



*Organic Chemistry*

*Chapter 2*

*Alkenes*

#### 4.1 Introduction

Molecules of the alkene (also called olefins) series of hydrocarbons are characterized by having two adjacent carbon atoms joined to one another by a double bond. The carbon-carbon double bond is unsaturated and hence highly reactive toward a wide variety of reagents.

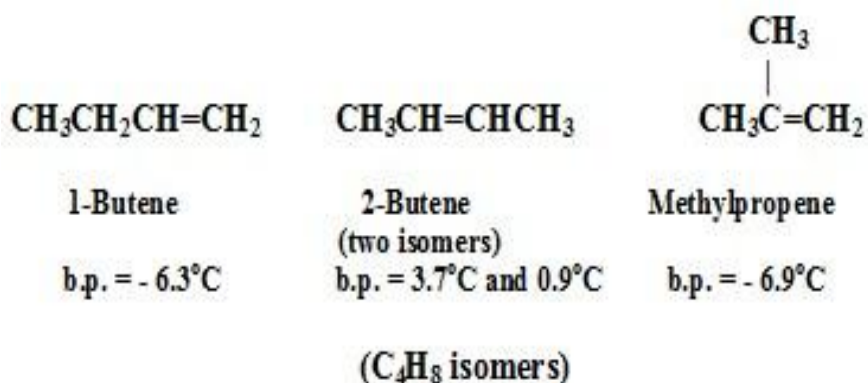
The general formula of alkenes is  $C_nH_{2n}$ , where  $n$  is the number of carbon atoms. The first nine members of this series are listed in Table 4.1.

**Table 4.1 The first nine member of the alkenes**

General formula	Structure	Name
$C_2H_4$	$CH_2 = CH_2$	Ethene
$C_3H_6$	$CH_2 = CHCH_3$	Propene
$C_4H_8$	$CH_2 = CHCH_2CH_3$	1-Butene
$C_5H_{10}$	$CH_2 = CH(CH_2)_2CH_3$	1-Pentene
$C_6H_{12}$	$CH_2 = CH(CH_2)_3CH_3$	1-Hexene
$C_7H_{14}$	$CH_2 = CH(CH_2)_4CH_3$	1-Heptene
$C_8H_{16}$	$CH_2 = CH(CH_2)_5CH_3$	1-Octene
$C_9H_{18}$	$CH_2 = CH(CH_2)_6CH_3$	1-Nonene
$C_{10}H_{20}$	$CH_2 = CH(CH_2)_7CH_3$	1-Decene

## 4.2 Isomerism in Alkenes

Isomeric compounds are also possible in the alkenes. For the molecular formula  $C_4H_8$ , there are three different ways of organizing the four carbon atoms and the double bond:



## 4.3 Nomenclature

Common names are seldom used except for three simple alkene; ethylene, propylene, and isobutylene. Most alkene are named by IUPAC system.

- 1- The longest continuous chain of carbon atoms containing the double bond serves as the parent compound.
- 2- The ending *-ane* of the corresponding alkane hydrocarbon name is replaced by the ending *-ene*.
- 3- The position of the double bond is indicated by the lower number of the numbers of the carbon atoms to which it is attached. The number that represents this position is placed before the parent compound name. Alkyl groups attached to the parent compound are designated as is done for the alkane.

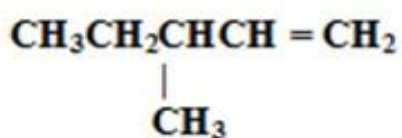
4- If a geometric isomer is designated, the name begins with *cis*- or *trans*-.



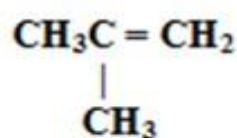
1- Hexene



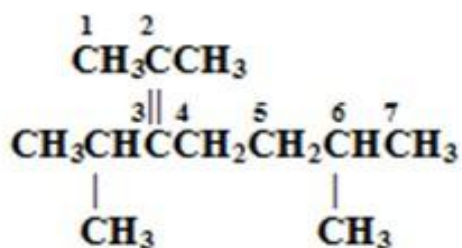
1-Butene



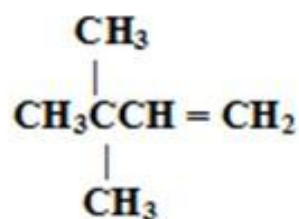
3-Methyl-1-pentene



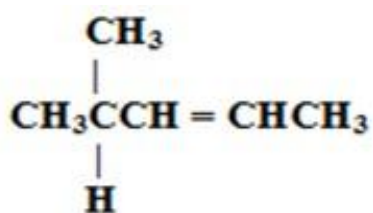
2-Methylpropene



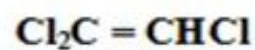
3-Isopropyl-2,6-dimethyl-2-heptene



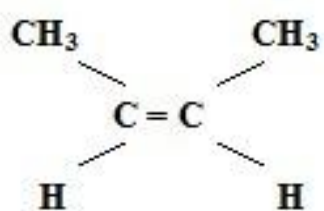
3,3-Dimethyl-1-butene



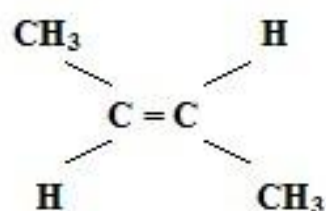
4-Methyl-2-pentene



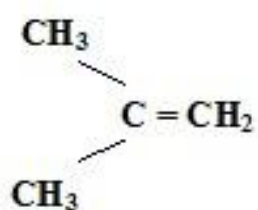
Trichloro ethene



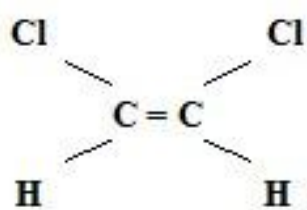
*cis*-2-Butene



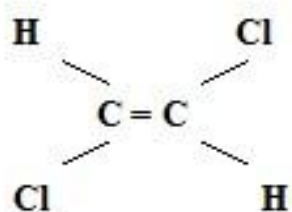
*trans*-2-Butene



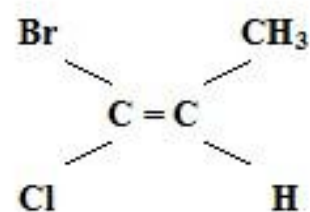
2-Methylpropene



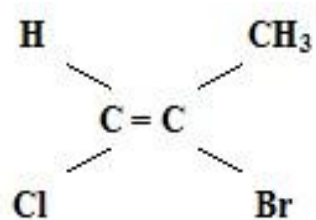
*cis*-1,2-Dichloroethene



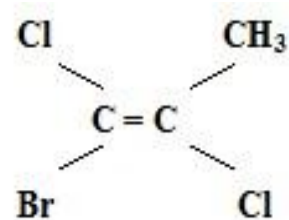
*trans*-1,2-Dichloroethene



1-Bromo-1-chloropropene



2-Bromo-1-chloropropene



1-Bromo-1,2-dichloropropene

#### 4.4 Physical Properties of Alkenes

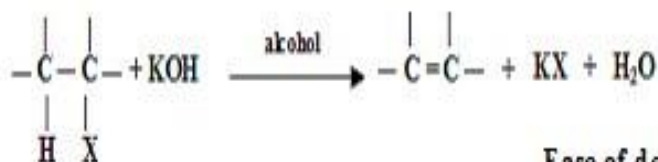
The alkenes possess physical properties that are essentially the same as those of the alkanes. They are insoluble in water, but quite soluble in non-polar solvents like benzene, ether, and chloroform. They are less dense than water. The boiling point rises with increasing carbon number; as with alkane, branching lowers the boiling point.

Like alkanes, alkenes are at most only weakly polar. Since the loosely held  $\pi$  electrons of the double bond are easily pulled or pushed, dipole moments are larger than for alkanes.

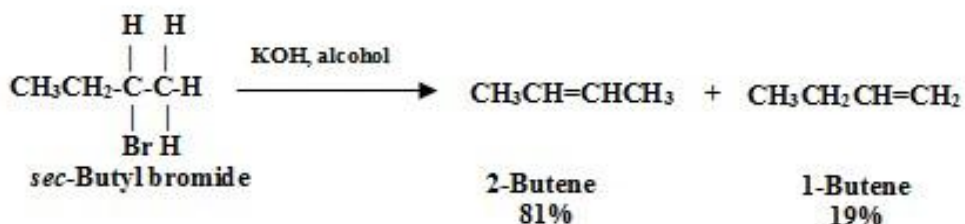
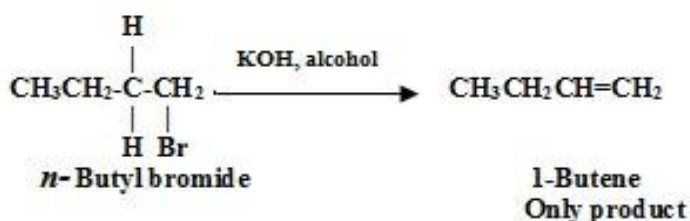
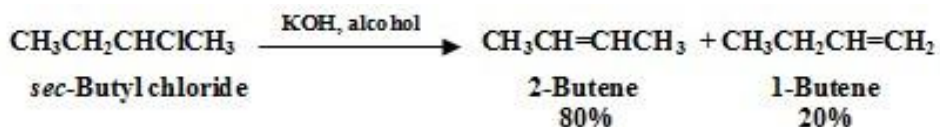
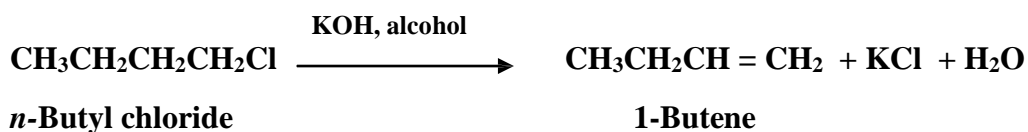
#### 4.5 Preparation of Alkenes

##### 1- Dehydrohalogenation of alkyl halides

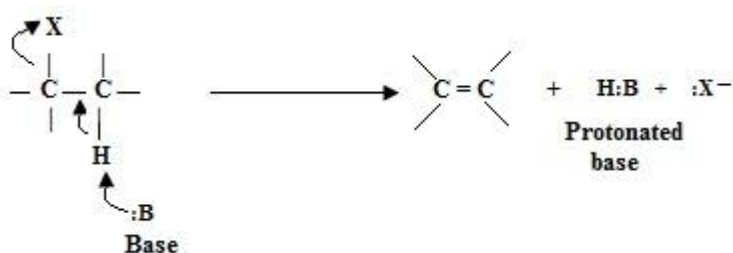
Dehydrohalogenation involves loss of the halogen atom and of hydrogen atom from a carbon adjacent to the one losing the halogen (*1,2-elimination*).



Ease of dehydrohalogenation  $3^\circ > 2^\circ > 1^\circ$   
of alkyl halides



### Mechanism:

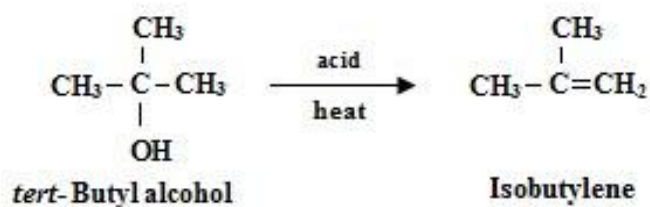
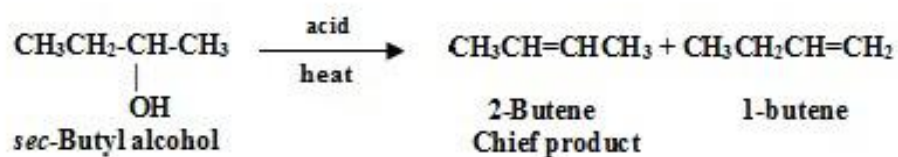
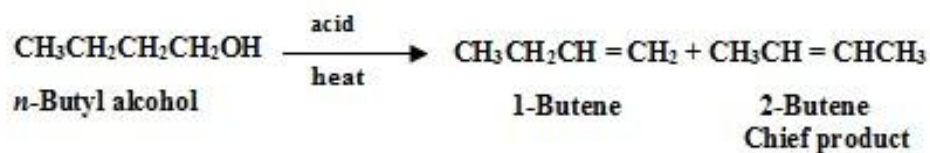
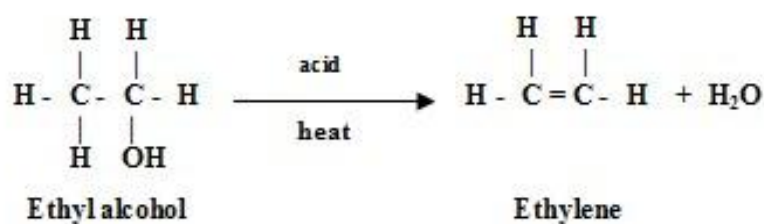
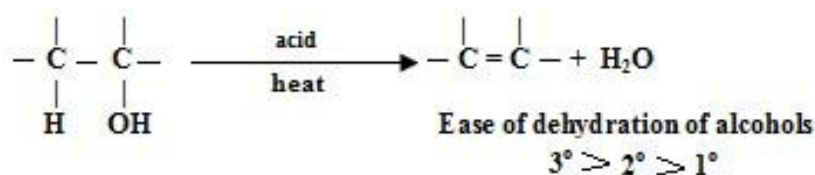


The base  $\text{:B}$  can be neutral or negatively charged: for example,  $\text{H}_2\text{O}$  or  $\text{OH}^-$ . The conjugate acid  $\text{H:B}$  will then be positively charged or neutral: for example,  $\text{H}_3\text{O}^+$  or  $\text{H}_2\text{O}$ .

Halogen leaves the molecule as halide ion, and hence must take its electron pair along. Hydrogen is abstracted by the base as a proton, and hence must leave its electron pair behind; it is this electron pair that is available to form the  $\pi$  bond between the carbon atoms.

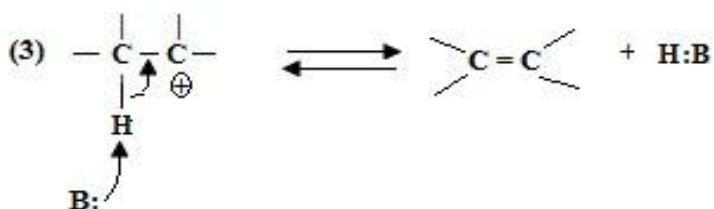
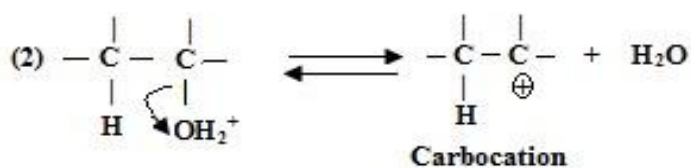
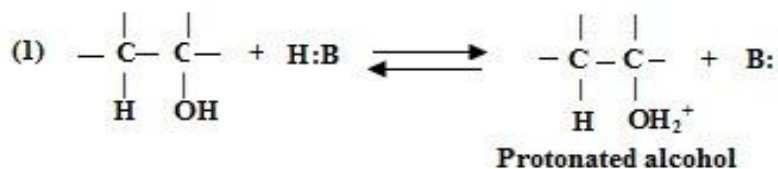
## 2- Dehydration of alcohols

In the dehydration of alcohols, the H and OH are lost from adjacent carbons (*1,2-elimination*). An acid catalyst is necessary and application of heat.





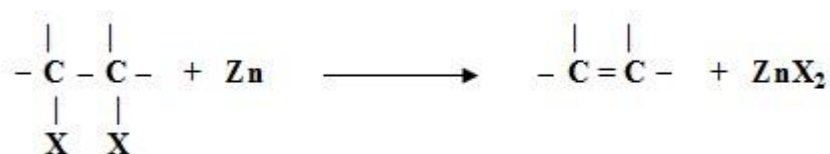
**Mechanism:**

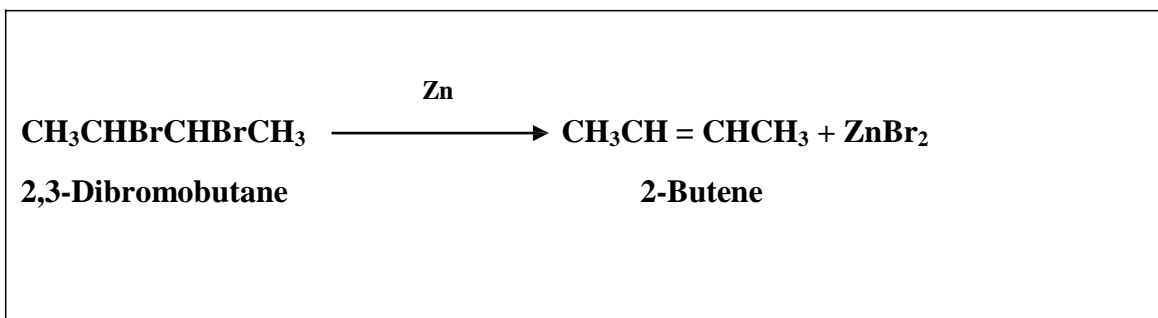


For secondary and tertiary alcohols the above mechanism is generally accepted. Step (1) is a fast acid-base reaction between the alcohol and the catalyzing acid which gives the protonated alcohol and the conjugate base of the acid. In step (2) the protonated alcohol undergoes heterolysis to form the carbocation and water. In step (3) the carbocation loses a proton to the base to yield alkene.

### 3- Dehalogenation of vicinal dihalides

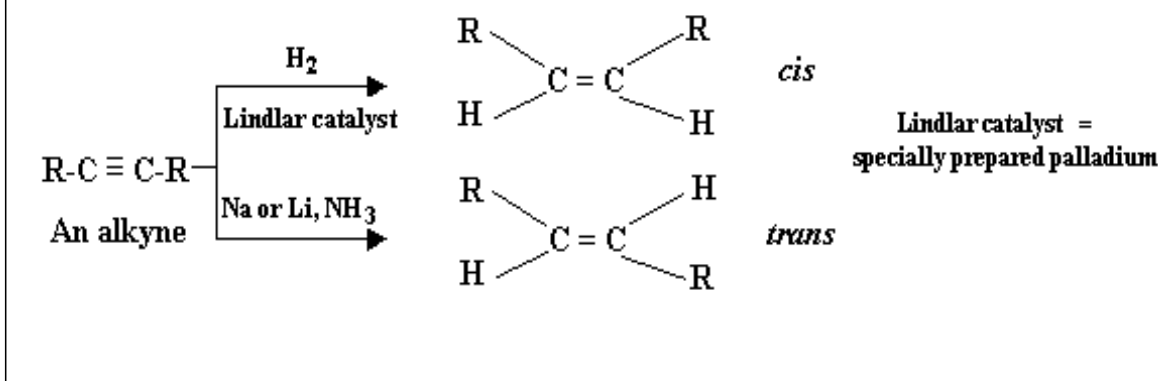
Alkenes can be prepared by elimination of two halide atoms from a vicinal (neighboring) dihalides.





#### 4- Reduction of alkynes

Trans alkene can be obtained by reduction of alkynes with sodium or lithium in liquid ammonia. Cis alkene is obtained by hydrogenation of alkynes with a specially prepared palladium called Lindlar catalyst.



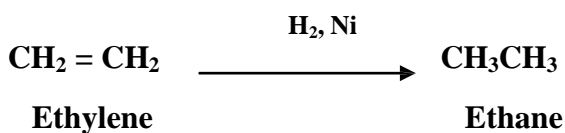
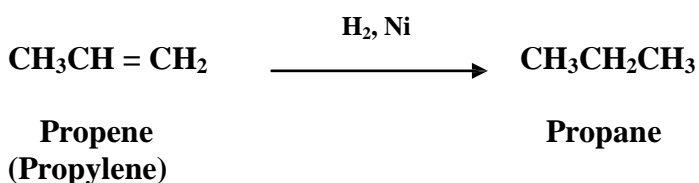
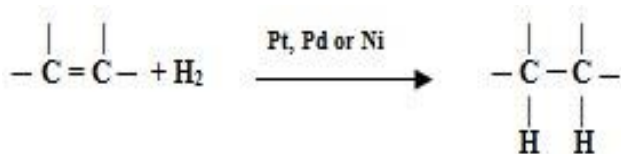
#### 4.6 Reactions of alkenes

The presence of the carbon-carbon double bond confers very considerable chemical activity on the alkenes and consequently they react with a much wider variety of reagents than do the alkanes. The  $\pi$ -bond component of the double bond is weaker than the  $\sigma$ -bond component and the  $\pi$ -electrons are more easily accessible to attacking reagents.

## (Addition Reactions)

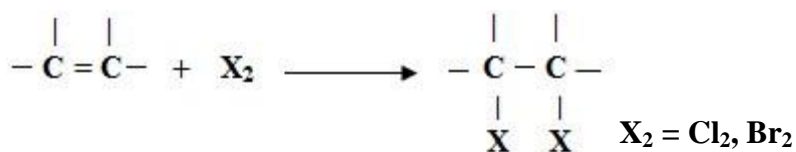
### 1- Addition of hydrogen

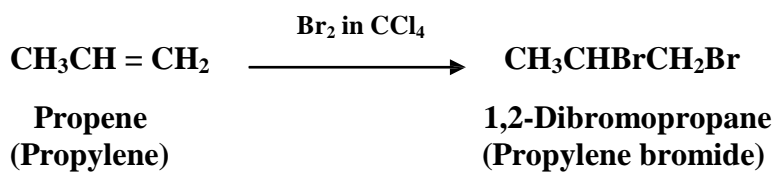
When an alkene is mixed with hydrogen, there is no appreciable reaction, but in the presence of certain metal catalysts such as nickel, platinum or palladium, a fairly rapid reaction occurs leading to the uptake of hydrogen.



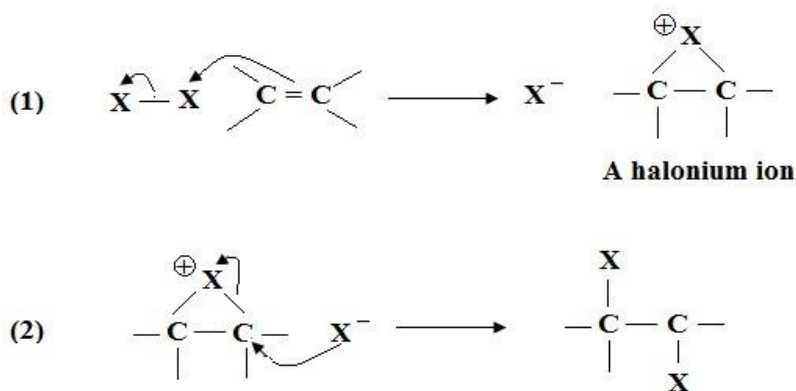
### 2- Addition of halogen

Chlorine and bromine react readily with alkenes, in the liquid or vapour states, to form dihalogeno addition products, the two halogen atoms are attached to adjacent carbons. Iodine generally fails to react.





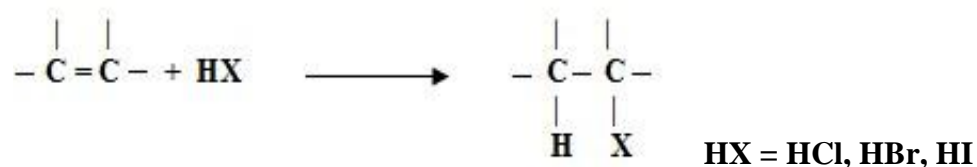
**Mechanism:**



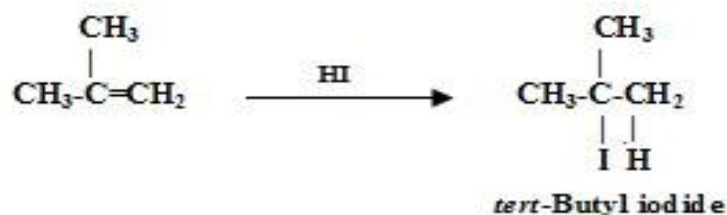
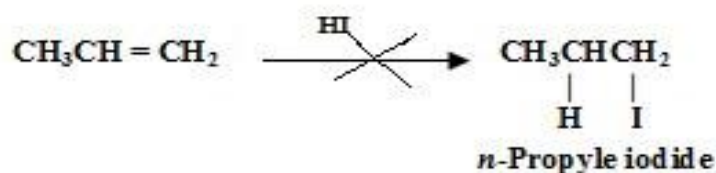
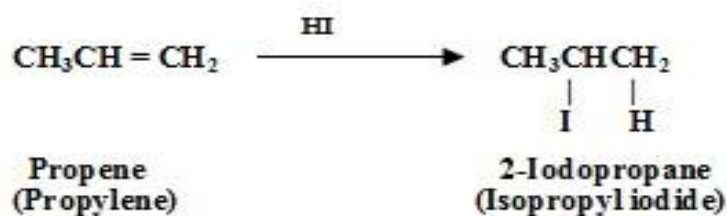
In step (1) a halogen is transferred, without a pair of electrons, from a halogen molecule to the carbon-carbon double bond; there is formed a halide ion and organic cation. In step (2) this cation reacts with a halide ion to yield the addition product.

### 3- Addition of hydrogen halides

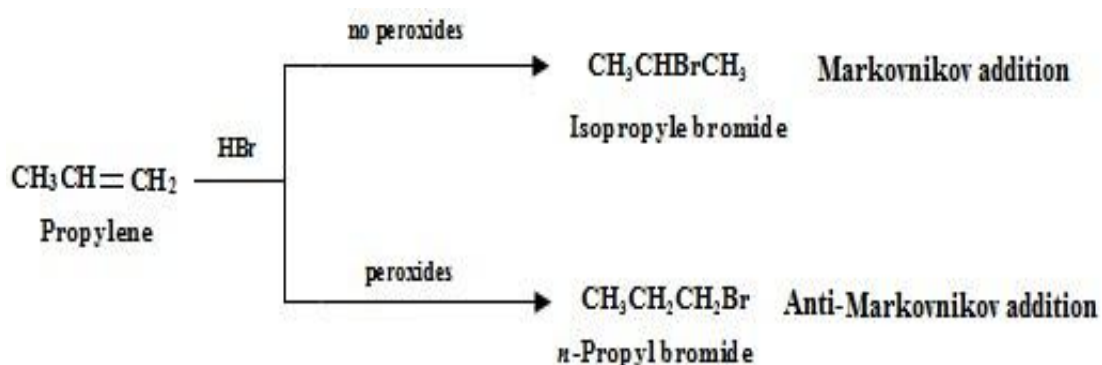
Alkenes react, usually on heating, with hydrogen halides (either gaseous or in concentrated solution) to form an addition product.



The hydrogen attaches itself to the carbon that already holds the greater number of hydrogens. This statement is called *Markovnikov's rule*.

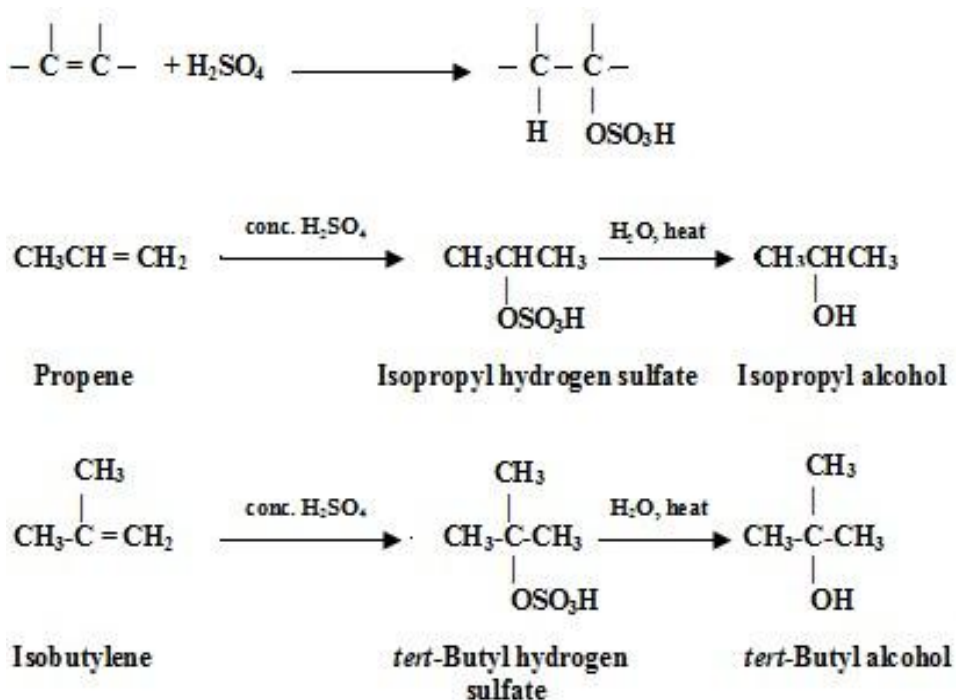


If the reaction takes place in the absence of peroxide, the addition of HBr, to alkenes follows Markovnikov's rule. On the other hand, if the reaction takes place in the presence of peroxide, HBr adds to alkenes in the reverse direction.



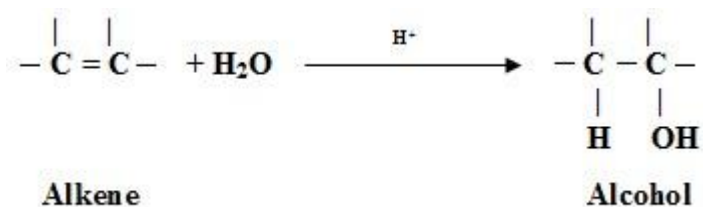
#### 4- Addition of sulfuric acid

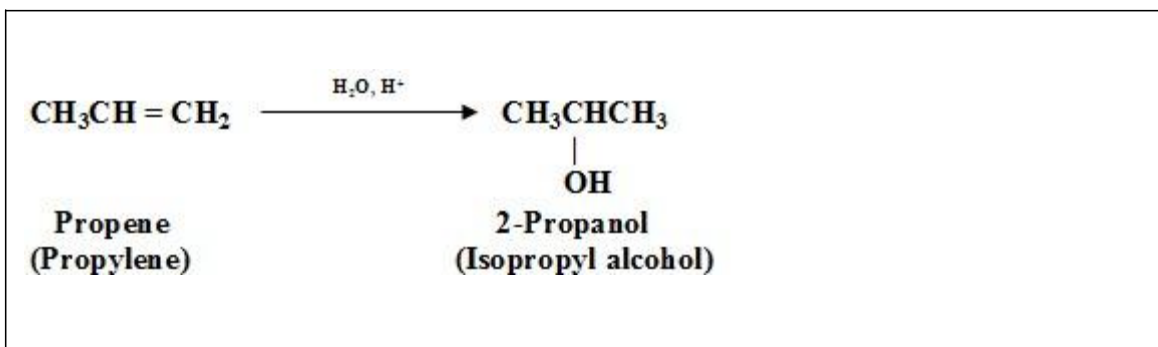
Alkenes are slowly absorbed when they are bubbled through, or shaken with, cold concentrated sulphuric acid. The reaction involves the addition of H and HSO<sub>4</sub> groups across the double bond, to form alkyl hydrogen sulfates, which is on dilution with water and heating yield alcohol.



#### 5- Addition of water. Hydration

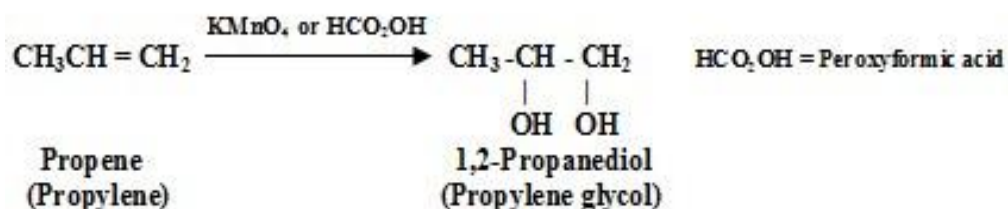
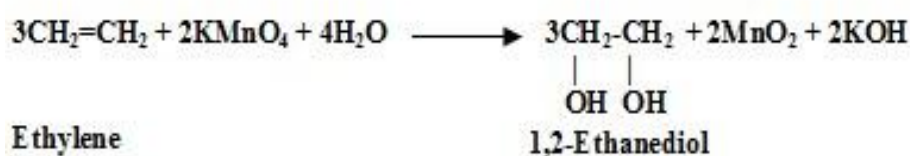
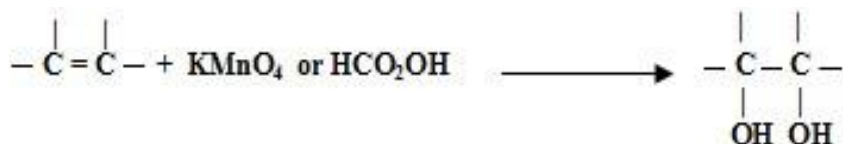
Alkenes are also reacting with water, and this reaction is carried out in a dilute acid medium. The reaction follows Markovnikov's rule.





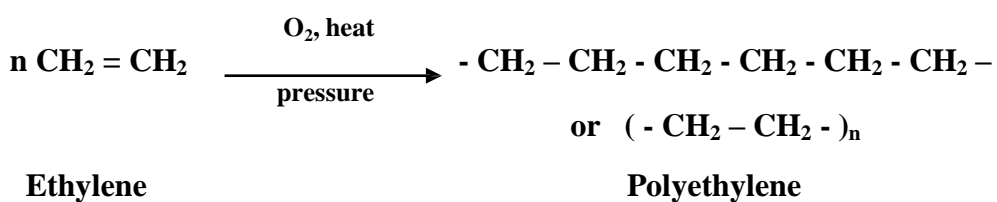
## 6- Hydroxylation – glycol formation

Alkanes are highly resistant to chemical oxidizing agents under normal conditions. In contrast, alkenes are quite sensitive to oxidation by several oxidizing agent. If an alkene is shaken with a few drops of a dilute acidified solution of  $\text{KMnO}_4$ , the purple solution is rapidly decolorized. The alkene is oxidized to an addition product, in which two hydroxyl groups have been added across the carbon-carbon double bond; the product is a di-alcohol or diol.



## 7- Polymerization

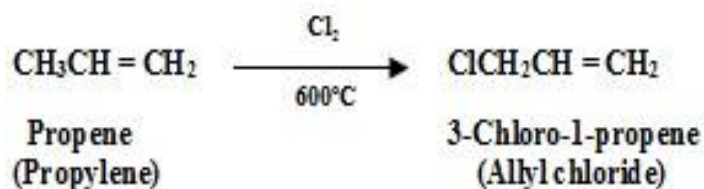
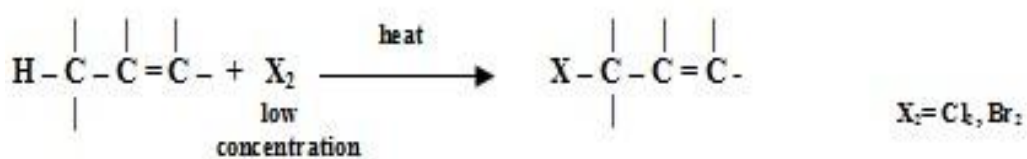
In the presence of a certain catalyst, alkene molecule can add on to each other in a head-to-tail fashion to form long-chain molecules of a very high relative molecular mass.



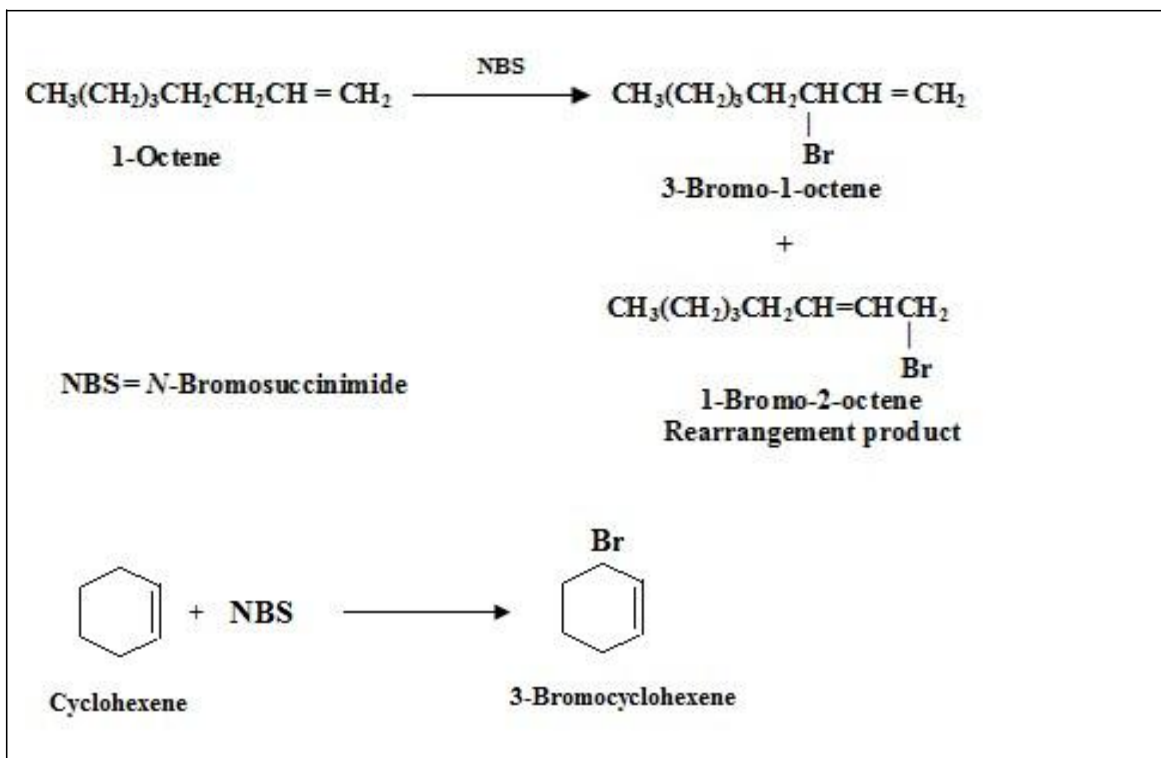
### *(Substitution Reactions)*

#### Halogenation. Allylic substitution

Alkenes react with halogens, substitution reaction. The reaction carried out as follow:







### (Cleavage Reactions)

#### Ozonolysis

$\text{O}_3$  (ozone) is produced by passage of an electric discharge through oxygen  $\text{O}_2$ . If the mixture of gases is bubbled through a solution of an alkene at low temperature, an unstable product known as an ozonide is formed. Ozonides are unstable and are readily hydrolysed to form aldehydes or ketones.

