

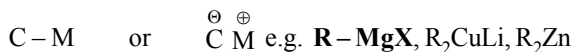
## CHEMISTRY FOR JEE MAIN &amp; ADVANCED

## ALKANES

## INTRODUCTION

## Introduction of Organometallic compounds

Organometallic compounds are the organic compounds in which a metal atom is directly attached to carbon atom through covalent bond or ionic bond. For example



(Where C is a carbon atom of an organic molecule and M is a metal atom)

If the metal atom is attached to oxygen, nitrogen, sulphur, etc., then such an organic compound is not regarded as an organometallic compound. The following structural formula do not belong to the family of organometallic compounds.

RONa (Sodium alkoxide),  $CH_3COONa$  (Sodium acetate),  $CH_3COOAg$  (Silver acetate), RSK (Potassium mercaptide) RNHK (N-Alkylpotassiumamide),  $(CH_3COO)_4Pb$  (Lead tetraacetate), etc.

## KEY POINTS

- (i) It should be noted that  $(CH_3)_4Si$  (Tetramethylsilane, TMS) is also not an organometallic compound because silicon is a nonmetal.
- (ii) Most important examples of organometallic compounds are Grignard's reagents. In Grignard's reagent, the carbon and magnesium atoms are bonded with each other through polar covalent bond and magnesium atom is attached to halogen by ionic bond.



- (iii) In organometallic compounds, the metal atom can be bonded to carbon atom of a hydrocarbon radical (Saturated, unsaturated, aliphatic, alicyclic or aromatic) or carbon atom of a heterocyclic radical.

## (I) Grignard Reagent

## 1. Saturated Aliphatic Grignard's reagent

$R-MgX$  (Alkylmagnesium halide)

$CH_3-MgI$  (Methylmagnesium iodide)

## 2. Unsaturated Aliphatic Grignard's reagent

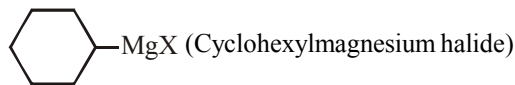
(i) Alkenyl Grignard's reagent

$CH_2=CH-CH_2-MgX$  (Allylmagnesium halide)

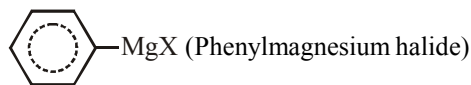
(ii) Alkynyl Grignard's reagent

$CH\equiv CH-CH_2-MgX$  (Propargylmagnesium halide)

## 3. Alicyclic Grignard's reagent

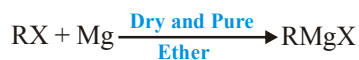


## 4. Aromatic Grignard's reagent

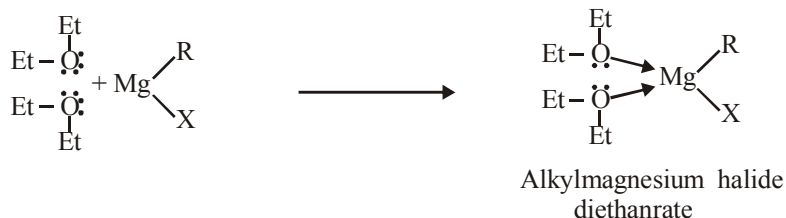


$C_6H_5CH_2MgCl$  (Benzylmagnesium halide)

### Preparation



Ether is used as a solvent because it is a Lewis base that donates its lone pair of electrons to electrondeficient magnesium atom, therefore providing stability to the Grignard's reagent by completing the octet on magnesium atom.

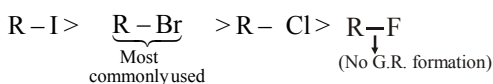


### Process

To an ethereal solution of alkyl halide Mg metal is added at very low temp. (0 . 5°C). A vigorous reaction takes place , and a solution of G.R. is obtained. It cannot be evaporated to obtain a solid state. The reaction will be explosive. It is **stable only in solution state**.

### Reactivity order with respect to X (For preparation of RMgX)

R - X :

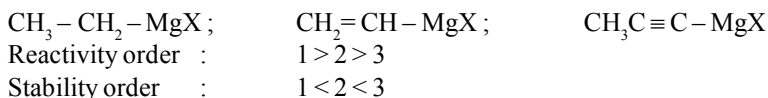


Iodides forms organometallic compounds at the fastest rate.

### Structural stability of G.R.

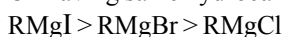
If the alkyl part has more stable negative charge, then RMgX is more stable. It will be less reactive

#### Ex.

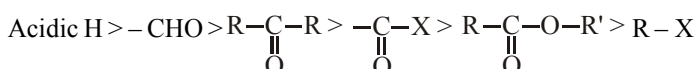


### Reactivity order of Grignard's reagent

On having same hydrocarbon radical, the order of reactivity of Grignard's reagents will be as follows :



### Reactivity order with respect to active H

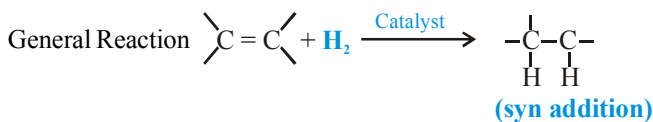


Except X (halogen) all other functional groups must be absent in the alkyl group otherwise. G.R. will be destroyed by internal reactions.

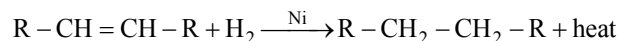
[- NO<sub>2</sub>, - CN must also be absent]

## (II) REDUCTION

### (a) CATALYTIC HYDROGENATION



Hydrogenation of an alkene is an **exothermic reaction** ( $\Delta H^\circ \cong -120 \text{ kJ mol}^{-1}$ )

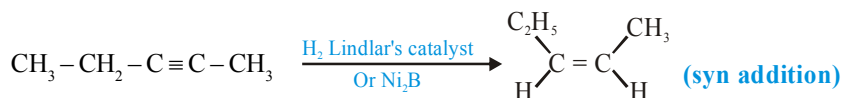


(b) **PARTIAL REDUCTION**

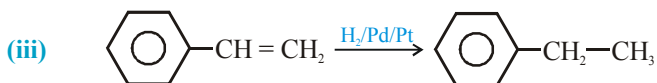
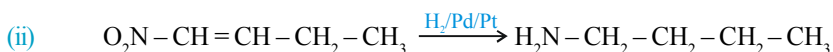
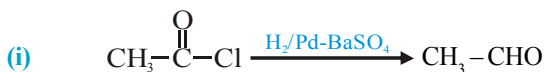
**Lindlar's catalyst**

It is a poisoned palladium catalyst (composed of powdered barium sulphate coated with palladium) poisoned with quinoline or sulphur. Nickel boride Ni<sub>2</sub>B (P-2 catalyst) (made from sodium acetate and sodium borohydride) is an excellent alternative catalyst for the conversion of alkyne into alkene. (syn addition)

The partial reduction of alkyne to alkene is heterogeneous hydrogenation with Lindlar's catalyst.

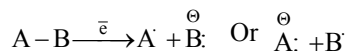


Acid chloride reduced to aldehyde by using Pd/BaSO<sub>4</sub> catalyst is called **Rosenmund Reduction**.



**Reduction by Dissolving Metals**

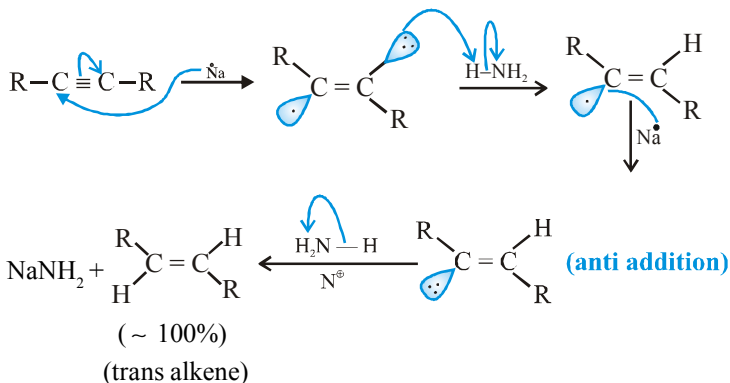
The general mechanism of reduction by dissolving metals is based on the fact that the metal acts as a source of electrons first an electron adds to the substrate causing fission of a single bond into a free radical and an anion or it can add to a double bond forming a resonance-stabilized radical ion.



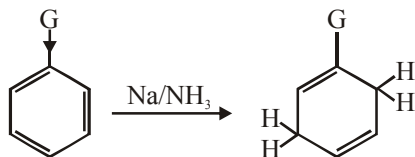
(c) **REDUCTION BY NA OR LI/NH<sub>3</sub> (BIRCH REDUCTION)**

**Mechanism**

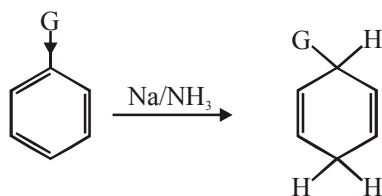
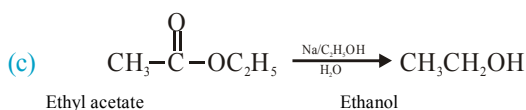
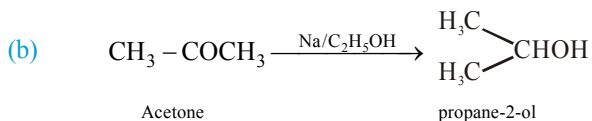
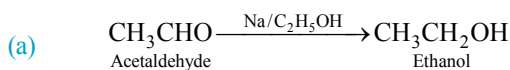
Reagents Na(or Li, K) + liq NH<sub>3</sub> → Na<sup>+</sup> e<sup>-</sup> (solvated electron)



Typical example of reduction for aromatic system :  
(electron releasing group - R, -OR, -NH<sub>2</sub>)

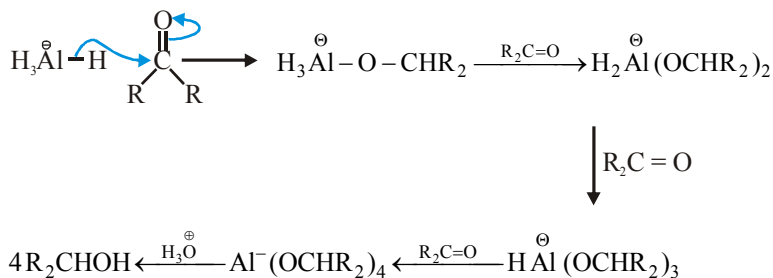


(electron withdrawing group - NO<sub>2</sub>, COOH, -CHO, -CN)

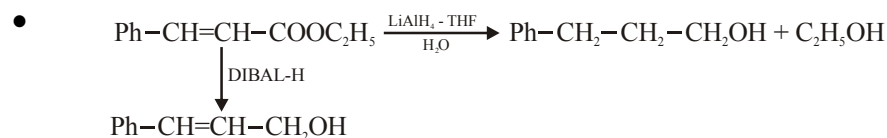
**(d) REDUCTION BY Na/C<sub>2</sub>H<sub>5</sub>OH [BOUVEALT-BLANC REDUCTION]****(e) REDUCTION BY METAL HYDRIDES AND ALKOXIDES**

LiAlH<sub>4</sub> (LAH) Lithium aluminium hydride (strong reducing agent) :

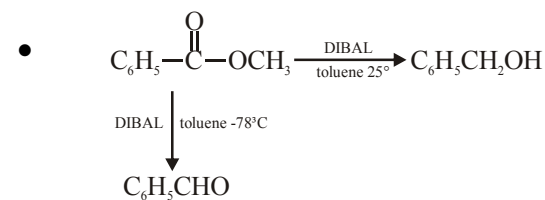
NaBH<sub>4</sub> Sodium borohydride (Mild reducing agent) :

**Mechanism****(f) DIBAL-H (DIISOBUTYLALUMINIUM HYDRIDE) (ALANE)**

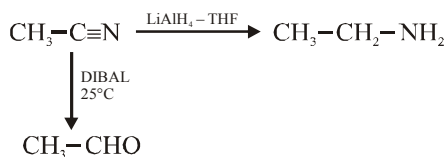
Most important alane is diisobutyl aluminium hydride. It runs parallel to LAH (Lithium aluminium hydride) as a reducing agent but it is more selective.



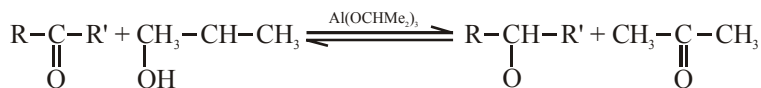
By DIBAL at ordinary temperature esters are reduced to alcohols but at low temperature esters are reduced to aldehyde.



LAH reduce RCN to amine but DIBAL is found to be reduce it to aldehyde.

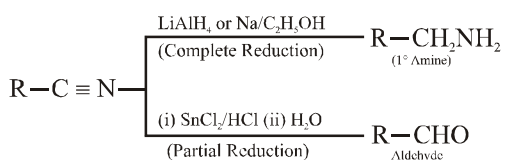


(g) **MPV REDUCTION (BY ISOPROPYLALCOHOL AND ALUMINIUM ISOPROPOXIDE)**



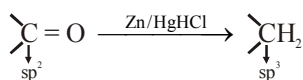
**Stephen's Reduction**

When reduction of compounds is carried out with acidified stannous chloride (SnCl<sub>2</sub>/HCl) at room temperature, imine hydrochloride is obtained which on subsequent hydrolysis with boiling water gives aldehyde. This specific type of reduction of nitrile is called Stephen's reduction.



**Clemmensen's Reduction**

Used to get alkane from carbonyl compounds :



Clemmensen reduction is not used for compounds which have **acid sensitive** group.

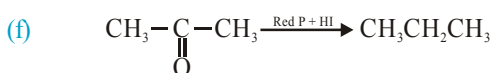
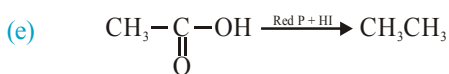
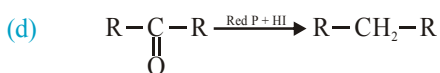
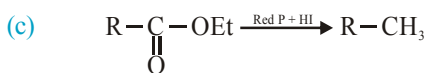
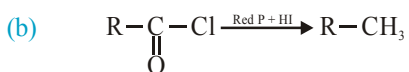
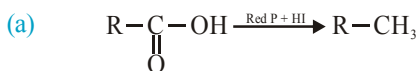
(h) **WOLFF-KISHNER REDUCTION (NH<sub>2</sub>NH<sub>2</sub>/KOH)**

Used to get alkane from carbonyl compounds

Wolff-kishner reduction is not used for compounds which have **base sensitive** groups.

**By Red P & HI**

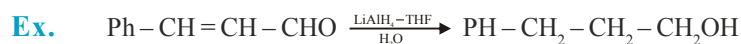
All the functional groups reduced into corresponding hydrocarbon



## Various functional groups and their products by the use of different reducing agents

S. No.	Group	Product	H <sub>2</sub> + Catalyst	LiAlH <sub>4</sub> in ether	NaBH <sub>4</sub> in EtOH	LiAlH(OBu) <sub>3</sub> in THF
1	-CHO	-CH <sub>2</sub> OH	+	+	+	+
2	$\begin{array}{c} \diagup \\ \text{C} = \text{O} \\ \diagdown \end{array}$	$\begin{array}{c} \diagup \\ \text{CHOH} \\ \diagdown \end{array}$	+	+	+	+
3	-CO <sub>2</sub> H	-CH <sub>2</sub> OH	-	+	-	-
4	-COOR'	-CH <sub>2</sub> OH	-	+	-	-
5	-CHNH <sub>2</sub>	-CH <sub>2</sub> NH <sub>2</sub>	-	+	-	-
6	-COCl	RCH <sub>2</sub> OH	+	+	+	+
7	-epoxide	alcohol	+	+	-	-
8	-CN	-CH <sub>2</sub> NH <sub>2</sub>	+	+	-	-
9	RNO <sub>2</sub>	RNH <sub>2</sub>	+	+	-	-
10	$\begin{array}{c} \diagup \\ \text{C} = \text{C} \\ \diagdown \end{array}$	$\begin{array}{c} \diagup \\ \text{CH}-\text{CH} \\ \diagdown \end{array}$	+	-	-	-

(\* ) double bond can be reduced by LiAlH<sub>4</sub>/THF only in cinnamic system.



## ALKANE

## Introduction

- Saturated hydrocarbons are known as alkanes or paraffins (Less reactive).
- Alkanes with carbon chains that are unbranched are called normal alkanes. Each member of the series differ from the next higher and next lower member by >CH<sub>2</sub> group.
- General formula : C<sub>n</sub>H<sub>2n+2</sub>
- All the carbon atoms in alkanes are in sp<sup>3</sup> state of hybridization and geometry is tetrahedral.
- All the bond angles are tetrahedral angles i.e., H-C-H or H-C-C bond angle is 109°28'

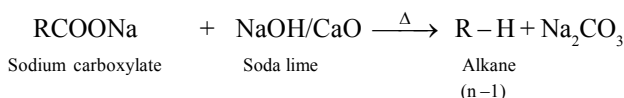
## Properties

	C-C	C-H
(i) Overlapping	sp <sup>3</sup> - sp <sup>3</sup>	sp <sup>3</sup> - s
(ii) Bond length	1.54 Å	1.112 Å
(iii) Bond energy	80 - 85 kcal	98.6 kcal

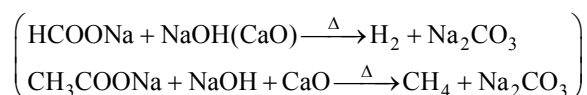
## Methods of Preparation

## (i) FROM CARBOXYLIC ACIDS

## (a) By de-carboxylation

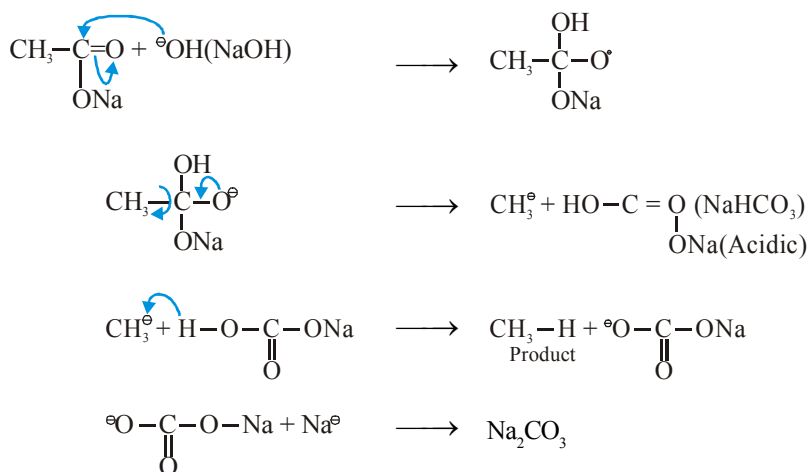


- The process of eliminatin of Carbon-di-oxide from Carboxylic acid called decarboxylation.
- Replacement of -COOH by hydrogen is known as decarboxylation.  
The alknae formed always contains one carbon atom less than the original acid.
- This reaction is employed for stepping down a homologous series.
- Soda lime is prepared by soaking quick lime CaO with NaOH solution and then drying the produces.
- Decarboxylation of sodium formate gives H<sub>2</sub>

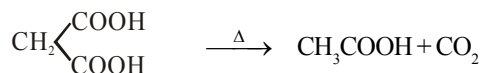


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**Mechanism** : Decarboxylation proceeds via the formation of carbanion intermediate as follows.



- (a) If in a compound two carboxylic groups are present and they are attached to same carbon atom then also decarboxylation of one of the carboxylic groups takes place simply on heating.

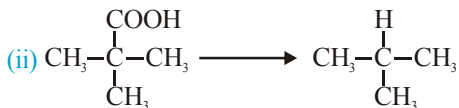
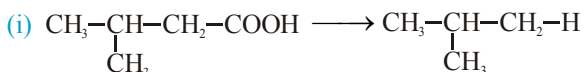


- (b)  $\text{CH}_4$  can be prepared by  $\text{CH}_3\text{COOH}$ .  
 (c)  $\text{C}_2\text{H}_6$  can be prepared by  $\text{CH}_3\text{CH}_2\text{COOH}$ .  
 (d)  $\text{CH}_3-\text{CH}_2-\text{CH}_3$  can be prepared by Butanoic acid and 2-Methyl propanoic acid.

**Ex.** How many acids can be taken to obtain isobutane from decarboxylation ?

- (A) 4                      (B) 3                      (C) 2                      (D) 5

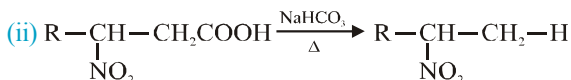
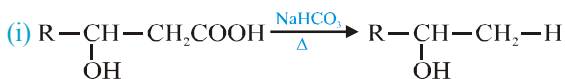
**Sol.** (C) To obtain isobutane the acids are



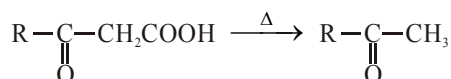
So two acids can be taken.

Reactivity of acid  $\propto$  stability of carbanion

Presence of electron attracting group ( $-I$ ) in the hydrocarbon part of the fatty acid increases the decarboxylation. If  $-I$  is more effective group then weak base may be taken.

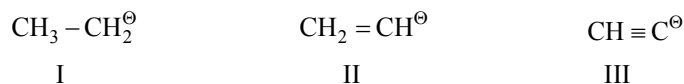


(iii)  $\beta$ -Keto acids are decarboxylated readily simply on heating (soda lime is not required)



- Ex.** Give reactivity order for decarboxylation ?  
 $\text{CH}_3-\text{CH}_2-\text{COOH}$        $\text{CH}_2=\text{CH}-\text{COOH}$        $\text{CH}\equiv\text{C}-\text{COOH}$   
 (A) I > II > III      (B) III > II > I      (C) III > I > II      (D) None is correct

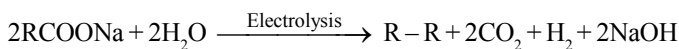
**Sol.** (B) In decarboxylation intermediates are ,



The stability order of carbanion – III > II > I

So reactivity order for acid is – III > II > I

### (b) Kolbe's electrolytic synthesis

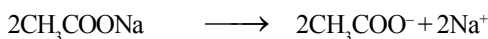


\* Methane cannot be prepared by this method.

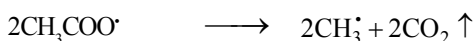
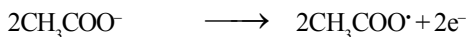


### Mechanism

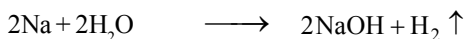
#### Ionic free radical



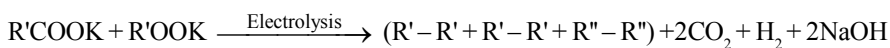
#### At anode



#### At cathode



- Methane can not be prepared by this method.
- Electrolysis of an acid salt gives symmetrical alkane, However in case of a mixture of Carboxylic acid salts, all probable alkanes are formed.



(c) Presence of alkyl groups in  $\alpha$ -position decreases the yield of alkanes.

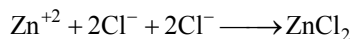
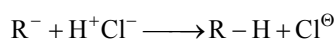
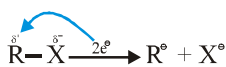
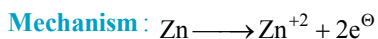
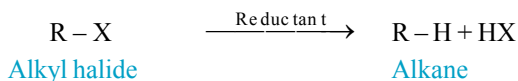
(d) True aromatic acids do not undergo Kolbe's electrolytic reaction.

(e) Free radical mechanism has been suggested for Kolbe reaction.

(f) At anode alkane (major) and  $\text{CO}_2$  gas is formed while at cathode NaOH and  $\text{H}_2$  gas is formed.

(g) The concentration of NaOH in solution is increased with time so pH solution is also increased.

### (ii) REDUCTION OF ALKYL HALIDES



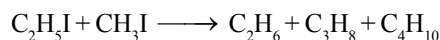
**Reductants :** Zn-Cu couple/EtOH, Na-EtOH, Zn-HCl, Pt or Pd or Ni/ $\text{H}_2$ Al-Hg/EtOH,  $\text{LiAlH}_4$  et.



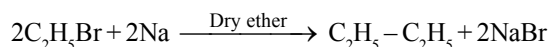
(iii) **WURTZ REACTION**



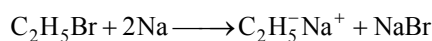
- Methane cannot be prepared by this method.
- The alkane produced is higher and symmetrical i.e., it contains double in the number of carbon atoms present in the alkyl halide taken.
- When the two reacting alkyl halides are different, a mixture of three different alkanes is obtained. So the Wurtz reaction is not useful for preparing alkanes containing odd no. of C atoms.



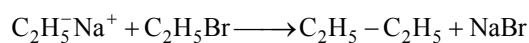
**Mechanism :** Wurtz reaction may proceed via the formation of organometallic compound or alkyl free radicals. [i.e. Both ionic and free radical mechanisms are proposed]



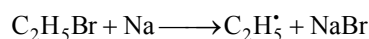
**Ionic Reaction Mechanism**



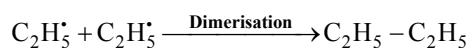
**Ethyl sodium**  
(organo metallic)



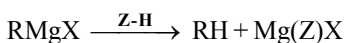
**Free radical Reaction Mechanism**



Ethyl free  
radical



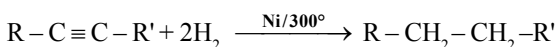
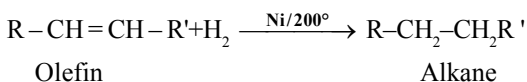
(iv) **FROM GRIGNARD REAGENT**



**Z-H [compound containing active hydrogen]**

HOH, NH<sub>3</sub>, RC≡CH, C<sub>6</sub>H<sub>5</sub>OH, CH<sub>3</sub>COOH, RNH<sub>2</sub>, R<sub>2</sub>NH, Pyrrole, C<sub>2</sub>H<sub>5</sub>OH etc.

(v) **FROM ALKENES AND ALKYNES (HYDROGENATION)**



- When the catalyst are Pt or Pd, hydrogenation proceeds smoothly at ordinary temperature and pressure.
- With Nickel catalyst, higher temperature (200° – 300°C) and pressure are needed. (In this case the reaction is known as **Sabatier Senderen's** reaction)
- With Raney Nickel, the reaction takes place at room temperature.



In this reaction following alkanes are not formed from unsaturated hydrocarbons

Alkene / Alkyne  $\longrightarrow$  Methane

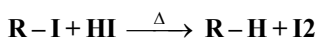
Alkene / Alkyne  $\longrightarrow$  Neopentane

Alkyne  $\longrightarrow$  Isobutane

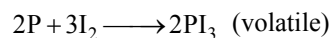
• The reaction is exothermic. The heat released in the reaction is known as heat of hydrogenation.

(vi) **REDUCTION OF ALCOHOLS, ALDEHYDES, KETONES AND ACIDS BY RED P AND HI (150°C)**

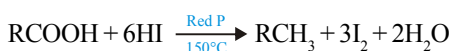
(a) **By the reduction of alcohols**



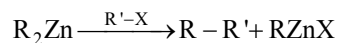
• Since iodine is produced during the reaction, it may react with the resulting alkane, so it is removed by adding red phosphorus.



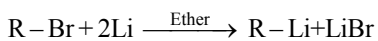
(b) **By reduction of acid**



(viii) **FROM DIALKYL ZINC : [FROM FRANKLAND REAGENT]**



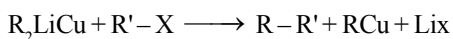
(ix) **COREY-HOUSE SYNTHESIS**



Alkyl bromide                      Alkyl lithium



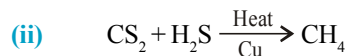
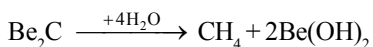
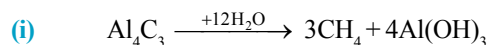
Lithium dialkyl  
cuprate



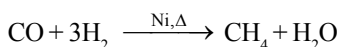
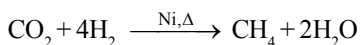
Alkane

• This method is useful for preparation of alkanes containing odd no. of c-atoms.

**SPECIFIC METHODS OF PREPARATION OF CH<sub>4</sub>**



(iii) **Sabatier Sendern's**



## PHYSICAL PROPERTIES

- (i) Alkanes from  $C_1$ – $C_4$  are gases.  
 $C_5$ – $C_{17}$  are liquids,  $C_{18}$ –onwards are waxy, white solids.  
**Note** : Neopentane is a gas.

(ii) **Boiling point**

Boiling point  $\propto$  molecular weight (for homologes)  $\propto \frac{1}{\text{Branches}}$  (for isomers)

**Ex.** order of boiling point

n-pentane > isopentane > neopentane

- (iii) **Melting point** : Alkanes containing even no. of carbon atoms have higher melting points than its next higher or next lower homologue having odd no. of carbon atoms. It is because of more symmetry of alkane molecules with even no. of carbon atoms as compared to alkanes with odd no. of carbon atoms.



(Both methyl groups are directed in opposite direction) (Both methyl groups are on the same side)

- Alkanes are colourless, odourless and tasteless.
- Alkanes are lighter than water. These are insoluble in water and soluble in organic solvents.

**Ex.** Alkanes are inert in nature, why?

**Sol.** Alkanes are quite inert substances with highly stable nature. Their inactiveness has been explained as:

- (i) Alkanes have all the C – C and C – H bonds being stronger  $\sigma$  bonds and are not influenced by acid, oxidants under ordinary conditions.  
 (ii) The C – C bond is completely non polar and C – H is weakly polar. Thus polar species i.e. electrophiles or nucleophiles are unable to attack these bonds under ordinary conditions.

## CHEMICAL REACTIONS

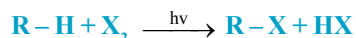
1. Stability
2. Substitution reactions :
  - (a) Halogenation
  - (b) Nitration
  - (c) Sulphonation
  - (d) Chlorosulphonation (Reed reaction)
3. Oxidation :
4. Isomerisation
5. Cracking / Pyrolysis :
6. Aromatization
7. Addition of  $CH_2$

### 1. STABILITY

Although alkanes are chemically unreactive under ordinary conditions due to the presence of strong C – C and C – H sigma  $\sigma$  bonds, yet they give following reactions under special conditions

### 2. SUBSTITUTION REACTION

#### Halogenation



- Reactivity order of hydrogen atoms in alkanes is  
 $3^\circ H > 2^\circ H > 1^\circ H$   
 $3^\circ H > 2^\circ H > 1^\circ H$
- Reactivity order of halogens is  
 $F_2 >> Cl_2 > Br_2 > I_2$

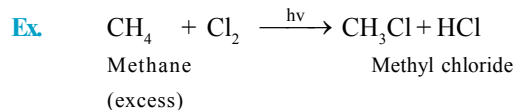
Fluorine can react in dark.  $Cl_2$  and  $Br_2$  require light energy.  $I_2$  does not show any reaction at room temperature, on heating it shows iodination.

**Fluorination**

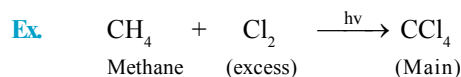
- Direct-fluorination of alkanes is usually explosive.  
 $\text{CH}_4 + \text{F}_2 \longrightarrow \text{Carbon black (explosive reaction)}$
- It is carried out successfully by diluting fluorine with nitrogen (Inert gas).  
 $\text{CH}_4 + \text{F}_2 \longrightarrow \text{CH}_3\text{F} + \text{HF}$

**Chlorination**

The monochloro derivative of alkane is obtained as a major product by taking alkane in excess.



- When chlorine is in excess, carbon tetrachloride will be the major product.

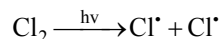


Chlorination of alkanes takes place in the following conditions.

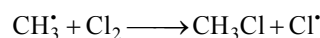
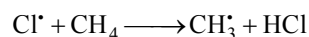
- No reaction at room temperature in darkness.
- At 300°C in darkness.
- At 100°C in the presence of organic peroxides.
- At 150°C in the presence of Tetra ethyl lead

⇒ Chlorination of methane is based on free radical mechanism and it completes in the following three steps :

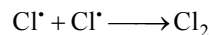
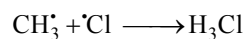
**(a)** Chain initiating (first) step



**(b)** Chain propagating (second) step



**(c)** Chain terminating (third) step

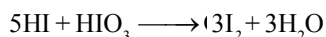


**Bromination :** Bromination of alkanes is similar to chlorination but not so vigorous.

**Iodination :** Iodination of alkanes is slow and reversible.



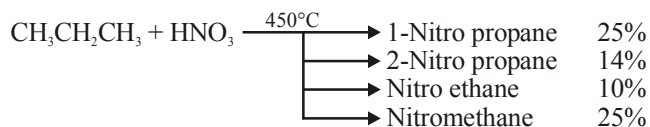
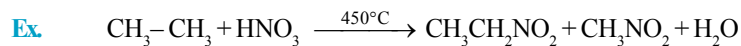
- Iodination may be carried out in the presence of an oxidising agent such as  $\text{HIO}_3$ ,  $\text{HNO}_3$ ,  $\text{HgO}$ , etc. which destroys the HI as it is formed and so drives the reaction to the right.

**KEY POINTS**

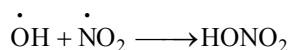
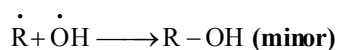
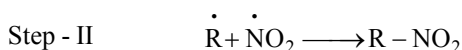
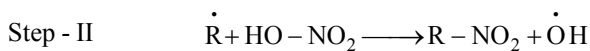
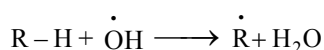
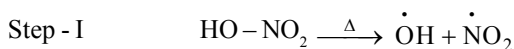
Halogenation is inhibited in presence of oxygen because oxygen reacts with alkyl free radicals to form less reactive peroxy alkyl radical  $\text{R-O-O}^\cdot$  which can not propagate the chain.



- (b) **Nitration** : When a mixture of vapour of alkane nitric acid is heated at high temperature (400°C – 450°C) a mixture of all possible nitroalkanes is obtained (The reaction involves both C–C and C–H bond cleavage).



**Mechanism** : (Free Radical substitution)



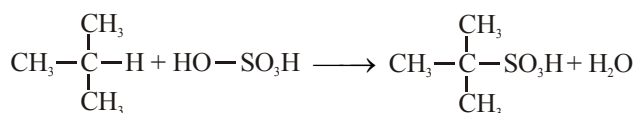
- (c) **Sulphonation** : In this reaction, hydrogen atom of the C–H bond is replaced by –SO<sub>3</sub>H group.



(Fluming) Alkane sulphonic acid

- Fuming H<sub>2</sub>SO<sub>4</sub> = mixture of SO<sub>3</sub> + Conc. H<sub>2</sub>SO<sub>4</sub> = H<sub>2</sub>S<sub>2</sub>O<sub>7</sub> (**Oleum**)
- Alkanes containing 6 or more carbon atom and lower branched alkenes (not lower unbranched) can be sulphonated).

Ex.

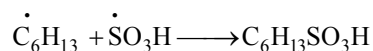
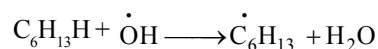
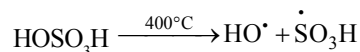


2-Methyl propane

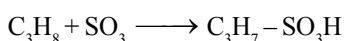
2-Methyl propane-2-sulphonic acid

The reactivity order for sulphonation is tert H > Sec. H > prim. H

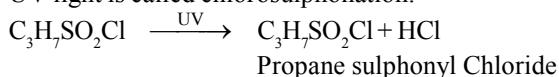
**Mechanism** : (Free Radical substitution)



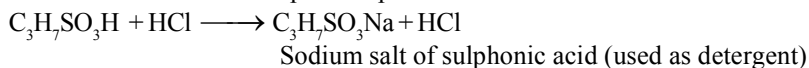
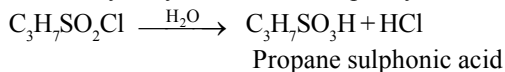
Lower member such as propane, butane, pentane etc. react with SO<sub>3</sub> in vapourphase to form sulphonic acids.



- (d) Chlorosulphonation (**Reed reaction**) : Reactoin with a mixture of  $\text{SO}_2$  and  $\text{Cl}_2$  at ordinary temp. in the presence of UV light is called chlorosulphonation.

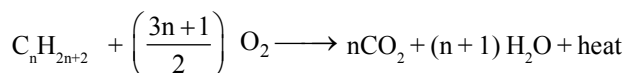


Further hydrolysis of alkane sulphonyl chloride gives alkane sulphonic acid.



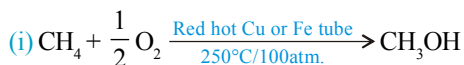
### (3) OXIDATION

(a) **Complete oxidation or combustion** : All alkanes readily burn in excess of air or oxygen to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

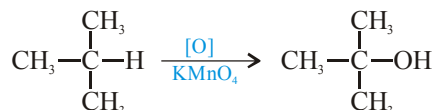


$$\frac{\text{Volume of alkane}}{\text{Volume of oxygen}} = \frac{2}{3n+1}$$

#### (b) Catalytic oxidation

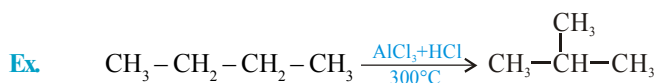


Tertiary alkanes are oxidized to give tertiary alcohols by  $\text{KMnO}_4$ .

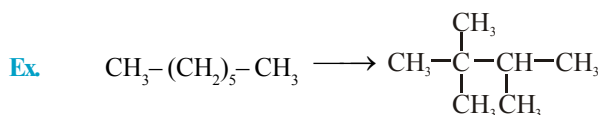


### (4) ISOMERISATION

Straight chain alkanes are converted into their branched chain isomers when heated in the presence of  $\text{AlCl}_3 + \text{HCl}$  at  $300^\circ\text{C}$ .

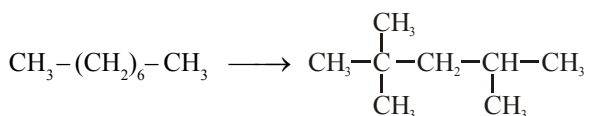


“If we take n-heptane then it converts into highly branched alkane (triptane).”



n-heptane Triptane [2,2,3-Trimethyl butane]

If we take n-octane then it convertes into most stable form iso-octane.

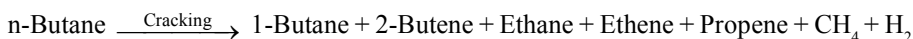
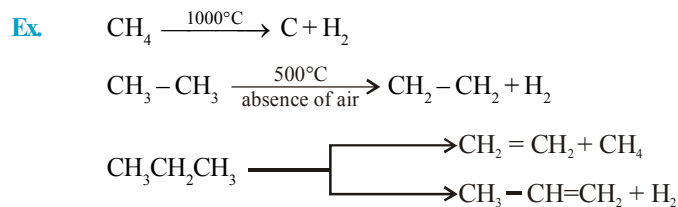


n-Octane iso-octane [2,2,4-Trimethyl pentane]

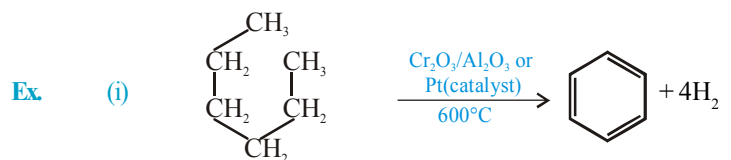
Isomerisation of alkanes is of great importance in petroleum industry to increas the octane number of petrol (gasoline).

**(5) PYROLYSIS OF CRACKING OR THERMAL DECOMPOSITION**

When alkanes are heated to 500–700°C they are decomposed into lower hydrocarbons. This decomposition is called pyrolysis. In petroleum industry it is also termed as cracking. Cracking is used for the manufacture of petrol, petrol gas/oil gas etc.

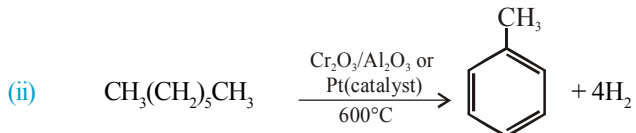

**(6) AROMATIZATION, HYDROFORMING OR CATALYTIC REFORMING**

The conversion of aliphatic compounds into aromatic compounds is referred to as aromatization. Alkanes having six or more carbon atoms are heated at 600°C in the presence of a catalyst such as  $\text{Cr}_2\text{O}_3$  supported over alumina or Pt, an aromatic hydrocarbon results.



n-Hexane

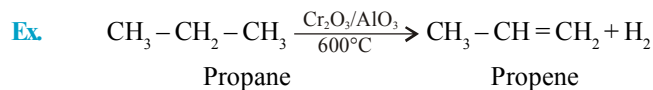
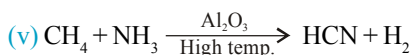
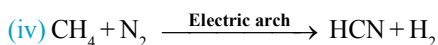
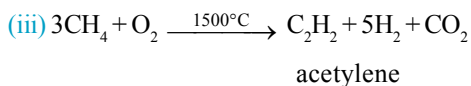
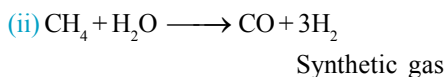
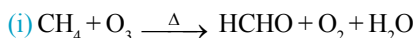
Benzene



n-Heptane

Toluene

Aromatization involves cyclization and dehydrogenation.

**Dehydrogenation**

**(7) SPECIAL PROPERTIES OF  $\text{CH}_4$** 




KEY POINTS

- (i) Methane is also called marsh gas or damp fire.
- (ii) CNG (Compressed nature gas)  $\Rightarrow$  CH<sub>4</sub> + Propane + butane + Higher alkane. 84%.
- (iii) LPG is called as liquified petroleum gas or kitchen gas or domestic gas. (Mixture of liquid propane + liquid butane and other liquid paraffines)  
The mixture of n-butane and isobutane called calor gas.

PRACTICE PROBLEMS

- Q.1** The Kolbe synthesis of alkane using a sodium salt of butanoic acid give –  
 (A) n-hexane                      (B) isobutane                      (C) n-butane                      (D) propane
- Q.2** Electrolysis of an aqueous solution of sodium butanoate gives main product –  
 (A) octane                      (B) heptane                      (C) hexane                      (D) butane
- Q.3** In Wurtz reaction if we take CH<sub>3</sub>Cl & C<sub>2</sub>H<sub>5</sub>Cl then product will be –  
 (A) Propane + Ethane  
 (B) Propane  
 (C) Propane + Ethane + Butane + Ethene + CH<sub>4</sub>  
 (D) Propane + Butane
- Q.4** Butane cannot be obtained by :  
 (A) Action of soda lime on sodium butanoate  
 (B) Clemmensen reduction (Zn amalgam in conc. HCl) of butanone  
 (C) Action of water on butyl magnesium iodide  
 (D) Sabatier Senderens hydrogenation of butene
- Q.5** The reaction condition leading to the best yields of C<sub>2</sub>H<sub>5</sub> are –  
 (A) C<sub>2</sub>H<sub>6</sub> (Excess) + Cl<sub>2</sub>  $\xrightarrow{\text{u.v.light}}$                       (B) C<sub>2</sub>H<sub>6</sub> + Cl<sub>2</sub>  $\xrightarrow{\text{dark room temp.}}$   
 (C) C<sub>2</sub>H<sub>6</sub> + Cl<sub>2</sub> (Excess)  $\xrightarrow{\text{u.v.light}}$                       (D) C<sub>2</sub>H<sub>6</sub> + Cl<sub>2</sub>  $\xrightarrow{\text{u.v.light}}$
- Q.6** C<sub>2</sub>H<sub>6</sub> + SO<sub>2</sub> + Cl<sub>2</sub>  $\xrightarrow{\text{U.V. Light}}$  product. In this reaction product will be –  
 (A) C<sub>2</sub>H<sub>4</sub>                      (B) CH<sub>3</sub>CH<sub>2</sub>Cl                      (C) CH<sub>3</sub>CH<sub>2</sub>SO<sub>2</sub>Cl                      (D) C<sub>2</sub>H<sub>2</sub>
- Q.7** Which of the following should be subjected to Wurtz reaction to obtain the best yield of n-hexane?  
 (A) Ethyl chloride and n-butyl chloride  
 (B) Methyl bromide and n-propyl bromide  
 (C) n-Propyl bromide  
 (D) Ethyl bromide and n-butyl bromide

- Q.8** 2-Methylbutane on reacting with bromide in the presence of sunlight give mainly –  
(A) 1-Bromo-3-methylbutane  
(B) 2-Bromo-3-methylbutane  
(C) 2-Bromo-2-methylbutane  
(D) 1-Bromo-2-methylbutane
- Q.9** Which of the following alkyl bromides may be used for the synthesis of 2,3-dimethylbutane by Wurtz reaction?  
(A) n-Propyl bromide (B) Isopropyl bromide  
(C) Isobutyl bromide (D) s-Butyl bromide

---

**ANSWER KEY**

- |            |     |            |     |            |     |            |     |            |     |
|------------|-----|------------|-----|------------|-----|------------|-----|------------|-----|
| <b>Q.1</b> | (A) | <b>Q.2</b> | (C) | <b>Q.3</b> | (C) | <b>Q.4</b> | (A) | <b>Q.5</b> | (A) |
| <b>Q.6</b> | (C) | <b>Q.7</b> | (C) | <b>Q.8</b> | (C) | <b>Q.9</b> | (B) |            |     |
-

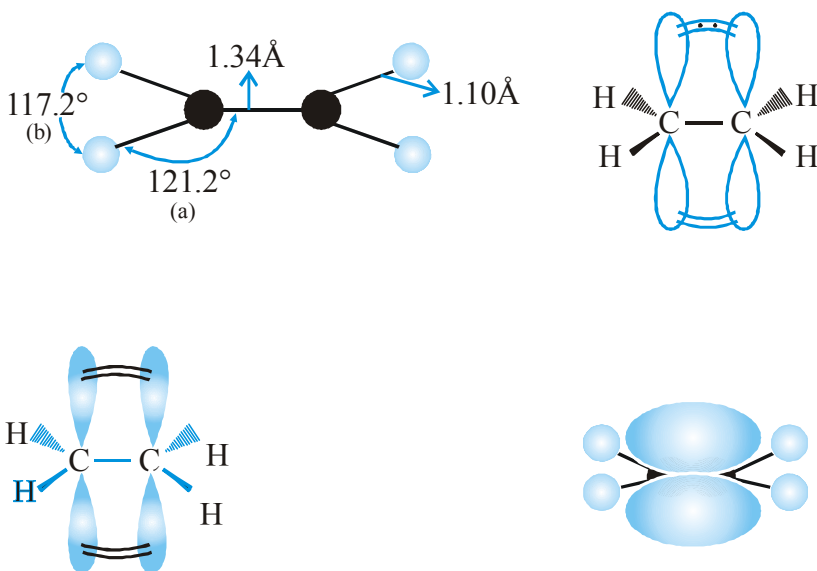
## ALKENE

### 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

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



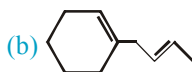
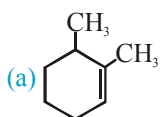
**Note :** That angle  $a < b$  since repulsion due to  $\pi$  electrons (double bond - single bond repulsion  $<$  single bond - single bond repulsion according to VSEPR theory.

## IUPAC Nomenclature alkenes and alkadienes

Table - 1

Sr. No.	Compound	Name	Type
1	$(\text{CH}_3)_2\text{C}=\text{CH}_2$	2-Methylpropane	Alkene
2	$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$	Hexa-1, 4-diene	Isolated diene
3	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	Buta-1, 3-diene	Conjugated diene
4	$\text{CH}_3-\text{CH}=\text{C}=\text{CH}-\text{CH}_3$	Penta-2, 3-diene	Cumulated diene
5		6-Chlorohept-3-ene	Alkene
6		4-methoxypenta-1, 3-diene	Conjugated diene
7		3-Ethynylpenta-1, 4-diene	Isolated diene
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

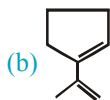
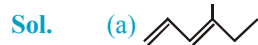
**Ex.** Write IUPAC names of :



**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 IN ALKENES

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

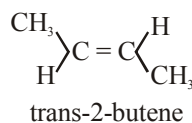
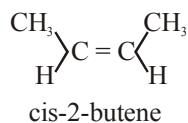
**Ex.** What is relation between  $\text{CH}_3\text{CH}=\text{CH}_2$ ,  $\text{CH}_2-\text{CH}_2$  ?  
 $\begin{array}{c} \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array}$

**Sol.** Ring chain isomerism

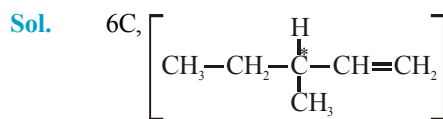
**Ex.** (a)  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$       (b)  $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$       (c)  $\text{CH}_3-\underset{\text{CH}_3}{\text{C}}=\text{CH}_2$       (d)  $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ | \quad | \\ \text{CH}_2-\text{CH}_2 \end{array}$

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



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



3-Methyl-1-Pentene

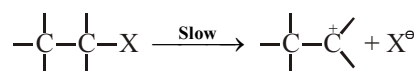
### METHOD OF PREPARATION

#### (I) By Elimination Reaction

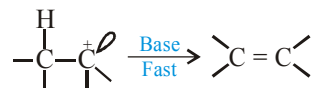
##### E-1 Mechanism

- (a) It is called unimolecular elimination reaction  
 (b) It takes place in two steps.

**Ist Step :** Departure of leaving group from a molecule to form carbocation.



**IInd Step :** Carbocation formed above loses a proton to the base and forms the alkene.



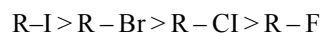
- (c) Ist step of E-1 mechanism is the rate determining step (R.D.S.)  
 (d) Since in R.D.S. only substrate undergoes covalency change  
 i.e. it follows first order kinetics with respect to substrate

$$\text{Rate} = K [\text{substrate}]$$

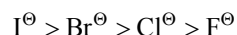
- (e) Since in R.D.S. carbocation is formed as an intermediate to the reactivity order of different substrate follows the stability of order of carbocation formed.

Allylic > Tertiary > Secondary > Primary

- (f) Loss of leaving group is the part of R.D.S. therefore the order of reactivity of alkyl halide in elimination reaction is



Above order is parallel to order of leaving group ability



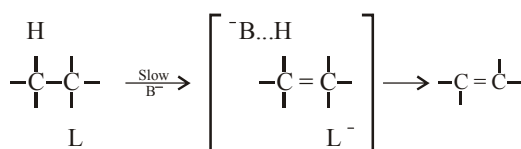
- (g) E-1 mechanism does not show isotopic effect as the loss of hydrogen is not the part of R.D.S.

$$\frac{K_H}{K_D} = 1$$

- (h) Since the ionization take place in step I. Therefore polar solvent favors the E-1 mechanism.  
 (i) E-1 mechanism involves carbocation as an intermediate so rearrangement of carbocation can take place if possible. More stable carbocation forms the major product in the reaction.

### E-2 Mechanism

- (a) It is known as bimolecular elimination mechanism.  
 (b) It take place in single step.  
 (c) It involves the formation of transition state



Transition State

- (d) Formation of transition state is the rate determination step.  
 (e) Rate of reaction depends on the concentration of substrate as well as of base i.e. it follows the second-order kinetics.

$$R = [\text{Substrate}] [\text{Base}]$$

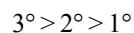
- (f) E-2 mechanism shows the isotopic effect as the loss of hydrogen is a part of R.D.S.

$$\frac{K_H}{K_D} = \frac{7}{1}$$

- (g) E-2 mechanism shows the halogen effect as loss of leaving group is a part of R.D.S.

∴ Reactivity of different alkyl halides follows the sequence

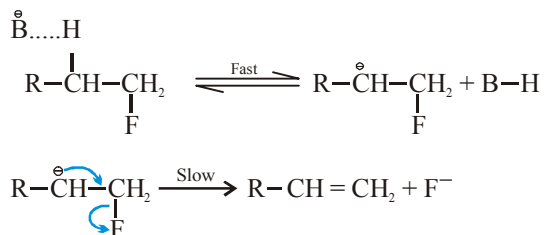
Reactivity order of different substrate follows



- (h) The rate of reaction increases with increasing strength and concentration of the base.  
 (i) Non-polar solvent favors the E-2 mechanism.  
 (j) Since E-2 mechanism involves the transition state rearrangement is not possible.

### E 1 CB Mechanism

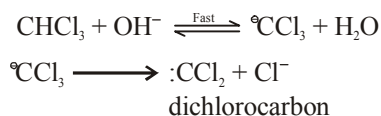
- (a) In this mechanism, the reaction take place in two steps.  
 (i) The first step involves rapid removal of a proton from the  $\alpha$ -carbon (carbon adjacent to the carbon bearing halogen atom) forming a carbanion.  
 (ii) The carbanion formed then loses the halides ion in the second rate determining step.



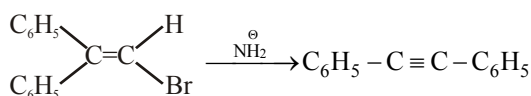
- (b) The overall rate of the reaction is limited to slower second step & hence the rate of reaction depends only on the concentration of carbanion.
- (c) Since carbanion is the conjugate base of the alkyl halide and rate of reaction depends on concentration of carbanion hence the mechanism is designated as E1 cB mechanism.

### Mechanism of $\alpha$ -Elimination

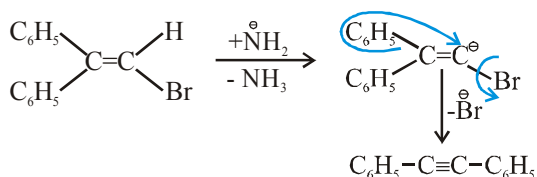
$\alpha$ -elimination does not occur frequently and completes in two stages, the second of which is rate determining. for eq.



Another example of  $\alpha$ -elimination of reactants formation of diphenylacetylene from 2, 2-diphenyl vinyl bromide and sodalime.



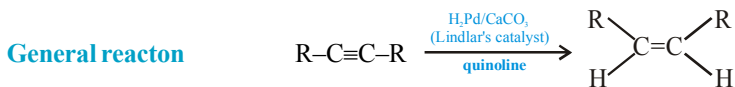
### Mechanism



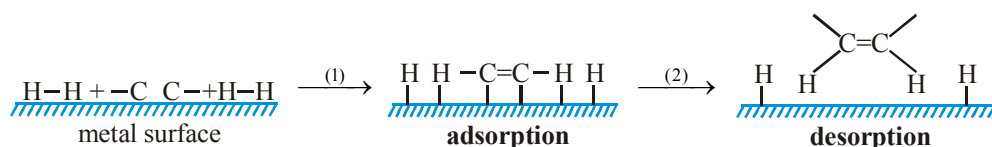
## (II) HYDROGENATION OF ALKYNE

### By partial reduction of Alkynes

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



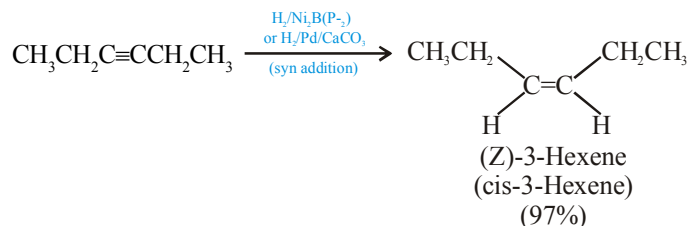
### Mechanism of hydrogenation



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

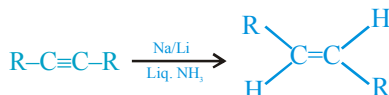
In this state, the reactants lie very close to each other and so the hydrogen atoms start forming bond with carbon. Two hydrogen atoms are added to two triply bonded carbon atoms from the same side of  $\pi$  bond and a **cis or syn addition product** is formed. The product alkene now escapes away from 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.

**Ex.**

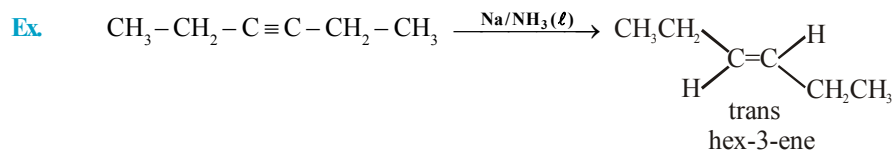
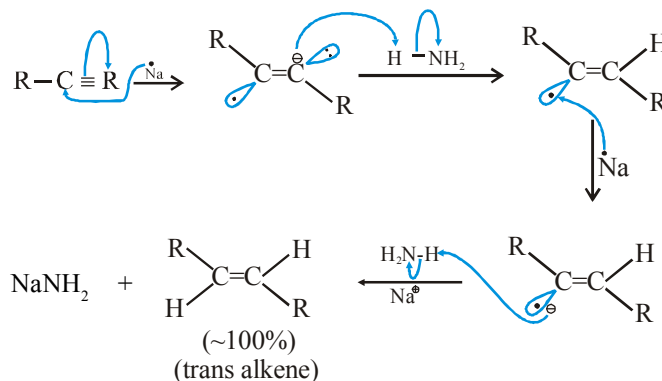


(b) **Birch Reduction** : (Anti addition of hydrogen : synthesis of trans-alkenes)

**General reaction**

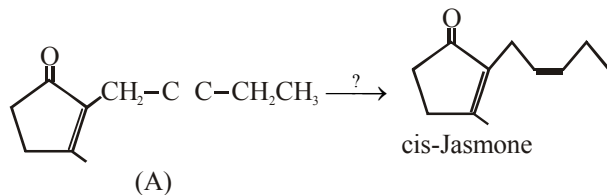


**Mechanism** : Reagents Na (or Li, K) + liq  $\text{NH}_3 \rightarrow \text{Na}^+ + \text{e}^-$  (solvated electron)

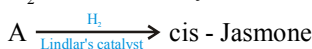


**Note :** This process of reduction is not eligible when terminal alkynes are taken ( $\text{R}-\text{C}\equiv\text{CH}$ ) because terminal alkynes form sodium salt with Na metal.

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



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

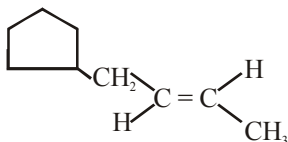




**Ex.** Identify the product in the following reaction :

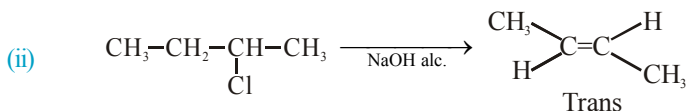
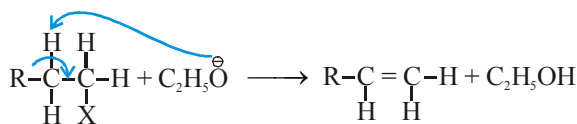
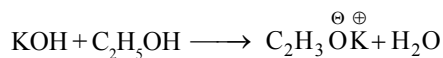
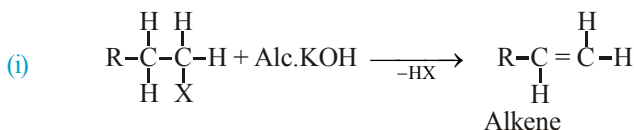


**Sol.**

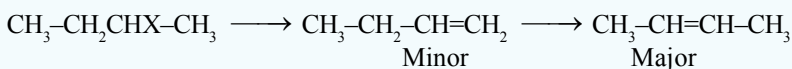


**(III) FROM ALKYL HALIDES**

**FROM MONO HALIDES :** When mono halide react with alcoholic KOH or NaOH then respective alkenes are formed



**KEY POINTS**

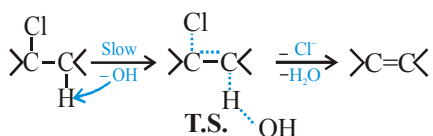


$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$  (Trans) is the major product because it is more stable as having six 'a' Hydrogen in the comparison to  $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$  having only two 'a' hydrogen.

This is in accordance with the saytzeff rule.

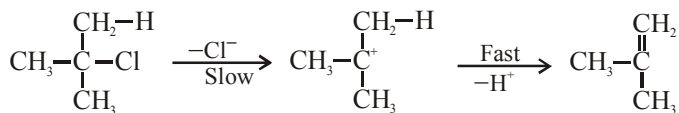
**Mechanism :**  $\text{E}_2$  and  $\text{E}_1$  are possible.

**$\text{E}_2$  Mechanism**



As molecularity of slowest step is two i.e.  $\text{E}_2$  mechanism.

**$\text{E}_1$  Mechanism**



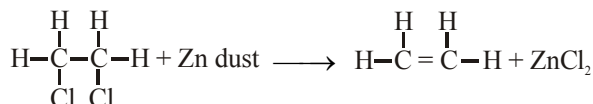
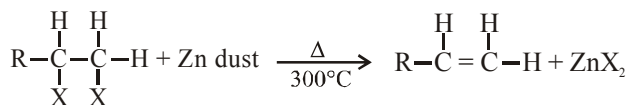
As molecularity of slowest step in one. That is why it is termed as  $E_1$ .

**Remember** : Possibility of  $E_1$  increases with increasing stability of carbo cation. Similarly possibility of  $E_2$  increases with decreasing stability of expected carbocation.

### From Dihalides

#### From vicinal dihalides

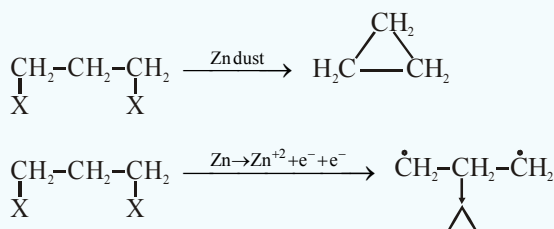
When vicinal dihalides are heated with Zn dust, alkene of same no. of carbon is obtained.



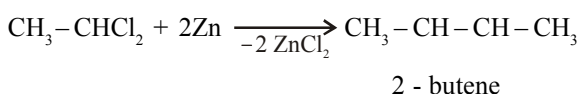
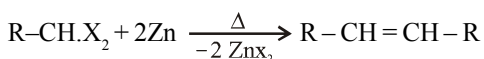
### KEY POINTS

Alkene is not formed from 1, 3 dihalides. Cyclo alkanes are formed by dehalogenation of it.

For ex.



**From gem dihalides** : When gem dihalides is heated with Na in ether then higher alkenes are formed.

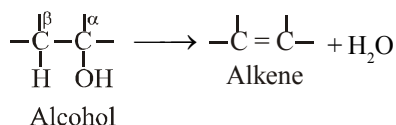


**Conclusion** – If we take two different types of gemdihalides then we obtain three different types of alkenes.

**Note** : The above reactin is used in the formation of symmetrical alkenes only because if we take two different types of halides then mixture of alkenes is obtained so the yield of are individual alkene is reduced and is improper to separate each alkene from the mixture because the difference of boiling points in alkenes is very less.

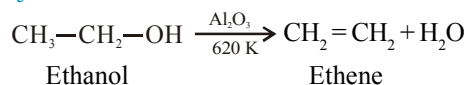
### (IV) FROM ALCOHOLS :

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**.

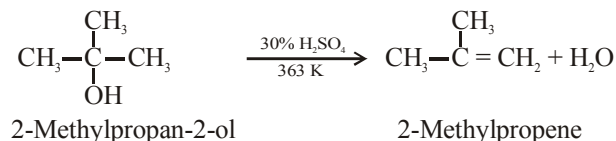
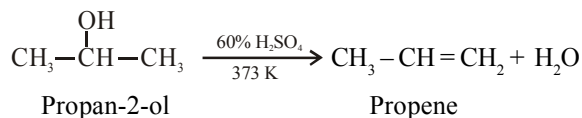
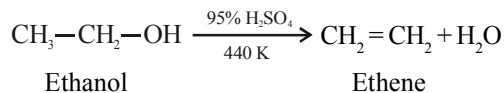


The dehydration can be carried with  $\text{Al}_2\text{O}_3$  or with **mineral acid** upon heating.

**(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.



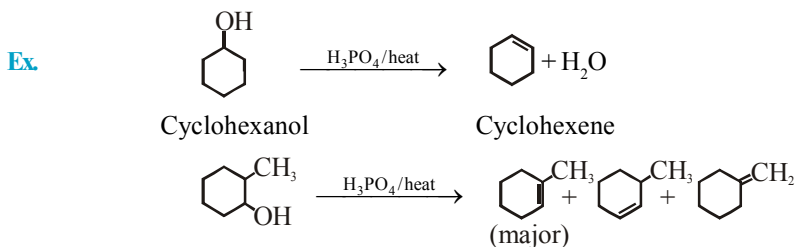
**(b) Dehydration with mineral acid :** Alcohols upon heating with conc.  $\text{H}_2\text{SO}_4$  form alkenes and the reaction is called **acidic dehydration**.



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

Tertiary > Secondary > Primary

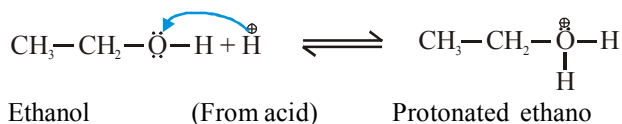
Cycloalkenes can be prepared in the same way by the dehydration of cycloalkanols.



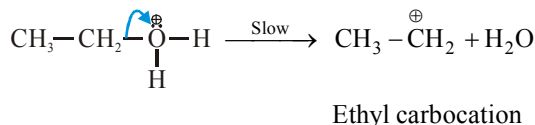
Regioselectivity of  $\beta$  elimination is governed by Zaitsev's Rule.

**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.

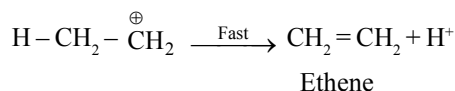


**Step - II :** Due to presence of positive charge on electronegative oxygen, its electron accepting tendency increases. As a result C – O bond becomes weak and cleaves as follows :



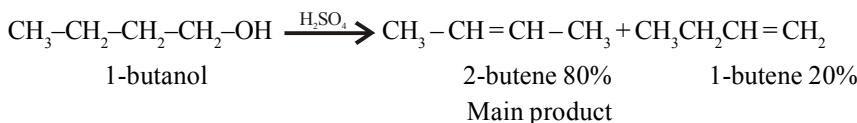
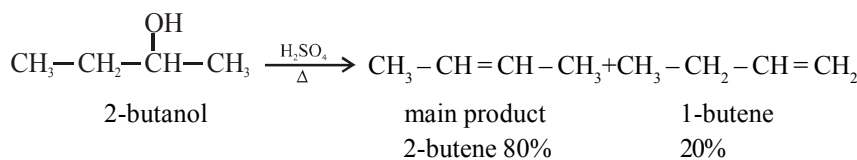
This is a slow and is regarded as rate determining step.

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

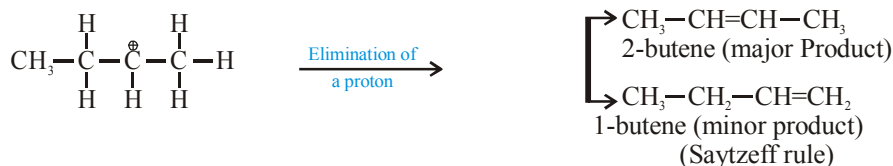
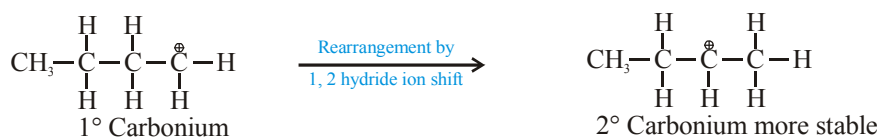
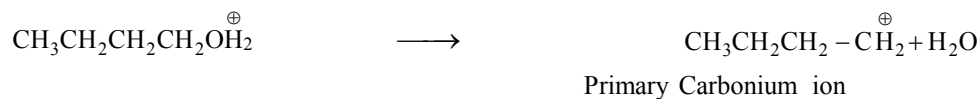
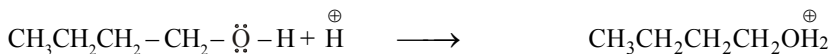


**Note :** Dehydration of secondary and tert alcohol is best carried out by using dil.  $\text{H}_2\text{SO}_4$ . Since alkenes produced from those alcohols have a tendency to form polymers under the influence of concentrated acid.

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



**Mechanism** : Acid catalyzed dehydration of alkanols proceeds via the formation of more stable carbonium ion.

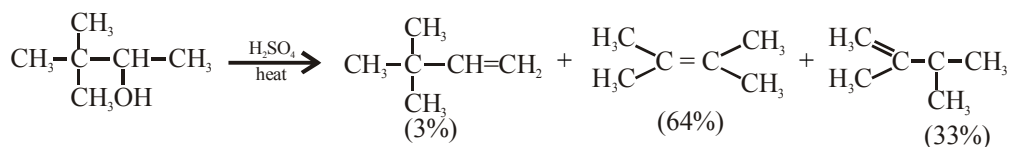


### Characteristic of dehydration of alcohol

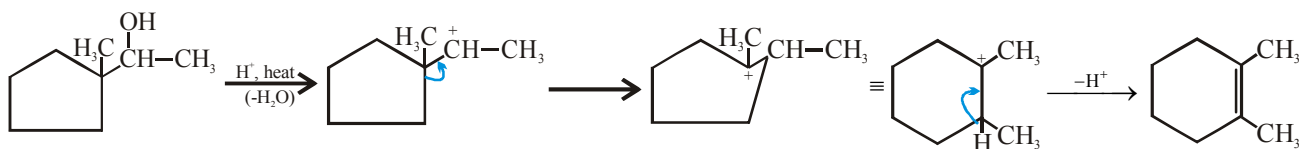
- Since the carbocation is formed as an intermediate in the R.D.S. of dehydration of alcohol the relative reactivity of alcohols decreases in the order.  
Tertiary > Secondary > Primary
- Since the R.D.S. is reversible it is necessary to remove the H<sub>2</sub>O molecule produced in the reaction. Therefore in experimental condition conc. H<sub>2</sub>SO<sub>4</sub> is added in a regular interval.
- For dehydration, different dehydrating agent like Al<sub>2</sub>O<sub>3</sub>, ThO<sub>2</sub> etc. also be employed.
- Rearrangement of carbocation can take place.
- OH is not a good leaving group. In alcohols so turn it into a good leaving group, it is converted into H<sub>2</sub>O by protonation.
- H<sub>2</sub>O is a good leaving group.

### Rearrangement in Alcohol Dehydration

- Some alcohols undergo dehydration to form alkene having carbon skeleton different from those of the straight alcohol.
- This is due to rearrangement of carbocation formed in the reaction to more stable carbocation.
- An example of alcohol dehydration that is accompanied by rearrangement is.

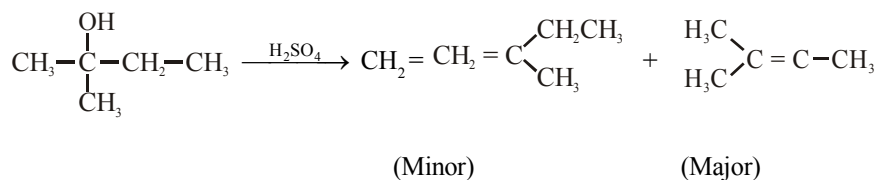


- (4) Percent yield of alkenes formed from rearranged carbocation is greater than the percent yield of alkene obtained from unrearranged carbocation.
- (5) Rearrangement of carbocation can also lead to a change in ring size, as the following example shows



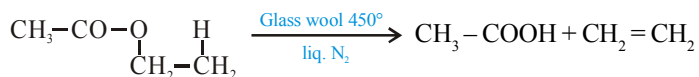
### Regioselectivity in alcohol dehydration

- In alcohols such as 2-methyl-2-butanol, dehydration can occur in two different directions to give alkenes that are constitution isomers.
- More substituted alkene forms the major product and is called Saytzeff alkene or Zaitsev alkene.
- Less substituted forms the minor product and is called Hofmann's alkene.



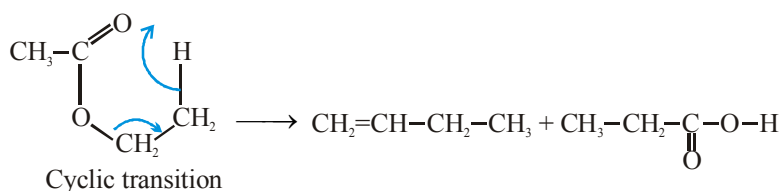
### (V) FROM ESTERS

When esters are heated in presence of liq.  $\text{N}_2$  and glass wool, then alkyl part of ester converts into respective alkene while alkanooate part of ester is converted into respective acid.

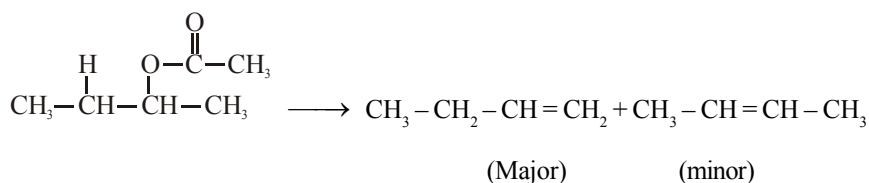


The reaction is called as 'Pyrolysis of Ester.'

**Mechanism** : Pyrolysis of Ester is a type of  $\text{E}_1$  elimination which proceeds via *cyclic T.S.* that is why the product becomes 'cis'.



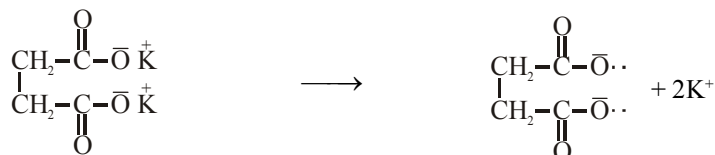
It is interesting to note that, in this case major product is 1-alkene in the comparison to 2-alkene.



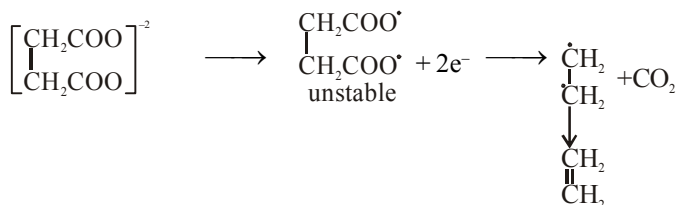
Major product is obtained by removal of  $-\text{H}$  from less hindered carbon.

## (VI) KOLBE'S SYNTHESIS

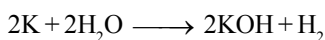
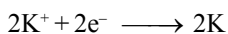
When aqueous solution of K or Na succinate is electrolysed, ethylene is released at anode.



## At Anode

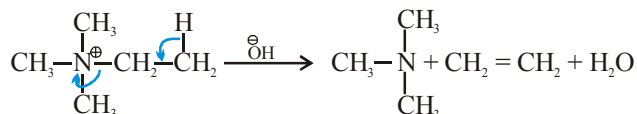


## At Cathode

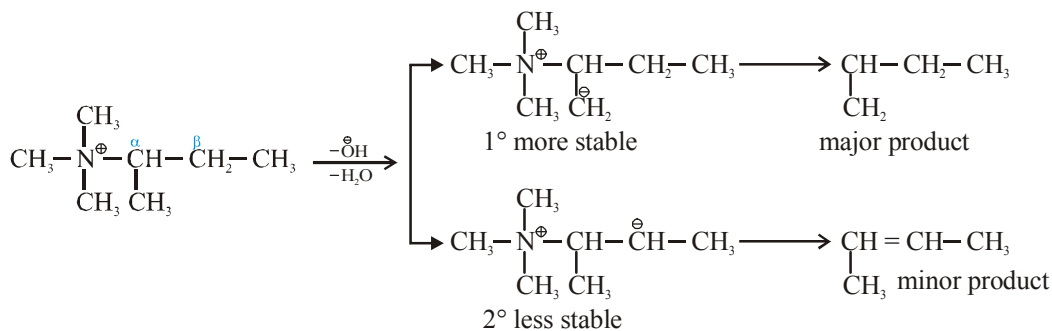


**Note :** If we use methyl succinic acid as reactant then propylene is formed.

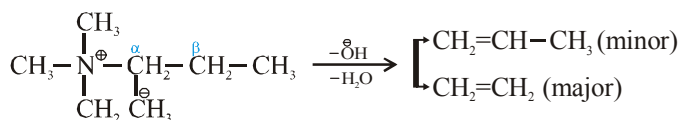
## (VII) FROM QUATERNARY AMMONIUM HYDROXIDE



**Ex.**



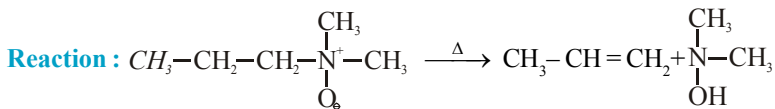
**Ex.**



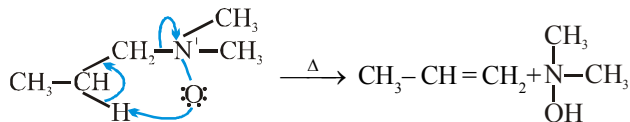
- (a) In this reaction  $\beta$ -hydrogen of tetra-alkyl ammonium ion is attached by a base and alkene is formed.  
 (b) In this reaction intermediate is carbanion. So yield of product depends on stability of carbanion.  
 (c) In this reaction Hoffmann's Rule is followed.

**(VIII) THE COPE ELIMINATION**

Tertiary amine oxide undergoes the elimination of a dialkylhydroxyamine when they heated. This reaction is called the Cope elimination.

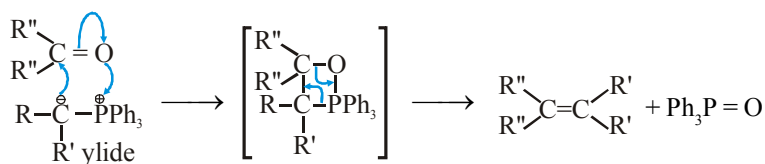


**Mechanism :**

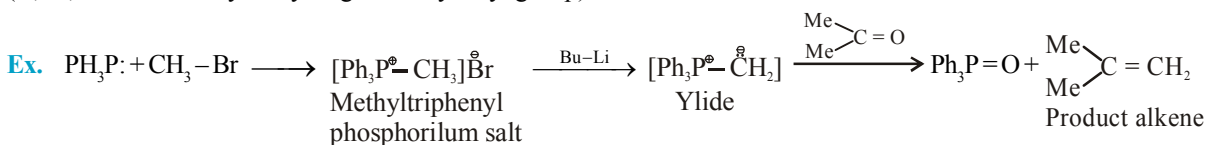

**(IX) WITTING REACTION**

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 cycli c transition state forming an alkene.



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


**PHYSICAL PROPERTIES OF ALKENES / HYDROCARBON**

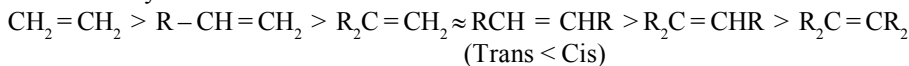
	Physical properties	Homologus series	Isomers
1.	Physical state	C <sub>1</sub> - C <sub>3</sub> gases C <sub>4</sub> - C <sub>20</sub> liquids > C <sub>20</sub> : solids	
2.	Dipolemoment (μ)		cis > trans
3.	Polarity	-	cis > trans (fro C <sub>ab</sub> = C <sub>ab</sub> type of alkenes)
4.	Melting point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

**CHEMICAL PROPERTIES OF ALKENES**

Alkenes are more reactive than alkane this is because –

- (a) The  $\pi$  electrons of double bond are located much far from the carbon nuclei and are thus less firmly bound to them.  
 (b)  $\pi$  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

- (i) Steric hinderence  
 (ii) Hyperconjugation  
 (iii) Heat of Combustion.

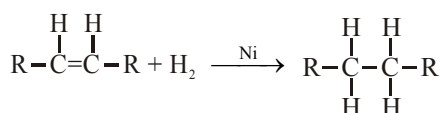
All four butenes may be compared, since all give the same products on combustion viz.  $4\text{CO}_2 + 4\text{H}_2\text{O}$

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

- (1) Addition reaction                      (2) Oxidation reaction                      (3) Ozonolysis  
 (4) Substitution reaction                      (5) Polymerization Reaction                      (6) Isomerisation

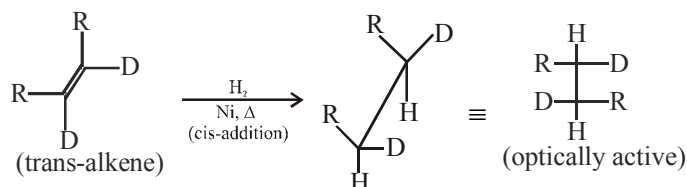
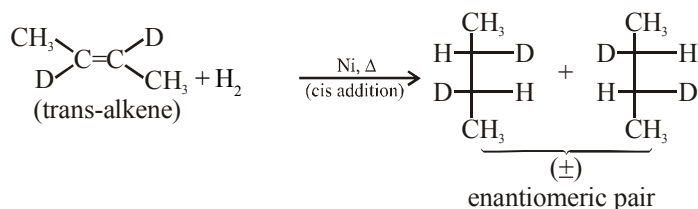
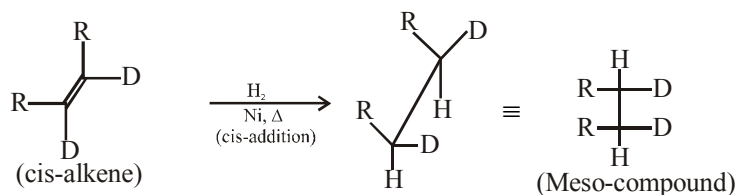
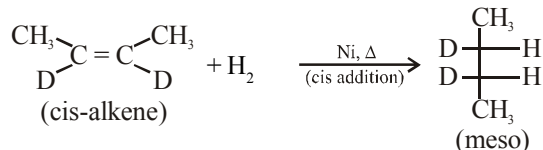
**(1) Addition Reaction**

**(a) REACTION WITH HYDROGEN –**



**Mechanism :** The reaction takes place at the surface of Ni, therefore the addition is cis addition.

**Ex.**





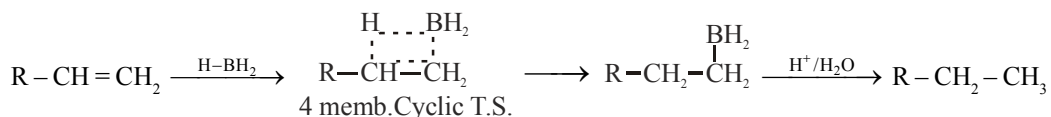
**KEY POINTS**

Hydrogenation (catalytic hydrogenation) of alkene is a cis addition and is an exothermic reaction. Thus the heat evolved decreases with increasing stability of alkene.

**Remember :** Stability of alkene depends upon hyperconjugation and type of geometrical isomerism

**Reduction of alkene via hydroboration**

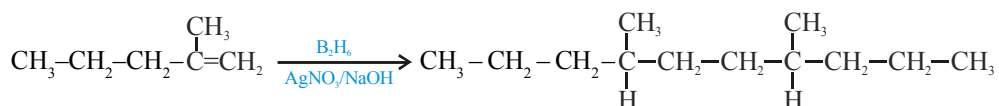
(i) Alkene can be converted in to alkane by hydroboration follwed by protolysis



This reaction is also represented as

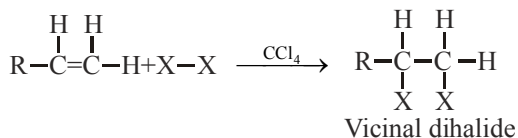


(ii) Alkene can be converted into alkane by hydroboration followed by treatment with  $AgNO_3 + NaOH$ .



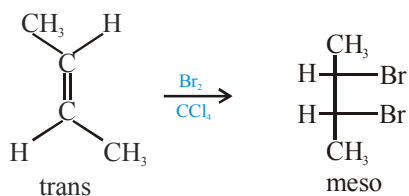
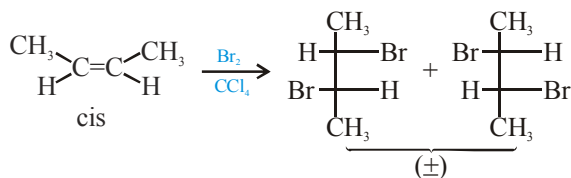
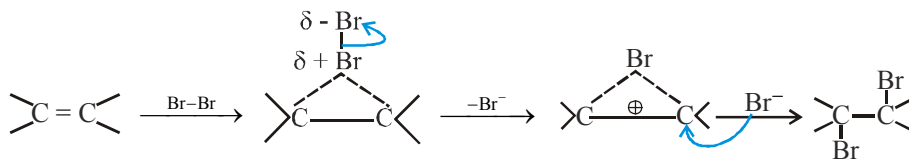
**(b) HALOGENATION**

In presence of polar of medium alkene form vicinal dihalide with halogen.



Order of reactivity of halogens is :  $F_2 > Cl_2 > Br_2 > I_2$

**Mechanism :** It is an electrophilic addition by molecular attack in which the addition takes place in trans manner.

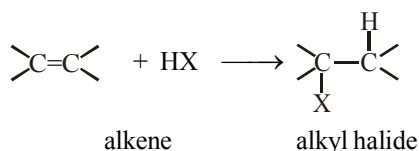


## KEY POINTS

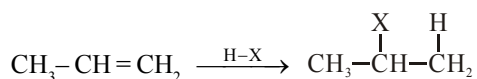
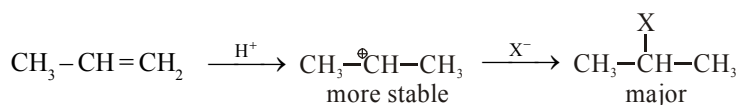
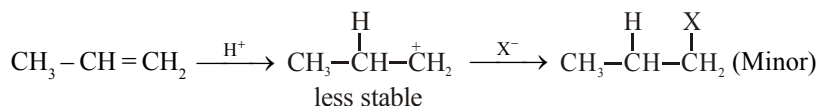
For suitable condition

- (i) Cis addition on cis form results meso
- (ii) Cis addition on trans form results ( $\pm$ )
- (iii) Trans addition on trans form results ( $\pm$ )
- (iv) Trans addition on trans form results meso.

## (c) REACTION WITH HX (HYDROHALOGENATION)

**Markovnikoff's Rule**

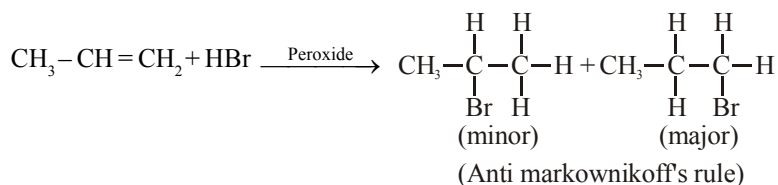
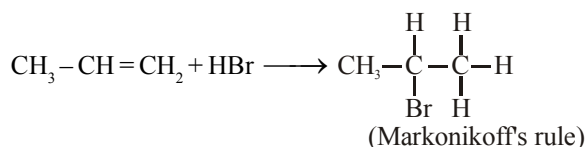
When an unsaturated unsymmetrical hydrocarbon reacts with HX then halogen goes on that unsaturated carbon which has minimum number of hydrogen atom. Mechanism of the reaction is based on  $-\text{C}^+$ .

**Mechanism**

- (i) Formation of Carbocation is Rate determining step.
- (ii) Rearrangement of carbocation to more stable carbocation can occur to form a more stable product.
- (iii) Regiochemistry - Markownikoff's Addition of HX.  
Addition of HX on unsymmetrical alkenes ( $\text{R}-\text{CH}=\text{CH}_2$ ) takes place according to Markownikoff's rule which states that, "the negative part of addendum is added on the carbon atom carrying lesser number of hydrogen atoms."
- (iv) Reactivity order of different hydrogen halide towards addition.  
 $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$

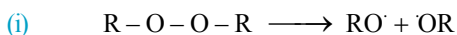
**Anti Markownikoff's Principle / Kharash Effect/ Peroxide Effect**

To understand antimarkownikoff's principle let us consider the following reactions

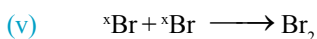
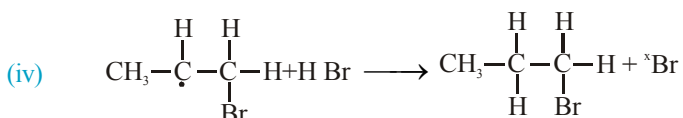
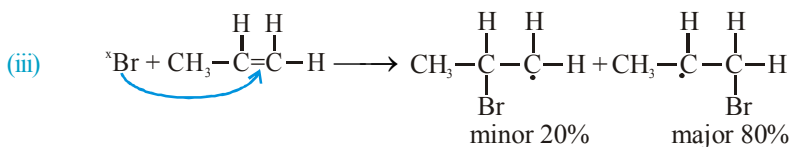


It is based on free radical mechanism.

(a) **Mechanism Concept –**

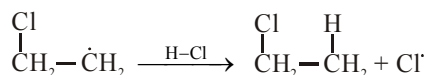


Peroxide



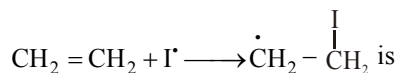
**Note:** It is interesting to note that anti markovnikov addition in the presence of peroxide is not applicable for HCl and HI

(i) In the case of H-Cl, the step



is endothermic (as  $\Delta H^\circ = +12.6 \text{ KJ mol}^{-1}$ )

(ii) In the case of H-I, the step

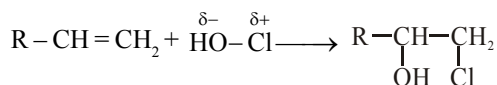


endothermic (as  $\Delta H = +46 \text{ KJ mol}^{-1}$ )

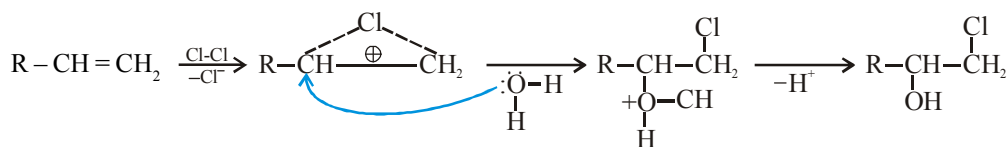
But in the case of HBr both of the steps are exothermic, which results spontaneous reaction

–  $CCl_4$ ,  $CBrCl_3$  etc. can also be added to alkene in anti markovnikov manner.

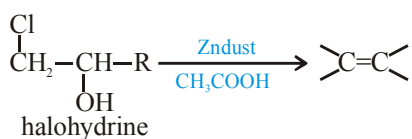
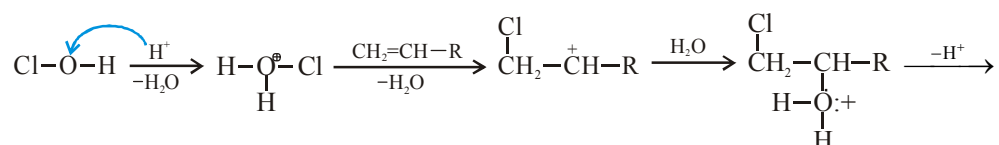
**(d) REACTION WITH HYPOHALOUS ACID –**



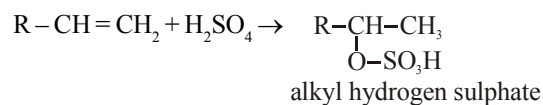
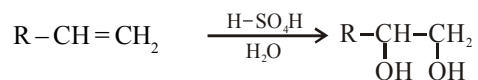
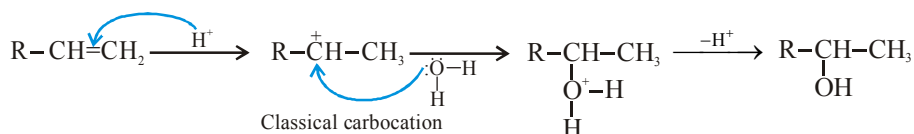
(i) When chlorine water or bromine water is used.



(ii) When aq. solution of HOCl is added in the presence of strong acid.

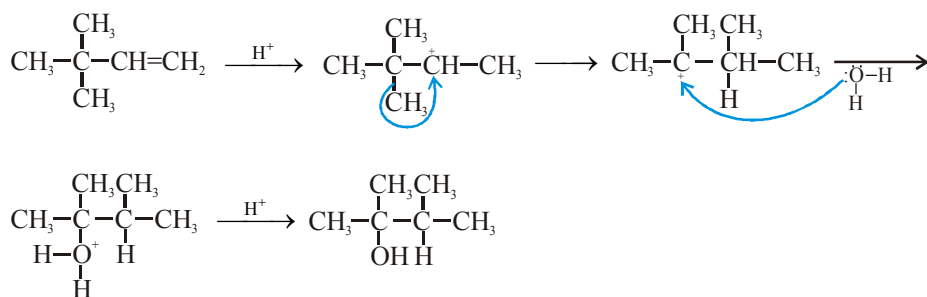


**(e) REACTION WITH H<sub>2</sub>SO<sub>4</sub> –**

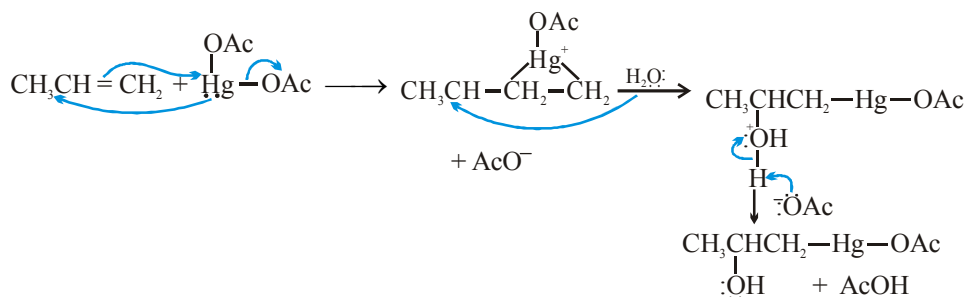
 (a) With conc. H<sub>2</sub>SO<sub>4</sub>

 (b) With dil. H<sub>2</sub>SO<sub>4</sub>

**Mechanism**


The hydration of alkene is not stereoselective, as in the case of HCl addition. This fact can be explained on the basis of classical carbon cation formation.

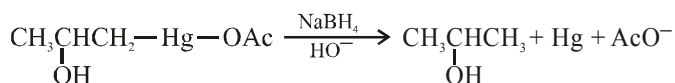
Since hydration proceeds via carbocation intermediate therefore rearrangement is always probable.



Rearrangement, however, may be avoided by treatment of alkene by *oxymercuration-demercuration method*.

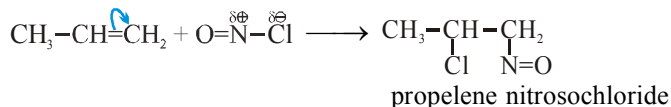
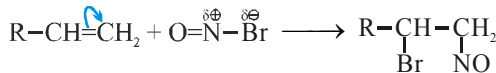
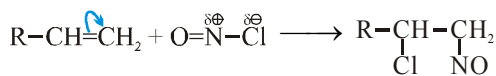


Sodium borohydride (NaBH<sub>4</sub>) converts the carbon-mercury bond into a carbon-hydrogen bond. Because the reaction results in the loss of mercury, it is called demercuration.

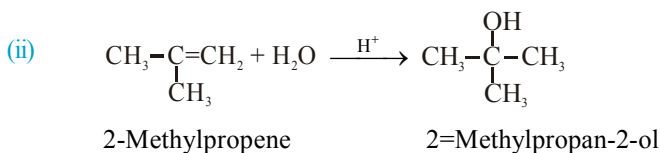
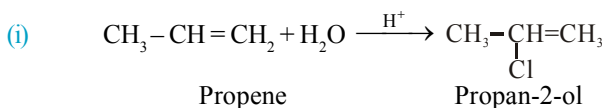


**(f) ADDITION OF NITROSYL HALIDE –**

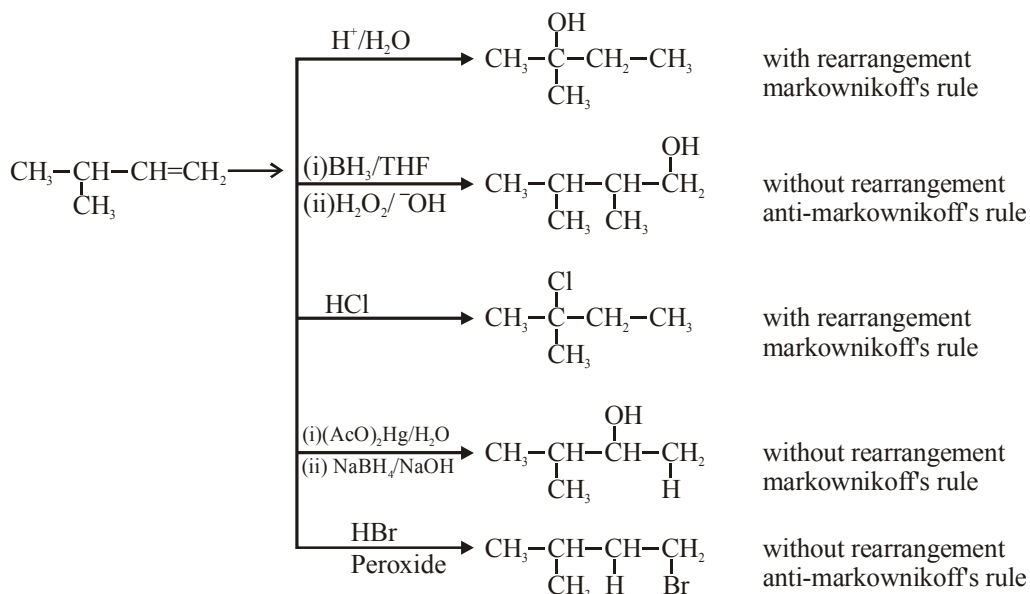
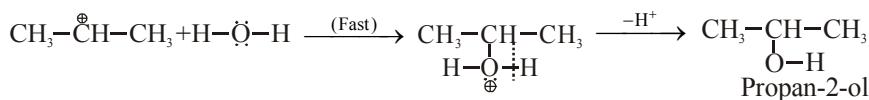
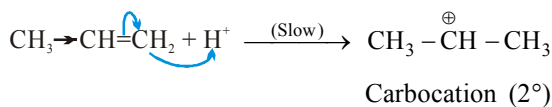
Alkene with nitrosyl bromide or nitrosyl chloride (Tilden reagent) react according to Markowinkoff's rule to give alkene nitrosobromide and alknene nitrosochloride respectively.



**(g) 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.

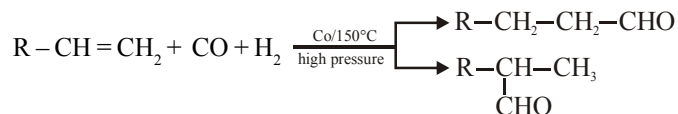


**Mechanism**

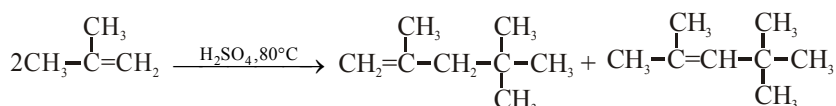


**(h) HYDROFORMYL OR OXO REACTION** : Alkenes react with Carbon monoxide and hydrogen at 100 - 150°C temperature and high pressure (1200 atm) in the presence of Cobalt catalyst to produce an aldehyde. It does not follow Markovnikov's rule.

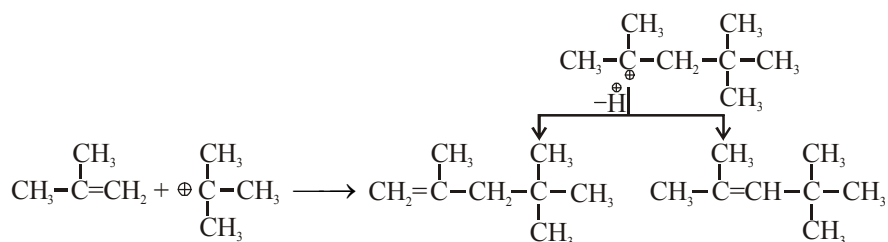
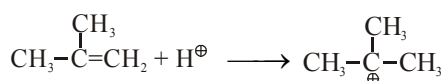
The net reaction is the addition of a H-atom to one of the Olefinic bond and a formyl (-CHO) group to the other.



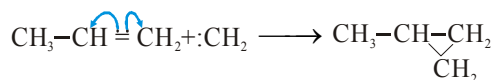
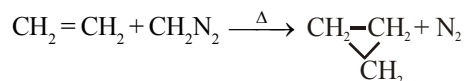
**(i) ALKENYLATION (ADDITION OF ALKENE)** In presence of  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$  at 80°C dimerisation of isobutylene takes place giving two isomers of octene.



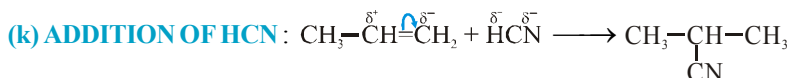
**Mechanism**



**(j) ADDITION OF CARBENE** : The addition of carbene to alkene is always carried by diazomethane  $\text{CH}_2\text{N}_2$ . Carbene group obtained from diazomethane is added to alkene and gives cycloalkanes.



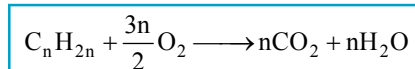
**Since** :  $\text{CH}_2$  is an electrophilic (neutral) and there is more electron density on double bond so first attack of  $\text{:CH}_2$  will be at double bond.



**(2) Oxidation Reaction :**

Alkenes are easily oxidised by oxidising agents. Oxidising agents attack on double bond and product formed during oxidation depends on oxidising agents.

**(a) ALKENE ON COMBUSTION GIVES  $\text{CO}_2$  AND  $\text{H}_2\text{O}$**



one mole of alkene requires  $\frac{3n}{2}$  moles of  $\text{O}_2$  for complete combustion.

## CHEMISTRY FOR JEE MAIN & ADVANCED

**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.

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

**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.

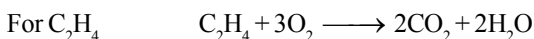
$\therefore$  for 1 mole of Alkene,  $\frac{3n}{2}$  mole of  $\text{O}_2$  is required for combustion.

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

**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 2 volume  $\text{C}_4\text{H}_8$ , 6 volume of  $\text{O}_2$  is required.

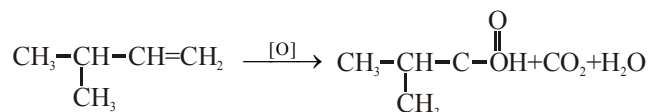
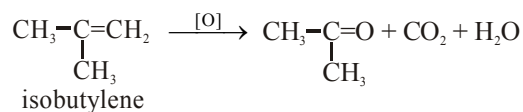
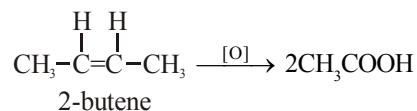
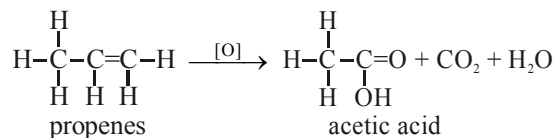
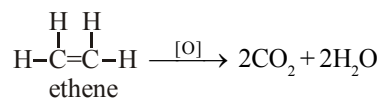
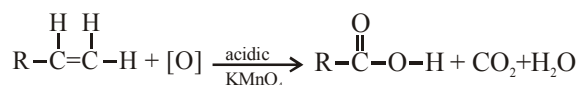
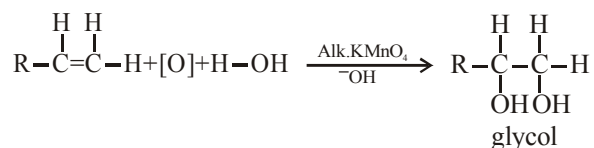
$\therefore$  for  $(30-x)$  mL " " , 6  $(30-x)$  mL of  $\text{O}_2$  is required.

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

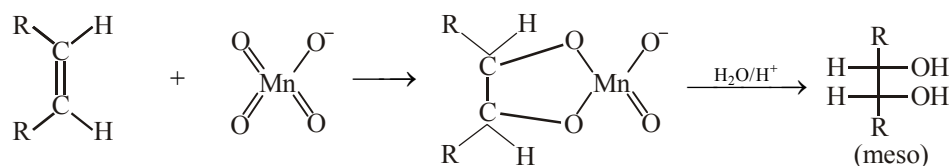
$$x = 10$$

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

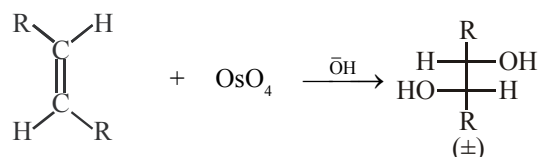
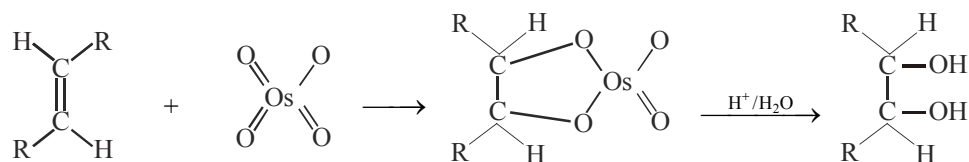
$\therefore$  Volume of  $\text{C}_4\text{H}_8$  in mixture is 20 mL

(b) WITH ACIDIC  $\text{KMnO}_4$  / HOT  $\text{KMnO}_4$ 

 (c) WITH ALKALINE  $\text{KMnO}_4$  / BAYER'S REAGENT


**Mechanism** : Hydroxylation by alkaline  $\text{KMnO}_4$  (Bayer's reagent) is cis addition and the mechanism is cyclic.

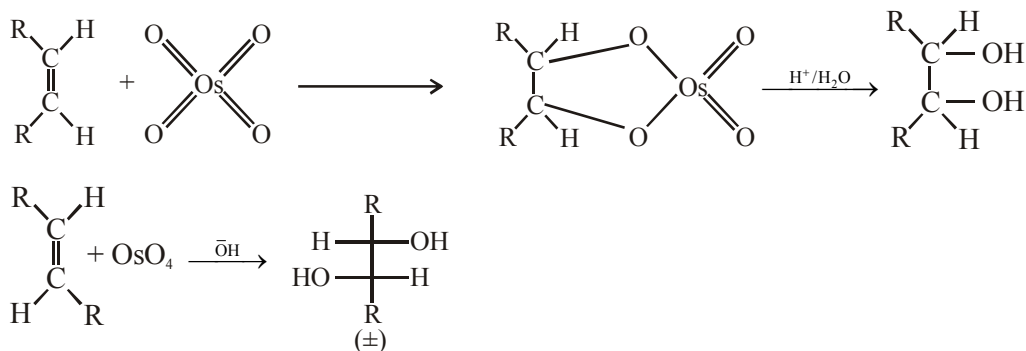


Similarly





(d) **HYDROXYLATION BY OSO<sub>4</sub>**

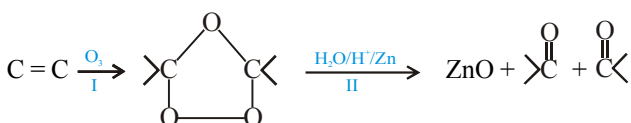


(3) **Ozonolysis**

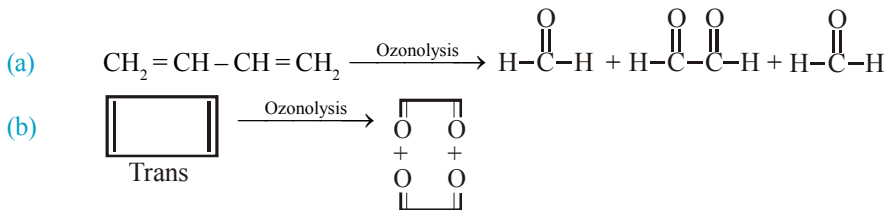
This is the two step reaction

(i) Ozonide formation

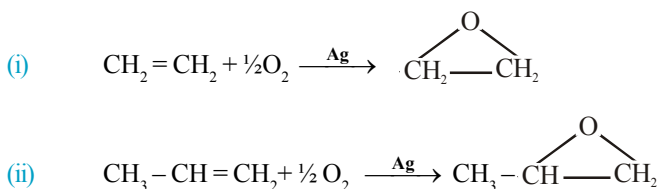
(ii) decomposition of ozonide (reductive hydrolysis)



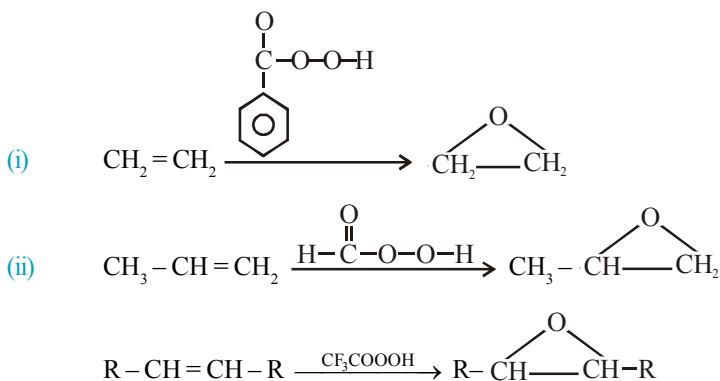
**Remember** : Ozonolysis gives oxidative cleavage of alkene to form two arbonyl group for each  $\text{>C}=\text{C}<$ . Whether it is in acyclic or cyclic or in aromatic compound. eg :-



**Epoxidation by O<sub>2</sub>/Ag**

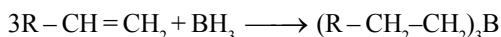


**Epoxidation by per acid**

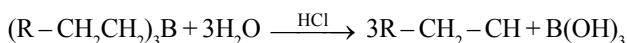


### Hydroboration

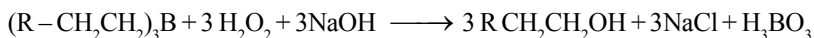
Alkene with borane hydride form an important compound called trialkyl borane.



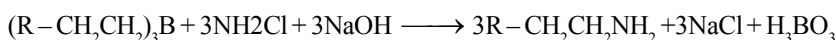
- (a) Trialkyl borane is an important compound because it gives respective alkane on acidic hydrolysis.



- (b) It gives respective alcohol on alkaline hydrolysis



- (c) It gives 1° amine on alkaline hydrolysis with chloramine



- (d)  $(R-CH_2CH_2)_3B \xrightarrow[NaOH]{AgNO_3} 3R-CH_2-CH_2-CH_2-CH_2-R$

- (e) In the overall hydroboration-oxidation reaction, three moles of alkene react with one mole of  $BH_3$  to form three moles of alcohol.

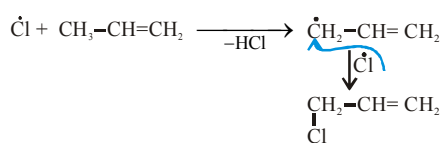
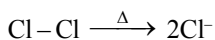
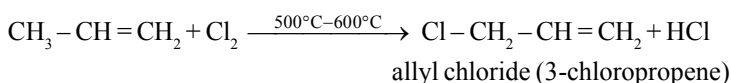
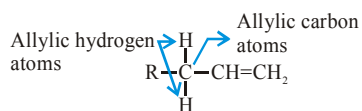
- (f) Because carbocation intermediates are not formed in the reaction carbocation rearrangements do not occur.

- (g) Regiochemistry Anti-Markovnikov's Addition of water.

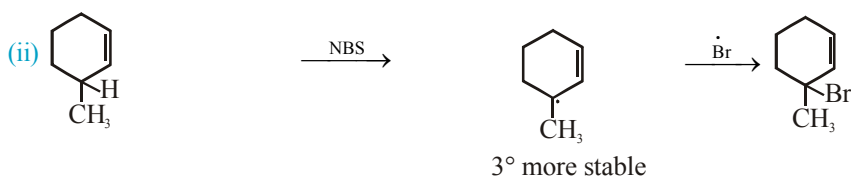
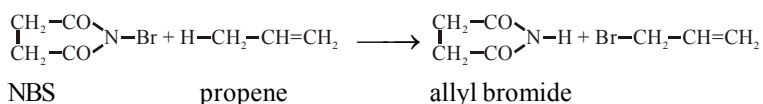
- (h) Alkyl boranes undergo coupling by means of silver nitrate in the presence of NaOH at 25°C. Higher alkanes are the products of this reaction.

### (4) Substitution Reaction

- (a) Except ethene other higher alkene having alkyl hydrogen when treated with chlorine or bromine 'α' H is substituted.



- (b) Allylic bromination can be easily done by NBS (N-bromo succinamide)



## CHEMISTRY FOR JEE MAIN & ADVANCED

### (5) Polymerization

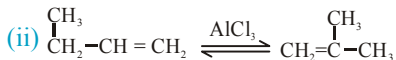
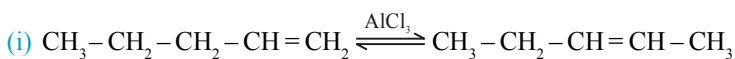
- (i) Two or more than two molecules of same compound unit with each other to form a long chain molecule with same empirical formula. This long chain molecules having repeating structural units called polymer, and the starting simple molecule as monomer and process is called addition polymerization.
- (ii) Molecular weight of polymer is simple multiple of monomer.
- (iii) The presence of oxygen initiates free radical mechanism.
- (iv) Addition polymerization can also be carried out by ionic mechanism by using Ziegler - Natta Catalysts ( $R_3Al + TiZl_4$ )

Name of polymer	Structure of monomer	Structure of Polymer	Properties	Uses Properties
1. Polyvinyl chloride (PVC)	$CH_2=CH-Cl$	$\left( H_2C-\underset{\text{Cl}}{\text{HC}} \right)_n$	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 inert to solvents, boiling acids, even quaregia stable upto 598K.	For making non-stick utensils coating
3. Natural rubber	$CH_2=CH-\underset{\text{isoprene}}{\overset{\text{CH}_3}{\text{C}}}=CH_2$		Waxy and non-elastic	Used as raw material for making vulcanised fubber which is strong and elastic vulcanised rubber is used in making tyres hose, pipes etc.
4. Orlon	acrylonitrile	$\left( H_2C-\underset{\text{CN}}{\text{HC}} \right)_n$	Fibrous	Used in making Fabrics
5. Poly methyl methacrylate (PMMA)	$CH_2=\underset{\text{Methyl methacrylate}}{\overset{\text{CH}_3}{\text{C}}}-\text{COOCH}_3$	$\left( CH_2-\underset{\text{OCH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{C=O} \right)_n$		

### (6) Isomerisation

Alkenes isomerise when heated at high temperature or at lower temperature in the presence of various catalysts as  $AlCl_3$ .

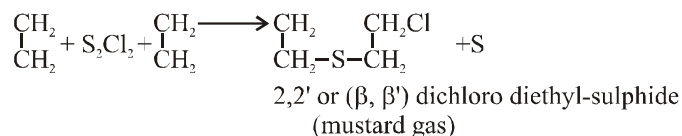
**Ex.**



the mechanism proceeds through carbocation

#### Uses

- (a) In plastic formation.
- (b) In oxy ethylene welding
- (c) As food preservatives and ripening fruits.
- (d) As general anaesthetic ( $C_2H_4$  with 8-10%  $O_2$ )
- (e) In preparation of mustard gas

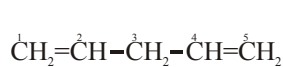


Functional Group	Reagent	Observation	Reaction	Remarks
$\begin{array}{c} \diagup \\ \text{C} = \text{C} \\ \diagdown \end{array}$	(1) Bayer's Reagent alk. dil. cold $\text{KMnO}_4$	Pink colour disappears	$\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} + \text{O} \xrightarrow[\text{OH} \quad \text{OH}]{\text{alk.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

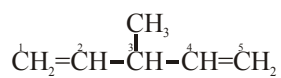
## DIENES

Dienes are the unsaturated hydrocarbons with carbon-carbon double bonds in the molecule. These are represented by the general formula  $\text{C}_n\text{H}_{2n-2}$  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 bonds, 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

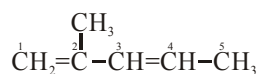


3-Methylpenta-1, 4-diene

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

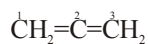


Buta-1, 3-diene

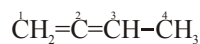


2-Methylpenta-1, 3-diene

**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 number are compared to the conjugated diene. The isolated diene is, therefore, less stable than a conjugated diene.

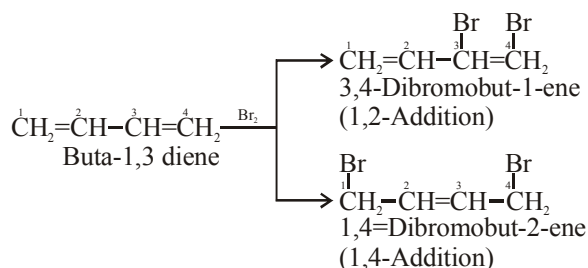
## PROPERTIES OF CONJUGATED DIENES

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.

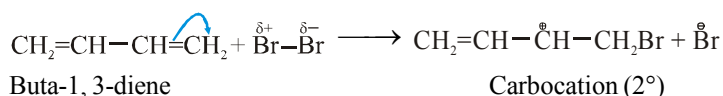
(A) **ELECTROPHILIC ADDITION REACTIONS** : The electrophilic addition is illustrated by the attack of halogen and halogen acid on buta-1,3-diene, a conjugated diene.

**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,

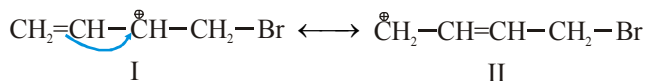


1, 2- addition is a normal addition in which one mole of halogen has been added to one of the double bond. But 1, 4- addition is somewhat unexpected.

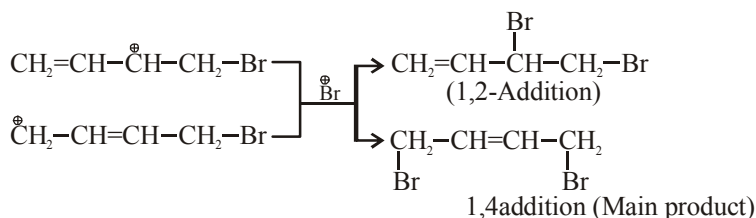
**Mechanism** : The addition is electrophilic in nature and the halogen molecule (bromine) provides the electrophilic for the attack.



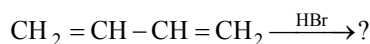
The 2° carbocation get stabilised by resonance as follows –



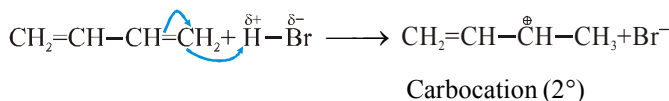
The attack of  $\overset{\ominus}{\text{Br}}$  ion on carbocation (I and II)



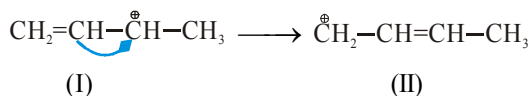
#### Addition of H - X



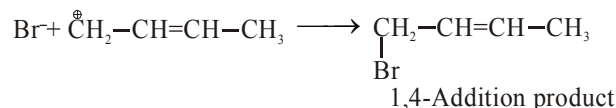
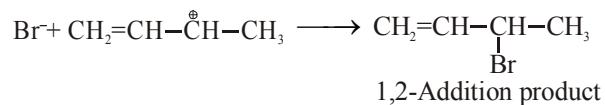
**Mechanism** : The addition is electrophilic in nature as  $\text{H}^+$  ion is the electrophilic



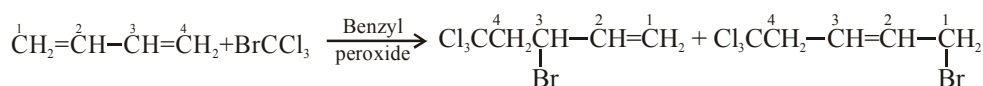
The carbocation gets resonance stabilised as follows :



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.



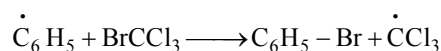
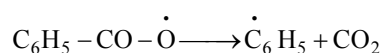
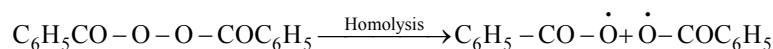
- (2) **Free Radical Addition Reaction :** The addition to conjugated dienes can also proceed by free radical mechanism provided it is carried in the presence of a suitable reagent which can help in forming a free radical. However, the addition also yields 1, 2 and 1, 4 addition products. The free radical 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.



Buta-1,3-diene      Bromotri-  
chloromethane

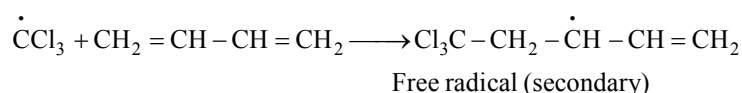
**Mechanism :** The mechanism of addition is free radical in nature which is initiated by benzoyl free radical. It is explained in the following steps :

**Step-I** Generation of free radical

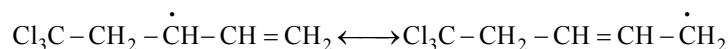


Trichloromethyl free radical

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

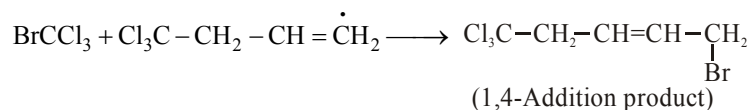
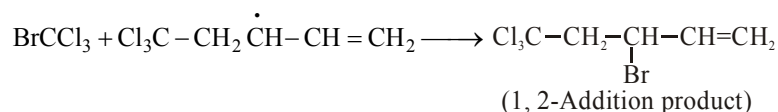


The free radical gets resonance stabilised



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

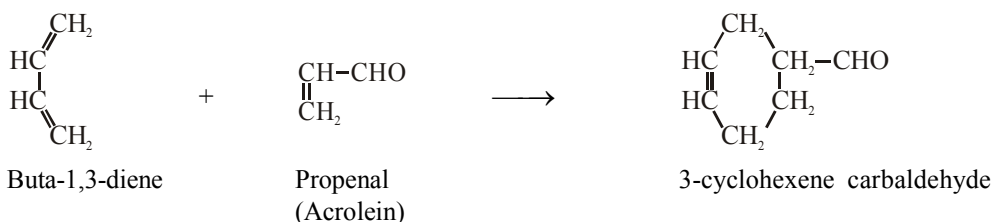
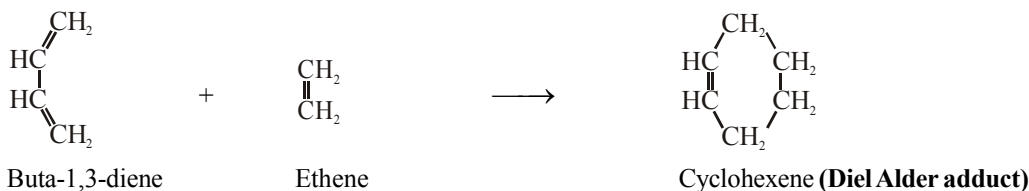
The free radical take up  $\dot{\text{Br}}$  from the attacking reagent to give the desired addition products. i.e. 1, 2 and 1, 4 addition products.



3. **Cyclo-Addition Reaction (Diel Alder Reaction)**

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 addition products is called **Diel Alder Adduct**. For example.

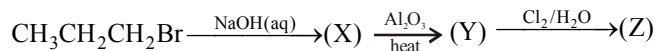


**PRACTICE PROBLEMS**

- Q.1**  $\text{R}-\text{CH}=\text{CH}_2 \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{Na/NH}_3(\text{l})} \text{RCH}_2\text{CH}_3$  is called  
 (A) Clemmensen's reduction (B) Fisher-Spier reduction (C) Birch reduction (D) Amdt-Eisher reduction
- Q.2** What would be the product when 2-pentene reacts with HBr –  
 (A) 2-bromo pentane (B) 3-bromo pentane (C) Both A and B (D) 1-bromo pentane
- Q.3** What would be the product when ethene is oxidised with ozone and forms ozonide which is hydrolysed in the presence of Zn and acetic acid?  
 (A)  $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$  (B)  $\text{CH}_3\text{OH}$  (C)  $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$  (D)  $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$
- Q.4** What would be the product when propene reacts with chlorine in presence of  $\text{CCl}_4$   
 (A)  $\text{CH}_3-\overset{\text{H}}{\underset{\text{Cl}}{\text{C}}}-\overset{\text{H}}{\underset{\text{Cl}}{\text{C}}}-\text{H}$  (B)  $\text{Cl}-\text{CH}_2-\text{CH}=\text{CH}_2$  (C)  $\text{CH}_3-\overset{\text{H}}{\text{C}}=\overset{\text{H}}{\text{C}}-\text{Cl}$  (D)  $\text{CH}_3-\overset{\text{H}}{\underset{\text{Cl}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{H}$
- Q.5** Propene on reaction with methylene iodide in presence of Zn-Cu couple gives :  
 (A) Cyclopropane (B) Cyclopropane (C) Methyl Cyclopropane (D) Cyclobutene
- Q.6** Propene + HOCl  $\rightarrow$  A  $\rightarrow$  Final product. In the above reaction A will be  
 (A)  $\text{CH}_3-\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}-\overset{\ominus}{\text{C}}-\text{H}$  (B)  $\text{CH}_3-\overset{\text{H}}{\text{C}}-\overset{\text{H}}{\underset{\text{Cl}}{\text{C}}}-\text{H}$  (C)  $\text{CH}_3-\overset{\text{H}}{\text{C}}-\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}-\text{H}$  (D)  $\text{CH}_3-\overset{\text{Cl}}{\text{CH}}-\overset{\oplus}{\text{C}}\text{H}_2$
- Q.7** In hydroboration it is evident that in the overall reaction a molecule of a water has been added to propene and the addition is :  
 (A) According to Markownikoff's rule (B) Contrary to Markownikoff's rule  
 (C) Not connected with Markownikoff's rule (D) None of these
- Q.8** NBS react with 1-butene to give –  
 (A) 3-bromobutene-1 (B) 1, 2-dibromobutane (C) 1-bromobutene (D) 1, 2-dibromobutene-1

- Q.9** Isobutane reacts with the following to form iso-octane :  
 (A) Isobutylene (B) n-Butene (C) n-Pentene (D) Isopentene
- Q.10** Reaction of alkene and peracid gives oxirane. This reaction is named as –  
 (A) Peroxidation (B) Oxidation (C) Priles chaiev (D) None
- Q.11** The compound which reacts with HBr obeying Markownikov's rule is –  
 (A)  $\text{CH}_2=\text{CH}_2$  (B)  $\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{H} \end{array} = \begin{array}{c} \text{C} \\ \diagdown \\ \text{H} \\ \diagup \\ \text{CH}_3 \end{array}$  (C)  $\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{H} \end{array} = \begin{array}{c} \text{H} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CH}_3 \end{array}$  (D)  $\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CH}_3 \end{array} = \begin{array}{c} \text{H} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{H} \end{array}$
- Q.12** Alkene and alkyne gives followed types of polymerisation –  
 (A) Addition (B) Condensation (C) Substitution (D) Replacement
- Q.13** Cyclic osmium ester of alkene after reacting with aqueous solution of sodium bisulphite gives –  
 (A) Diol (B) Cis-diol (C) Tran-diol (D) Salt
- Q.14** The minimum number of C atoms required to be present in an optically active alkene are :  
 (A) 4 (B) 6 (C) 8 (D) 10
- Q.15** Chloroethane reacts with alcoholic KOH to form –  
 (A) Propyl chloride (B) Ethyl chloride (C) Ethene (D) None
- Q.16** The synthesis of ethene from electrolysis of an aqueous solution of potassium succinate is known as :  
 (A) Faraday's electrolysis (B) Kolbe - Schmidt reaction  
 (C) Hoffmann's rearrangement (D) Kolbe's electrolytic Synthesis
- Q.17**  $\begin{array}{c} \text{H} \quad \text{Cl} \\ | \quad | \\ \text{CH}_2 - \text{CH}_2 \end{array} \xrightarrow[\text{alk.}]{\text{NaOH}} \text{CH}_2 = \text{CH}_2$ . Most probable mechanism for this reaction is –  
 (A) E 1 (B) E 2 (C) E1 CB (D)  $\alpha$  elimination
- Q.19** If we take ethylidene chloride and isopropylidene chloride with zinc and dust then product will be –  
 (A) 2-butene  
 (B) 2-butene + 2,3-dimethyl-2butene  
 (C) 2-methyl-2-butene  
 (D) 2-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene

**Q.20** Identify 'Z' in the following reaction series,



- (A) Mixture of  $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 \\ | \quad | \\ \text{Cl} \quad \text{Cl} \end{array}$  and  $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 \\ | \quad | \\ \text{OH} \quad \text{Cl} \end{array}$  (B)  $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 \\ | \quad | \\ \text{OH} \quad \text{Cl} \end{array}$
- (C)  $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 \\ | \quad | \\ \text{Cl} \quad \text{OH} \end{array}$  (D)  $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 \\ | \quad | \\ \text{Cl} \quad \text{Cl} \end{array}$

ANSWER KEY

Q.1	(C)	Q.2	(C)	Q.3	(A)	Q.4	(A)	Q.5	(C)
Q.6	(D)	Q.7	(B)	Q.8	(A)	Q.9	(A)	Q.10	(C)
Q.11	(D)	Q.12	(A)	Q.13	(B)	Q.14	(B)	Q.15	(C)
Q.16	(D)	Q.17	(B)	Q.19	(D)	Q.20	(B)		



## ALKYNE

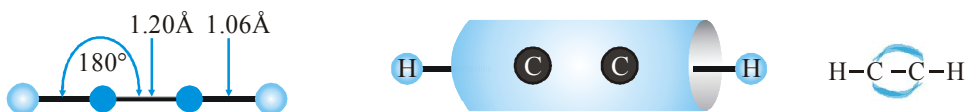
### GENERAL INTRODUCTION

A triple bond gives an alkyne four fewer hydrogen atoms than the corresponding alkane. Therefore, the triple bond contributes two degrees of unsaturation (DU).

Alkynes are not as common in nature as alkenes, but some plants do use alkynes to protect themselves against disease or predators. Acetylene is by far the most important commercial alkyne. Acetylene is an important industrial feedstock, but its largest use is as the fuel for the oxyacetylene welding torch.

### STRUCTURE AND BONDING IN ALKYNES

- (a) Alkynes are also hydrocarbons that contain carbon-carbon triple bond.
- (b) Alkynes are also called acetylenes because they are derivatives of acetylene.
- (c) The general formula is:  $C_n H_{2n+2}$  (one triple bond)
- (d) In alkyne C  $\equiv$  C bond length is 1.20 Å
- (e) Its bond energy is 192 kcal. mol<sup>-1</sup>
- (f) The hybridization of carbon atoms having triple bond (C  $\equiv$  C) in alkynes is sp.
- (g) Overlapping of these sp hybrid orbitals with each other and with the hydrogen orbitals gives the sigma bond framework which is linear (180°) structure.
- (h) Two  $\pi$  bonds result from overlap of the two remaining unhybridized p orbitals on each carbon atom. These orbitals overlap at **right angles** (90°) to each other, forming one  $\pi$  bond with electron density above and below the C-C sigma bond, and the other with electron density in front and in back of the sigma bond. This results in a cylindrical  $\pi$  electron cloud around  $\sigma$  bonded structure.



**Note :** Any type of stereoisomerism does not arise in acetylenic bond due to linearity of C  $\equiv$  C bond.

### IUPAC NOMENCLATURE OF ALKYNES

S. No.	Compound	Name
1.	CH $\equiv$ CH	Ethyne
2.	CH <sub>2</sub> - C $\equiv$ H	Propyne
3.	HC $\equiv$ C - CH <sub>2</sub> - CH <sub>3</sub>	But-1-yne
4.	CH <sub>3</sub> - C $\equiv$ C - CH <sub>3</sub>	But-2-yne
5.	$  \begin{array}{c}  \text{CH}_3 \\    \\  \text{CH}_3 - \text{CH} - \text{C} \\    \\  \text{C} - \text{CH}_2 - \text{CH} - \text{CH}_3 \\    \\  \text{Br}  \end{array}  $	6-Bromo-2methylhept-3-yne

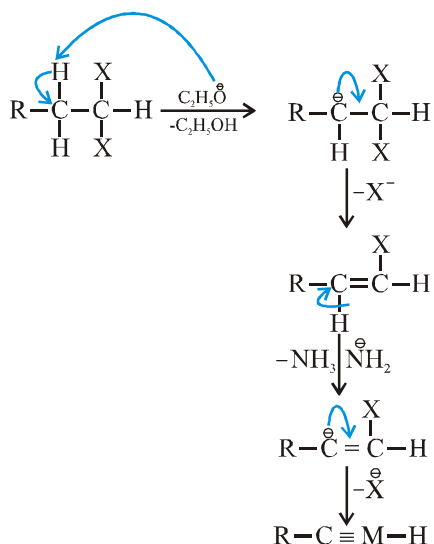
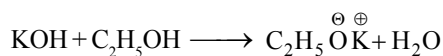
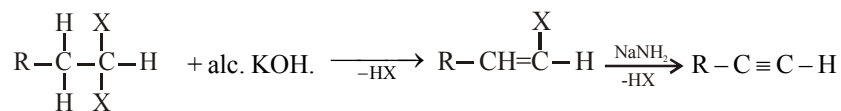
### ISOMERISM IN ALKYNES

Type	Category	Examples
Structural Isomerism	(i) Chain isomerism	CH <sub>3</sub> - CH <sub>2</sub> - CH <sub>2</sub> - C $\equiv$ CH & CH <sub>3</sub> - CH - C $\equiv$ CH <div style="margin-left: 150px;">  CH<sub>3</sub></div>
	(ii) Positional	CH <sub>3</sub> - CH <sub>2</sub> - CH <sub>2</sub> - C $\equiv$ CH & CH <sub>3</sub> - C $\equiv$ C - CH <sub>3</sub>
	(iii) Functional group isomerism	CH <sub>3</sub> - CH <sub>2</sub> - C $\equiv$ C - CH <sub>3</sub> & CH <sub>3</sub> - C = C = CH - CH <sub>3</sub> &

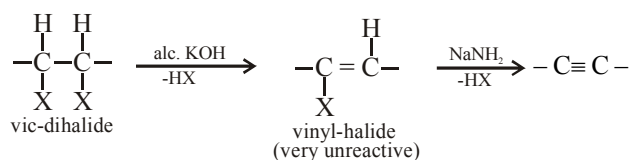
## METHOD OF PREPARATION

## (1) Dehydrohalogenation

## (a) FROM GEM DIHALIDES

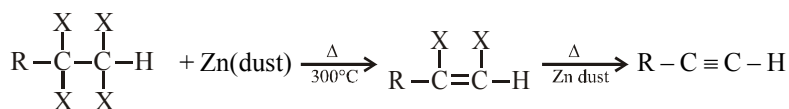


## (b) FROM VICINAL DIHALIDES



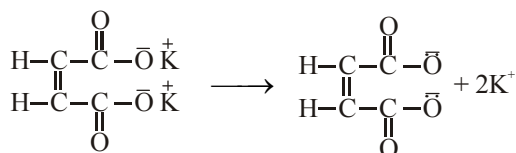
The elimination of one molecule of hydrogen halide yields vinyl halide which is very unreactive. Under mild conditions, the dehydrohalogenation stops at vinylic halide stage but more vigorous conditions – like the use of a stronger base like amide ion ( $\text{NH}_2^-$ ) – are required for alkyne formation.

## (c) FROM TETRAHALOALKANES (DEHALOGENATION)



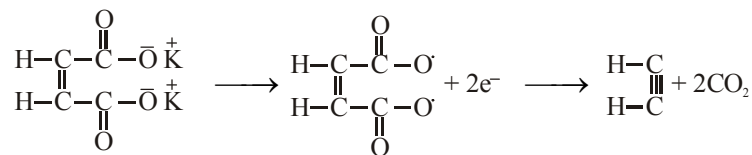
In the above reaction it is necessary that the four halogen atoms must be attached at vicinal carbons. If they are attached at the two ends then the product alkene is obtained.

## (2) From Kolbe's Synthesis

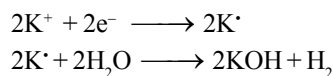


Potassium Malaete

**At Anode**

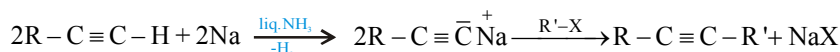
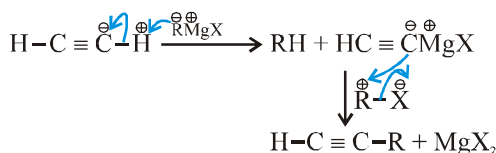
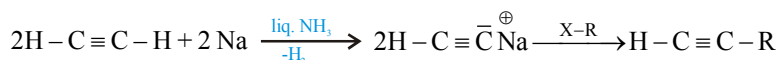


**At Cathode**



**(3) From Alkynes : (To form higher Alkyne)**

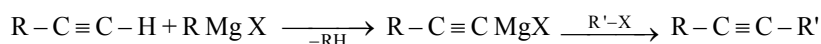
**(i) With Na :** When acetylene or 1-alkyne react with Na in presence of liq.  $\text{NH}_3$  then an intermediate compound sodium acetylide or sodium alkyne is formed which gives higher alkyne with alkylhalide.



**(ii) With Grignard reagent :** When acetylene or 1-alkyne react with GR then alkyne and unsaturated GR is formed which further react with alkyl halide and form higher alkyne.

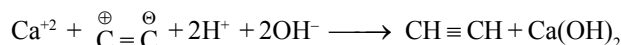
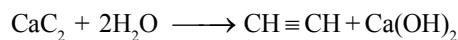


acetylene

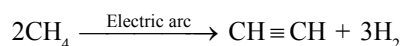


**(4) Preparation of Ethyne of Acetylene**

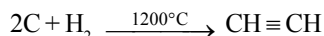
**(a) From Metal carbide [Laboratory method] :** Acetylene is prepared in the laboratory by the action of water on calcium carbide.



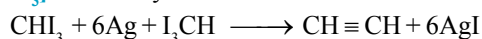
**(b) Manufacture :** Acetylene is manufactured by heating methane or natural gas at  $1500^{\circ}\text{C}$  in the electric arc



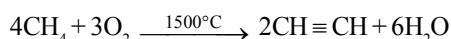
**(c) Berthelot's process :** Acetylene is synthesized by striking an electric arc between carbon electrodes in presence of hydrogen.



**(d) From haloform [ $\text{CHI}_3$ ,  $\text{CHCl}_3$ ] :** Pure acetylene is obtained when iodoform or chloroform is heated with Silver powder



**(e) Partial oxidation of methane :** A recent method for manufacturing of acetylene is the controlled partial oxidation of method at high temperature.



## PHYSICAL PROPERTIES

- (a) Alkynes are colourless, odourless and tasteless.
- (b) Lower alkynes are partially soluble in  $H_2O$ . (It is due to its polarisability).
- (c) Higher alkynes are insoluble in water due to more % of covalent character.
- (d) Completely soluble in organic solvents.
- (e) Melting point and boiling point increases with molecular mass and decreases with number of branches.
- (f) Upto  $C_4$  alkynes are gaseous  $C_5 - C_{11}$  are liquid,  $C_{12}$  & above are solids.
- (g) Pure acetylene is odourless and impure acetylene has odour like garlic. It is due to impurities of Arsene ( $AsH_3$ ) & Phosphine ( $PH_3$ ).
- (h) Acetylene & 1-alkyne are acidic in nature. It is due to greater electronegativity of  $sp$  hybridised 'C'.
- (i) Acetylene has two acidic hydrogen atoms. It can neutralise two equivalents of base at the same time. So it is also called as dibasic acid But the base should be very stronger as ' $NH_2$  or  $^-CH_3$ ' etc.

## CHEMICAL PROPERTIES

The chemical properties of alkyne are due to two factors :

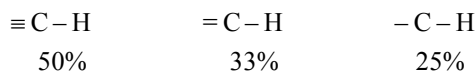
**Presence of  $\pi$  electrons :** Due to presence of loosely bond  $\pi$  electrons, alkynes like alkenes, undergo easily electrophilic addition reaction.

Carbon-carbon triple bond is less reactive than the carbon-carbon double bond towards electrophilic addition reaction.

In addition to electrophilic additions, alkynes also undergo nucleophilic addition with nucleophiles

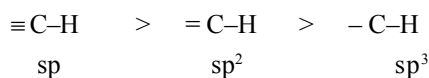
**Presence of acidic hydrogen atom :** The hydrogen atom attached to the triple bonded carbon can be easily removed by a strong base and hence acetylene and 1-alkynes are considered as weak acids.

**Ex :** The amounts of s-character in various types of C-H bonds is as-



Since s electrons are closer to the nucleus than the p electrons, the electrons in a bond having more s-character will be more closer to nucleus. Due to high s-character of the C-H bond in alkyne (s-50%) the electrons constituting this bond are more strongly held by the carbon nucleus, with the result the H present on CH can be easily removed as proton.

The acidic nature of the three types of C-H bonds as



Relative acidic order

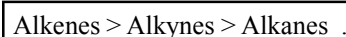


### (1) Addition Reaction

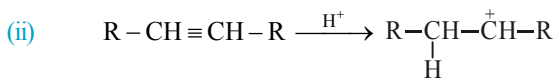
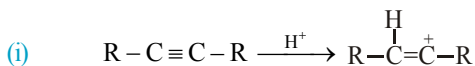
**ELECTROPHILIC ADDITION :** Addition reactions where the addition is initiated electrophilic (positive group).

The characteristic reaction of alkynes is electrophilic addition but the reactivity of alkynes towards electrophilic addition is less than alkenes because in  $C \equiv C$ , the  $\pi$  electrons are tightly held by carbon nuclei and so they are less easily available for reaction for reaction with electrophilic.

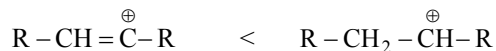
Reactivity order of hydrocarbos for electrophilic addition



**Another reasons is :** The intermediates when an electrophile attack on alkene and alkynes are :



### Stability of intermediates



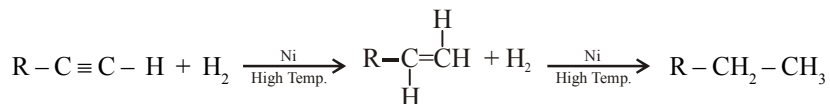
(+) ve on more En                      more stable

atoms is less stable

So we can say that alkenes are more reactive towards electrophilic addition reaction.

### (a) ADDITION OF HYDROGEN

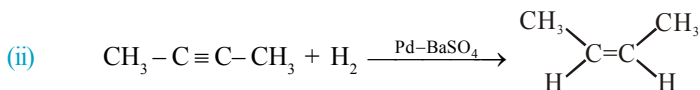
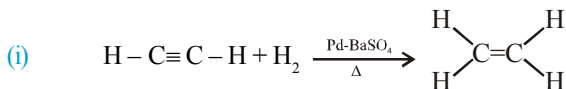
#### Hydrogenation



The above reaction is called as Sabatier Senderson's reaction.

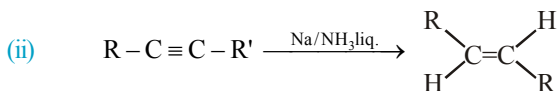
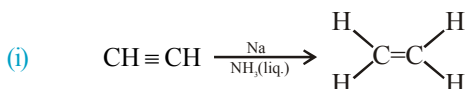
#### Hydrogenation in the presence of lindlar's Catalyst

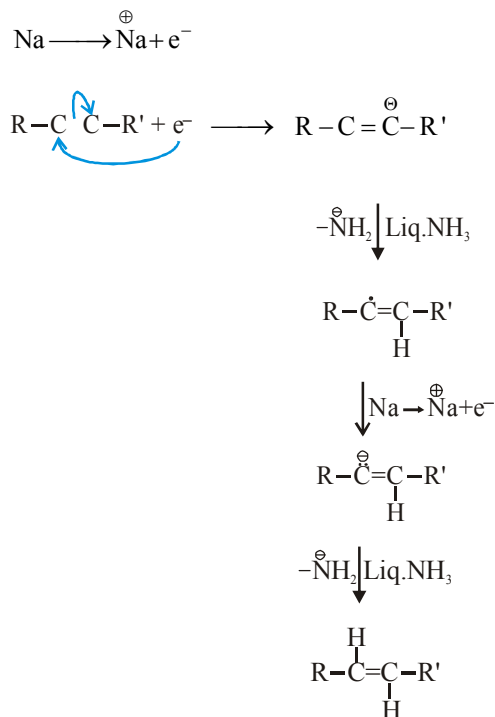
Addition up to alkene takes place in cis manner.



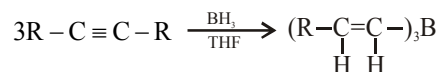
#### Hydrogenation by Na + NH<sub>3</sub> (liq.)

Addition upto alkene takes place in trans manner

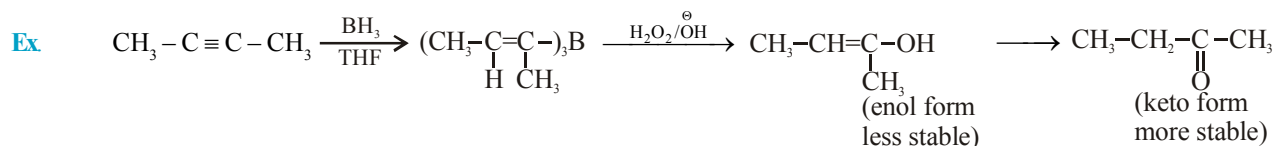
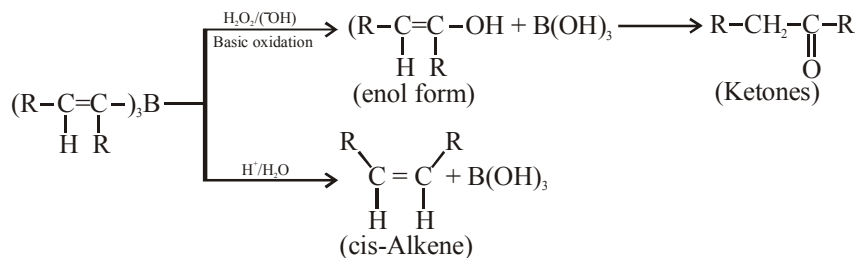
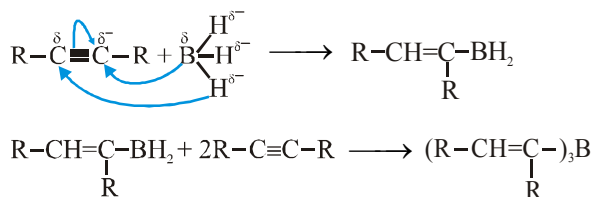


**Mechanism**


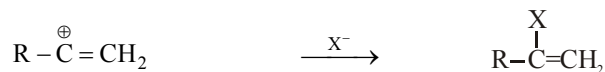
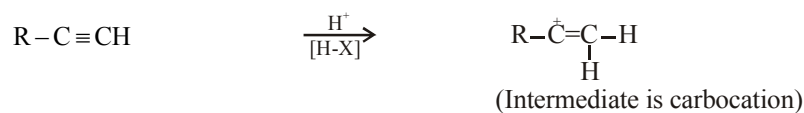
(b) **ADDITION OF  $\text{BH}_3$  / THF OR  $\text{B}_2\text{H}_6$  (HYDROBORATION)**: THF – Tetrahydrofuran is used as solvent.



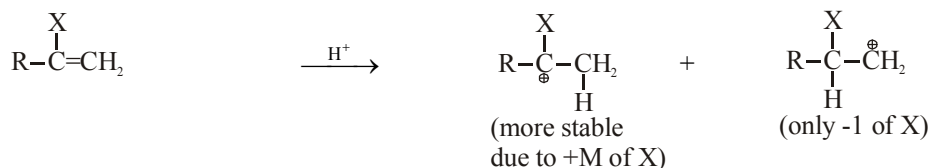
Since  $\text{BH}_3$  is not available as monomer so a solvent THF is used for the stability of  $\text{BH}_3$ .



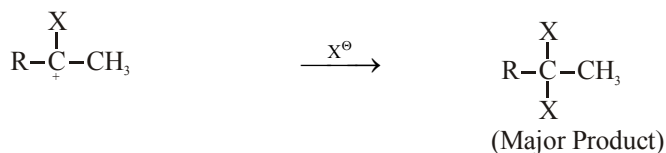


**Mechanism**


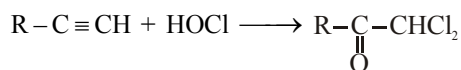
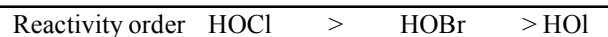
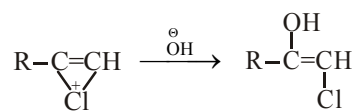
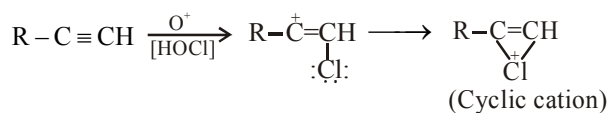
Further



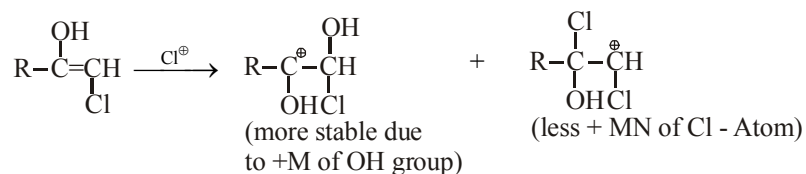
so



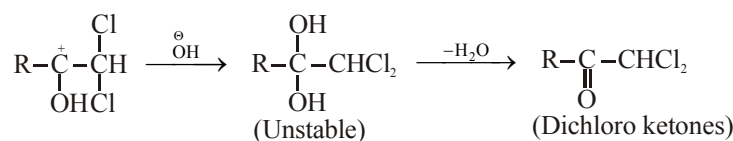
- (e) **ADDITION OF HOX** : Alkynes react with hypohalous acids according to markwonikoff's rule and form gem diol, which are unstable, lose a molecule of water and form halo aldehyde or halo ketones.


**Mechanism**


Further



so

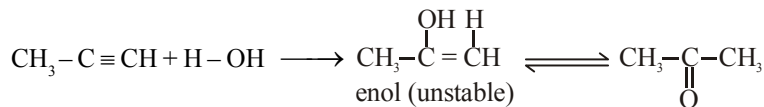
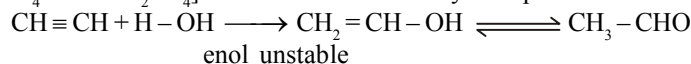




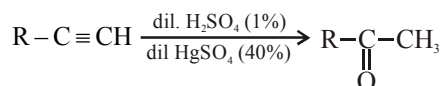
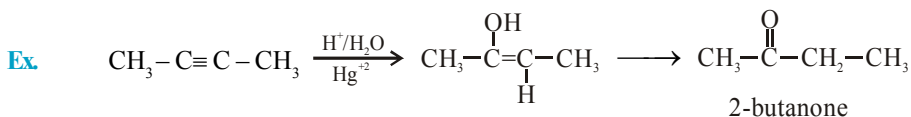
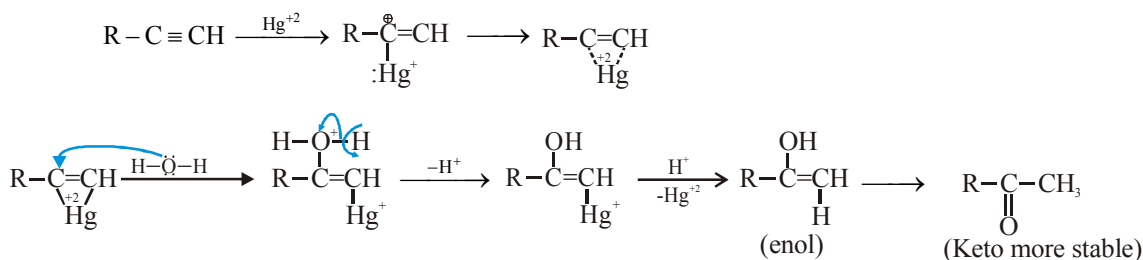
**(2) Nucleophilic Addition Reaction**

In these reactions some heavy metal cation like  $Hg^{+2}$ ,  $Pb^{+2}$ ,  $Ba^{+2}$  are used. These cation attracts the  $\pi$   $e^-$  of alkynes and decrease the  $e^-$  density and hence a nucleophilic can attack an alkynes.

**(a) ADDITION OF DIL.  $H_2SO_4$  (HYDRATION)** : The addition of water takes place in the presence of  $Hg^{+2}$  and  $H_2SO_4$  [ $1\% HgSO_4 + 40\% H_2SO_4$ ]. In this reaction carbonyl compounds are obtained.



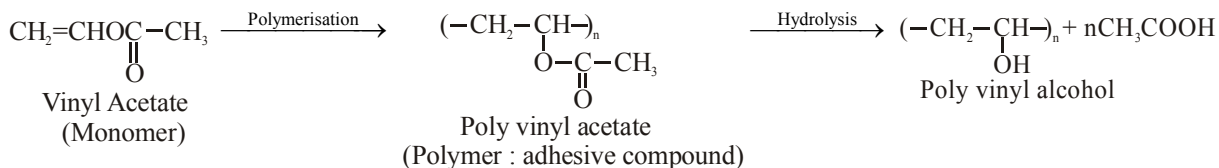
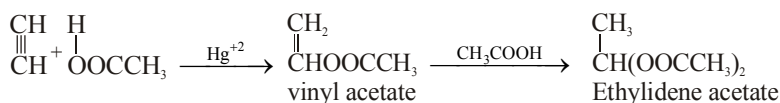
A structure in which  $-OH$  group is attached to double bond carbon is called as enol (enol + - ol). This reaction is used for preparation of aldehyde and ketone.


**Mechanism**

**(b) ADDITION OF HCN**

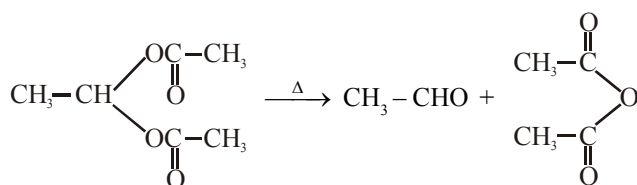
Addition takes place in the presence of  $CuCl$



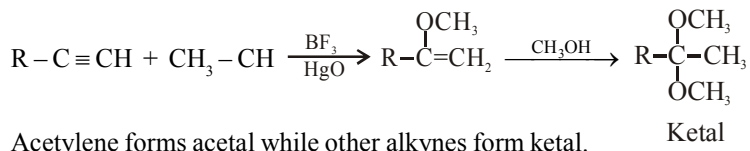
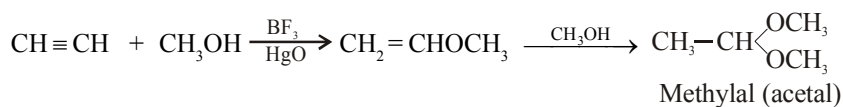
**(c) ADDITION OF ACETIC ACID** : Acetylene combines with acetic acid in presence of mercuric sulphate. It first forms vinyl acetate and then ethylidene acetate.



When ethylidene acetate is heated it gives acetaldehyde and acetic anhydride



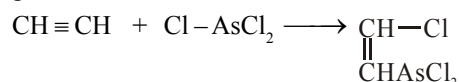
**(d) ADDITION OF ALCOHOLS:** In presence of  $\text{BF}_3$  and  $\text{HgO}$  alkynes react with alcohols and form acetal and ketal



Acetylene forms acetal while other alkynes form ketal.

### (3) Addition of $\text{AsCl}_3$

In presence of  $\text{AlCl}_3$  or  $\text{HgCl}_2$  acetylene combines with  $\text{AsCl}_3$  to yield Lewisite gas. It is four times poisonous than mustard gas.



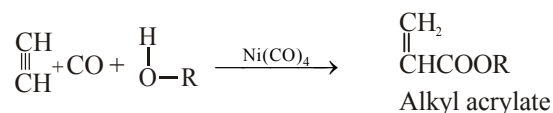
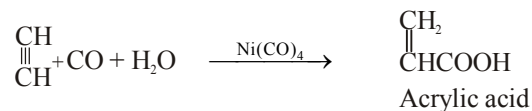
2-Chlorovinyl dichloro arsine (Lewisite gas)

The action of Lewisite may be checked by its antidote BAL (British Anti Lewisite). BAL combines with the Lewisite to form a cyclic non toxic compound.



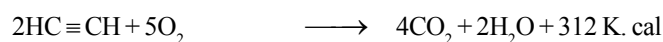
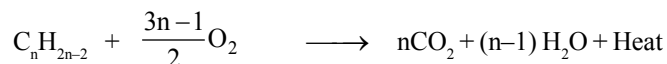
### (4) Carbonylation

Reaction of alkynes with CO in presence of  $\text{Ni}(\text{CO})_4$



### (5) Oxidation Reactions

#### (a) COMBUSTION

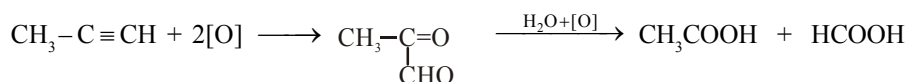
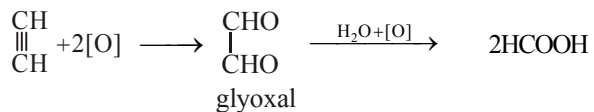
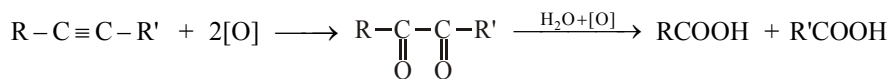


The combustion of acetylene is used for welding and cutting of metals in which oxy-acetylene flame having high temp ( $3000^\circ\text{C}$ ) is produced.

**(b) OXIDATION WITH ALKALINE  $\text{KMnO}_4$ :** Oxidation with alkaline  $\text{KMnO}_4$  gives carboxylic acids.

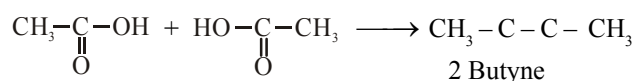


- (c) **OXIDATION WITH ACIDIC KMnO<sub>4</sub> OR K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>:** In presence of acidic KMnO<sub>4</sub> or acidic K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, Alkynes are oxidised to monocarboxylic acids.

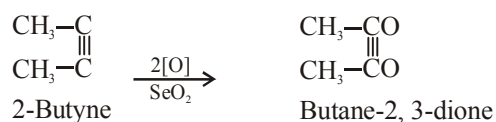
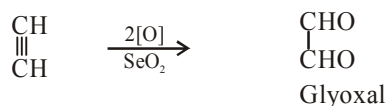


**Ex.** An alkyne on oxidation with acidic KMnO<sub>4</sub>, only acetic acid is obtained what is given alkynes ?

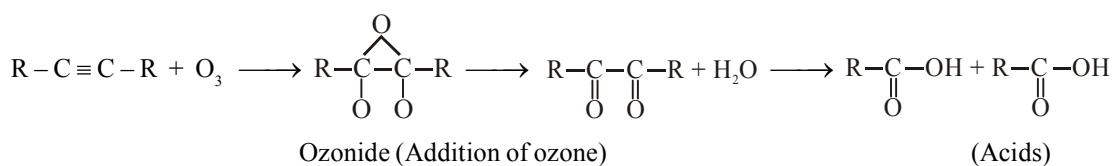
**Sol.** In Oxidation of alkynes two moles of mono carboxylic acids are obtained.



- (d) **OXIDATION WITH SELENIUM DIOXIDE:** Selenium dioxide alkynes to the dicarbonyl compounds.

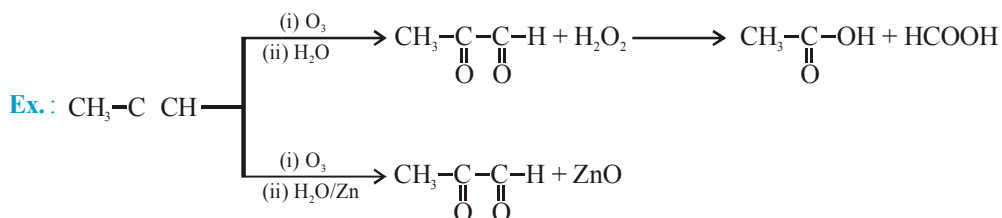
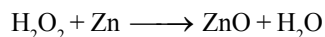


- (e) **OXIDATION WITH OZONE (O<sub>3</sub>):** In the ozonolysis both sp-C-atoms are converted into  $-\overset{\text{O}}{\parallel}{C}-\overset{\text{O}}{\parallel}{C}-$  group.



In this reaction H<sub>2</sub>O<sub>2</sub> is oxidant which oxidise  $R-\overset{\text{O}}{\parallel}{C}-\overset{\text{O}}{\parallel}{C}-R$  into acids.

But if we use some amount of Zn as reductant with H<sub>2</sub>O then it reduce H<sub>2</sub>O<sub>2</sub> so oxidation does not take place

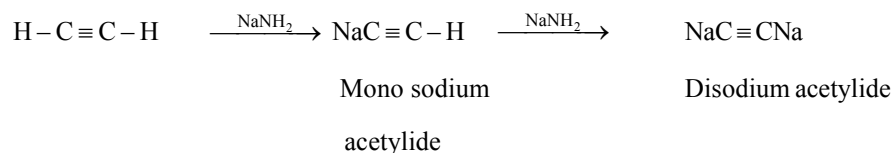


**(3) Substitution Reaction : (Formation of metallic derivatives)**

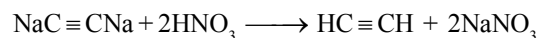
Only 1-alkynes gives substitution reaction and show acidic characters  $\equiv \overset{\delta^-}{\text{C}}-\overset{\delta^+}{\text{H}}$

Acetylene is dibasic acid where as propyne is monobasic means acetylene can give two  $\text{H}^+$  where as propyne can give one  $\text{H}^+$ .

**(a) FORMATION OF SODIUM ACETYLIDES :** Acetylene and 1-alkynes react with sodamide to form acetylides

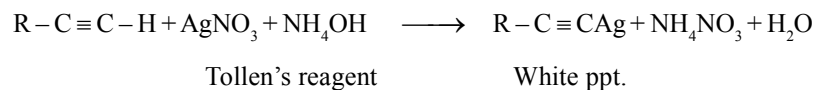
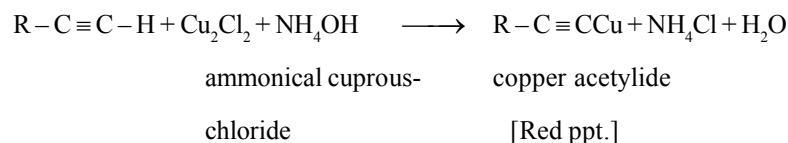


Dry alkynides are generally unstable and explosive. These are easily converted in to original alkynes when heated with dilute acids.



This reaction can be used for the purification, separation and identification of 1-alkynes.

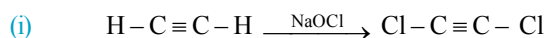
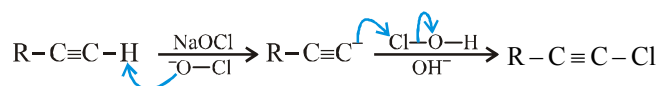
**(b) FORMATION OF COPPER AND SILVER ACETYLIDES :** Copper and silver acetylides are obtained by passing 1-alkynes in the ammonical solution of cuprous chlorides and silver nitrate (Tollen's reagent) respectively.



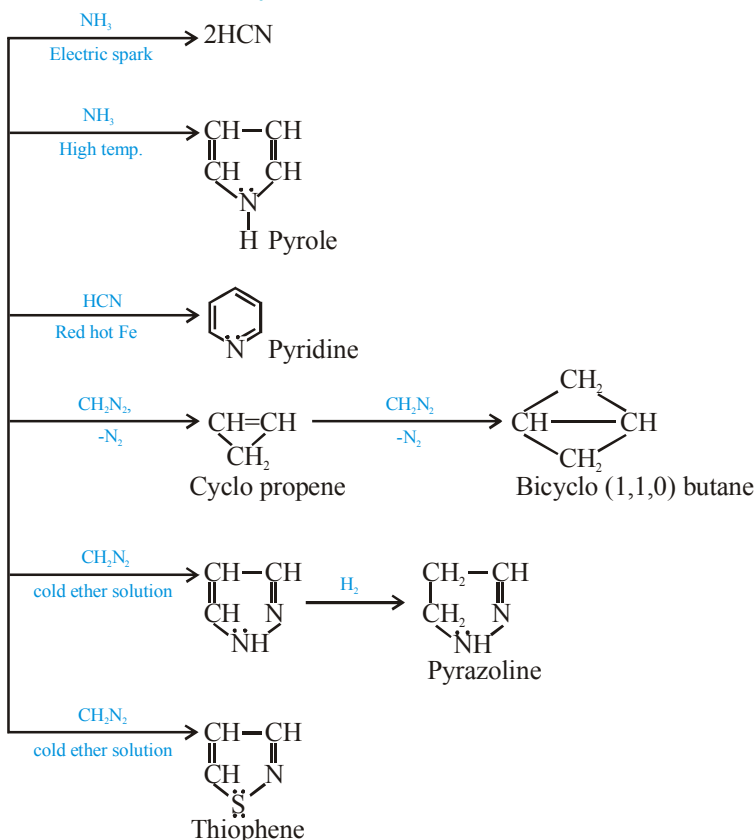
These reactions are used for detecting the presence of acetylenic hydrogen. These are test for distinguish alkenes and alkynes or 1-alkynes and 2-alkynes.

**(4) Reaction with NaOCl**

Acidic hydrogen is substituted by 'Cl'

**Mechanism**

(5) Other reactions of acetylene



(6) **Reaction with HCHO** : This reaction is called ethynylation.



**Uses of Acetylene**

- (i) Oxyacetylene flame used in welding and cutting
- (ii) Acetylene is used as an illuminant
- (iii) Acetylene is used for artificial ripening of fruits
- (iv) Used for manufacture of acetaldehyde, acetic acid, ethyl alcohol, westron, westrosol, PVC, PVA, Chloroprene, butadiene, Lewisite etc.
- (v) It is used as a general anaesthetic.

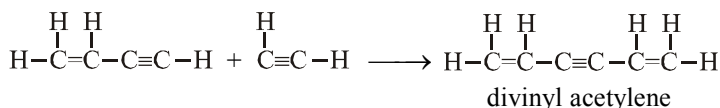
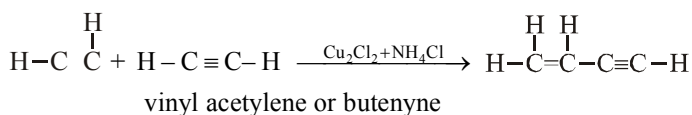
(7) **Polymerisation**

**Polymerisation Reactions** : Alkyne mainly shows addition polymerisation reactions.

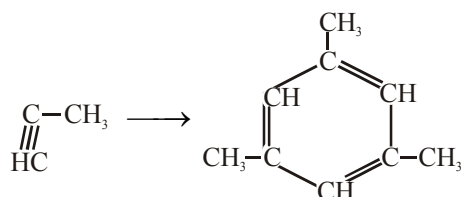
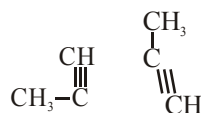
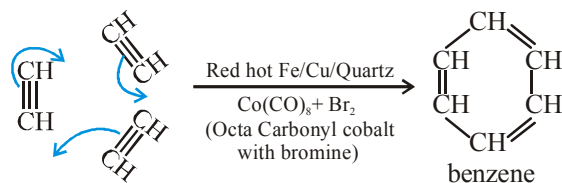
**Dimerisation and Cyclization**

(a) **DIMERISATION** : Two mole acetylene reacts with  $\text{Cu}_2\text{Cl}_2$  &  $\text{NH}_4\text{Cl}$  and forms vinyl acetylene.

**Note** : If acetylene would be in excess then product would be divinyl acetylene and the reaction is called trimerisation.



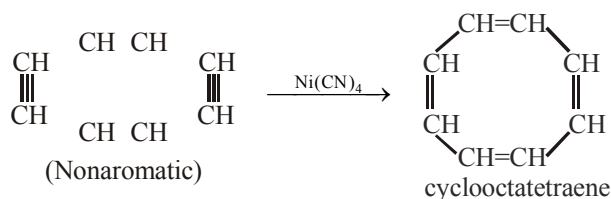
- (b) **TRIMERISATION** : If three mole of acetylene is passed into red hot iron or Cu or quartz tube, then a cyclic trimer is formed which is called benzene.



mesitylene (having 3-1°, 3-2° & 3-3° carbons)

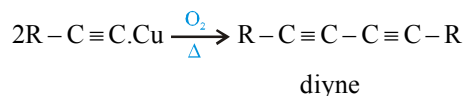
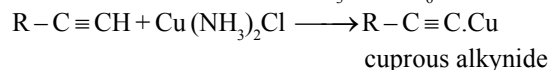
**Important** : Mesitylene can also be obtained from acetone by condensation polymerisation.

- (c) **TETRAMERISATION** : According to the name four moles of acetylene are heated with nickel tetra cyanide, then acetylene forms a cyclic tetramer cyclo octa tetraene.

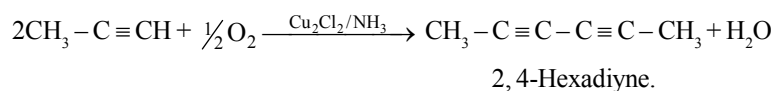
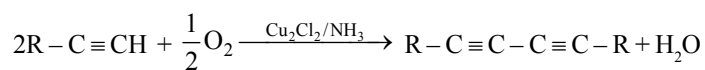


## (8) Coupling

- (a) Alkyne form respective cuprous alkynide with ammonical cuprous chloride solution. When cuprous alkynide is reacted with potassium ferri cyanide  $[K_3Fe(CN)_6]$  they converted into conjugated diyne.

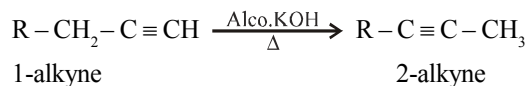


- (b) Coupling is also done easily by 1-alkyne in the presence of  $Cu_2Cl_2$  (cuprous compound) and amine (ie. pyridine + air) cuprous alkynide is formed (this coupling is known as oxidative coupling or glase coupling)

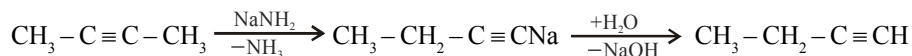


**(9) Isomerisation**

(a) When 1-alkyne is treated with alcoholic KOH 2-alkyne is formed.



(b) When 2-alkyne is treated with sodamide then it is converted into 1-alkyne.

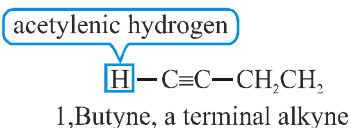


**LABORATORY TEST FOR ALKYNES**

Functional Group	Reagent	Observation	Reaction	Remarks
-C≡C-	(1) Bayer's Reagent alk. dil. Cold KMnO <sub>4</sub>	Pink Colour disappears	$\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} + \text{O} \xrightarrow{\text{alk.KMnO}_4}$ $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\   \quad   \\ \text{OH} \quad \text{OH} \end{array}$	Hydroxylation
	(2) Br <sub>2</sub> /H <sub>2</sub> O	Red Colour decolourises	$\text{Br}_2 + \text{CH}_2=\text{CH}_2 \longrightarrow$ $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\   \quad   \\ \text{Br} \quad \text{Br} \\ \text{White ppt} \end{array}$	Bromination
	(3) O <sub>3</sub> (ozone)	Acid Formed	$\text{R}-\text{C}\equiv\text{C}-\text{R}' \xrightarrow{\text{O}_3} \text{RCOOH} + \text{R}'\text{COOH}$	Ozonolysis

**LABORATORY TEST OF TERMINAL ALKYNES**

When triple bond comes at the end of a carbon chain. The alkyne is called a terminal alkyne.



Functional Group	Reagent	Observation	Reaction
R-C≡C-H	(1) Cuprous chloride  + NH <sub>4</sub> OH	Red ppt.	$\text{R}-\text{C}\equiv\text{CH} + \text{CuCl} \xrightarrow{\text{NH}_4\text{OH}}$ $\text{R}-\text{C}\equiv\text{C} \text{Cu} \downarrow (\text{red})$
	(2) AgNO <sub>3</sub> + NH <sub>4</sub> OH	White ppt.	$\text{R}-\text{C}\equiv\text{CH} + \text{Ag}' \rightarrow \text{R}-\text{C}\equiv\text{C} \text{Ag} \downarrow (\text{white})$
	(3) Na in ether	Colourless gas	$\text{HC}\equiv\text{CH} + 2\text{Na} \rightarrow \text{Na}-\text{C}\equiv\text{C}-\text{Na} + \text{H}_2 \uparrow$

(i) Decolourization of Br<sub>2</sub> in CCl<sub>4</sub> solution.

(ii) Decolourisation of 1% alkaline KMnO<sub>4</sub> solution.

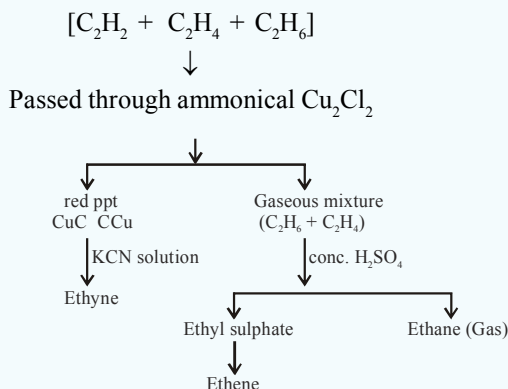
(iii) 1-alkynes give white ppt. with ammonical AgNO<sub>3</sub> and red ppt with ammonical cuprous chloride solution.

**Note :** (i) and (ii) tests are used for determination of unsaturation (i.e., presence of double or triple bond in any compound.)

(iii) Test is used for distinguish between alkenes and 1-alkynes or 1-alkyne and 2-alkyne.

## KEY POINTS

## Separation of Ethane, Ethene and Ethyne



## PRACTICE PROBLEMS

- What happens when 2-butyne reacts with  $H_2$  in presence of Nickle Boride or lindlar's catalyst ( $Pd/CaCO_3-PbO$ ) –
 

(A)  $CH_3-C \equiv C-H$   
 $CH_3-C \equiv C-H$

(B)  $CH_3-C \equiv C-H$   
 $H-C \equiv C-CH_3$

(C)  $CH_3-CH_2-CH_2-CH_3$

(D)  $CH_2=CH$   
 $CH=CH_2$
- What will be the product of chlorine water and acetylen –
 

(A) Dichloro propanol

(B) Dichloroethanol

(C) Propanol

(D) 2-Chloro ethanol
- Product formed by the oxidation of acetylene in the presence of alkaline  $KMnO_4$ 

(A) Glyoxal

(B) Oxyrane

(C)  $CO_2 + H_2O$

(D) Oxalic acid
- Acetylene on treating with HI gives –
 

(A) 1, 1-Diiodoethane

(B) Ethylene

(C) Iodoethane

(D) Ethane
- Acetylene and ethylene react with alk  $KMnO_4$  to give –
 

(A) Oxalic acid and formic acid

(B) Acetic acid and ethylene glycol

(C) Ethyl alcohol and ethylene glycol

(D) None
- When 2-butyne reacts with sodamide in an inert solvent in the presence of dilute HCl, the product formed si
 

(A) n-Butane

(B) 2-Butene

(C) 1-BHutyne

(D) 1-Propyne
- Which of the following can not react with ammonical silver nitrate –
 

(A) Acetylene

(B) Hexyne -1

(C) Phenyl acetaldehyde

(D) hept-4-yne-2-ene
- The hydrocarbon that reacts with ammonical cuprous chloride is –
 

(A) Essentially aromatic

(B) Ethane

(C) Ethyne

(D) Ethene
- The product of reaction  $CH_3CH_2CH_2MgB_4 + HC \equiv CCH_3 \rightarrow$  is
 

(A)  $CH_3CH_2CH_3$

(B)  $CH_3CH_2CH_2C \equiv CCH_3$

(C)  $CH_3CH_2CH_2OH$

(D)  $CH_3CH_2CHO$



## CHEMISTRY FOR JEE MAIN & ADVANCED

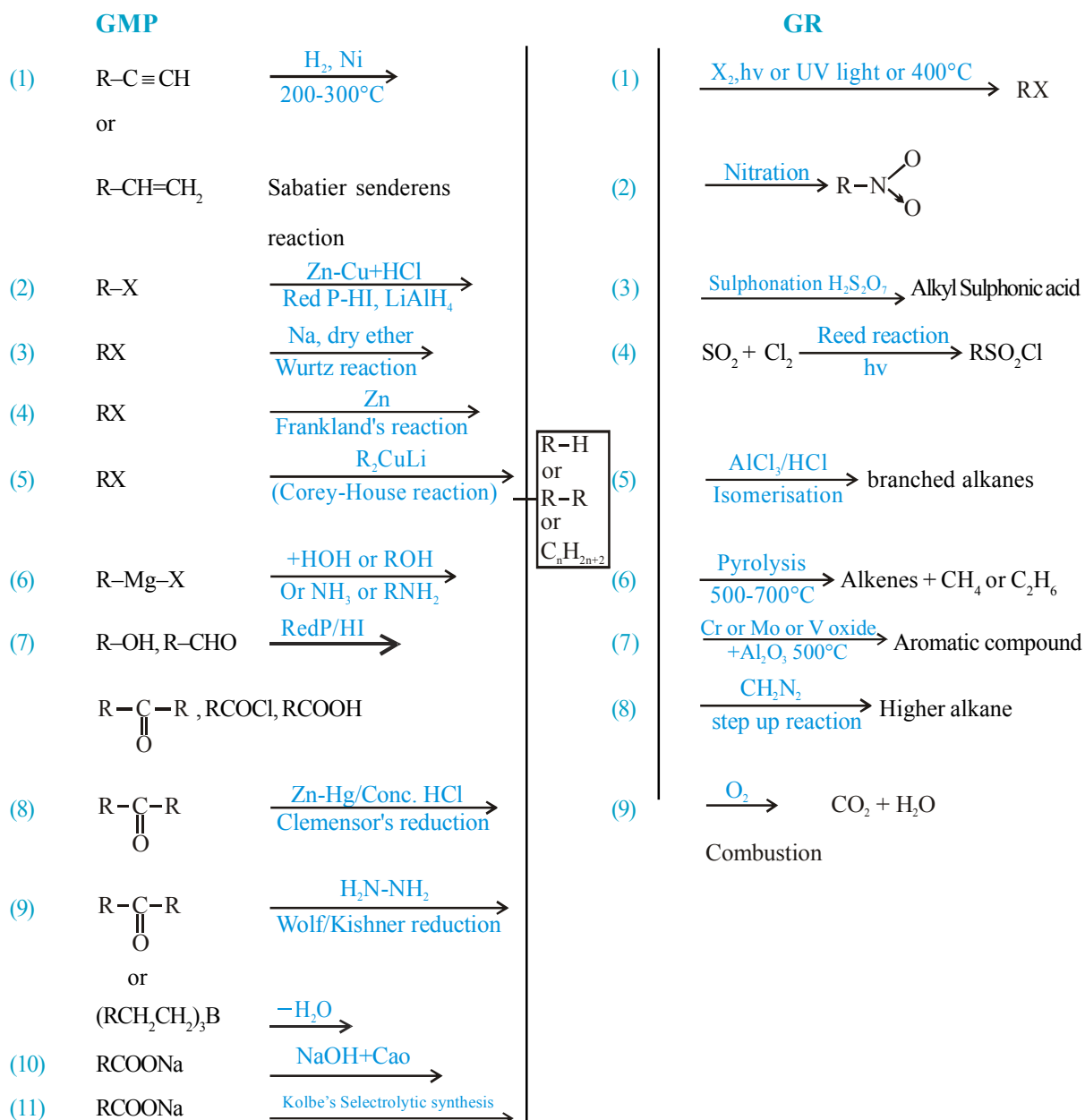
10. 1-butyne can be distinguished from 2-butyne by using  
(A) bromine water ( $\text{Br}_2$  in  $\text{CCl}_4$ )  
(B) cold alk.  $\text{KMnO}_4$  (Baeyer's Reagent)  
(C) ammoniacal solution  
(D) diethyl ether
11. What is the chief product of reaction between  $\beta$ -butylene chloride and alc.  $\text{KOH}/\text{NaNH}_2$   
(A) 1,2-butadiene      (B) 1,3-butadiene      (C) 2-butyne      (D) 1-buthne
12. Chloroform is heated with Ag powder in laboratory what will be the product –  
(A) Acetylene      (B)  $\text{Ag}_2\text{O}$       (C)  $\text{CH}_2\text{Cl}_2$       (D)  $\text{CH}_4$
13. Ethylene dibromide on treating with alcoholic  $\text{KOH}$  gives –  
(A)  $\text{C}_2\text{H}_6$       (B)  $\text{CH}_4$       (C)  $\text{C}_2\text{H}_4$       (D)  $\text{C}_2\text{H}_2$
14. Treatment of an alkyne with  $\text{H}_2$  in presence of palladised coke results in the formation of –  
(A) Alkane      (B) Alkane vigorously      (C) Trans-alkene      (D) cis-alkene

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### ANSWERS

- |     |     |     |     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1.  | (A) | 2.  | (B) | 3.  | (D) | 4.  | (A) | 5.  | (A) |
| 6.  | (C) | 7.  | (D) | 8.  | (C) | 9.  | (A) | 10. | (C) |
| 11. | (C) | 12. | (A) | 13. | (D) | 14. | (D) |     |     |
-

## REACTION CAHRT FOR ALKANES

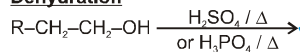


# Tips

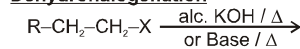
## PREPARATION AND PROPERTIES OF ALKENES

### General Method of Preparation (GMP)

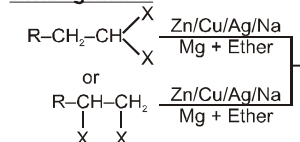
#### Dehydration



#### Dehydrohalogenation



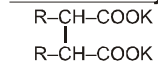
#### Dehalogenation



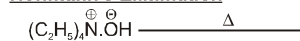
#### Partial Reduction



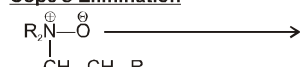
#### Kolbe's Electrolysis



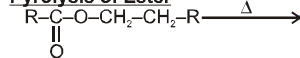
#### Hoffmann's Elimination



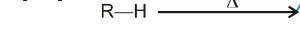
#### Cope's Elimination



#### Pyrolysis of Ester



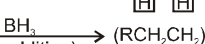
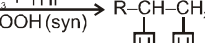
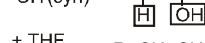
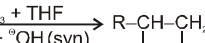
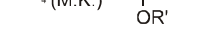
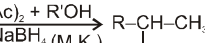
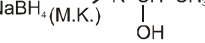
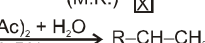
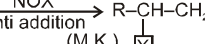
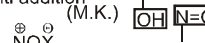
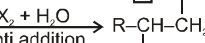
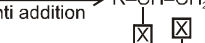
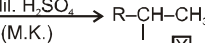
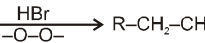
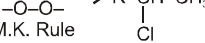
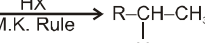
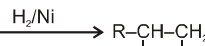
#### Pyrolysis



#### Non Terminal alkyne then Birch



### General Reactions (GR)



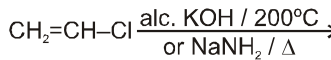
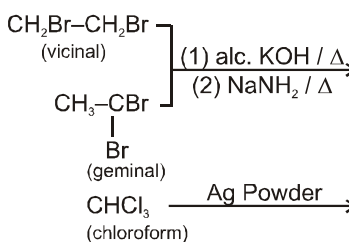
**RCH=CH<sub>2</sub>**  
or  
**C<sub>n</sub>H<sub>2n</sub>**

# Tips

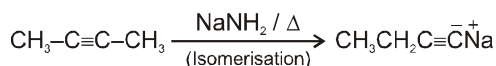
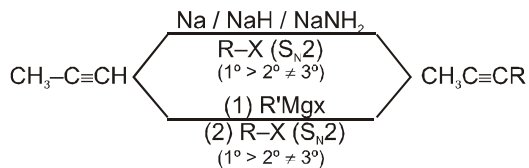
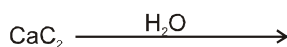
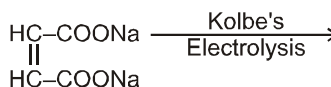
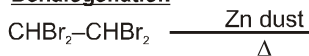
## PREPARATION AND PROPERTIES OF ALKYNES

### General Method of Preparation (GMP)

#### Dehydrohalogenation



#### Dehalogenation



### General Reactions (GR)

