoffman elimination of quaternary ammonium salt of cyclopropane



- Dehydrohalogenation of cycloalkane halide



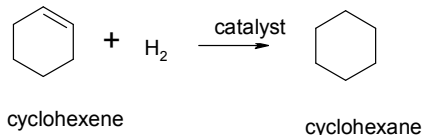
- Dehydration of cycloalkanol



(3) Chemical Properties

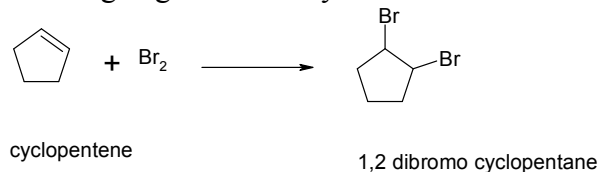
a) Hydrogenation

cycloalkenes react with hydrogen in presence of catalyst to form cycloalkane.

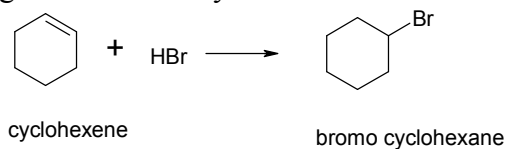


b) Addition of Halogens and halogen acids.

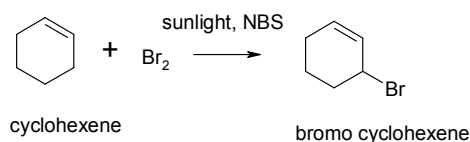
Cycloalkenes on addition of halogen give dihalo cycloalkanes



And on addition of haloacid give monohalo cycloalkanes



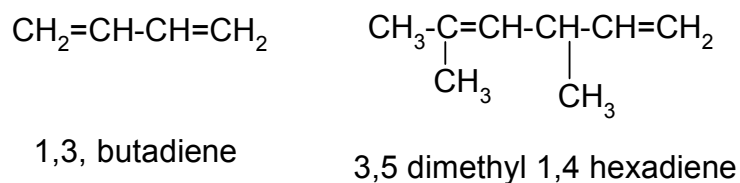
c) Allylic halogenations: under suitable conditions sunlight and N-bromosuccinamide cycloalkenes undergo substitution of H from allylic position.



3.3 Alkadienes:

Aliphatic hydrocarbons containing two double bonds in their molecules are called alkadienes.

Nomenclature: The alkadienes are named by selecting the longest possible chain of carbons with both the double bonds and then naming the compound as a derivative of the parent hydrocarbon and adding the number indicating the position of the double bonds with lowest possible number and then adding the suffix as diene.



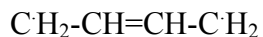
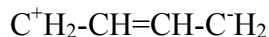
(2) Classification:

Based on the position of the double bonds, dienes are classified into three classes:

1. Isolated diene: dienes in which the two double bonds are separated by more than one single bonds.
Eg. Penta-1,4,diene
 $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$
2. Conjugated diene: dienes in which the two double bonds are separated by only one single bond.
Eg. Buta-1,3 diene Penta-1,3,diene
 $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$
3. Cumulative diene: dienes in which the two double bonds are in succession.
Eg. Allene or propadiene
 $\text{CH}_2=\text{C}=\text{CH}_2$

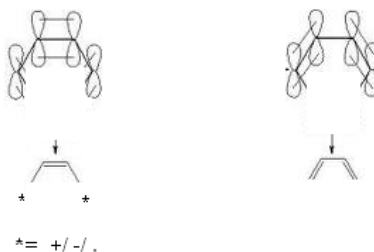
(3) Buta-1,3-diene : C_4H_6 : $CH_2=CH-CH=CH_2$

a) Structure: The actual structure of the butadiene is resonance hybrid of the following resonating structures



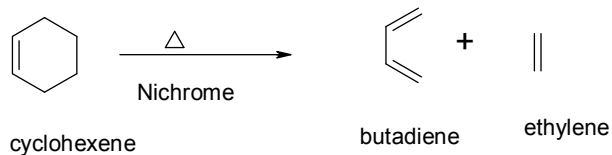
This explains the bond length of C_1-C_2 and C_3-C_4 as 1.35 \AA than expected 1.33 \AA and bond length of C_2-C_3 as 1.46 \AA than expected 1.54 \AA .

This is further explained by Molecular orbital theory. Every carbon in butadiene is sp^2 hybridised and has one unhybridised P_z orbital on every carbon atom which is laterally overlapped to have delocalization of pi electrons over all the four carbon atoms.



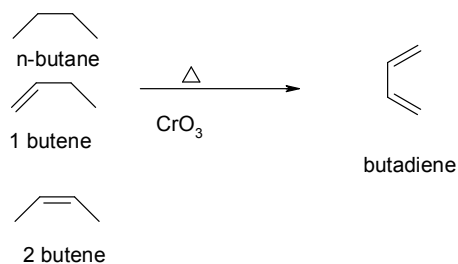
b) Methods of formation:

i) From cyclohexane: when vapours of cyclohexene are passed over nichrome alloy butadiene is formed.

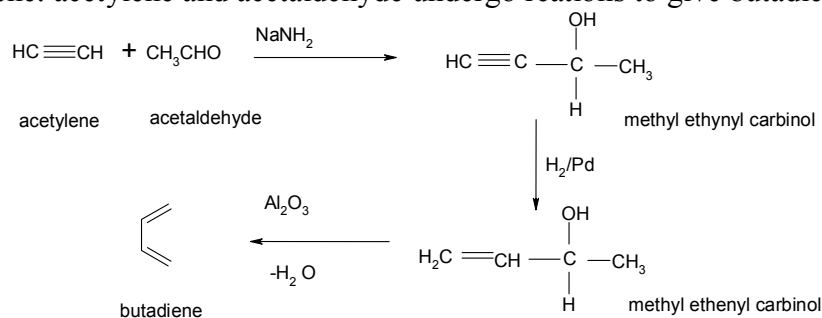


ii) From Butane by dehydrogenation:

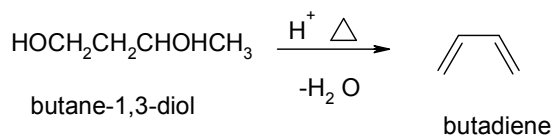
butane or butene when passed over chromium oxide catalyst, undergo dehydrogenation to give butadiene.



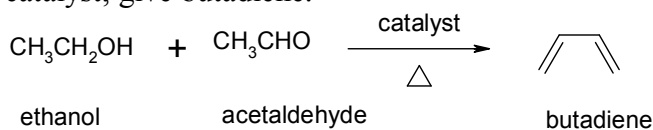
iii) From acetylene: acetylene and acetaldehyde undergo reactions to give butadiene



iv) From Butane-1,3-diol: butane-1,3 diol on heating with acid catalyst, undergo dehydration to give butadiene

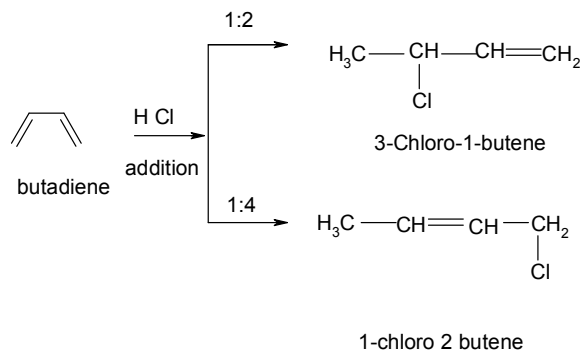


v) From ethanol and acetaldehyde (Industrial method) when mixture of ethanol and acetaldehyde passed over the heated catalyst, give butadiene.



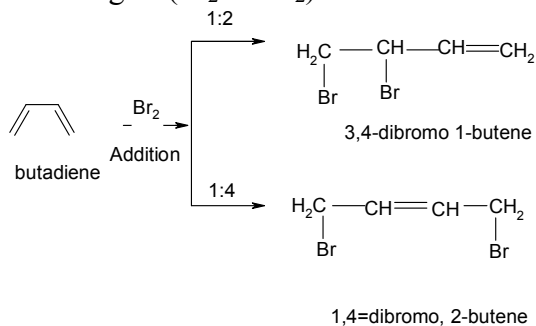
(4) Chemical Properties

a) Reaction with hydrogen halide:

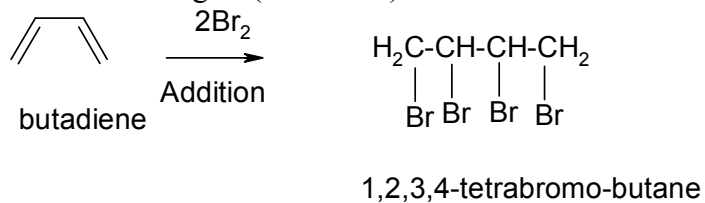


b) Reaction with halogens

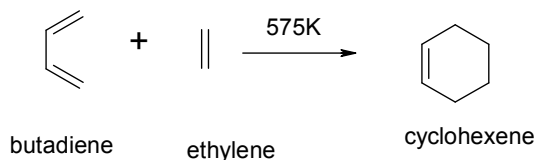
i) With one molar equivalent of halogens(Cl₂ or Br₂)



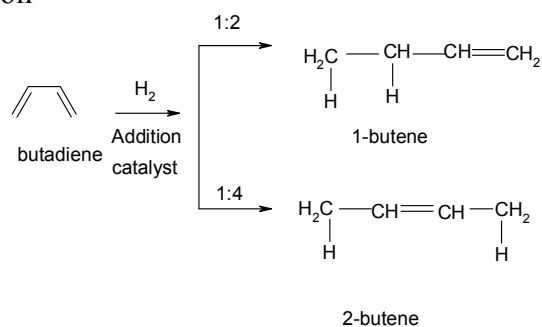
ii) With two molar equivalent of halogens(Cl_2 or Br_2)



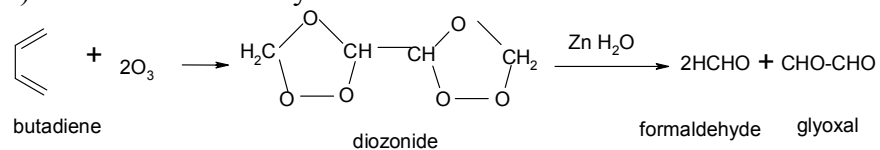
c) Diels- Alder reaction



d) Reduction – hydrogenation



e) Oxidation – Ozonolysis:



f) Polymerization

