

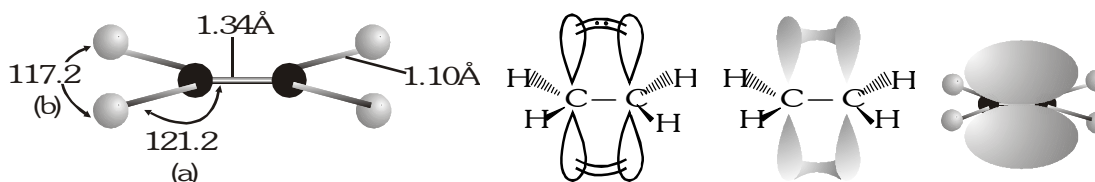
## ALKENE

### □ Introduction :

Alkenes are hydrocarbons with carbon-carbon double bonds, Alkenes are sometimes called olefins, a term derived from olefiant gas, meaning 'oil forming gas'. Alkenes are among the most important industrial compounds and many alkenes are also found in plants and many alkenes are also found in plants and animals. Ethylene is the largest-volume industrial organic compound, used to make polyethylene and a variety of other industrial and consumer chemicals. Alkenes polymerise to give many important polymers.

### □ Structure and bonding in Alkenes :

- (a) Alkenes are unsaturated hydrocarbons having at least one double bond.
- (b) They are represented by general formula (G.F.)  $C_n H_{2n}$  (one double bond)
- (c) In Ethene  $C = C$  bond length is  $1.34 \text{ \AA}$
- (d) Its bond energy is  $146 \text{ kcal. mol}^{-1}$
- (e) The hybridization of  $(C = C)$  alkenic carbon is  $sp^2$
- (f) The  $\pi e^-$  cloud is present above and below the plane of  $\sigma$ -bonded skeleton.
- (g) They are also known as olefins since ethene, the first member of the homologous series forms oily liquid substance when treated with halogens.
- (h) Compounds may exist as conjugated polyenes or as cumulated polyenes or as isolated polyenes

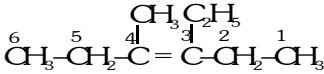
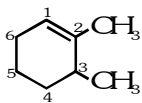


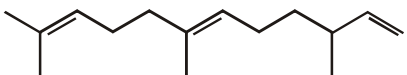


**Note :** That angle  $a < b$  since repulsion due to  $\pi$  electrons (double bond - single bond repulsion)  $>$  single bond - single bond repulsion according to VSEPR theory.

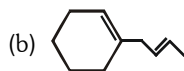
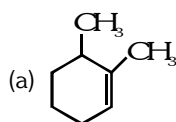
### □ IUPAC Nomenclature of alkenes and alkadienes :

Table - I

| S.No. | Compound  | Name                      | Type             |
|-------|---|---------------------------|------------------|
| 1.    | $(CH_3)_2C = CH_2$  | 2-Methylpropene           | Alkene           |
| 2.    | $CH_3-CH=CH-CH_2-CH=CH_2$   | Hexa-1, 4-diene           | Isolated diene   |
| 3.    | $CH_2=CH-CH=CH_2$   | Buta-1, 3-diene           | Conjugated diene |
| 4.    | $CH_3-CH=C=CH-CH_3$   | Penta-2, 3-diene          | Cumulated diene  |
| 5.    | $  \begin{array}{ccccccc}  & & & & Cl & & \\  & & & &   & & \\  1 & 2 & 3 & 4 & 5 & 6 & 7 \\  CH_3 & -CH_2- & CH= & CH- & CH_2- & CH- & CH_3  \end{array}  $    | 6-Chlorohept-3-ene        | Alkene           |
| 6.    | $  \begin{array}{ccccccc}  1 & 2 & 3 & 4 & 5 \\  CH_2 & =CH- & CH= & C- & CH_3 \\  & & &   & \\  & & & OCH_3 &  \end{array}  $                                  | 4-methoxypenta-1, 3-diene | Conjugated diene |
| 7.    | $  \begin{array}{ccccccc}  1 & 2 & 3 & 4 & 5 \\  CH_2 & =CH- & CH- & C \equiv & CH \\  & &   & & \\  & & CH & & \\  & &    & & \\  & & CH_2 & &  \end{array}  $ | 3-Ethynylpenta-1, 4-diene | Isolated diene   |

| S.No. | Compound  | Name                                     | Type            |
|-------|---|--|-----------------|
| 8.    |  | 3-Ethyl-4-methylhex-3-ene                | Alkene          |
| 9.    |  | 2, 3-Dimethylcyclohex-1-ene              | Cycloalkene     |
| 10.   | $\text{CH}_2 = \text{C} = \text{CH}_2$  | Propadiene                               | Cumulated diene |
| 11.   | $\text{CH}_2 = \text{C} = \text{O}$   | Ethenone                                 | Alkene          |
| 12.   |  | Methylenecyclopentane                    | Alkene          |
| 13.   |  | Cyclopentylethene                        | Alkene          |
| 14.   |  | 3, 7, 11-trimethyldodeca-1, 6, 10-triene | Isolated triene |

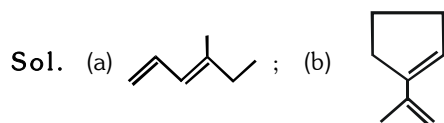
Ex. Write IUPAC names of :



Sol. (a) 2, 3-Dimethylcyclohexene; (b) 1-(2-butenyl) cyclohex-1-ene

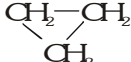
Ex. Give the structure for each of the following

(a) 4-Methyl-1, 3-hexadiene ;(b) 1-Isopropenylcyclopentene

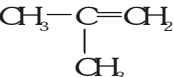
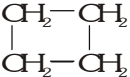


□ **Isomerism** :

Alkenes show chain, Ring chain or functional, Position, Geometrical isomerism and optical isomerism. For more details refer to isomerism provided to you in study material.

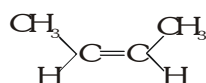
Ex. What is relation between  $\text{CH}_3\text{CH}=\text{CH}_2$  ,  ?

Sol. Ring chain isomerism

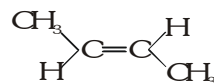
Ex. (a)  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$  (b)  $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$  (c)  (d) 

Define relations between a,b,c,d ?

**Sol.** a and b – Position isomerism ; a and c – Chain isomerism  
a and d – Ring chain isomerism ; b also show Geometrical isomerism

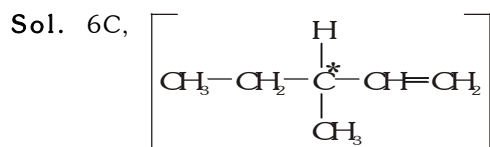


cis-2-butene



trans-2-butene

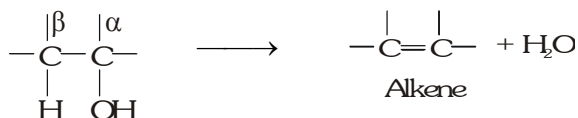
**Ex.** How many minimum carbon atom present in optically active alkene?



3-Methyl-1-Pentene

### □ Preparation of Alkenes :

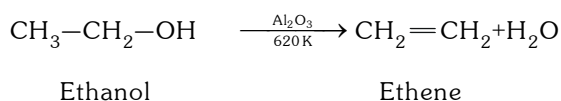
(1) **From Alcohols** : Alkenes can be prepared from monohydric alcohols or alkanols by the loss of  $\text{H}_2\text{O}$  and the reaction is known as **dehydration reaction**.



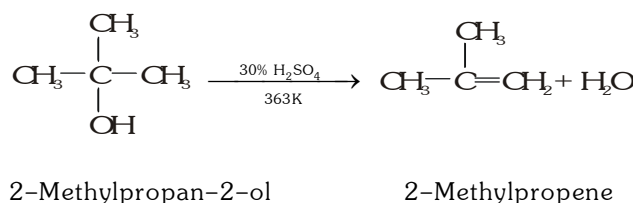
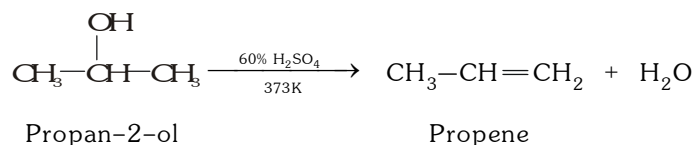
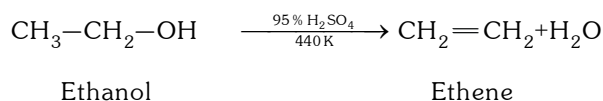
Alcohol

The dehydration can be carried with  $\text{Al}_2\text{O}_3$  or with **mineral acid** upon heating.

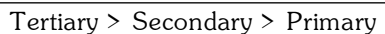
(a) **Dehydration with  $\text{Al}_2\text{O}_3$**  : Ethene is prepared by heating ethanol with  $\text{Al}_2\text{O}_3$  at 620 K.



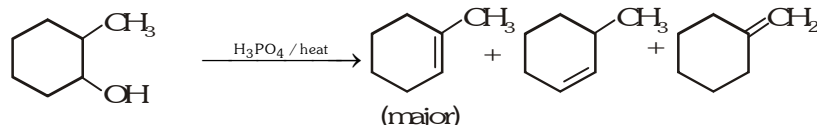
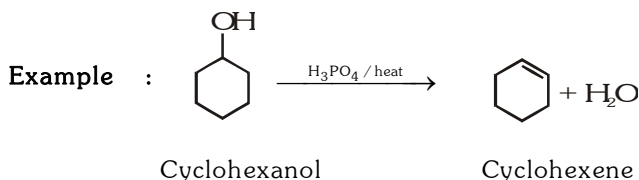
(b) **Dehydration with mineral acid** : Alcohols upon heating with conc.  $\text{H}_2\text{SO}_4$  form alkenes and the reaction is called **acidic dehydration**.



From the above reactions, it is clear that the order of acidic dehydration in different alcohols is



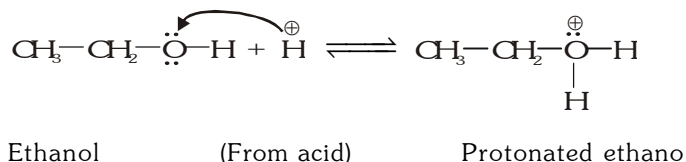
Cycloalkenes can be prepared in the same way by the dehydration of cycloalkanols.



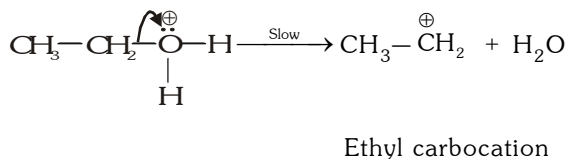
Regioselectivity of  $\beta$  elimination is governed by Zaitsev's Rule.

**Mechanism of Reaction:** The acidic dehydration of alcohol proceeds through the formation of a carbocation intermediate and is explained as follows :

**Step I :** Alcohol being a Lewis base accepts a proton ( $\text{H}^+$ ) from the acid in a reversible step as follows:

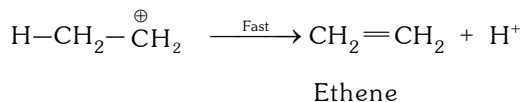


**Step II :** Due to presence of positive charge on electronegative oxygen, its electron accepting tendency increases. As a result C - O bond becomes weak and cleaves as follows :



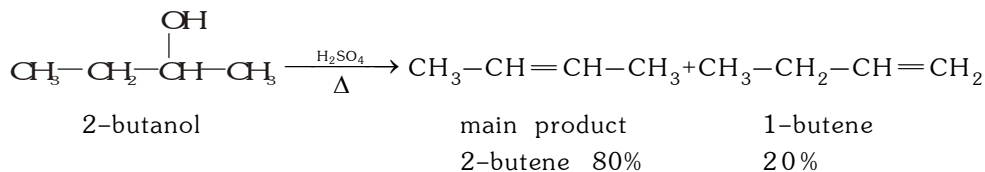
This is a slow and is regarded as **rate determining step**.

**Step III :** Carbocation is unstable in nature and loses a  $\text{H}^+$  and changes into ethene in a fast step as follows:

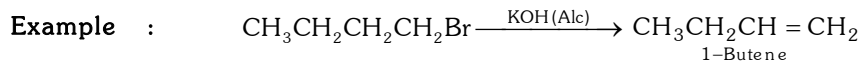


**Note:** Dehydration of secondary and tert alcohol is best carried out by using dil.  $\text{H}_2\text{SO}_4$ . Since alkenes produced from those alcohols have a tendency to form polymers under the influence of concentrated acid.

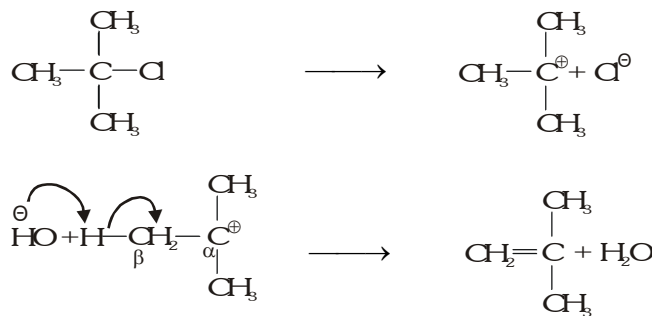
**Saytzeff Rule :** When two possible alkenes are obtained by the elimination reaction than that alkene will be in good yield, containing maximum number of alkyl group on double bonded C-atoms



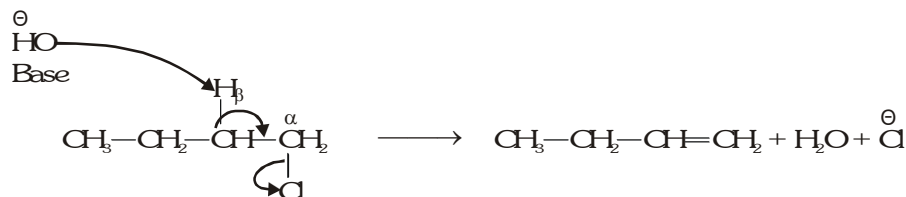




Primary and secondary alkyl halides undergo elimination reaction by  $\text{E}_2$  mechanism.  $\text{E}_1$  elimination reactions are shown by tertiary alkyl halides which are capable of producing stable (tert) Carbonium ion on ionization.



**$\text{E}_2$  mechanism :** Those alkyl halides which do not give Stable Carbonium ion on ionization show  $\text{E}_2$  elimination.

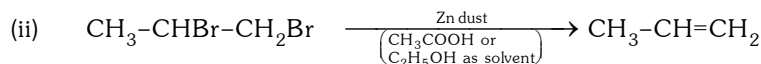
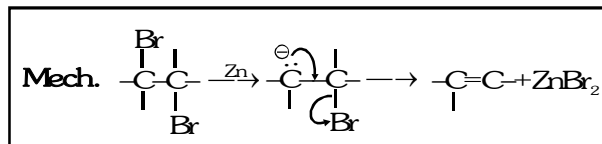
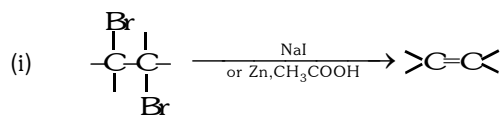


**(A) Dehalogenation of vicinal dihalides :**

There are two types of dihalides namely gem (or geminal) dihalides in which the two halogen atoms are attached to the same carbon atom and vicinal dihalides in which the two halogen atoms are attached to the adjacent carbon atoms.

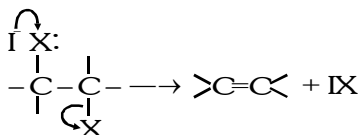
Dehalogenation of vicinal dihalides can be effected either by NaI in acetone or zinc in presence of acetic acid or ethanol.

◆ **General Reaction**



**Mech.**

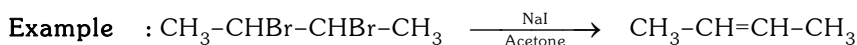
With NaI in acetone :



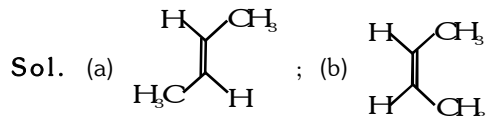
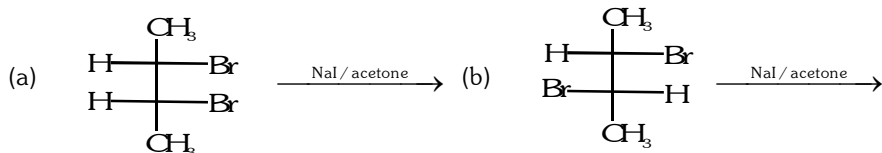
It involves an **antielimination** of halogen atoms

**Remarks :**

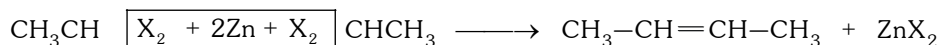
- (i) Both are  $E_2$  elimination.
- (ii) Both are stereospecific antielimination.



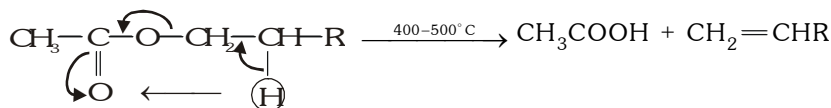
**Ex.** Identify the product in the following reactions :



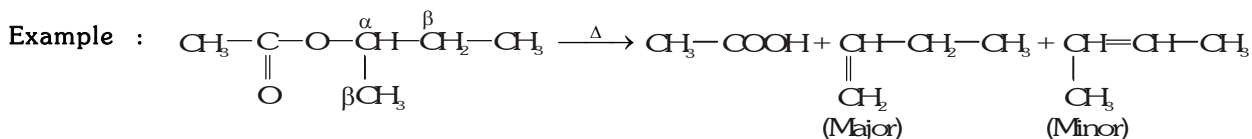
**(B)** From **gem dihalide** : Higher alkene obtained



**(3)** By **Pyrolysis of ester** :

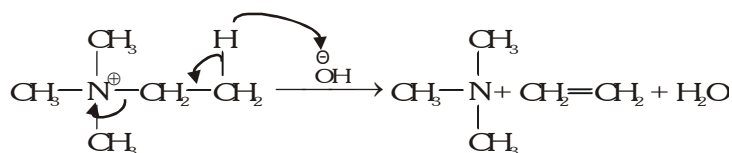


**Hoffmann's Rule** : Less substituted or less stable alkene is major product.

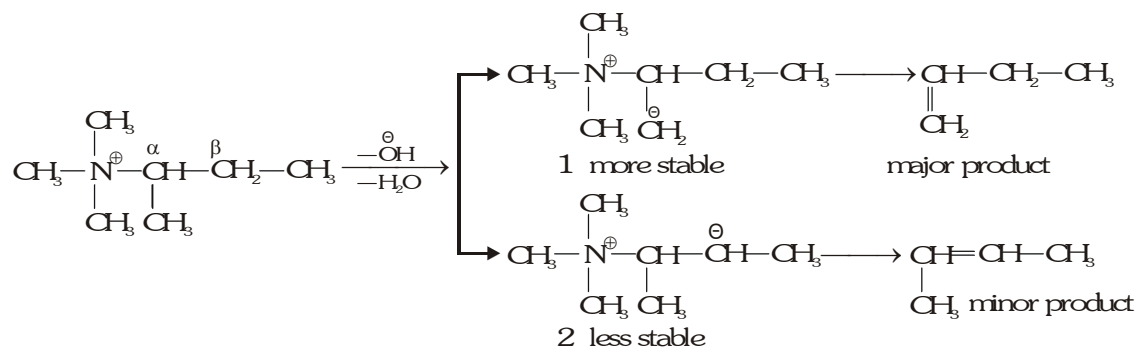


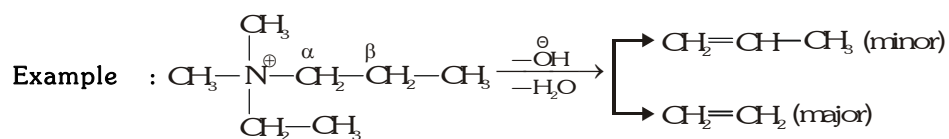
In the reaction to form an alkene a  $\beta$ -hydrogen from alkyl ester is attracted by oxygen atom of keto group & Hoffmann's alkene will be the major product.

**(4)** By **Pyrolysis of tetra alkyl ammonium ion** :



**Example :**

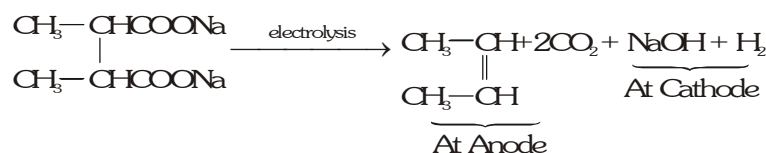
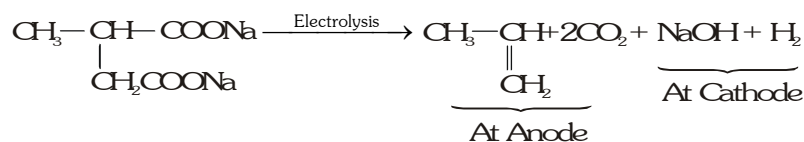
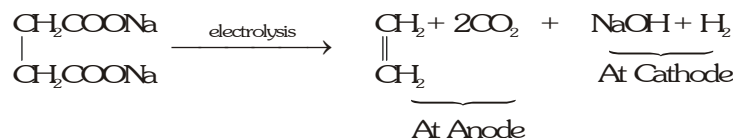




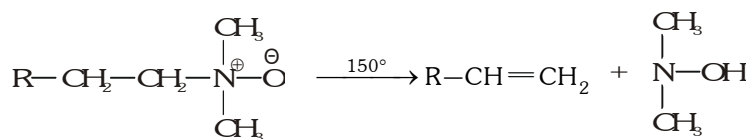
- In this reaction  $\beta$ -hydrogen of tetra-alkyl ammonium ion is attracted by a base and alkene is formed.
- In this reaction intermediate is carbanion. So yield of product depends on stability of carbanion.
- In this reaction Hoffmann's Rule is followed.

**(6) By Kolbe's method:**

Electrolysis of potassium or sodium salt of saturated dicarboxylic acid gives alkene.



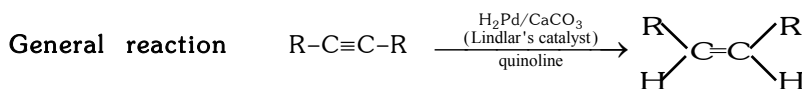
**(7) Pyrolysis of Tri alkyl amine Oxide : (Cope Reaction)**



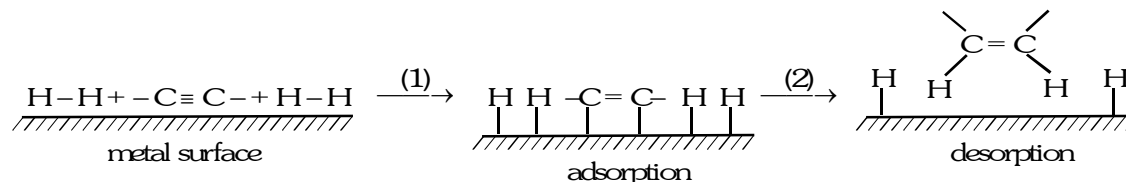
**(8) Hydrogenation of alkyne :**

By partial reduction of Alkynes -

- By catalytic Hydrogenation of Alkynes in presence of poisoned catalyst** (A Syn Addition of Hydrogen : Synthesis of cis-Alkenes : This is performed by)
  - Lindlar's catalyst** : Metallic palladium deposited on calcium carbonate conditioned with lead acetate and quinoline.
  - $\text{P}_2$  catalyst ( $\text{Ni}_2\text{B}$  nickel boride)



**Mechanism of hydrogenation :**

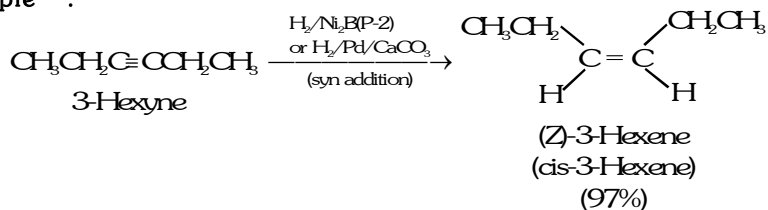




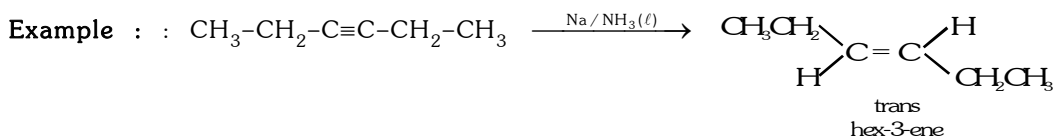
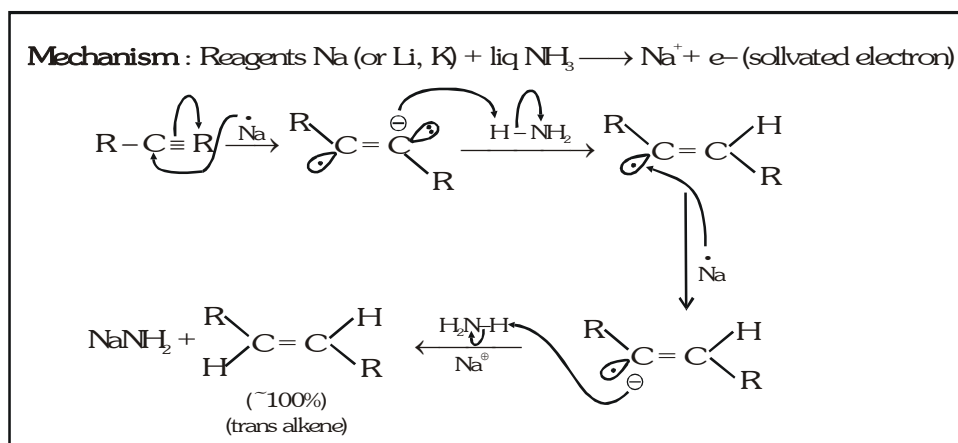
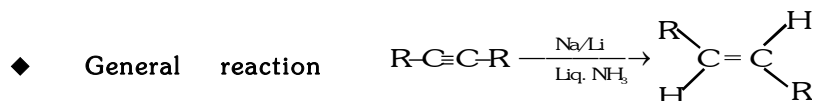
**Steps :** The reactant alkyne molecules and hydrogen molecules get adsorbed at the surface of metal catalyst. It is chemical adsorption (chemisorption).

In this state, the reactants lie very close to each other and so the hydrogen atoms start forming bond with carbon. Two hydrogen atoms are added to two triply bonded carbon atoms from the same side of  $\pi$  bond and a **cis or syn addition product** is formed. The product alkene now escapes away from the surface of the catalyst. Quinoline occupies the metal surface inhibiting further reduction to alkanes **Quinoline** therefore is called catalyst poison and such palladium is called deactivated catalyst or poisoned catalyst.

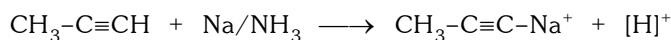
**Example :**



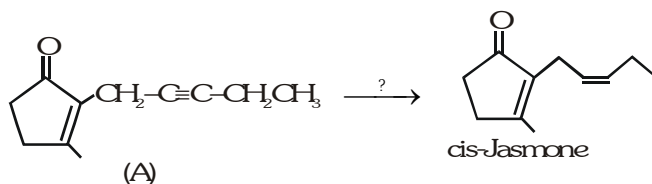
(b) **Birch Reduction :** (Anti addition of hydrogen : synthesis of trans-alkenes)



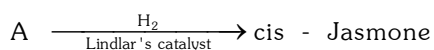
**Note :** This process of reduction is not eligible when terminal alkynes are taken ( $\text{R}-\text{C}\equiv\text{CH}$ ) because terminal alkynes form sodium salt with Na metal.



**Ex.** Identify the reagent for following synthesis



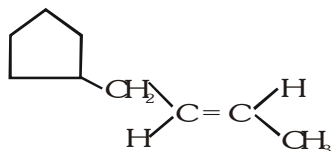
**Sol.**  $\text{H}_2/\text{Lindlar's catalyst}$



Ex. Identify the product in the following reaction :



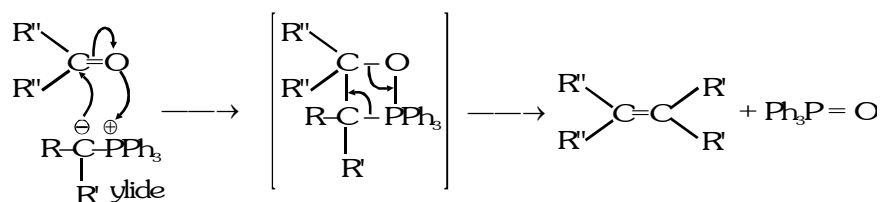
Sol.



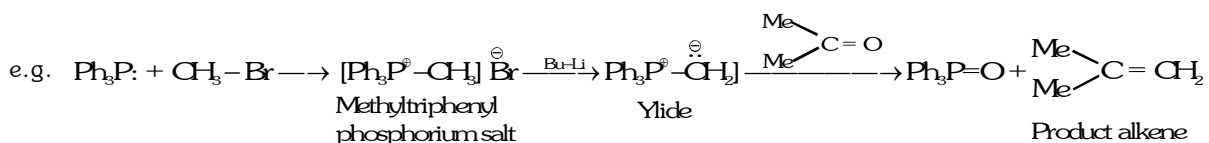
### (9) Wittig Reaction :

The aldehydes and ketones are converted into alkenes by using a special class of compounds called **phosphorus ylides**, also called Wittig reagents.

The Triphenyl group of phosphorane has a strong tendency to pull oxygen atom of the aldehyde or ketone via a cyclic transition state forming an alkene.



(R, R', R'' and R''' may be hydrogen or any alkyl group)



### Physical Properties of Alkenes / Hydrocarbons :

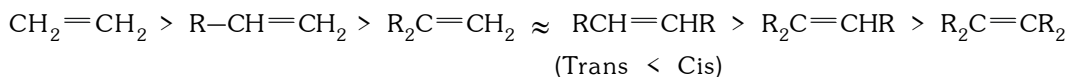
|    | Physical properties     | Homologus series  | Isomers   |
|----|-------------------------|---|---|
| 1. | Physical state          | $\text{C}_1 - \text{C}_3$ gases<br>$\text{C}_4 - \text{C}_{20}$ liquids<br>$> \text{C}_{20}$ : solids     |   |
| 2. | Dipole moment ( $\mu$ ) |   | cis > trans   |
| 3. | Polarity                | —   | cis > trans (for $\text{C}_{ab}=\text{C}_{ab}$ type of alkenes)   |
| 4. | Melting point           | increases with M.W.   | trans > cis<br>(due to more packing capacity)   |
| 5. | Boiling point           | increases with M.W.   | cis > trans<br># branching decreases B.P.   |
| 6. | Solubility              | Practically insoluble in water but fairly soluble in nonpolar solvents like benzene petroleum ether, etc. | $\text{C}-\text{C}=\text{C} < \text{C}-\text{C}=\text{C}-\text{C}$<br>Polarity increases, boiling point increases<br>cis > trans<br>Polarity increases, solubility in polar solvents increases. |
| 7. | Stability               |   | trans > cis (cis isomers has more Vander Waals repulsion)   |

## ❑ Chemical Properties :

Alkenes are more reactive than alkane this is because -

- The  $\pi$  electrons of double bond are located much far from the carbon nuclei and are thus less firmly bound to them.
- $\pi$  bond is weaker than  $\sigma$  bond and more easily broken.

The reactivity order for alkenes -



The reactivity order of alkenes has been delt in terms of heat of hydrogenation of alkene, more is the heat of hydrogenation ( $\Delta H = -ve$ ), more is the reactivity, the reactivity of alkene is however also related to

- Steric hinderence
- Hyperconjugation
- Heat of Combustion.

All four butenes may be compared, since all give the same products on combustion viz.  $4\text{CO}_2 + 4\text{H}_2\text{O}$

**Alkenes give the following type of reactions :**

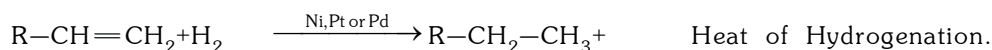
- Addition reaction
- Oxidation reaction.
- Substitution reaction.
- Polymerization Reaction.
- Isomerisation

| Alkene         | Heat of combustion (kJ/mol) | Heat of hydrogenation (kcal/mol) |
|----------------|-----------------------------|----------------------------------|
| 1-Butene       | 2719                        | 30.3                             |
| Isobutene      | 2703                        | 27.2                             |
| Cis-2-butene   | 2712                        | 28.6                             |
| trans-2-butene | 2707                        | 27.6                             |

### (A) Addition Reaction :

[A<sub>1</sub>] free radical addition :

◆ Addition of H<sub>2</sub> :



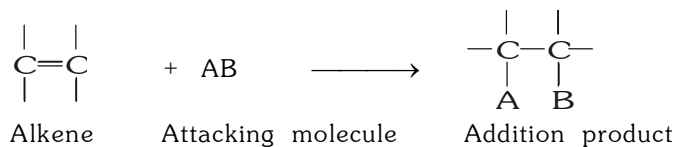
**Note:**(a) Reaction is exothermic, It is called heat of hydrogenation.

$$(b) \quad \text{Stability of alkene} \propto \frac{1}{\text{heat of hydrogenation}} \propto \frac{1}{\text{reactivity of alkene with H}_2}$$

(c) The process is used to obtain vegetable (saturated fats) ghee from hydrogenation of oil.

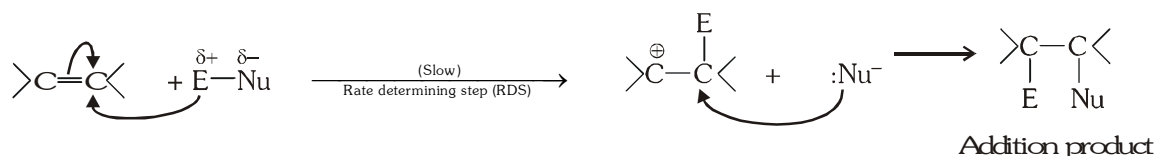
### (B) [A<sub>2</sub>] Electrophilic addition reactions :

Because of the presence of  $>\text{C}=\text{C}<$  bond in molecules, alkenes generally take part in the **addition reactions**.



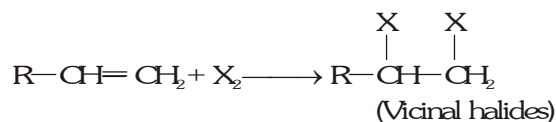
From mechanism point of view, the addition in alkenes is generally **electrophilic in nature** which means that attacking reagent which carries the initial attack is an electrophile ( $E^+$ ). This is quite expected also as there is high electron density in the double bond. The mechanism proceeds in two steps.

**Step I :** The  $\pi$ -electron cloud of the double bond causes the polarisation of the attacking molecule ( $E-Nu$ ) which cleaves to release the electrophile ( $E^+$ ) for the attack. The double bond simultaneously undergoes electromeric effect and the attack by the electrophile is accomplished in slow step (also called rate determining step) to form a **carbocation** intermediate.



**Step II :** The nucleophile ( $:Nu^-$ ) released in the slow step combines with the carbocation to give the desired addition product in the fast step.

1. **Addition of Halogen :** It is an electrophilic addition reaction.

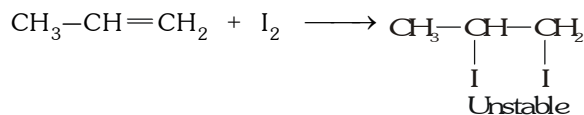


**Note:**(a) Reactivity order of halogen is :  $Cl_2 > Br_2 > I_2$

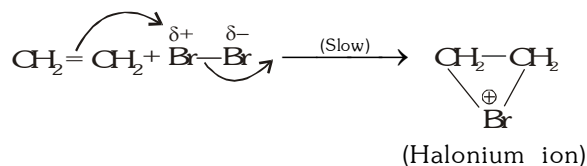
(b) Addition of  $F_2$  is exothermic reaction so it is difficult to control.

(c) The addition of  $Br_2$  on alkenes provides a useful test for unsaturation in molecule. The brown colour of the bromine being rapidly discharged. Thus decolorization of 5%  $Br_2$  in  $CCl_4$  by a compound suggests unsaturation in it. Colourless dibromo compound is formed.

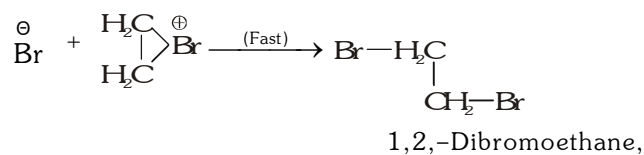
(d)  $I_2$  reacts slowly with alkenes to form Vicinal di-iodides which are unstable and eliminated  $I_2$  molecule very readily to give original alkene due to large size of Iodine they overlap.



◆ **Mechanism :** It is interesting to note that product which is mainly formed as a result of addition is **trans** in nature whereas the cis isomer is obtained in relatively smaller proportions. Since carbocation intermediate is planar ( $sp^2$  hybridised), both cis and trans addition products must be formed almost in equal proportions. The trans product can be justified in case a cyclic ion is formed by the initial electrophile attack.

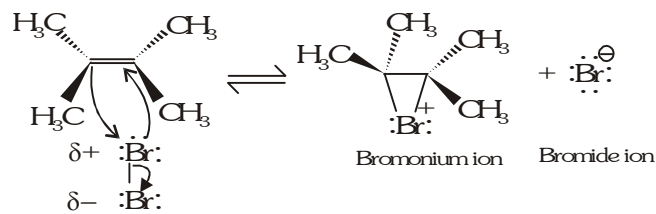


The attack of  $Br^-$  ion on the cyclic ion takes place from the side opposite to side where bromine atom is present in order to minimise steric hindrance.



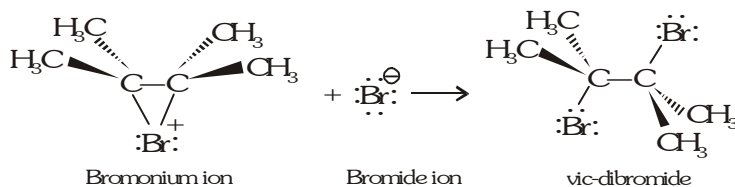
For 2, 3-dimethylbut-2-ene :

Step I :



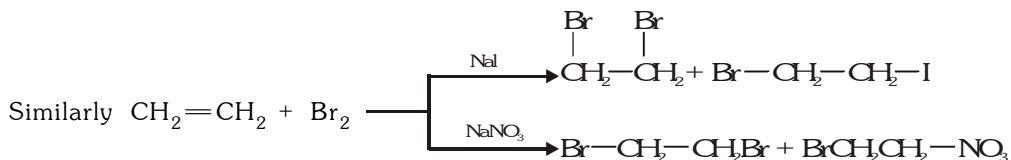
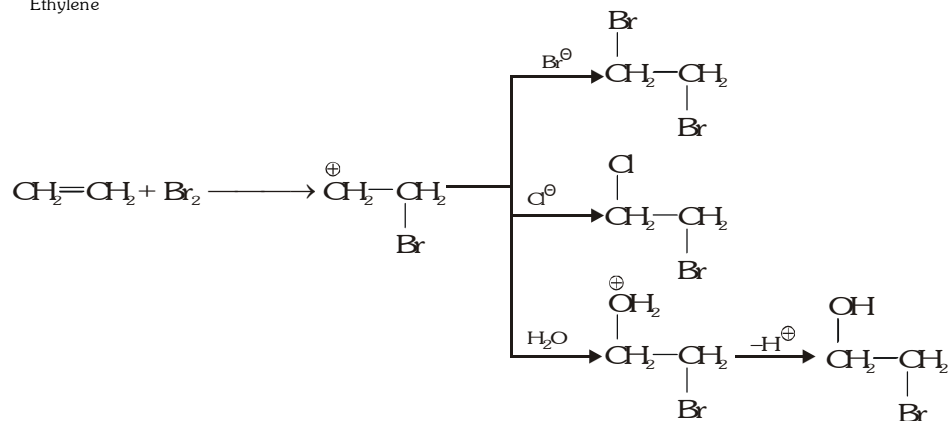
A bromine molecule becomes polarized as it approaches the alkene. The polarized bromine molecule transfers a positive bromine atom (with six electrons in its valance shell) to the alkene resulting in the formaiton of bromonium ion.

Step II :

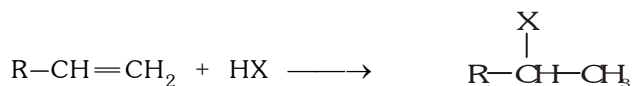
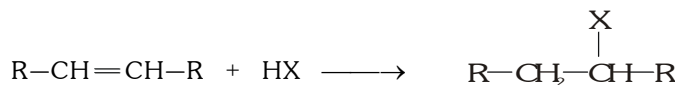


Ex.  $\text{CH}_2=\text{CH}_2 + \text{Br}_2 \xrightarrow{\text{aq. NaCl}}$  Products, what are the products?  
Ethylene

Sol.



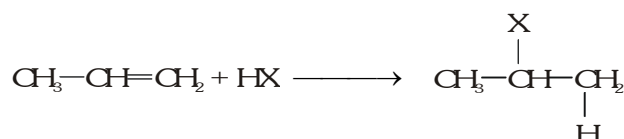
2. Addition of halogen acid :



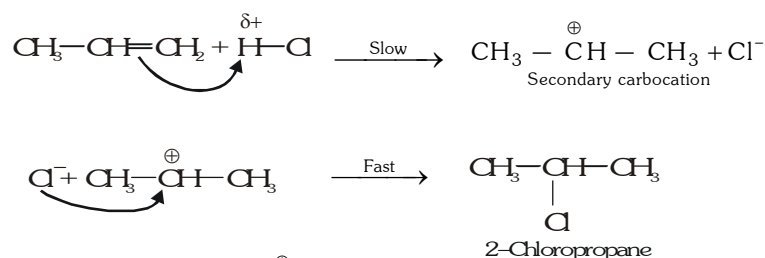
- Note:**(i) The order of reactivity of hydrogen halide is :  $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$
- (ii) Their addition is an example of electrophilic addition.
- (iii) Addition on alkene proceeds via the formation of more stable carbonium ion.
- (iv) Addition of  $\text{HX}$  on unsymmetrical alkenes ( $\text{R}-\text{CH}=\text{CH}_2$ ) takes place according to Markownikoff's rule.

□ **MARKOWNIKOFF'S RULE :**

- (a) **First Rule :** When molecule of a  $\text{HX}$  add up on unsymmetrical unsaturated hydrocarbon, the halogen atom goes to the unsaturated carbon atom bearing lesser number of hydrogen atoms.



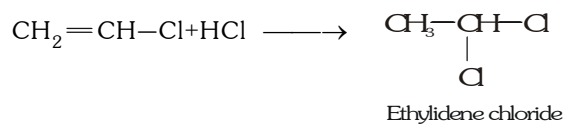
**Mechanism :** It is electrophilic addition and is illustrated by the action of  $\text{HCl}$  to propene.



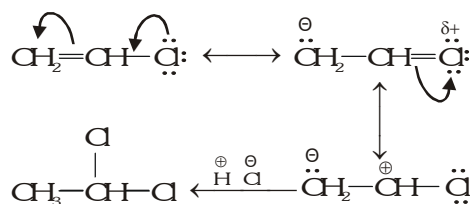
Primary carbocation ( $\text{CH}_3-\text{CH}_2-\overset{\oplus}{\text{CH}_2}$ ) is formed but only in very small proportion since it is less stable than the secondary carbocation. Markownikff's rule can also be stated as :

**The electrophilic addition to unsymmetrical alkenes always occurs through the formation of a more stable carbocation intermediate.**

- (b) **Second Rule :** In the addition of  $\text{HX}$  to vinyl halide and analogous compounds, the halogen attaches itself to the carbon atom, on which the halogen atom is already present.



◆ **Mechanism :**



In vinyl chloride two effects operate simultaneously in opposite direction-

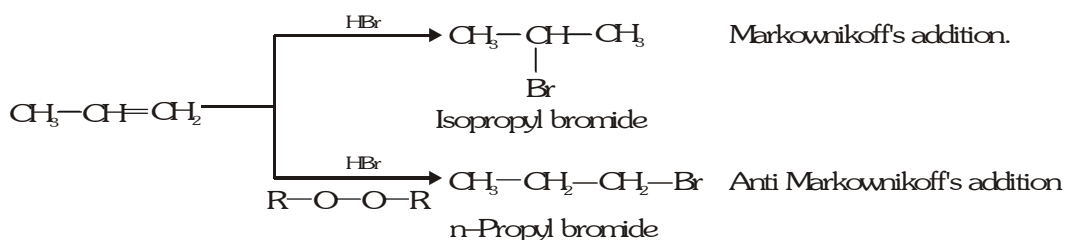
- (i) Inductive effect - electron attracting (-I) effect of chlorine.
- (ii) Resonance effect - electron pair releasing (+R) effect of chlorine.

The resonance effect is much more than the -I effect of Chlorine at the time of attack. This creates centres of +ve and -ve charges.

All polar reagents of the general structure  $\overset{\oplus}{Y} \overset{\ominus}{Z}$  (such as  $\overset{\oplus}{H}-\overset{\ominus}{X}$ ,  $\overset{\oplus}{H}-\overset{\ominus}{OH}$ ,  $\overset{\oplus}{H}-\overset{\ominus}{SO_3H}$ ,  $\overset{\oplus}{X}-\overset{\ominus}{OH}$ ) add on unsymmetrical unsaturated compound in accordance with Markownikoff's rules. Such additions are called normal Markownikoff's rule, where as additions in the opposite manner are referred to as abnormal or **antimarkownikoff's additions**.

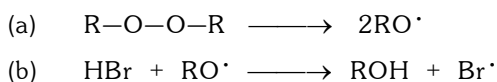
❑ **ANTI MARKONIFF'S RULE OR PEROXIDE EFFECT OR KHARASCH RULE :**

- (i) In the presence of oxygen or peroxides the addition of HBr on unsaturated unsymmetrical compound takes place contrary to Markownikoff's rule. This is called peroxide effect and is due to the difference in the mechanism of the addition.
- (ii) In the normal Markownikoff's addition the mechanism is ionic.
- (iii) In the presence of peroxide the addition of HBr takes place via free radicals.

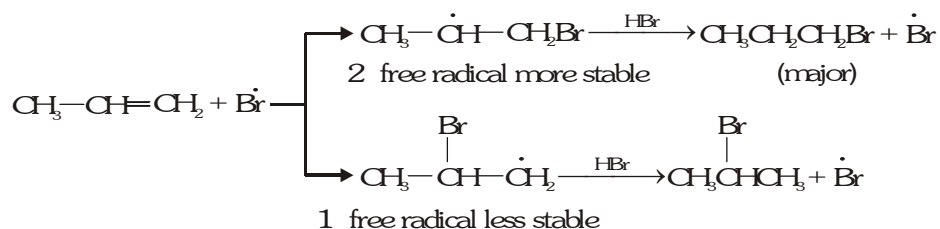


◆ **Mechanism :**

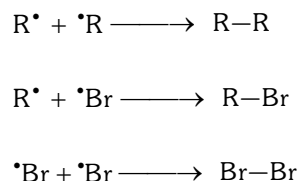
(i) **Chain initiation -**



(ii) **Chain propagation**



(iii) **Chain termination :**

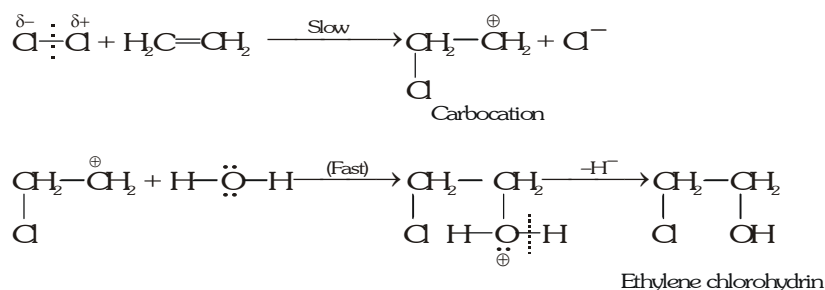


**Ex.** Why HCl and HI do not give antimarkownikoff products in the presence of peroxides.?

**Sol.** (a) The H-Cl bond is stronger than H-Br.

- (b) The H-I bond is weaker than H-Br bond. It is broken by the alkoxy free radicals obtained from peroxides, but the addition of iodine atom on alkene is endothermic as compared to Br atom therefore iodine atoms so formed combine with each other to yield iodine.

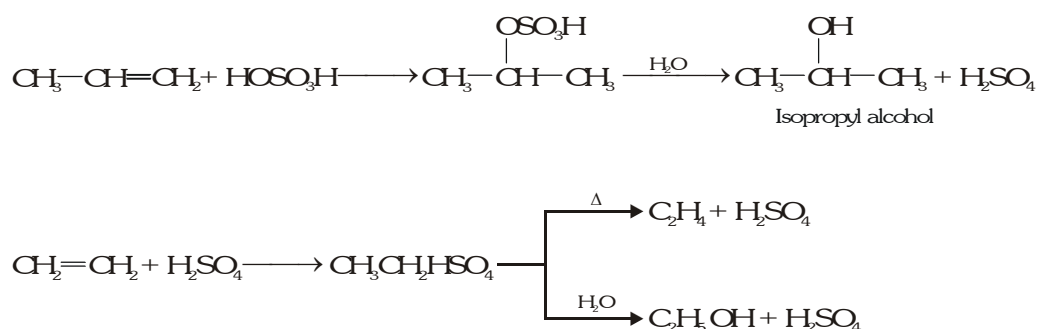
3. **Addition of Hypohalous acid (or  $X_2/H_2O$ , or  $HOX$ )** : It is a electrophilic addition and follows Markownikoff's rule.



In the fast step, there is competition between  $\text{Cl}^-$  ion and  $\text{H}_2\text{O}$  molecule to act as nucleophile but  $\text{H}_2\text{O}$  is a better nucleophile.

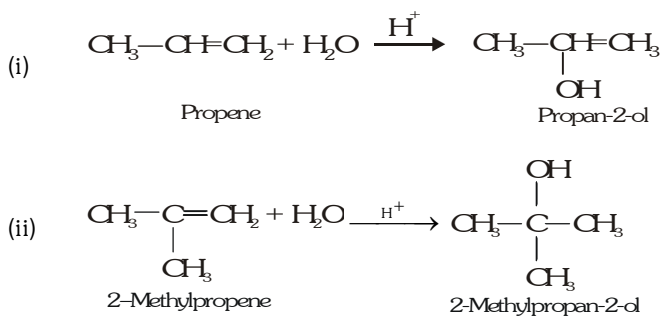
|  |
|--|
| Reactivity order is $\text{HOCl} > \text{HOBr} > \text{HOI}$ |
|--|

4. **Addition of  $\text{H}_2\text{SO}_4$** : Alkene react with conc.  $\text{H}_2\text{SO}_4$  to produce alkyl hydrogen sulphate. Which gives alcohols on hydrolyses. This reaction used to separate alkene from a mixture of alkane and alkene.

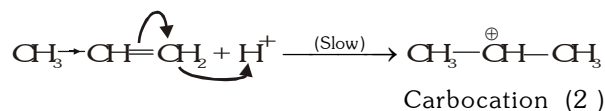


Ethyl hydrogen sulphate give ethylene when heated 430-440K while ethanol is obtained on boiling it with water.

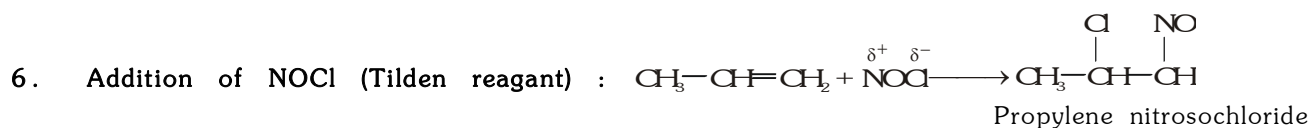
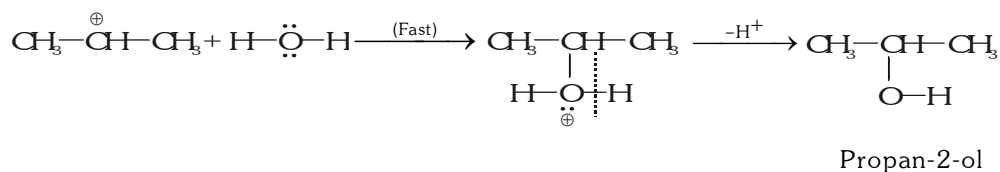
5. **Addition of water (Hydration of alkenes)** : Propene and higher alkenes react with water in the presence of acid to form alcohol. This reaction is known as the **hydration reaction** . Intermediate in this reaction is carbo cation, so rearrangement will take place.



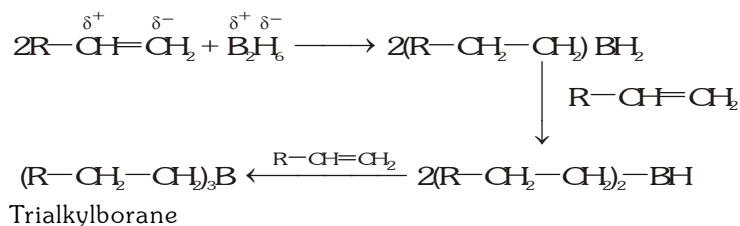
◆ **Mechanism** :



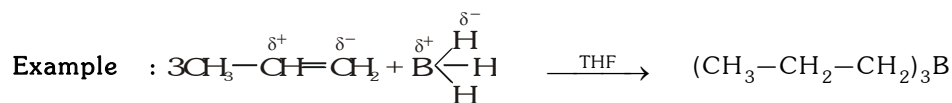




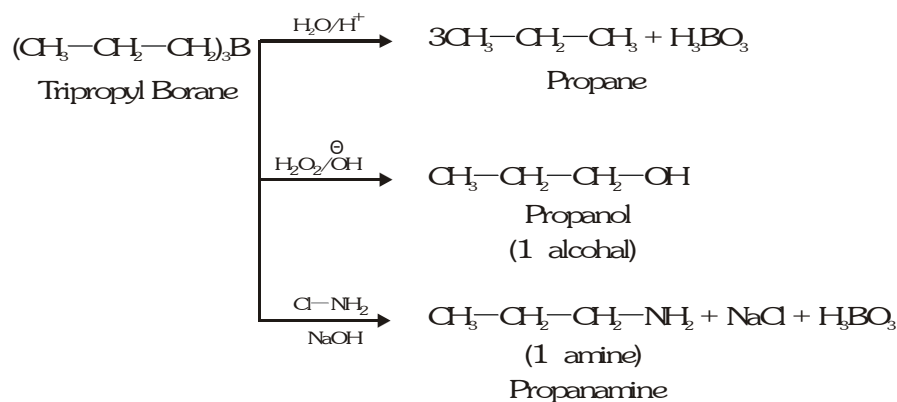
7. **Hydroboration** : It obeys markoni'koff's rule. Diborane readily reacts with alkenes giving trialkyl boranes. The reaction is called hydroboration.



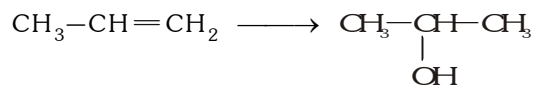
$\text{BH}_3$  does not exist or stable as monomer so a solvent THF (tetra hydro furane) is used.



$\text{BHR}_2$  also can be taken.



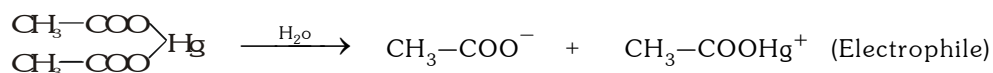
8. **Oxymercuration - demercuration** : Mercuric acetate in tetrahydro furan (THF) is treated with an alkene. The addition product on reduction with sodium Boro hydride in aqueous NaOH solution gives alcohol. It follows the markonikoff's rule.

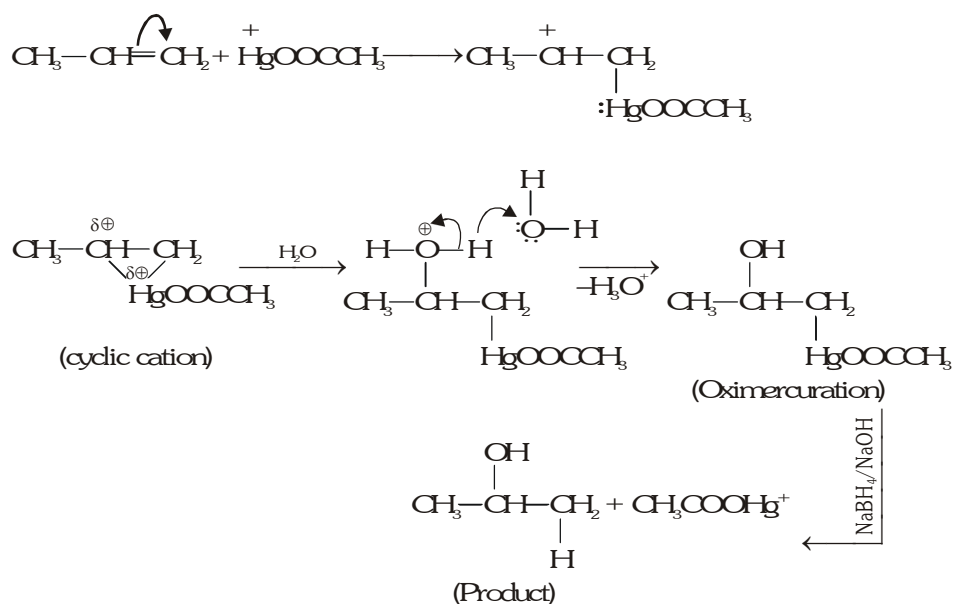


(i)  $(\text{AcO})_2\text{Hg}/\text{H}_2\text{O}$  (Mercuric acetate) or  $(\text{CH}_3\text{COO})_2\text{Hg}/\text{H}_2\text{O}$

(ii)  $\text{NaBH}_4/\text{NaOH}$

◆◆ **Mechanism** :







**Ex :** 90 mL of oxygen is required for complete combustion of unsaturated 20 mL gaseous hydrocarbon, hydrocarbon is ?

**Sol.** Following two formulae can be used for solution of the above asked question.

$$\frac{\text{Volume of Hydrocarbon}}{\text{Volume of O}_2} = \frac{2}{3n} \quad (\text{for Alkene})$$

$$\frac{\text{Volume of Hydrocarbon}}{\text{Volume of O}_2} = \frac{2}{3n-1} \quad (\text{for Alkyne})$$

By putting the values in above formulae we can find the hydrocarbon for which n is natural number.

$$\frac{20}{90} = \frac{2}{3n} \quad n = 3 \text{ So hydrocarbon is Propene [C}_3\text{H}_6\text{].}$$

**Ex.** How many mole of oxygen is required for complete combustion of 1 mole of Alkene.

**Sol.**  $2\text{C}_n\text{H}_{2n} + 3\text{nO}_2 \longrightarrow 2\text{nCO}_2 + 2\text{nH}_2\text{O}$

keeping in mind, the above equation.

$\therefore$  for 2 mole of Alkene, 3n mole of  $\text{O}_2$  is required for combustion.

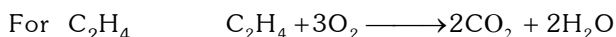
$\therefore$  for 1 mole of Alkene,  $\frac{3n}{2}$  mole of  $\text{O}_2$  is required for combustion.

$$= 1.5n \text{ mole of O}_2$$

**Ex.** 30 mL mixture of ethylene and Butylene is burnt in presence of oxygen then 150 mL of oxygen is required, what is the volume of Ethylene & Butylene in mixture.

**Sol.** Let the volume of  $\text{C}_2\text{H}_4 = x$  mL

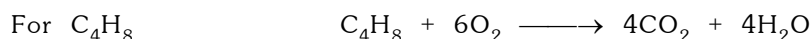
So volume of Butylene = (30-x) mL



from equation

$\therefore$  for 1 volume  $\text{C}_2\text{H}_4$ , 3 volume of  $\text{O}_2$  is required.

$\therefore$  for x mL vol. of  $\text{C}_2\text{H}_4$ , 3x ml volume of  $\text{O}_2$  is required.



$\therefore$  for 1 volume  $\text{C}_4\text{H}_8$ , 6 volume of  $\text{O}_2$  is required.

$\therefore$  for (30-x) mL " " , 6 (30-x) mL of  $\text{O}_2$  is required.

$$\text{Total volume of O}_2 = 3x + 6 (30-x) \text{ mL} = 150 \text{ mL (Given)}$$

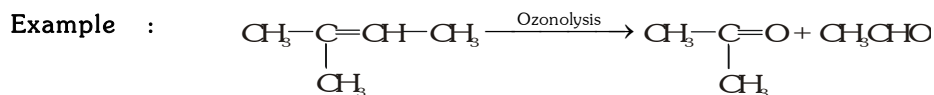
$$x = 10$$

$\therefore$  Volume of  $\text{C}_2\text{H}_4$  in mixture is 10 mL

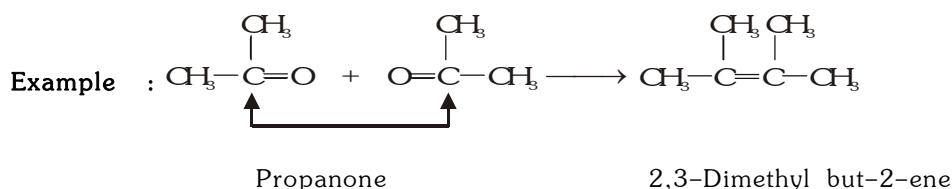
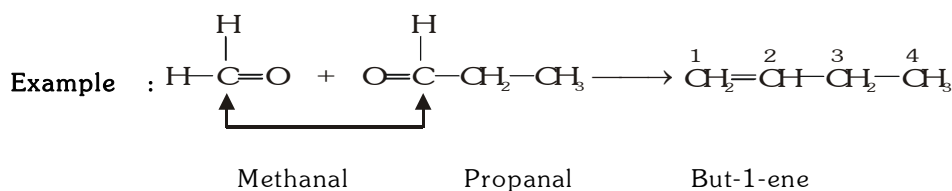
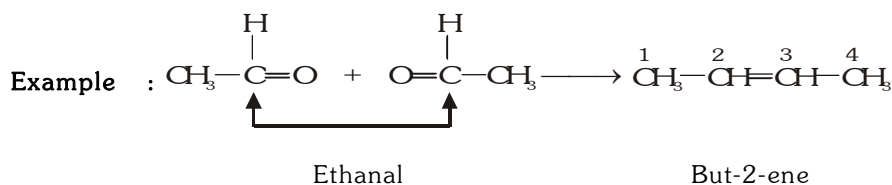
$\therefore$  Volume of  $\text{C}_4\text{H}_8$  in mixture is 20 mL

**(2) Ozonolysis :** (A test for unsaturation in molecule)

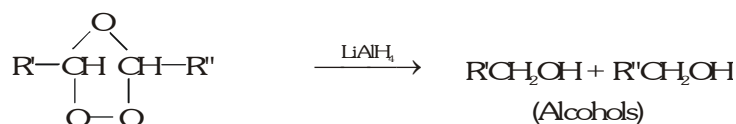
- The addition of ozone on the double bonds and subsequent a reductive hydrolysis of the ozonide formed is termed as ozonolysis.
- When ozone is passed through an alkene in an inert solvent, it adds across the double bond to form an ozonide. Ozonides are explosive compound they are not isolated.
- On warming with Zn and  $\text{H}_2\text{O}$ , ozonides cleave at the site of the double bond, the products are carbonyl compound (aldehyde or ketone) depending on the nature of the alkene.



- (iv) Ozonolysis of alkenes helps in locating the position of double bond in an alkene. It can be achieved by joining together the carbon atoms of the two carbonyl compounds formed as the products of ozonolysis with double bond.

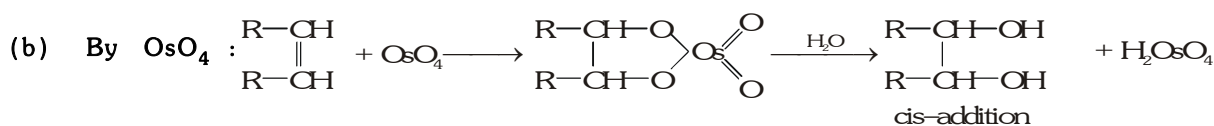
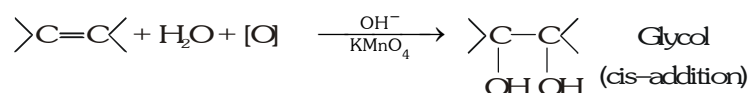


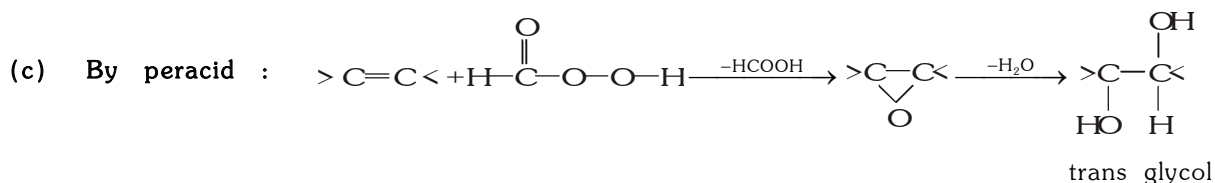
It may be noted that reaction with bromine water or Baeyer's reagent detects the presence of double bond (or unsaturation) in an alkene while ozonolysis helps in locating the position of the double bond. In an reduction of ozonide by  $\text{LiAlH}_4$  or  $\text{NaBH}_4$  gives corresponding alcohols.



- (3) **Hydroxylation :** Oxidation of carbon-carbon double bond to  $\begin{array}{cc} | & | \\ -\text{C} & -\text{C}- \\ | & | \\ \text{OH} & \text{OH} \end{array}$  is known as hydroxylation.

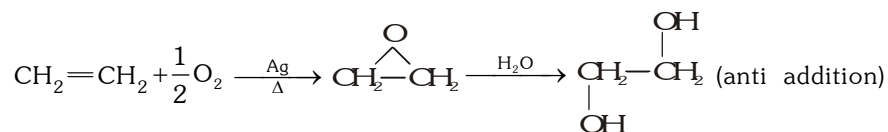
- (a) **Oxidation by Baeyer's reagent** (A test for unsaturation) : Alkenes on passing through dilute alkaline 1% cold  $\text{KMnO}_4$  (i.e., Baeyer's reagent) decolourise the pink colour of  $\text{KMnO}_4$  and gives brown ppt  $\text{MnO}_2$  and glycol.



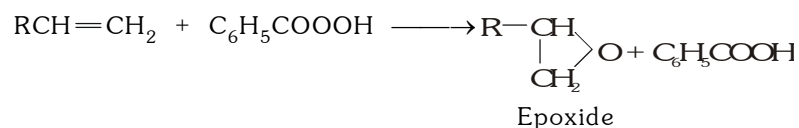


(4) Epoxidation :

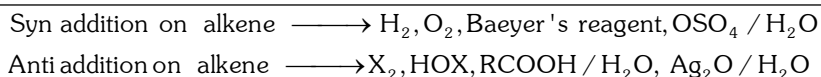
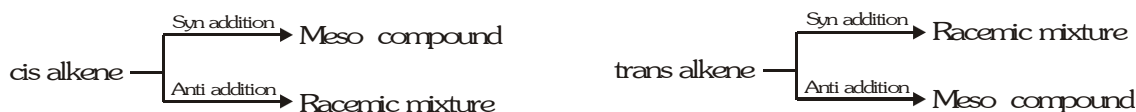
(a) Alkenes reacts with oxygen in the presence of Ag catalyst at 250 -400 °C to form epoxide.



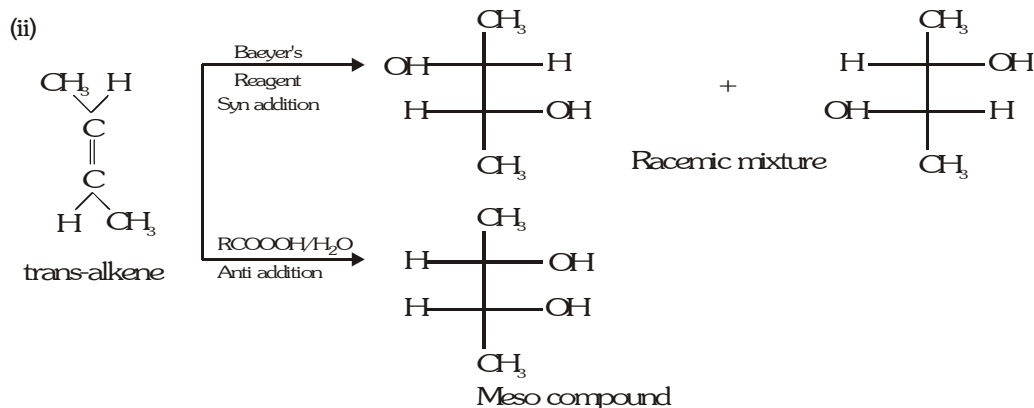
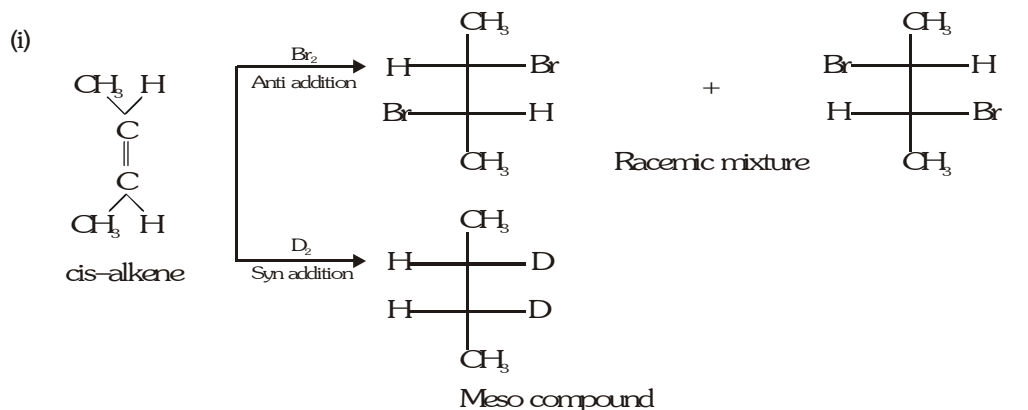
(b) **Prileschiaev reaction:** When an alkene is treated with perbenzoic acid an epoxide is formed. Such an epoxidation is known as Prileschiave reactions.



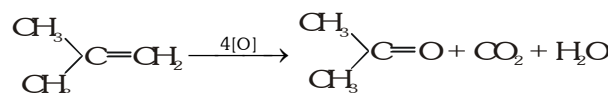
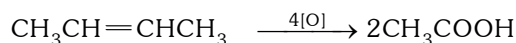
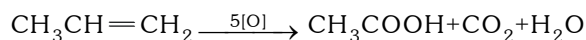
Emmons have found that perbenzoic oxy trifluoroacetic acid ( $\text{CF}_3\text{COO}_2\text{H}$ ) is a very good reagent for epoxidation and hydroxylation.



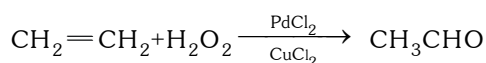
Example :



- (5) **Oxidation by strong oxidising agent (Oxidative cleavage)** : The alkenes themselves are readily oxidised to acid or ketone by means of acid permagnate or acid dichromate. If HCOOH is formed, it further oxidized to CO<sub>2</sub> and H<sub>2</sub>O. Keep it in mind that no further oxidation of ketones will takes place.

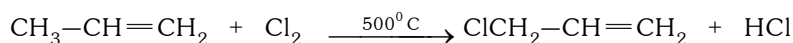


- (6) **Oxidation with retention of Carbon-Carbon bond - (Waker process)** :



- (C) **SUBSTITUTION REACTION (Allylic substitution)** :

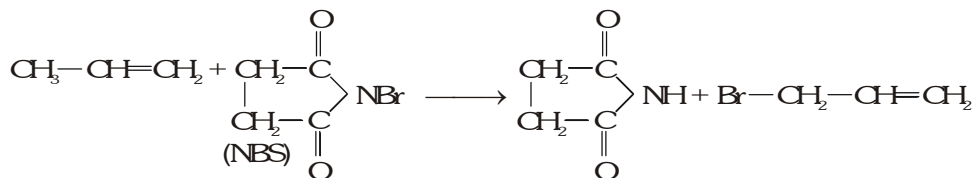
When alkenes are treated with Cl<sub>2</sub> or Br<sub>2</sub> at high temp., one of their allylic hydrogen is replaced by halogen atom. Allylic position is the carbon adjacent to one of the unsaturated carbon atoms. It is free radical substitution.



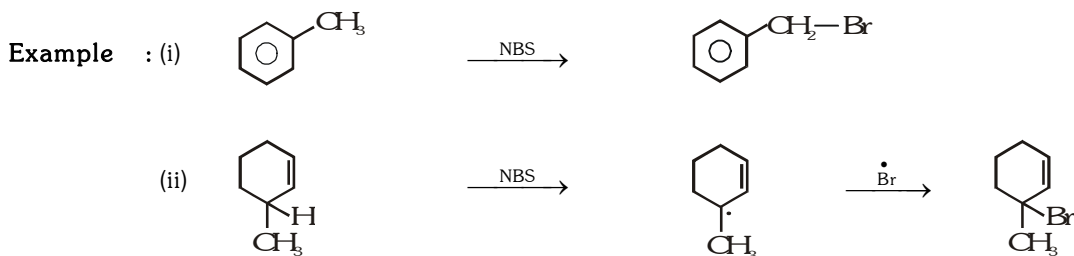
Allyl chloride

(3-Chloro-1-propene)

N-Bromosuccinimide (NBS) is an important reagent used for allylic bromination and benzylic substitution.



Substitution reaction is not given by ethene.



3 more stable

- (D) **POLYMERIZATION** :

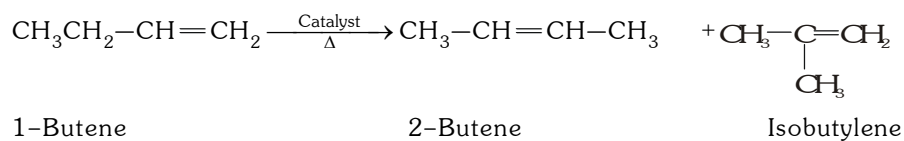
- (i) Two or more than two molecules of same compound unit with each other to form a long chain molecule with same empirical formula. This long chain molecule having repeating structural units called polymer, and the starting simple molecule as monomer and process is called addition polymerization.

- (ii) Molecular weight of polymer is simple multiple of monomer.
- (iii) Polymerization can be carried out by free radical or ionic mechanism.
- (iv) The presence of oxygen initiates free radical mechanism.
- (v) Addition polymerization can also be carried out by ionic mechanism by using Ziegler - Natta Catalysts ( $R_3Al+TiZCl_4$ )

| Name of polymer                             | Structure of monomer   | Structure of Polymer  | Properties   | Uses Properties  |
|---|--|---|--|--|
| 1. Polyvinyl chloride (PVC)                 | $CH_2=CH-Cl$   | $\left( \begin{array}{c} H_2C-CH \\   \\ Cl \end{array} \right)_n$                            | Pliable (easily moulded)   | Used in handbag, raincoats, vinyl flooring, good electrical insulator for wires  |
| 2. Polytetrafluoroethylene or Teflon (PTFE) | $F_2C=CF_2$  | $\left( F_2C-CF_2 \right)_n$  | Flexible and <b>inert</b> to solvents, boiling acids, even aquaregia stable upto 598K. | For making non-stick utensils coating  |
| 3. Natural rubber                           | $\begin{array}{c} CH_3 \\   \\ CH_2=CH-C=CH_2 \\ \text{isoprene} \end{array}$                    |   | Waxy and non-elastic   | Used as raw material for making vulcanised rubber which is strong and elastic vulcanised rubber is used in making tyres hose, pipes etc. |
| 4. Orlon                                    | acrylonitrile  | $\left( \begin{array}{c} H_2C-CH \\   \\ CN \end{array} \right)_n$                            | Fibrous  | Used in making Fabrics   |
| 5. Poly methyl methacrylate (PMMA)          | $\begin{array}{c} CH_3 \\   \\ CH_2=C \\   \\ COOCH_3 \\ \text{Methyl methacrylate} \end{array}$ | $\left( \begin{array}{c} CH_3 \\   \\ CH_2-C \\   \\ C=O \\   \\ OCH_3 \end{array} \right)_n$ |  |  |

#### (E) ISOMERISATION :

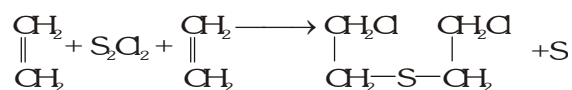
Alkene on heating to 500 to 700 C or on heating in presence of catalyst  $[AlCl_3$  or  $Al_2(SO_4)_3]$  undergo isomerisation.





❑ **Uses :**

- In plastic formation.
- In oxy ethylene welding
- As food preservatives and ripening fruits.
- As general anaesthetic ( $C_2H_4$  with 10%  $O_2$ )
- In preparation of mustard gas



2,2' or ( $\beta$ ,  $\beta'$ ) dichloro diethyl-sulphide  
(mustard gas)

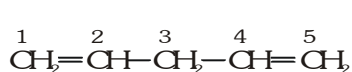
❑ **Laboratory test of alkene :**

| Functional Group                        | Reagent  | Observation                                | Reaction  | Remarks         |
|---|--|--|---|-----------------|
| $\diagup \text{C} = \text{C} \diagdown$ | (1) Bayer's Reagent alk. dil. cold $\text{KMnO}_4$ | Pink colour disappears                     | $\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} + \text{O} \xrightarrow{\text{alk. KMnO}_4} \begin{array}{c} \text{CH}_2-\text{CH}_2 \\   \quad   \\ \text{OH} \quad \text{OH} \end{array}$ | Dihydroxylation |
|   | (2) $\text{Br}_2/\text{H}_2\text{O}$               | Red colour decolourises                    | $\text{Br}_2 + \text{CH}_2=\text{CH}_2 \longrightarrow \begin{array}{c} \text{CH}_2-\text{CH}_2 \\   \quad   \\ \text{Br} \quad \text{Br} \end{array}$<br>White ppt.                      | Dibromination   |
|   | (3) $\text{O}_3$ (ozone)                           | $\diagup \text{C} = \text{O}$<br>Compounds | $\text{CH}_2=\text{CH}_2 + \text{O}_3 \xrightarrow{\text{Zn}/\text{H}_2\text{O}} 2\text{HCHO}$  | Ozonolysis      |

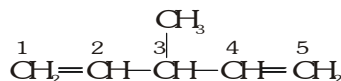
**: DIENES :**

Dienes are the unsaturated hydrocarbons with carbon-carbon double bonds in their molecules. These are represented by the general formula  $C_nH_{2n-2}$  which means that they are isomeric with alkynes (functional isomers). However, their properties are quite different from those of alkynes. Depending upon the relative positions of the two double bond, dienes are classified in three types :

**Isolated dienes or non conjugated dienes :** In an isolated diene, the two double bonds are separated by more than one single bond. For example,

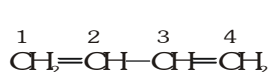


Penta-1,4-diene

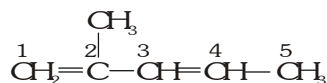


3-Methylpenta-1, 4-diene

**Conjugated dienes :** In a conjugated diene, the two double bonds are present in the conjugated or alternate position and are separated by a single bond.

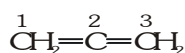


Buta-1,3-diene

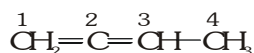


2-Methylpenta-1,3-diene

**Commulate dienes** : In this case, the two double bonds in the molecules are present at adjacent positions. For example,



Propa-1,2-diene



Buta-1, 2-diene

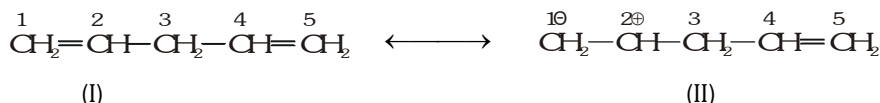
□ **Comparison of relative stabilities of isolated and conjugated dienes :**

**Resonance Theory** : The relative stabilities of the two types dienes can also be justified on the basis of the theory of resonance. Penta-1,3-diene (conjugated diene) is a hybrid of the following contributing structures.



The delocalisation of  $\pi$ -electron charge because of resonance decreases the energy of the molecule or increases its stability.

Penta-1, 4-diene (isolated diene) has only two contributing structures.



Since the carbon atom  $\text{C}_3$  is not involved in any resonance, the contributing structures are less in number are compared to the conjugated diene. The isolated diene is, therefore, less stable than a conjugated diene.

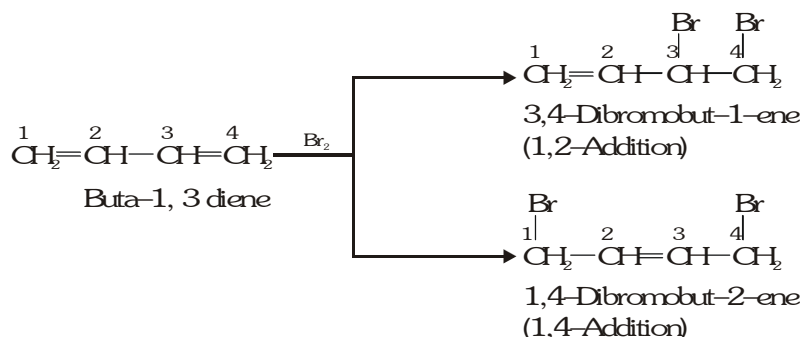
□ **Properties of Conjugated Dienes :**

The properties of the isolated dienes are similar to those of simple alkene but those of conjugated dienes are somewhat modified because of delocalisation of the  $\pi$ -electron charge. However, they also participate in the addition reactions. The important chemical characteristics of the conjugated dienes are briefly discussed.

1. **Addition Reaction** : Conjugated or 1,3-dienes take part in the addition reactions which can proceed by electrophilic as well as free radical mechanism depending upon the nature of the attacking reagent and the reaction conditions.

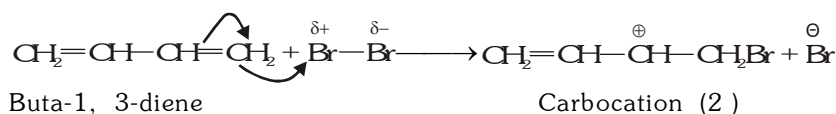
(A) **Electrophilic Addition Reactions** : The electrophilic addition is illustrated by the attack of halogen and halogen acid on buta-1,3-diene, a conjugated diene.

(a) **Addition of halogen** : If one mole of halogen attacks per mole of the diene, two types of addition products are formed. There are 1, 2 and 1, 4 addition products. For example,

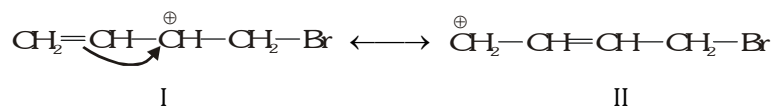


1, 2-addition is a normal addition in which one mole of halogen has been added to one of the double bond. But 1, 4-addition is somewhat unexpected.

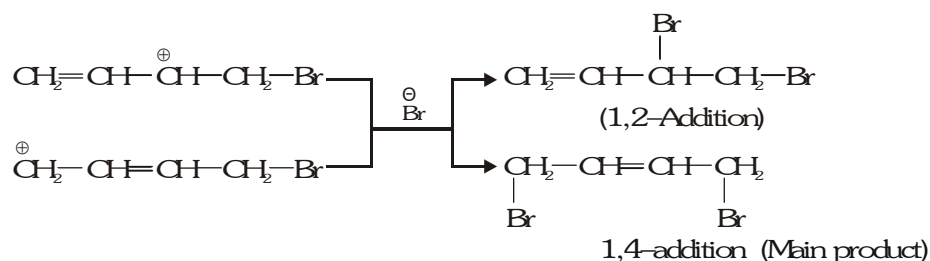
◆ **Mechanism** : The addition is electrophilic in nature and the halogen molecule (bromine) provides the electrophile for the attack.



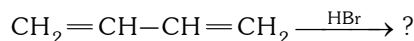
The 2 carbocation gets stabilised by resonance as follows -



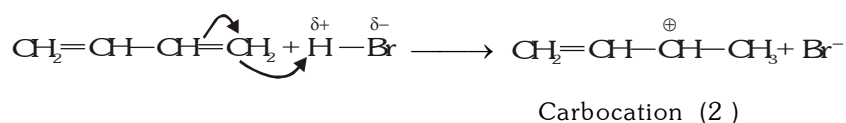
The attack of  $\text{Br}^-$  ion on carbocation (I and II)



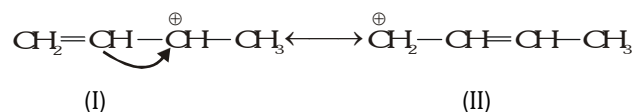
(b) Addition of H - X :



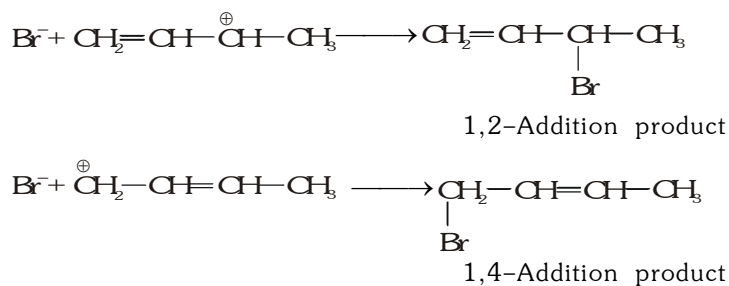
◆ **Mechanism :** The addition is electrophilic in nature as  $\text{H}^+$  ion is the electrophile.



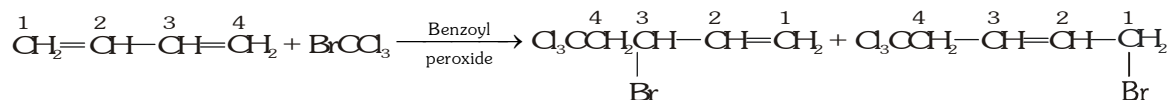
The carbocation gets resonance stabilised as follows :



The attack of  $\text{Br}^-$  ion on the carbocation (I) gives 1,2-addition product whereas the attack on the carbocation (II) yields 1,4-addition product.

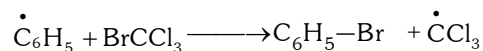
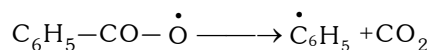


(B) **Free Radical Addition Reaction :** The addition to conjugated dienes can also proceed by free radical mechanism provided it is carried in the presence of a suitable reagent which can help in forming a free radical. However, the addition also yields 1,2 and 1,4 addition products. The free radical addition is illustrated by the attack of bromotrichloromethane ( $\text{BrCCl}_3$ ) on buta-1,3-diene in the presence of an organic peroxide such as benzoyl peroxide.



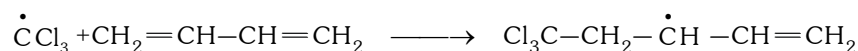
- ◆ **Mechanism** : The mechanism of addition is free radical in nature which is initiated by benzoyl free radical. It is explained in the following steps :

**Step I** Generation of free radical



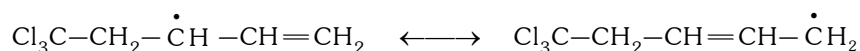
Trichloromethyl free radical

**Step II** Attack of free radical on buta-1, 3-diene



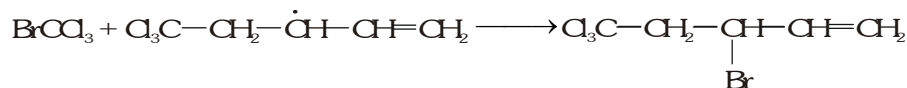
Free radical (secondary)

The free radical gets resonance stabilised

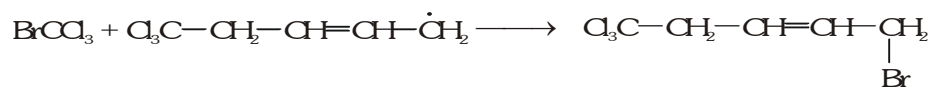


**Step III** Change of free radical into addition product

The free radicals take up  $\dot{\text{Br}}$  from the attacking reagent to give the desired addition products. i.e. 1,2 and 1,4 addition products.



(1,2-Addition product)

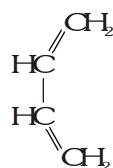


(1,4-Addition product)

## 2. Cyclo-Addition Reaction (Diel Alder Reactions) :

Cyclo-addition reactions are one of the most important reactions of conjugated dienes. Cyclo-addition involves the combination between a conjugated diene ( $4\pi$ -electron system) and a compound containing a double bond ( $2\pi$ -electron system) called **dienophile** which means a diene loving or attracting molecule. As a result, a six membered ring gets formed and the reaction is therefore known as **cyclo-addition reaction**. It is quite often termed as **(4 + 2) cyclo-addition reaction** because four  $4\pi$ -electron system adds to a two  $2\pi$  electron system. The reactions of this type are known as : Diel Alder Reaction.

The addition product is called **Diel Alder Adduct**. For example.



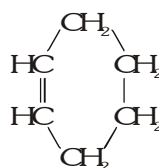
Buta-1,3-diene

+

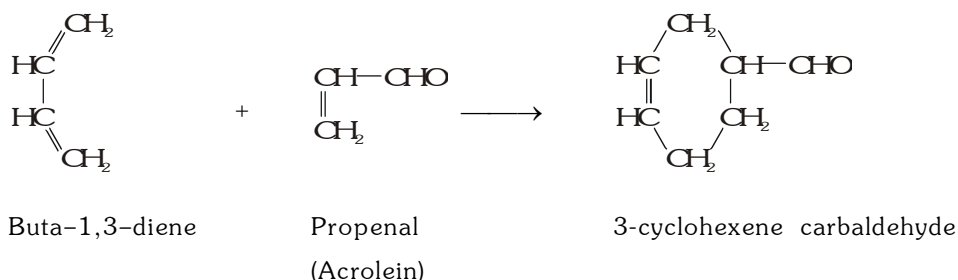


Ethene

→



Cyclohexene (Diel Alder adduct)



**Ex.** The density of a hydrocarbon at N.T.P. 2.5 gram/litre. What is hydrocarbon?

**Sol.** Density of 1 litre hydrocarbon = 2.5 gram/litre

$\therefore$  molecular weight of hydrocarbon =  $2.5 \times 22.4 = 56$

After molecular weight, we calculate the molecular formula.

$\text{C}_n\text{H}_{2n+2}$  = molecular weight (Alkane) or  $14n+2$  = molecular weight

$\text{C}_n\text{H}_{2n}$  = molecular weight (alkene) or  $14n$  = molecular weight

$\text{C}_n\text{H}_{2n-2}$   $\text{C}_n\text{H}_{2n-2}$  = molecular weight (Alkyne) or  $14n-2$  = molecular weight

with the help of above three formulae, we can identify the given hydrocarbon

$14n = 56$  (Alkene)  $\therefore$  Hydrocarbon is  $\text{C}_4\text{H}_8$  (Butene).

$n = 4$

Volume of hydrocarbon will be given and volume of  $\text{O}_2$  for complete combustion will also be given.

What is hydrocarbon is to be asked ?

The above question may be solved with the help of following three formulae.

$$\text{Formula No. 1} \quad \frac{\text{Volume of H.C.}}{\text{Volume of O}_2} = \frac{2}{3n+1} \quad (\text{for Alkane})$$

$$\text{Formula No. 2} \quad \frac{\text{Volume of H.C.}}{\text{Volume of O}_2} = \frac{2}{3n} \quad (\text{for Alkene})$$

$$\text{Formula No. 3} \quad \frac{\text{Volume of H.C.}}{\text{Volume of O}_2} = \frac{2}{3n-1} \quad (\text{for Alkyne})$$

**Ex.** How much propanol is required for dehydration to get 2.24 litre of Propene at N.T.P. if yield is 100%.

**Sol.**  $\text{C}_3\text{H}_8\text{O} + \text{H}_2\text{SO}_4 \longrightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O} + \text{H}_2\text{SO}_4$

Molecular weight of propanol = 60

from the equation given above we can see that from dehydration of 1 mole or 60 gram of propanol we get 1 mole (22.4lit.) of propene as product.

$\therefore$  22.4 litre of  $\text{C}_3\text{H}_6$  can be get from dehydration of 60 g of propanol.

$\therefore$  1 litre of propene can be get from dehydration of  $\frac{60}{22.4}$  g of propanol

$\therefore$  2.24 litre of propene can be get from dehydration of  $\frac{60}{22.4} \times 2.24$  g of propanol

**Ans.** = 6 g