which are very important industrial compounds.

CYCLOALKENES

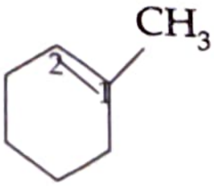
1.10. INTRODUCTION

Cycloalkenes are unsaturated alicyclic hydrocarbons having a carbon-carbon double bond i their molecules (*general formula* = C_nH_{2n-2}). They are named by adding the word **cyclo** to the nam of straight chain alkene having the same number of carbon atoms as the ring. The double bond i always taken to be located between carbons 1 and 2 and, therefore, its position need not be specifie

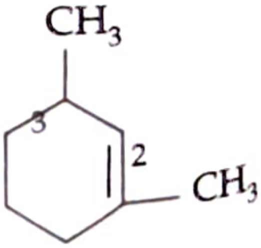

Cyclopropene


Cyclobutene


Cyclopentene



1-Methylcyclohexene

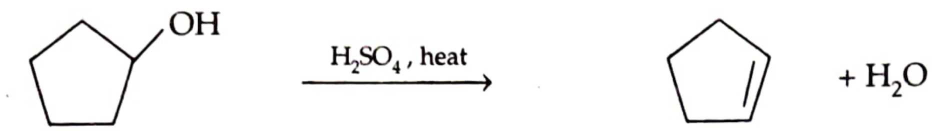


1, 3-Dimethylcyclohexene

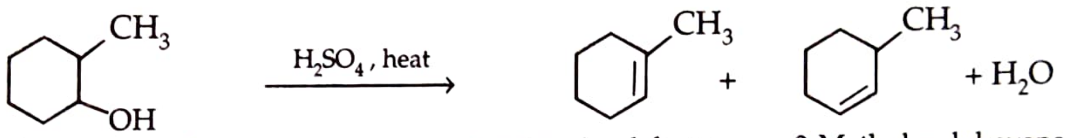
1.10.1. Methods of Preparation

Cycloalkenes are generally prepared from other cyclic compounds by β-elimination reactions such as dehydration and dehydrohalogenation as given below :

(1) By the dehydration of alicyclic alcohols. As in case of open chain alcohols, dehydration of alicycli alcohols to form alkenes is brought about by heating with concentrated sulphuric acid. For example :



Cyclopentanol Cyclopentene

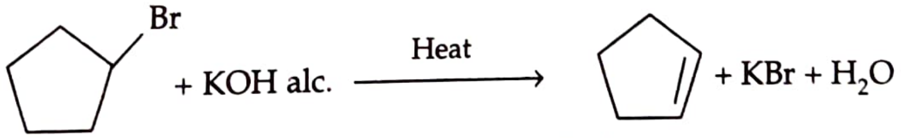


2-Methylcyclohexanol 1-Methylcyclohexene (84%) 3-Methylcyclohexene (16%)

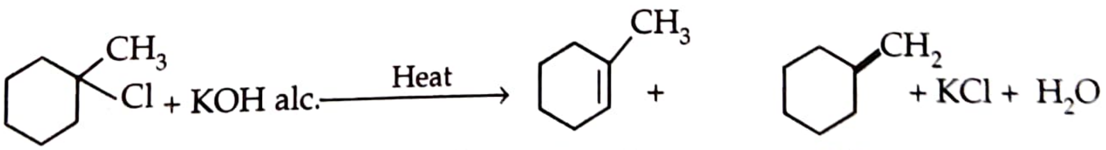
(More highly substituted cycloalkene)

It may be noted from the dehydration of 2-methylcyclohexanol that in the *dehydration of substituted alicyclic alcohols, the more* **highly substituted cycloalkene** *is the major product.*

(2) By the dehydrohalogenation alicyclic halides. When treated with bases such as alcoholic KOH, cyclic halides form cycloalkenes. For example :



Cyclopenty bromide Cyclopentene

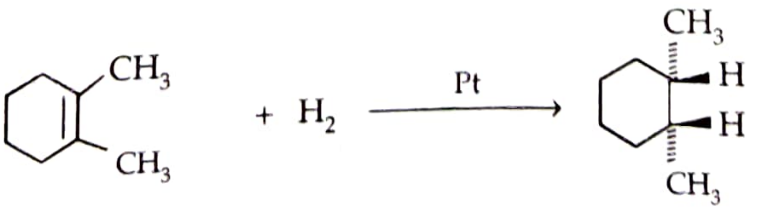


1-Chloro-1methylcyclohexane 1-Methylcyclohexene (94%) Methylene cyclohexane (6%)

1.10.2. Chemical Properties of Cycloalkenes

Cycloalkenes exhibit the usual properties of alkenes. They undergo electrophilic addition reactions in which the using remains intact. The important reactions of cycloalkenes are given below.

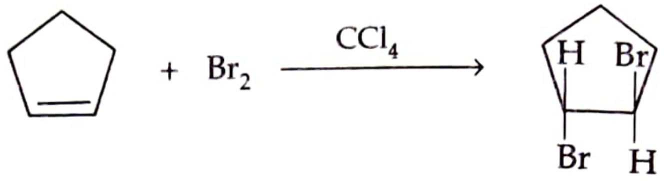
(1) Addition of hydrogen. Cycloalkenes undergo catalytic hydrogenation to form cycloalkanes. For example :



1, 2 Dimethylhexene cis-1, 2-Dimethylcyclohexane

It may be noted that the addition of both hydrogens to the double bond takes place from the same side *i.e.* **cis addition** takes place.

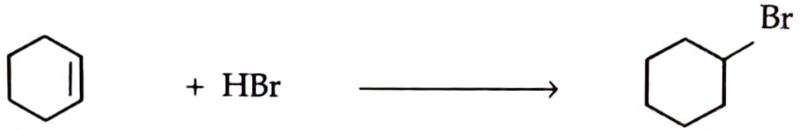
(2) Addition of halogens. Cycloalkenes add on halogens to form dihalocyclo alkanes. In con to hydrogenation of cycloalkenes, addition of halogens to cycloalkenes is a **trans-addition** rea *i.e.* the two halogens are added from the opposite sides of the double bond. For example :



Cyclopentene

Trans-1, 2-dibromo-cyclopentane

(3) Addition of halogen acids. Like alkenes, cycloalkenes undergo electrophilic additi halogen acids according to Markownikoff's rule. This reaction also involves **trans-addition** example :



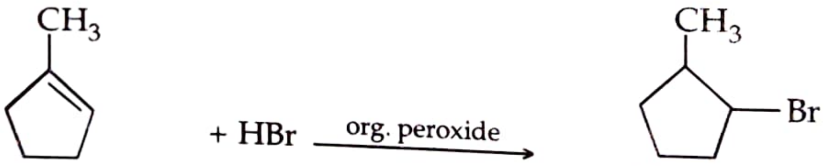
Cyclohexene

Cyclohexyl bromide

Methylcyclopentene

1-Chloro-1-methylcyclopentane

But addition of HBr in the presence of peroxides takes place to against the Markowni rule and follows free radical mechanism. For example :



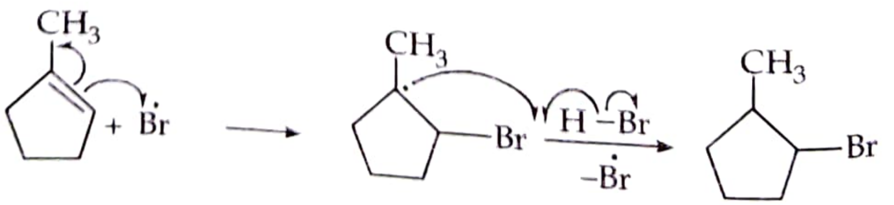
1- Methyl cyclopentene

1- Bromo -2- methyl cyclopentane

The reaction takes place by the following mechanism :

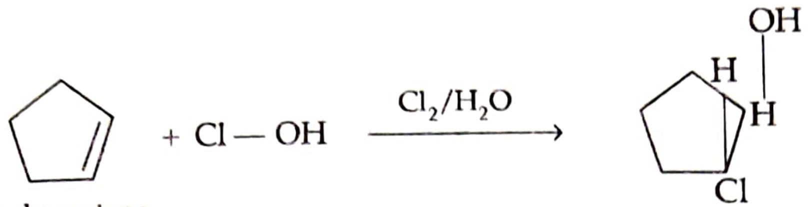
$$RO-OR \xrightarrow{Heat} 2R\dot{O}$$

$$R\dot{O} + HBr \longrightarrow ROH + \dot{Br}$$



1- Bromo - 2- methylcyclopentane

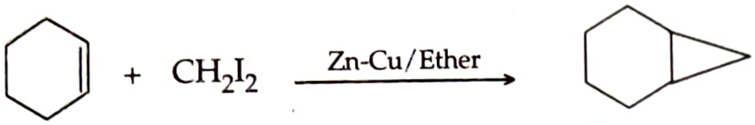
(4) Addition of hypohalous acid (Formation of halohydrins). Cyclo alkenes react hypochlorous acid (Cl$_2$/H$_2$O) and hypobromous acid (Br$_2$/H$_2$O) to form **trans** halohydrins example :



Cyclopentene

Trans-2-chlorocyclopentanol

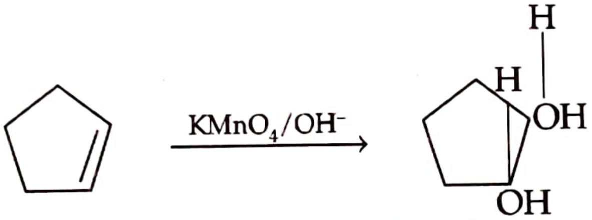
(5) Addition of carbenes or carbenoids. Cycloalkenes undergo addition of carbenes or carbenoids to form bicyclic compounds. For example, cyclohexene undergoes Simmons-Smith reaction with di-iodomethane in the presence of Zn-Cu couple as shown below :



Cyclohexene

Bicyclo [4.1.0] heptane

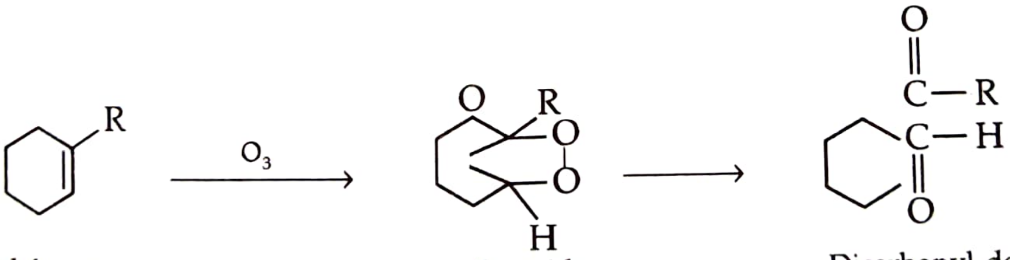
(6) Hydroxylation. Cycloalkenes undergo hydroxylation on treatment with potassium permanganate ($KMnO_4$) or osmium tetroxide (OsO_4) to form **cis-glycols or diols.** For example :



Cyclopentene

Cis-cyclopentane-1, 2-diol

(7) Ozonolysis. Ozonolysis of cycloalkenes results in the cleavage of the ring system at the site of double bond forming dicarbonyl derivative with the same number of carbon atoms. The reaction can be used to locate the position of the double bond. For example :

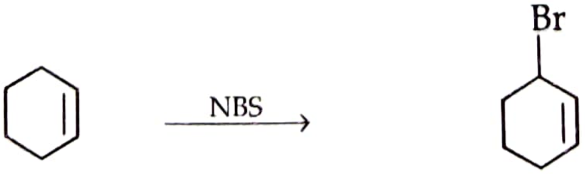


Alkyl cyclohexene

Ozonide

Dicarbonyl derivative

(8) Allylic halogenation. Like alkenes, cycloalkenes also undergo allylic halogenation under suitable conditions. For example :



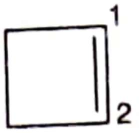
Cyclohexene

3-Bromocyclohexene

1.10.3. Conformations of Cycloalkenes

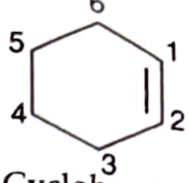
Due to sp^2 hybridisation of the carbon atoms constituting the double bond of cycloalkenes, these two carbon atoms and the atoms **directly** attached to them must lie in the same plane. Therefore for the first two cycloalkenes (*i.e.* cyclopropene and cyclobutene), all the ring carbon atoms lie in one plane. On account of large angle strain in them, these molecules are highly strained. Cyclopentene is also supposed to be nearly planar but has very little angle strain.

Cyclopropene
(Planar)



Cyclobutene
(Planar)

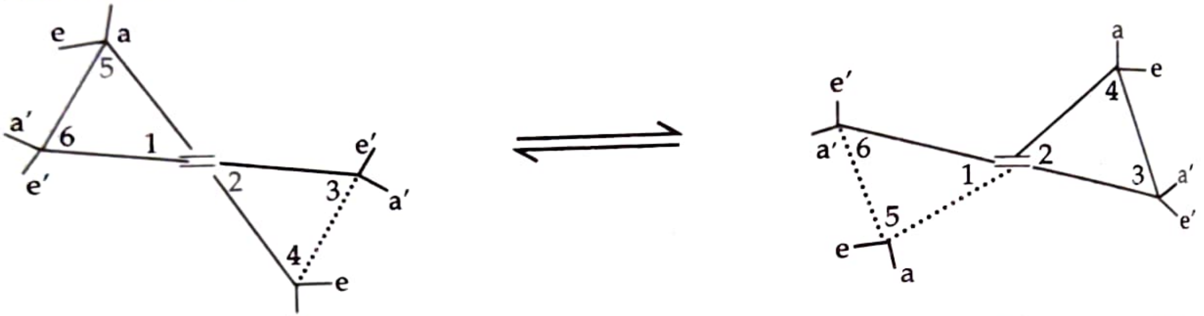
Cyclopentene
(Nearly planar)



Cyclohexene
(Non-planar)

In contrast with smaller ring cycloalkenes, cyclohexene and larger cycloalkenes exist in stra free non-planar or puckered conformation.

In cyclohexene, carbon atoms 1, 2 (which are sp^2 hybridised) and 3, 6 (which are direct attached to 1 and 2 respectively) lie in the same plane. But, in order to maintain proper bond angle out of carbon atoms C_4 and C_5, one lies above and other below this plane. This causes the ring assume "half-chair" conformation. Two such conformations become possible which are in rap equilibration with each other.



In both these conformations, bonds to C_4 and C_5 are normal axial (a) and equatorial (e) but th bonds to C_3 and C_6 are *pseudo or quasi axial* (a′) and *pseudo or quasi equatorial* (e′).

It may be noted that the conformation in which both C_4 and C_5 are above the plane of C_1, C_2, C_3 and C_6 would be highly strained. Such a conformation (known as **half-boat** conformation) is highly unstable