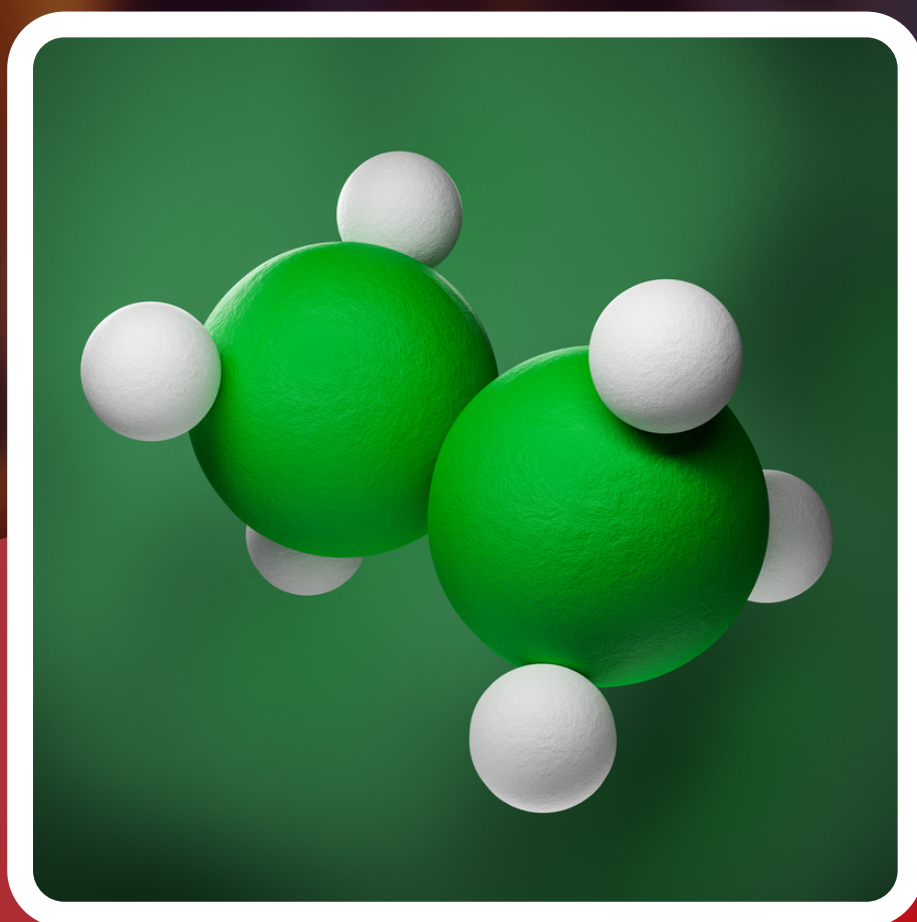


# ORGANIC CHEMISTRY

ENTHUSIAST | LEADER | ACHIEVER



**STUDY MATERIAL**

Hydrocarbons

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ENGLISH MEDIUM

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## HYDROCARBONS

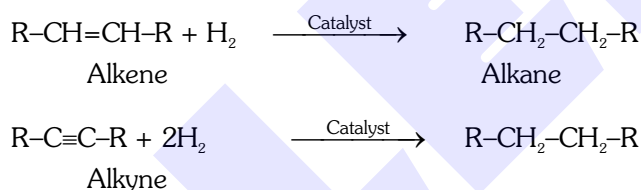
### 5.0 ALKANES

#### 5.1.1 Introduction of Alkanes

- (a) Branched and unbranched aliphatic saturated open chain hydrocarbons are called member of alkanes.
- (b)  $\text{CH}_4$  is also known as Marsh gas (fire damp).
- (c) Calore gas : Mixture of n-butane and isobutane.
- (d) LPG (Liquefied petroleum gas) : liquid propane, isobutane.
- (e) Natural gas : 80% methane + 10% ethane + 10% propane + small amounts of  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$  etc.
- (f) Water gas :  $\text{CO} + \text{H}_2$  (1:1)
- (g) Synthesis gas :  $\text{CO} + 3\text{H}_2$  (1:3)

#### 5.1.2 General Methods of Preparation

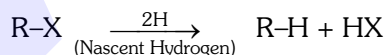
- (1) From alkenes and alkynes (Sabatier and Senderens reaction) or (By hydrogenation of alkenes and alkynes) :** Alkenes and alkynes on catalytic hydrogenation give alkanes.



**Catalyst :**

- (a) Pd/Pt at ordinary temperature and pressure
- (b) Ni, 200–300° C (Sabatier and Senderens reaction)
- (c) Raney Nickel at room temp.
- (d) Methane can not be prepared by this method

- (2) From alkyl Halides (By reduction) :**



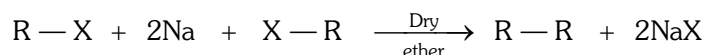
**Catalyst :**

- |                                 |   |   |
|---------------------------------|---|---|
| (i) $\text{Zn} + \text{HCl}$    | (ii) $\text{Zn} + \text{CH}_3\text{COOH}$ | (iii) $\text{Zn}-\text{Cu}$ couple in $\text{C}_2\text{H}_5\text{OH}$ |
| (iv) $\text{Red P} + \text{HI}$ | (v) $\text{Al}-\text{Hg}$ + ethanol       |   |

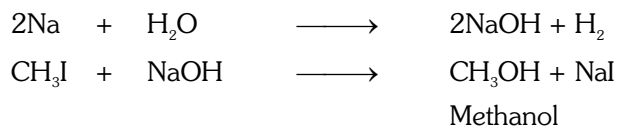
### GOLDEN KEY POINTS

- Alkyl halides can also be reduced to alkane by  $\text{H}_2/\text{Pd}$  or  $\text{LiAlH}_4$  or  $\text{H}_2/\text{Ni}$ .
- Halogen atom of alkyl halide is replaced by hydrogen atom to obtain an alkane.

**(3) From alkyl halide (By Wurtz reaction) :** A solution of alkyl halide in ether on heating with sodium gives alkane.

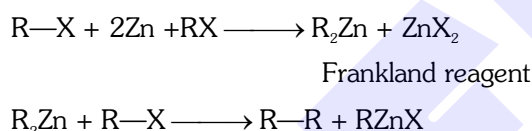


- (a) Two moles of alkyl halide are treated with Na in presence of dry ether. If ether is wet then we obtain alcohol.

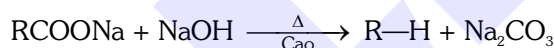


- (b) Methane can not be prepared by this method. The alkane produced is higher and symmetrical i.e. it contains double the number of carbon atoms present in the alkyl halide taken.
- (c) Two different alkyl halides, on wurtz reaction give all possible alkanes.
- (d) The separation of mixture into individual members is not easy because their B.P. are near to each other and thus wurtz reaction is not suitable for the synthesis of alkanes containing odd number of carbon atom.

**(4) From Frankland Reagent:**



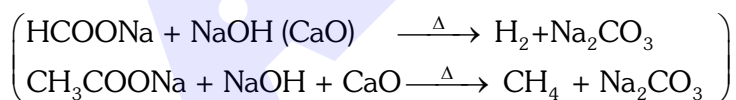
**(5) From Carboxylic Acid (By decarboxylation) :** Sodium salt of saturated monocarboxylic acid on dry distillation with sodalime give alkane.



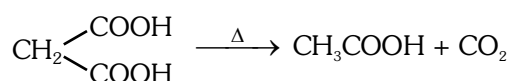
**Note :-** Sodalime  $\Rightarrow NaOH + CaO$

### GOLDEN KEY POINTS

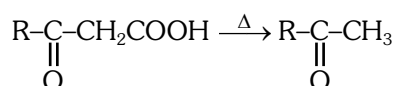
- The process of elimination of Carbon-di-oxide from Carboxylic acid called decarboxylation.
- The alkane formed by decarboxylation contains one carbon atom less than the original acid.
- Decarboxylation of sodium formate gives  $H_2$



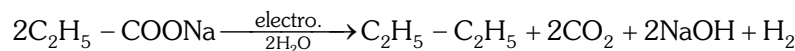
- If in a compound two carboxylic groups are present and they are attached to same carbon atom then decarboxylation of one of the carboxylic groups takes place simply on heating.



- $CH_3-CH_2-CH_3$  can be prepared by Butanoic acid and 2-Methyl propanoic acid.
- $\beta$ -Keto acids are decarboxylated readily simply on heating (soda lime is not required)

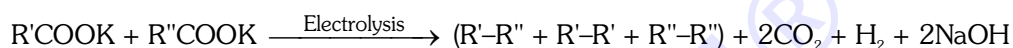


**(6) From carboxylic acid (By Kolbe's electrolysis process) :** Alkanes are formed on electrolysis of concentrated aqueous solution of sodium or potassium salt of saturated monocarboxylic acids.



### GOLDEN KEY POINTS

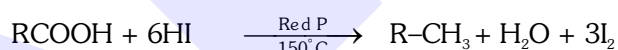
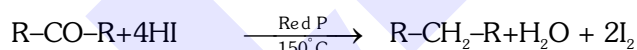
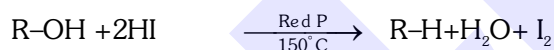
- Electrolysis of an acid salt gives symmetrical alkane, However in case of a mixture of Carboxylic acid salts, all probable alkanes are formed.



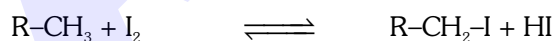
- At anode alkane and  $\text{CO}_2$  gas is formed while at cathode  $\text{NaOH}$  and  $\text{H}_2$  gas is formed.
- The concentration of  $\text{NaOH}$  in solution is increased with time so pH of solution is also increased.

### (7) From alkanol, alkanals, Alkanone and alkanoic acid (By reduction) :

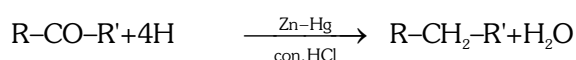
The reduction of either of the above compound in presence of red P and HI gives corresponding alkane.

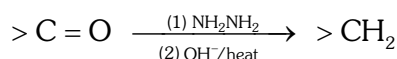


In the above reaction  $\text{I}_2$  is formed which may react with alkane to form alkyl halide. So red P is added in the reaction to remove  $\text{I}_2$  formed in the reaction.

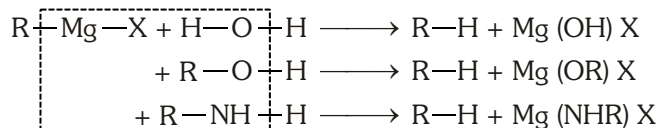


**(8) From alkanones (By Clemmensen's method) :** Carbonyl compound may also be reduced with Zinc amalgam and concentrated  $\text{HCl}$  ( $\text{Zn-Hg/HCl}$ ), this reaction is called Clemmensen reduction.



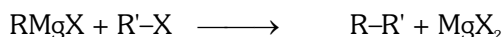
**(9) From alkanals and alkanones (By Wolf Kishner reaction) :**

**(10) From G.R. :**

- (a) Formation of alkanes with same number of C atoms :** Grignard reagent reacts with the compounds having active hydrogen to form alkane.

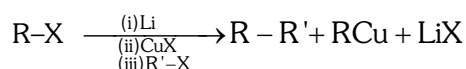


This reaction is used to determine the number of active H-atoms in the compound this is known as Zerewitnoff's method.

- (b) G.R. react with alkyl halide to give higher alkanes :**



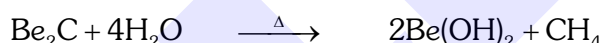
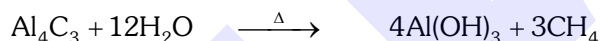
- (11) Corey-House Synthesis :** This method is suitable for the preparation of unsymmetrical alkanes i.e. those of type R-R'



**Note:** In Corey-House reaction symmetrical and unsymmetrical alkane both can be formed.

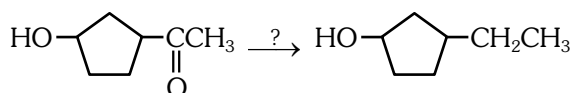
**(12) From metal carbide (By hydrolysis) :**

Only  $CH_4$  can be obtained by the hydrolysis of Be or Al carbides


**BEGINNER'S BOX-1**

- If two moles of Isopropyl chloride reacts with Na in presence of dry ether, which alkane is obtained.
  - Hexane
  - 2, 3-Dimethyl butane
  - Isopentane
  - Neopentane
- If isopropyl chloride and ethyl chloride both react with Na in presence of dry ether which alkanes are obtained.
  - n-Butane
  - 2-Methyl butane
  - 2, 3-Dimethyl butane
  - All of them
- Which of the following compound can not be obtained from single alkyl halide by wurtz reaction.
  - ethane
  - butane
  - isobutane
  - hexane
- Which of the following acids on decarboxylation gives isobutane
  - 2,2-Dimethyl butanoic acid
  - 2,2-dimethyl propanoic acid
  - 3-Methyl pentanoic acid
  - 2-Methyl butanoic acid

5. Which of the following reagent can be used for following conversion



- (1) Zn – Hg/HCl      (2) Red P + HI      (3)  $\text{NH}_2 - \text{NH}_2/^{\circ}\text{OH}$       (4) All of them

HC0007

6. Which of the following does not give alkane with  $\text{R}-\text{Mg}-\text{X}$ .

- (1)  $\text{Ph}-\text{OH}$       (2)  $\text{C}_6\text{H}_6$       (3)  $\text{CH}_3\text{COOH}$       (4)  $\text{HCl}$

7. Which of the following reaction can not be used to obtained propane in good yield.

- (1) Wurtz reaction      (2) Corey-House reaction  
(3) Decarboxylation of acid salt      (4) All of them

### 5.1.3 Physical & Chemical Properties of alkane

#### Physical properties

- (i) **Solubility** : Alkanes being non polar and thus insoluble in water but soluble in nonpolar solvents

Ex.  $\text{C}_6\text{H}_6$ ,  $\text{CCl}_4$ , ether etc.

- (ii) **Boiling point** -  $\propto$  molecular weight (for n-alkanes)

$$\therefore \boxed{\text{Vander Waals force of attraction} \propto \text{molecular weight} \propto \text{surface area of molecule.}}$$

i.e. boiling point      Pentane < hexane < heptane

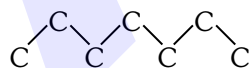
$$\text{Also boiling point} \propto \frac{1}{\text{number of side chain}}$$

because the shape approaches to spherical which results in decrease in van der Waal's forces (as surface area decreases)

Thus boiling point n-Pentane > Isopentane > neopentane

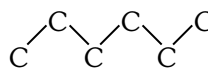
- (iii) **Melting Point** : M.P. of alkanes do not show regular trend. Alkanes with even number of carbon atoms have higher M.P. than their adjacents alkanes of odd number of carbon atoms.

The abnormal trend in M.P. is due to the fact that alkanes with odd carbon atoms have their end carbon atom on the same side of the molecule and in even carbon atom alkane the end Carbon atom on opposite side. Thus alkanes with even carbon atoms are packed closely in crystal lattice to permit greater intermolecular attractions.



Odd number of carbon

<

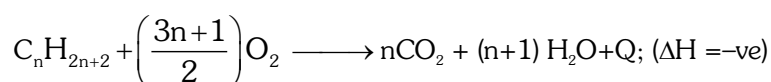


Even number of carbon

#### Chemical Properties

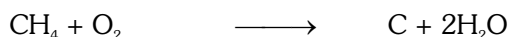
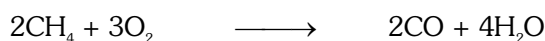
##### (1) Oxidation :

- (a) **Complete oxidation or combustion** : Alkanes burn readily with non-luminous flame in presence of air or oxygen to give  $\text{CO}_2$  and water with evolution of heat. Therefore, alkanes are used as fuels.





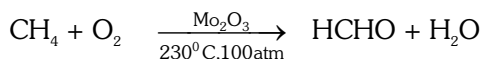
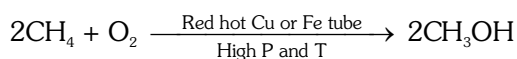
- (b) **Incomplete oxidation :** In limited supply of air, alkane gives carbon black and CO.



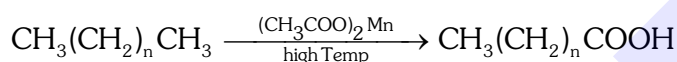
C-black (used in printing ink)

- (c) **Catalytic oxidation :**

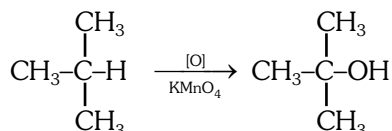
- (i) Alkanes are easily converted to alcohols and aldehydes under controlled catalytic oxidation.



- (ii) Alkanes on oxidation in presence of manganese acetate give fatty acids.

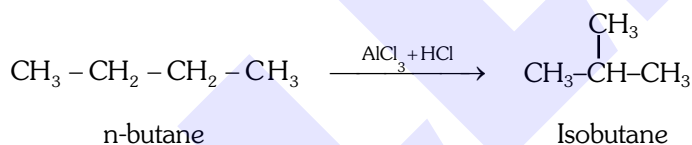


- (iii) Tertiary alkanes are oxidized to give tertiary alcohols by  $\text{KMnO}_4$ .

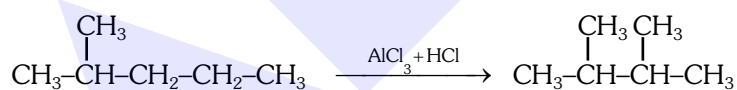


- (2) **Substitution Reactions :** Substitution reaction in alkanes shows free radical mechanism.

- (3) **Isomerization:** Unbranched chain alkanes on heating with  $\text{AlCl}_3 + \text{HCl} / 200^\circ\text{C}$  are converted into branched chain alkanes

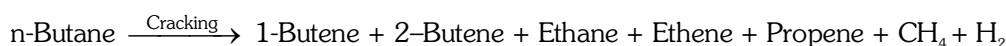
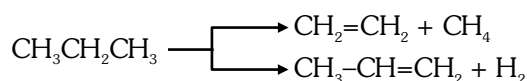
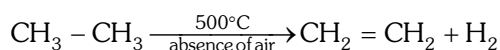
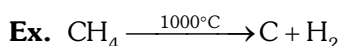


Branched chain alkanes converted to more branched alkane.



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

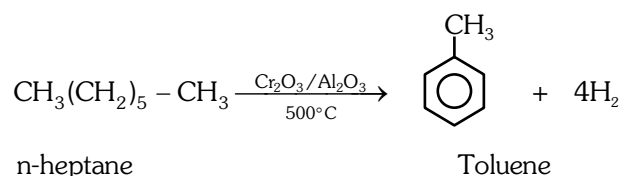
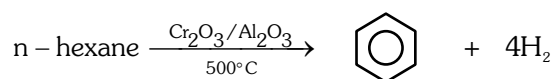
- (4) **Pyrolysis or Cracking or thermal decomposition :** When alkanes are heated to  $500-700^\circ\text{C}$  they are decomposed into lower hydrocarbon. This decomposition is called pyrolysis.





**(5) Aromatization:**

Unbranched higher alkanes (from 6 to 10 carbon atoms) when heated in presence of oxides of Cr, Mo, V on  $\text{Al}_2\text{O}_3$  support at  $500^\circ\text{C}$  aromatic hydrocarbons are formed.



#### 5.1.4 PETROLEUM

**Flash Point :** Flash point of an oil is that minimum temperature at which the oil gives so much vapour that it starts burning in the presence of air when it comes in contact with a spark. Flash point depends on local temperature of countries.

Flash point of kerosene in **India**  $\Rightarrow 44^{\circ}\text{C}$ ,    in **France**  $\Rightarrow 35^{\circ}\text{C}$ ,    in **England**  $\Rightarrow 23^{\circ}\text{C}$

**Knocking :** Preignition of the fuel-air mixture in the cylinder ahead of the flame causes knocking. Knocking reduces efficiency of the engine and also damages the cylinder and piston of the engine.

**Octane Number (Quality of Gasoline) :** Octane no. is a scale which is used to determine the quality of a fuel in an internal engine. Two pure hydrocarbons are selected as standard.

- (i) n - heptane – straight chain hydrocarbon knocks very badly have octane no. zero
- (ii) Iso-octane – branched hydrocarbon, good antiknocking properties, have octane no. 100.

**Octane no. of a fuel :** The percentage of iso-octane by volume in a mixture of iso-octane and n-heptane which has the same antiknocking properties as the fuel under examination.

For example – Let knocking of a fuel is same as a mixture of 70% iso-octane and 30% n-heptane, then its octane no. is 70.

**Order of quality of Gasoline or petrol :** (i) Length of chain  $\uparrow$ , the octane no.  $\downarrow$   
(ii) branches  $\uparrow$  octane no.  $\uparrow$

Straight chain alkane < branched chain alkane < olefins < cycloalkane < aromatic compound

**Octane number can be increased by :** (i) Cracking      (ii) Isomerization      (iii) Aromatization

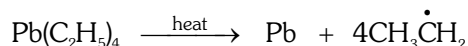
**Antiknocking agents - (Gasoline additives) :** Quality of a fuel is increased by :

- (i) By using fuel of higher octane no.
- (ii) By addition of certain compounds to the gasoline which reduce knocking. These are called antiknocking agents.

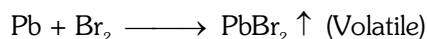
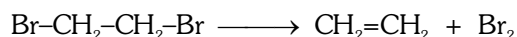
**Ex.** Tetraethyl lead (TEL) –  $\text{Pb}(\text{C}_2\text{H}_5)_4$   
Tetra methyl lead –  $\text{Pb}(\text{CH}_3)_4$

## Pre-Medical

In cylinder of engine  $\text{Pb}(\text{C}_2\text{H}_5)_4$  decomposes in ethyl radicals which combine with the radicals produced due to irregular combustion and this prevents knocking.



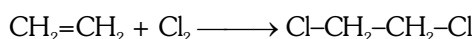
but combustion of TEL with petrol gives Litharge ( $\text{PbO}$ ) which deposited in cylinder walls and piston has jammed. So Ethylene dibromide is added with petrol.


**BEGINNER'S BOX-2**

- Which of the following reactions of alkanes involve free radical intermediates
  - Halogenation
  - Pyrolysis
  - Nitration
  - All of the above
- $(\text{CH}_3)_3\text{CMgCl}$  on reaction with  $\text{D}_2\text{O}$  produces
  - $(\text{CH}_3)_3\text{CD}$
  - $(\text{CH}_3)_3\text{OD}$
  - $(\text{CD}_3)_3\text{CD}$
  - $(\text{CD}_3)_3\text{OD}$
- The compound with the highest boiling point is—
  - n-hexane
  - n-pentane
  - 2,2-dimethyl propane
  - propane
- Photochemical chlorination of alkane is initiated by a process of
  - pyrolysis
  - substitution
  - Homolysis
  - Peroxidation
- The highest boiling point is expected for
  - Isooctane
  - 2,2,3,3-tetramethylbutane
  - n-octane
  - n-butane
- The antiknocking compound is
  - TEL
  - Diethylzinc
  - Dimethylcadmium
  - Tetramethyl tin

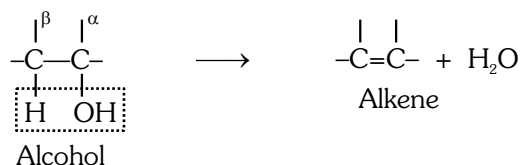
**HC0013**
**HC0015**
**5.2 ALKENES (OLEFINS)**
**5.2.1 Introduction of Alkenes**

Alkene are also called olefins (oil forming) since the first member ethylene ( $\text{C}_2\text{H}_4$ ) was found to form an only liquid on reaction with chlorine.



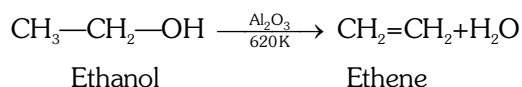
### 5.2.2 General Methods of Preparation

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

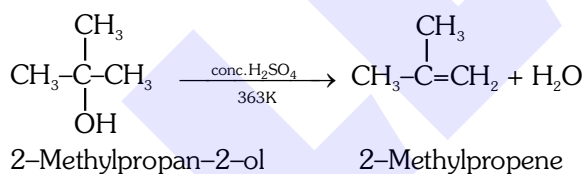
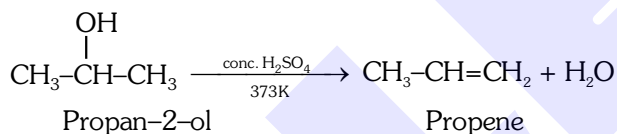
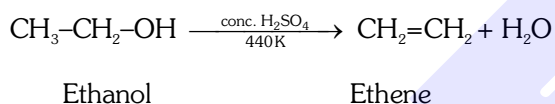


The dehydration can be carried with  $\text{Al}_2\text{O}_3$  or with **mineral acid** upon heating.

- (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.



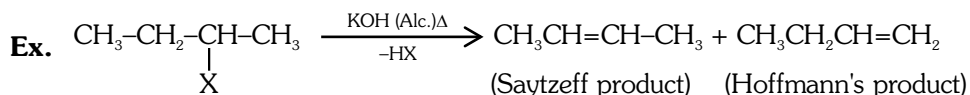
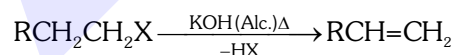
- (b) Dehydration with mineral acid :** Alcohols upon heating with conc.  $\text{H}_2\text{SO}_4$  form alkenes and the reaction is called **acidic dehydration**.



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

Tertiary > Secondary > Primary

- (2) From Alkyl halide (By dehydrohalogenation):** Removal of  $\text{HX}$  from a substrate by alcoholic  $\text{KOH}$  or  $\text{NaNH}_2$



The ease of dehydrohalogenation show the order

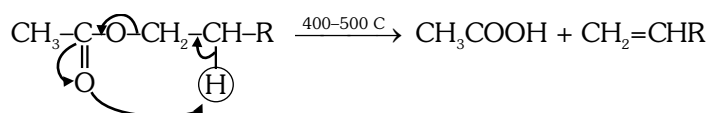
For alkyl group

tertiary > secondary > primary

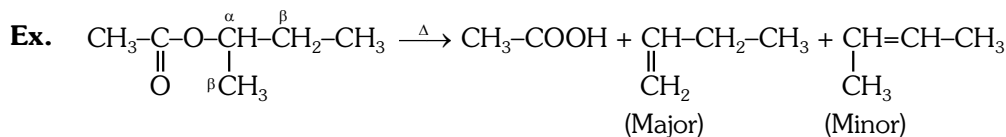
For halogen in halide

Iodide > Bromide > Chloride > fluoride



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

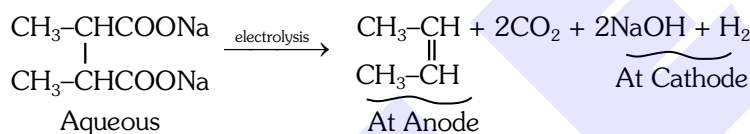
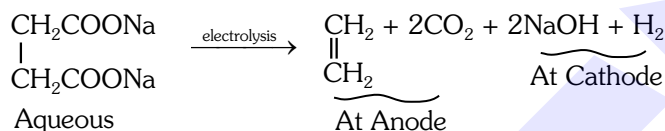
**Hoffmann's Rule :** Less substituted or less stable alkene is major product.



In the reaction to form an alkene a  $\beta$ -hydrogen from alkyl ester is attracted by oxygen atom of keto group.

**(6) By Pyrolysis of tetra alkyl ammonium hydroxide :**

**(7) By Kolbe's method:** Electrolysis of potassium or sodium salt of saturated dicarboxylic acid gives alkene.

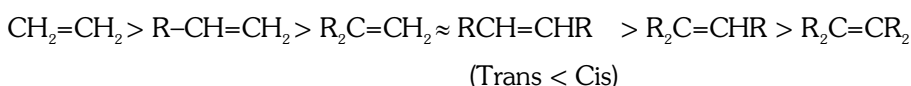
**5.2.3 PHYSICAL & CHEMICAL PROPERTIES OF ALKENES****Physical Properties**

- (1) All are colourless and have no characteristic odour. Ethene has pleasant smell.
- (2) Lower members ( $\text{C}_2$  to  $\text{C}_4$ ) gaseous medium ( $\text{C}_5$  to  $\text{C}_{17}$ ) liquid and higher members are solid.
- (3) The B.P., M.P. and specific gravity show a regular increase with increase in molecular weight
- (4) The increase in branching in carbon chain decreases the B.P. among isomeric alkenes.
- (5) The B.P. and M.P. of alkenes are slightly higher than the corresponding alkanes because the intermolecular forces of attraction are stronger due to the presence of easily polarizable  $\pi$  bond.
- (6) Insoluble in water because they can not form H-bond with water molecule, they dissolve freely in organic solvent like benzene,  $\text{CHCl}_3$ ,  $\text{CCl}_4$  etc.

**Chemical Properties :** 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 hinderance                      (ii) Hyperconjugation

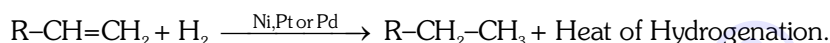
**Alkenes give the following type of reactions :**

- (A) Addition reaction.                      (B) Oxidation reaction.                      (C) Substitution reaction.  
(D) Polymerization Reaction.                      (E) Isomerisation

**(A) Addition Reaction :**

**[A<sub>1</sub>] Free Radical Addition**

**(1) Addition of H<sub>2</sub> :**



- (a) Reaction is exothermic, Heat released in reaction is called heat of hydrogenation.

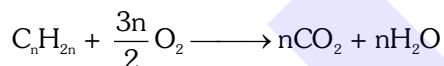
(b) Stability of alkene $\propto \frac{1}{\text{heat of hydrogenation}} \propto \frac{1}{\text{reactivity of alkene with } H_2}$
--

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

**[A<sub>2</sub>] Electrophilic Addition Reactions:**

**(B) Oxidation Reaction:** Alkenes are easily oxidised by oxidising agents. Oxidising agents attack on double bond and product formed during oxidation depends on oxidising agents.

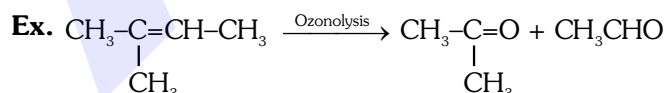
**(1) Combustion:**



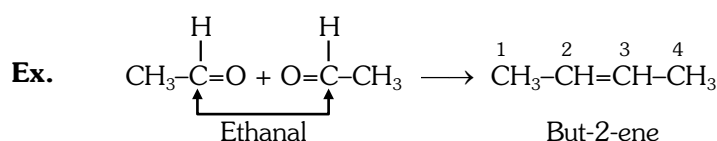
One mole of alkene requires  $\frac{3n}{2}$  moles of O<sub>2</sub> for complete combustion.

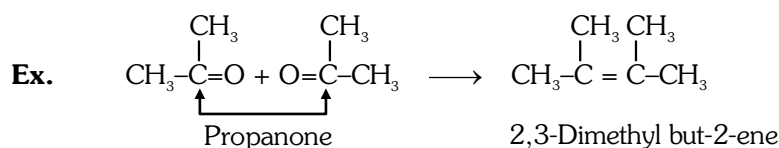
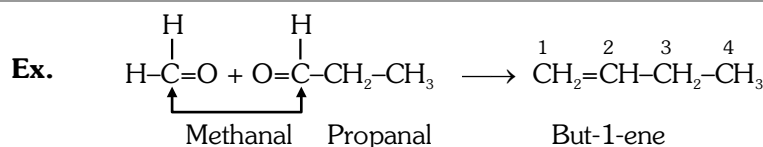
**(2) Ozonolysis :** (A test for unsaturation in molecule)

- (i) The addition of ozone on the double bonds and subsequent a reductive hydrolysis of the ozonide formed is termed as ozonolysis.  
(ii) Ozonides are explosive compound.  
(iii) On warming with Zn and H<sub>2</sub>O, ozonides cleave at the site of the double bond, the products are carbonyl compound (aldehyde or ketone) depending on the nature of the alkene.



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

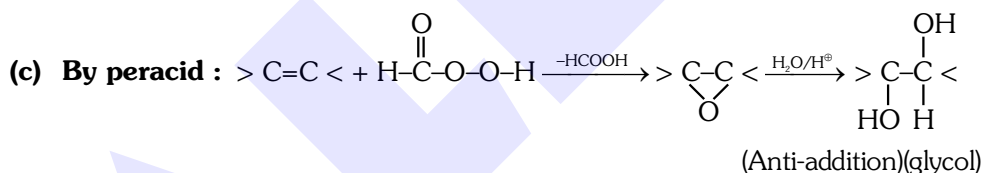
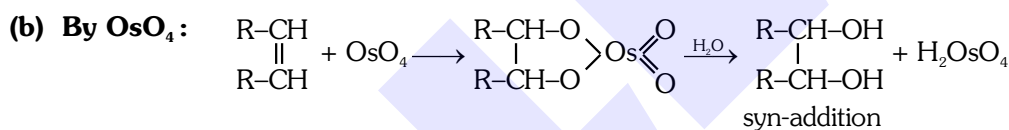
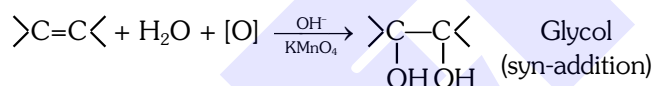




It may be noted that reaction with bromine water or Baeyer's reagent detects the presence of double bond (or unsaturation) in an alkene while ozonolysis helps in locating the position of the double bond.

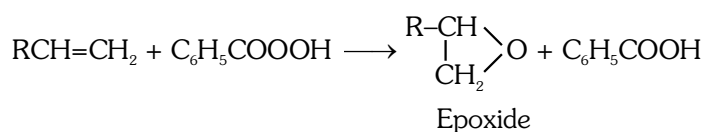
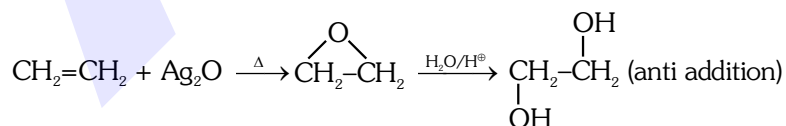
**(3) Hydroxylation :** Oxidation of carbon-carbon double bond to  $\begin{array}{c} | & | \\ -\text{C}-\text{C}- \\ | & | \\ \text{OH} & \text{OH} \end{array}$  is known as hydroxylation.

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

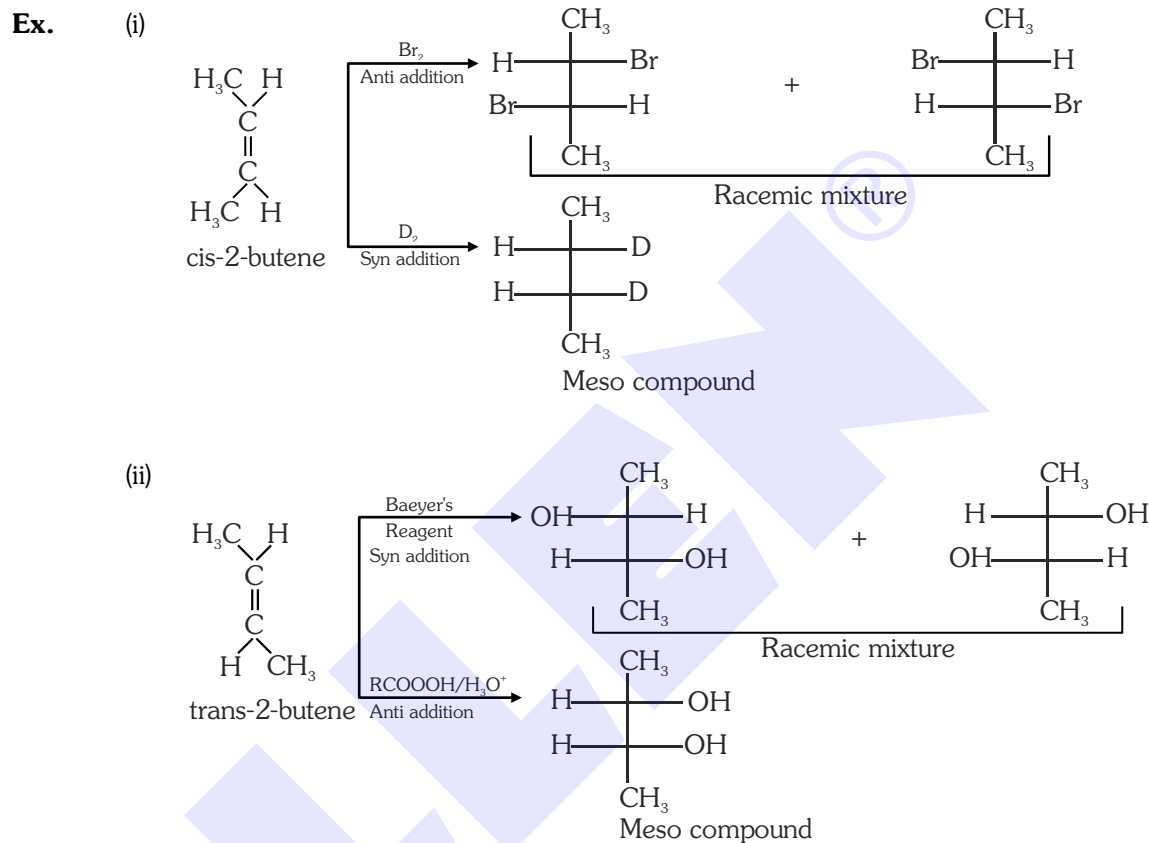
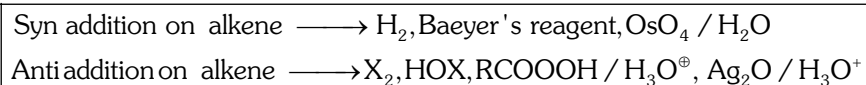


**(d) By  $\text{Ag}_2\text{O}/\Delta$  :**

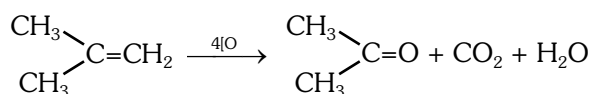
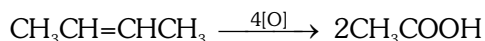
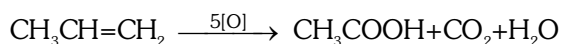
(a) Alkenes reacts with oxygen in the presence of Ag catalyst at  $250^\circ\text{--}400^\circ\text{C}$  to form epoxide.





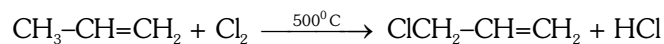


**(4) Oxidation by strong oxidising agent (Oxidative cleavage):** The alkenes themselves are readily oxidised to acid or ketone by means of acid permanganate. If  $\text{HCOOH}$  is formed, it further oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Keep it in mind that no further oxidation of ketones will takes place.



**(C) Substitution Reaction (Allylic Substitution):**

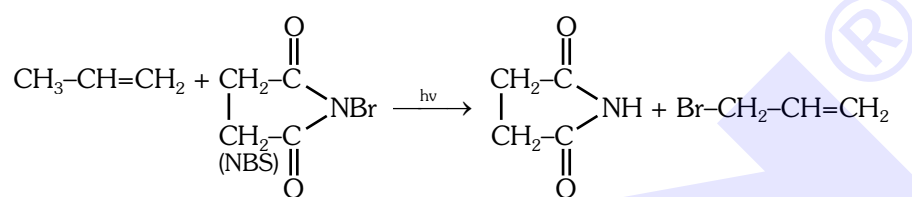
When alkenes are treated with low concentration of  $\text{Cl}_2$  or  $\text{Br}_2$  at high temperature or with NBS/hv one of their allylic hydrogen is replaced by halogen atom. Allylic position is the carbon adjacent to one of the unsaturated carbon atoms. It is free radical substitution.



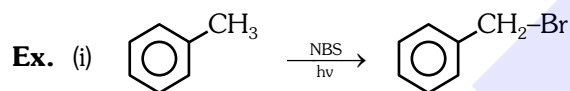
Allyl chloride

(3-Chloro-1-propene)

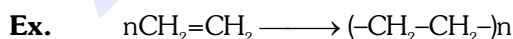
N-Bromosuccinimide (NBS) is an important reagent used for allylic bromination and benzylic substitution.



Substitution reaction is not given by ethene.

**(D) Polymerization:**

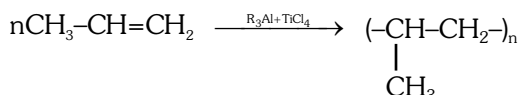
- Two or more than two molecules of same compound unit with each other to form a long chain molecule with same empirical formula. This long chain molecule having repeating structural units called polymer, and the starting simple molecule as monomer and process is called addition polymerization.
- Molecular weight of polymer is simple multiple of monomer.
- Polymerization can be carried out by free radical or ionic mechanism.
- The presence of oxygen initiates free radical mechanism.
- Addition polymerization can also be carried out by ionic mechanism by using Ziegler - Natta Catalysts ( $\text{R}_3\text{Al} + \text{TiCl}_4$ )



ethene

Poly ethene

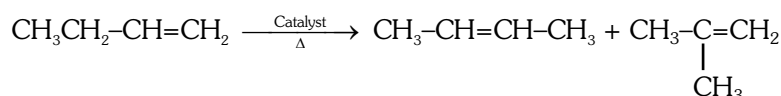
used in the manufacture of insulating Coating,  
sheeting and moulded products.



Polypropene or Koylene (Plastic)

**(E) Isomerisation :**

Alkene on heating to 500° to 700 °C or on heating in presence of catalyst [AlCl<sub>3</sub> or Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>] undergo isomerisation.

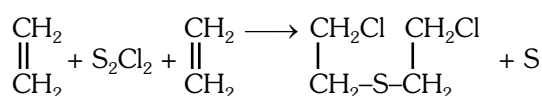


1-Butene

2-Butene

Isobutylene

- Uses:**
- (1) In plastic formation.
  - (2) In oxy ethylene welding
  - (3) As food preservatives and ripening fruits.
  - (4) As general anaesthetic (C<sub>2</sub>H<sub>4</sub> with 10% O<sub>2</sub>)
  - (5) In preparation of mustard gas



2,2' or (β, β') dichloro diethyl-sulphide  
(mustard gas)

**BEGINNER'S BOX-3**

- The treatment of (CH<sub>3</sub>)<sub>2</sub>C=CHCH<sub>3</sub> with boiling KMnO<sub>4</sub> produces
  - (1) CH<sub>3</sub>COCH<sub>3</sub> + CH<sub>3</sub>COOH
  - (2) CH<sub>3</sub>COCH<sub>3</sub> + CH<sub>3</sub>CHO
  - (3) CH<sub>3</sub>CHO + CO<sub>2</sub>
  - (4) CH<sub>3</sub>COCH<sub>3</sub> only
- Which alkene gives only acetone on ozonolysis ?
  - (1) Isobutylene
  - (2) 2,3-Dimethyl-1-butene
  - (3) 2,3-Dimethyl-2-butene
  - (4) 3,3-Dimethyl-1-butene
- Which of the following reactions is used for locating the position of double bond in an alkene ?
  - (1) Hydroboration
  - (2) Hydroxylation
  - (3) Chlorohydroxylation
  - (4) Ozonolysis
- The molecules having dipole moment are :-
  - (1) 2,2-dimethylpropane
  - (2) trans pent-2-ene
  - (3) cis-hex-3-ene
  - (4) 2 and 3
- When ethene reacts with bromine in aqueous sodium chloride solution, the product(s) obtained is (are)
  - (1) Ethylene dibromide only
  - (2) Ethylene dibromide and 1-bromo-2-chloro ethane
  - (3) 1-bromo-2-chloroethane only
  - (4) Ethylene dichloride only

HC0018

HC0020

HC0024

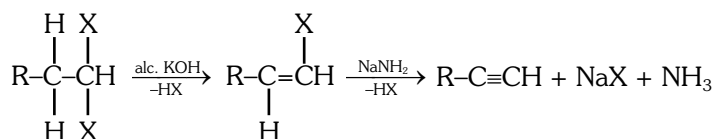
## 5.3 ALKYNES

## 5.3.1 Introduction of Alkynes

Alkynes are unsaturated hydrocarbons and characterised by the presence of a triple bond between the two carbon atoms ( $C \equiv C$ ). The carbon-carbon triple bond is also called acetylenic bond. It consists of a strong  $\sigma$  and two weak  $\pi$  bonds. Alkynes are isomers of alkadienes and cycloalkenes.

## 5.3.2 General Methods of Preparation

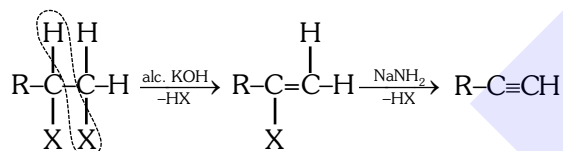
**(1) From Gem dihalides (by dehydrohalogenation) :** Dehydrohalogenation agents are :  $NaNH_2$  (Sodamide) or Alc. KOH or  $ROH + RONa$ .



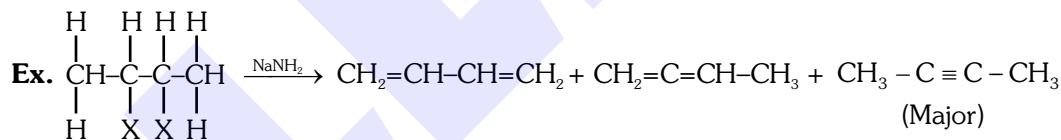
(Stable by resonance)

(Vinyl halide)

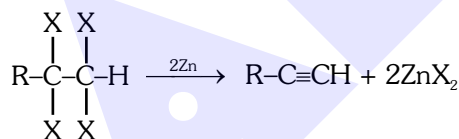
**(2) From Vicinal dihalides (by dehydrohalogenation) :**



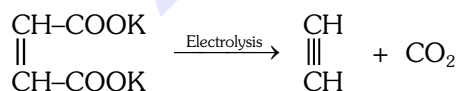
(a) Elimination of Vic. dihalides gives also alkadiene (1, 2 and 1, 3 alkadienes) but the major product is alkyne.



**(3) Dehalogenation of tetrahalo alkane :** By heating 1, 1, 2, 2 - tetra halo alkane with Zn dust.

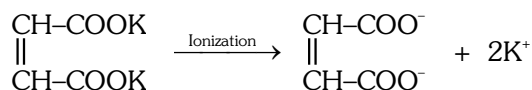


**(4) From Kolbe's electrolysis :** By the electrolysis of aqueous Solution of sodium or potassium fumarate or maleate, acetylene is formed at anode.



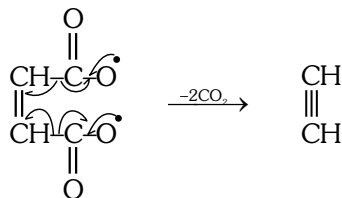
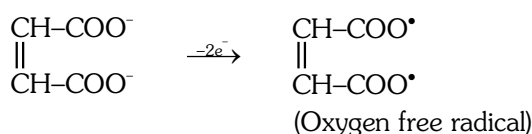
(Aqueous)

**Mechanism :**

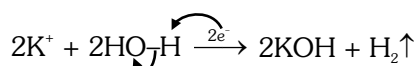


(Aqueous)

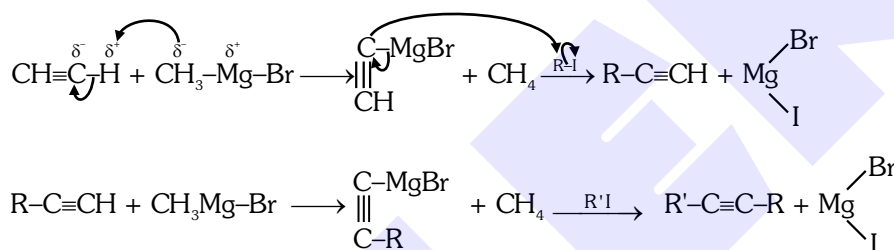
at **anode** (Alkyne and  $\text{CO}_2$  gas is formed)



at **cathode** ( $\text{KOH}$  and  $\text{H}_2$  gas is formed)

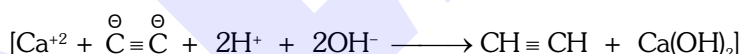


**(5) Preparation of higher alkynes by Grignard reagent :** By this method lower alkyne is converted in to higher alkyne

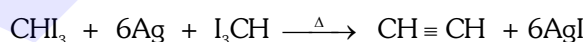


**(6) Preparation of Ethyne or Acetylene :**

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



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



### 5.3.3 Physical & Chemical Properties of Alkynes

#### Physical Properties

- (i) First three members [ $\text{C}_2$  to  $\text{C}_4$ ] are gases, from  $\text{C}_5$  to  $\text{C}_{12}$  are liquid and after that they are solid.
- (ii) Alkynes are slightly soluble in  $\text{H}_2\text{O}$  but soluble in  $\text{CCl}_4$ , benzene, acetone and alcohol.
- (iii) B.P., M.P. and densities of alkynes are comparatively more than alkenes and alkanes due to more polarisation.

$\text{B.P.} \propto \text{mol.wt.} \propto \frac{1}{\text{number of side chains}}$
---

### Chemical Properties

The chemical properties of alkynes are due to two factors

- (a) Presence of  $\pi$  electrons :** Due to presence of loosely bonded  $\pi$  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 reactions.

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

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

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

$\equiv\text{C-H}$	$=\text{C-H}$	$-\text{C-H}$
50%	33%	25%

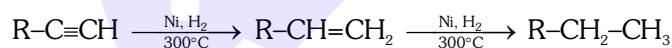
Since s electrons are closer to the nucleus than the p electrons, the electrons present in a bond having more s-character will be closer to nucleus. Due to high s-character of the C—H bond in alkyne (s=50%) the electrons constituting this bond are more strongly held by the carbon nucleus, with the result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

### GOLDEN KEY POINTS

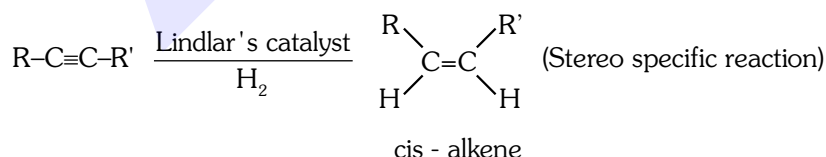
- The acidic nature of the three types of  $-\text{C-H}$  bonds are  
 $\begin{array}{ccccc} \equiv\text{C-H} & > & =\text{C-H} & > & -\text{C-H} \\ \text{sp} & & \text{sp}^2 & & \text{sp}^3 \end{array}$
- Relative acidic order  $\text{H}_2\text{O} > \text{ROH} > \text{HC} \equiv \text{CH} > \text{HNH}_2 > \text{CH}_2 = \text{CH}_2 > \text{CH}_3 - \text{CH}_3$

#### (1) Addition reaction

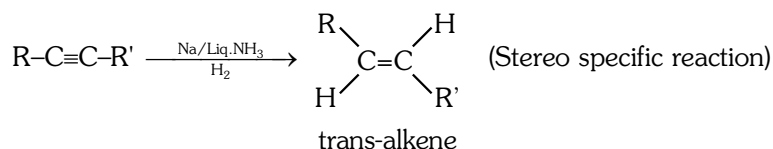
- (a) Addition of hydrogen :** Alkynes reacts with hydrogen in presence of a catalyst. In presence of Pt., Pd or Ni alkynes give alkanes with  $\text{H}_2$



In presence of Lindlar's catalyst [ $\text{Pd}/\text{CaCO}_3 + \text{quinoline}$ ] or Nickle boride alkynes give cis - alkene

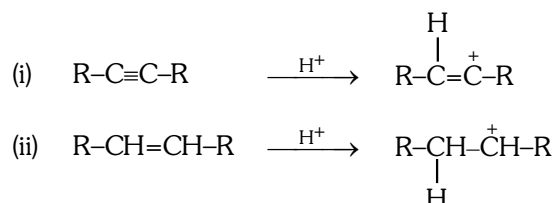


In presence of  $\text{Na}/\text{NH}_3$  alkynes give trans-alkene. **(Birch Reduction)**

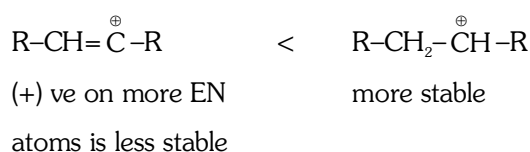


**(b) Electrophilic addition :** Addition reactions where the addition is initiated by electrophile (positive group). The characteristic reaction of alkynes is electrophilic addition but the reactivity of alkynes towards electrophilic addition is less than alkenes because in  $C\equiv C$ , the  $\pi$  electrons are tightly held by carbon nuclei and so they are less easily available for reaction with electrophiles.

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

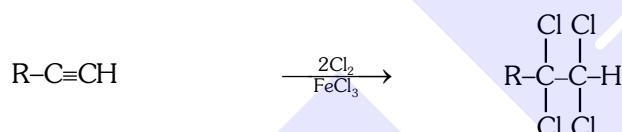


**Stability of intermediates :**

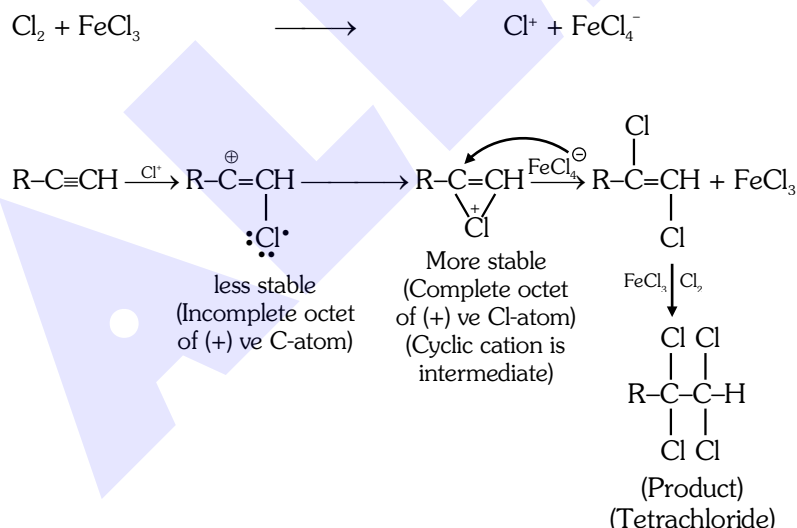


So we can say that alkenes are more reactive towards electrophilic addition reaction.

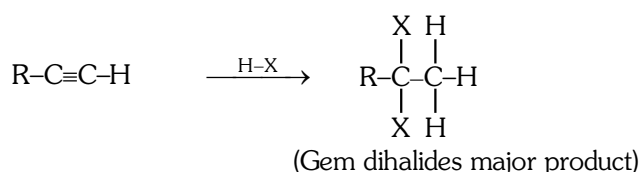
**(i) Addition of Halogens :** Alkynes react with  $Cl_2$  or  $Br_2$  in dark in presence of metal halide and form di and tetra halo derivatives.



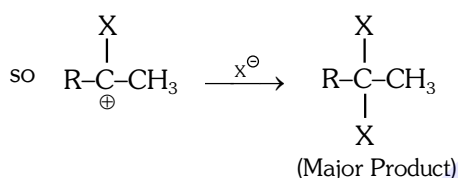
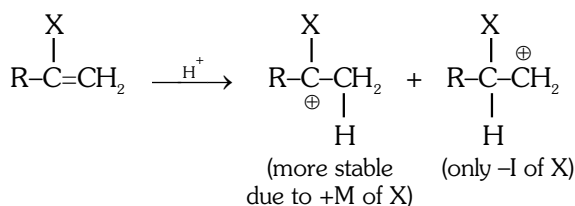
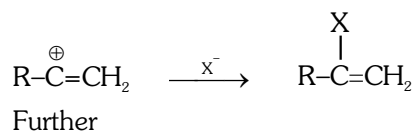
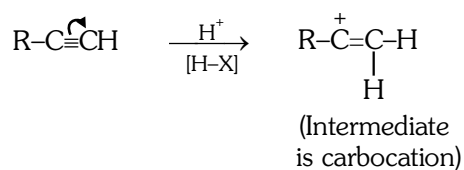
**Mechanism :**



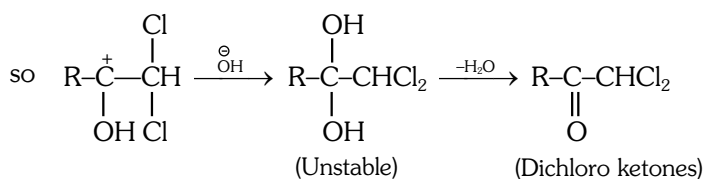
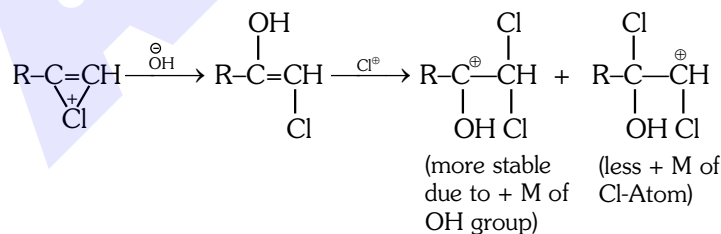
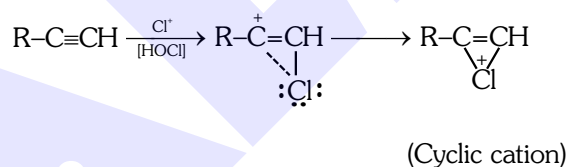
**(ii) Addition of halogen acids (H - X) :** Addition according to Markovnikov's Rule.



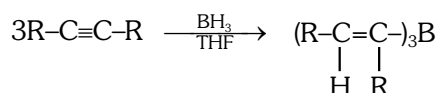


**Mechanism :**

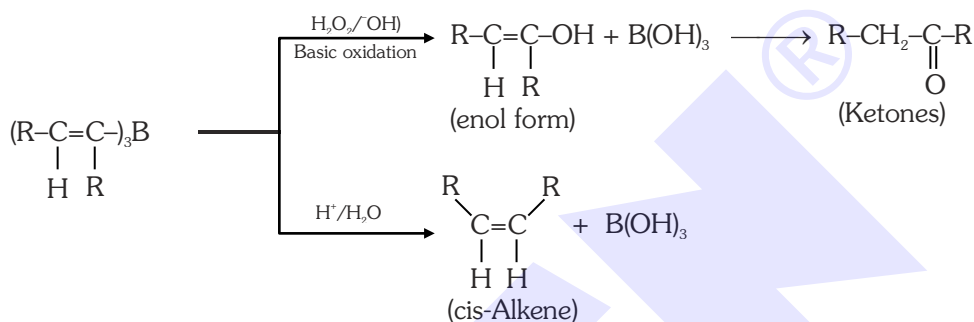
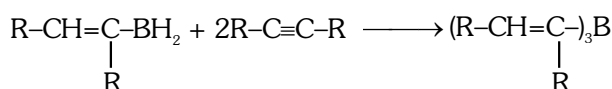
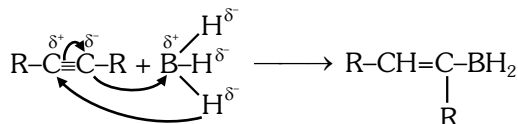
- (iii) **Addition of HOX :** Alkynes react with hypohalous acids according to Markovnikov's rule and form gem diol, which are unstable, lose a molecule of water and form dihalo aldehyde or dihalo ketones.

**Mechanism :**

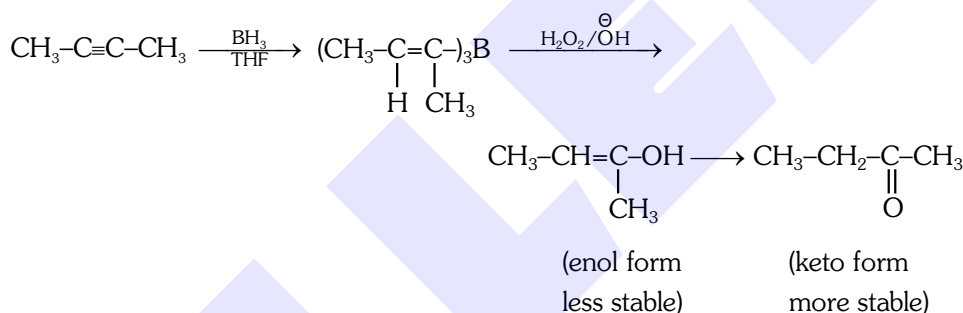
(iv) **Addition of  $\text{BH}_3$  / THF or  $\text{B}_2\text{H}_6$  (Hydroboration)** : THF - Tetrahydrofuran is used as solvent.



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

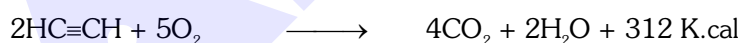
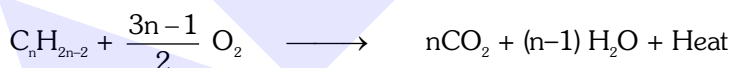


Ex.



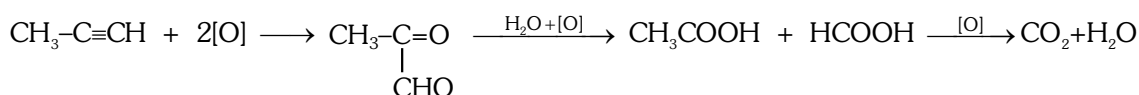
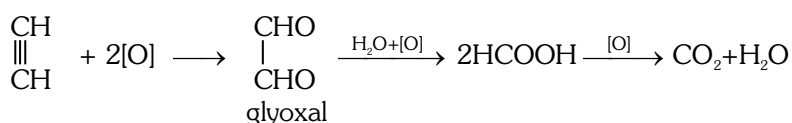
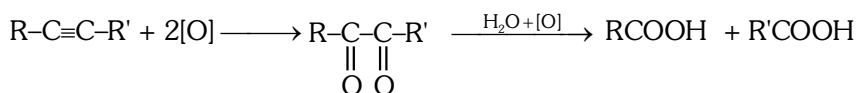
## (2) Oxidation Reactions

### (a) Combustion :

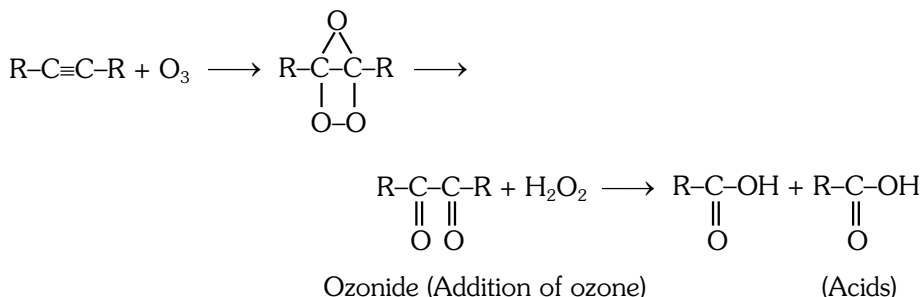


The combustion of acetylene is used for welding and cutting of metals in which oxy-acetylene flame having high temp ( $3000^\circ\text{C}$ ) is produced.

(b) **Oxidation with acidic  $\text{KMnO}_4$**  : In presence of acidic  $\text{KMnO}_4$ , alkynes are oxidised to monocarboxylic acids.

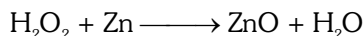


(c) **Oxidation with ozone (O<sub>3</sub>)** : In the ozonolysis both sp-C-atoms are converted into  $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{C} \\ \parallel \\ \text{O} \end{array}$  group.

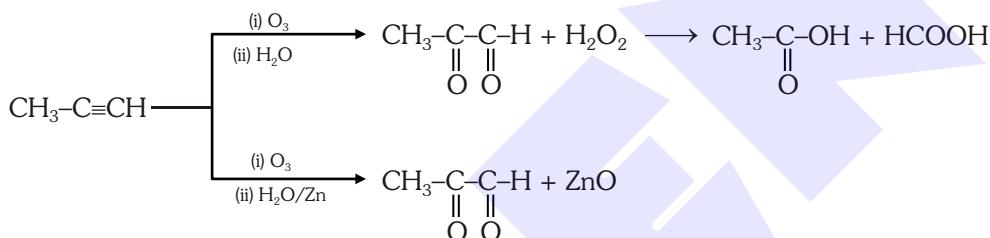


In this reaction H<sub>2</sub>O<sub>2</sub> is oxidant which oxidise  $\begin{array}{c} \text{R}-\text{C}-\text{C}-\text{R} \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$  into acids.

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



**Ex.**

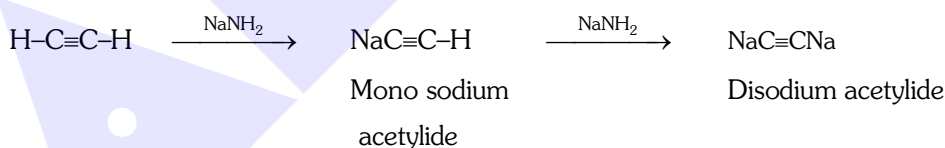


### (3) Substitution Reaction : (Formation of metallic derivatives)

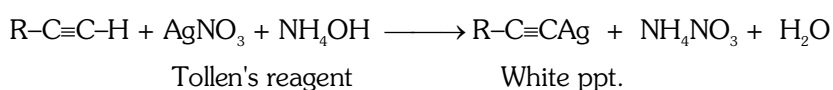
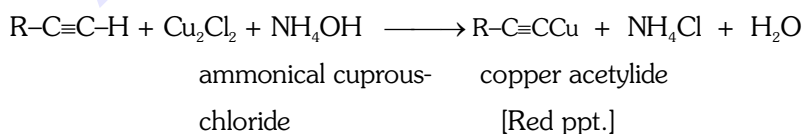
Only 1-alkynes give substitution reaction and show acidic characters  $\equiv \overset{\delta-}{\text{C}}-\overset{\delta+}{\text{H}}$

Acetylene is dibasic acid where as propyne is monobasic means acetylene can give two H<sup>+</sup> where as propyne can give one H<sup>+</sup>.

(a) **Formation of sodium acetylides** : Acetylene and 1-alkynes react with sodamide to form acetylides

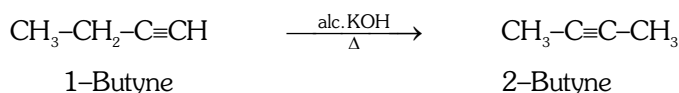


(b) **Formation of copper and silver acetylides** : Copper and silver acetylides are obtained by passing 1-alkynes in the ammonical solution of cuprous chloride and silver nitrate (Tollen's reagent) respectively.

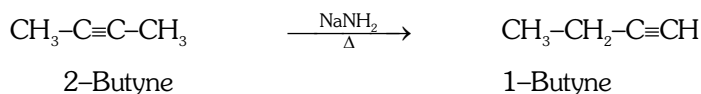


These reactions are used for detecting the presence of acetylenic hydrogen. These are test to distinguish alkenes and alkynes or 1-alkynes and 2-alkynes.

(4) **Isomerisation:** When alkyne-1 is heated with alc. KOH alkyne-2 is obtained.



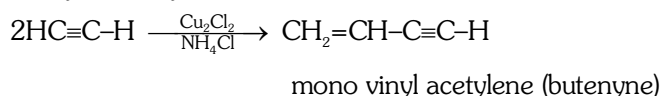
When alkyne-2 is heated with NaNH<sub>2</sub> alkyne-1 is obtained



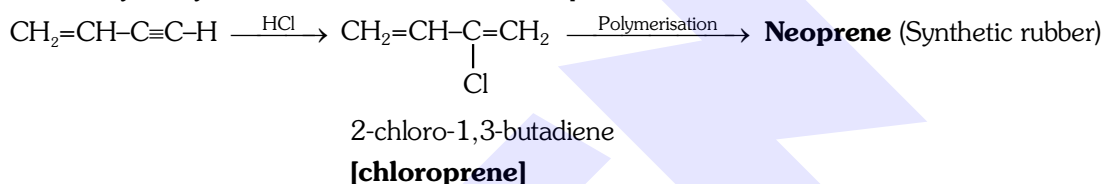
(5) **Polymerisation :**

(a) **Linear polymerisation :**

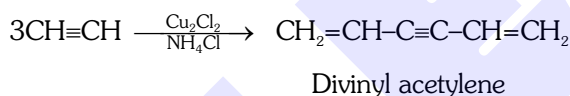
**Dimerisation :** When two molecules of acetylene passed through a solution. of Cu<sub>2</sub>Cl<sub>2</sub> and NH<sub>4</sub>Cl a vinyl acetylene is obtained.



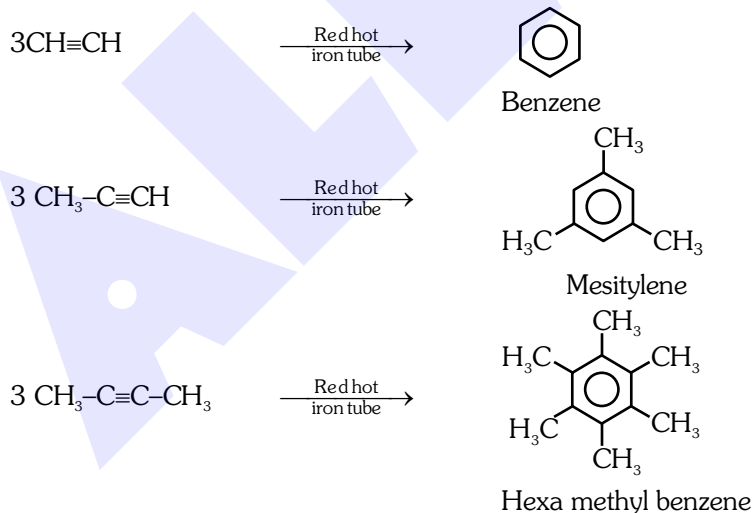
When vinyl acetylene react with HCl then chloroprene is obtained.



**Trimerisation :** 3 molecules of acetylene.



(b) **Cyclic polymerisation :** When alkyne is passed through red hot metallic tube, cyclic polymerisation takes place with the formation of aromatic compound



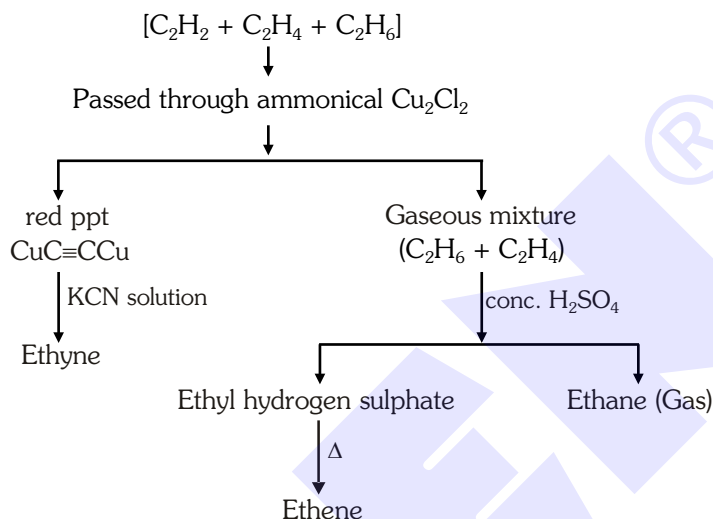
### Uses of Acetylene

- (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.

**Test for alkynes :**

- (i) Decolourization of  $\text{Br}_2$  in  $\text{CCl}_4$  Solution..
- (ii) Decolourisation of 1% alkaline  $\text{KMnO}_4$  Solution..
- (iii) 1- alkynes give white ppt. with ammonical  $\text{AgNO}_3$  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.

**Separation of ethane, ethene and ethyne :****BEGINNER'S BOX-4**

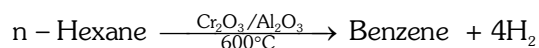
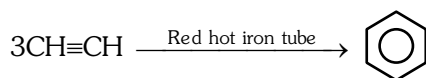
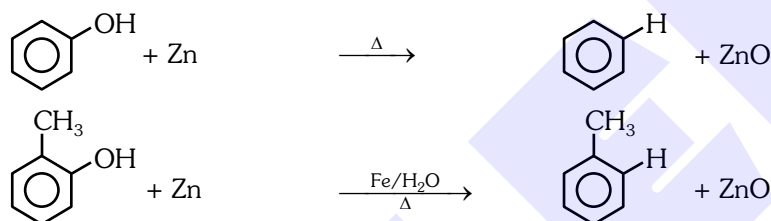
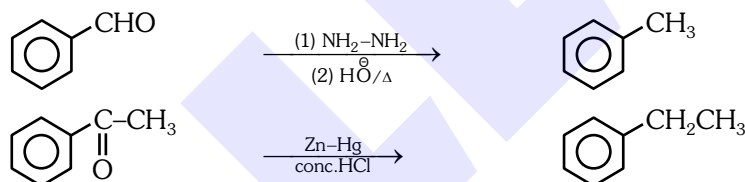
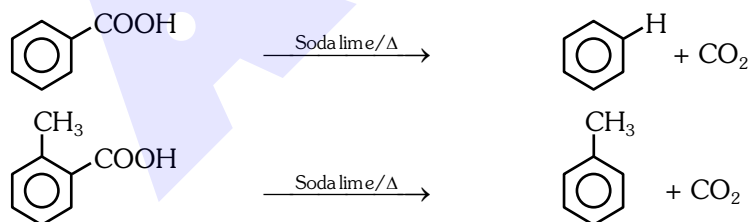
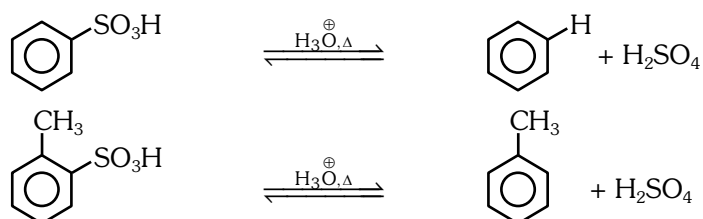
1. Propyne and HCl in presence of peroxide gives :  
 (1) 1,1-dichloro propane (2) 1,2-dichloro propane (3) 1,3-dichloro propane (4) 2,2-dichloro propane
2. When treated with ammonical cuprous chloride, which one among the following forms red precipitate ?  
 (1)  $\text{C}_2\text{H}_6$  (2)  $\text{C}_2\text{H}_4$  (3)  $\text{C}_2\text{H}_2$  (4)  $\text{C}_6\text{H}_6$
3. Which of the following decolourise 1% alkaline  $\text{KMnO}_4$  ?  
 (1) Propene (2) Propyne (3) 2-butyne (4) All of them
4. 1-Alkyne and 2 -Alkyne can not be distinguished by :  
 (1) Ammonical  $\text{AgNO}_3$  (2) Baeyer's reagent (3)  $\text{Br}_2$  in  $\text{CCl}_4$  (4) 2 and 3 both
5.  $\text{CH}\equiv\text{CH} \xrightarrow{\text{CH}_3\text{MgBr}} \text{A (gas)} + \text{B}$ ,  $\text{B} \xrightarrow{\text{CH}_3\text{-I}} \text{C}$ . C is :  
 (1)  $\text{CH}_4$  (2)  $\text{CH}_3\text{-CH}_3$  (3)  $\text{CH}\equiv\text{C-CH}_3$  (4)  $\text{CH}_3\text{-C}\equiv\text{C-I}$

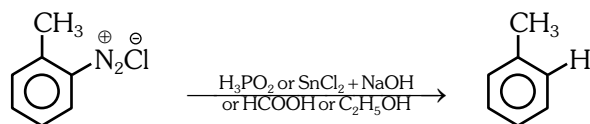
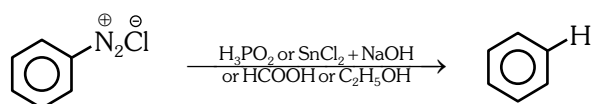
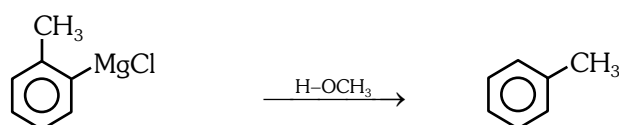
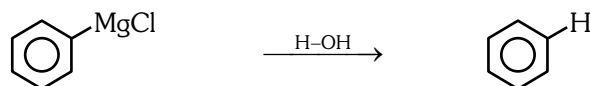
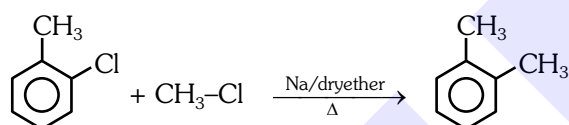
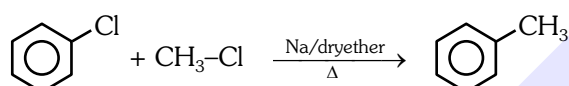
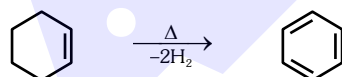
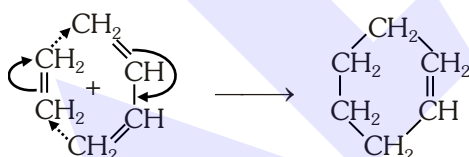
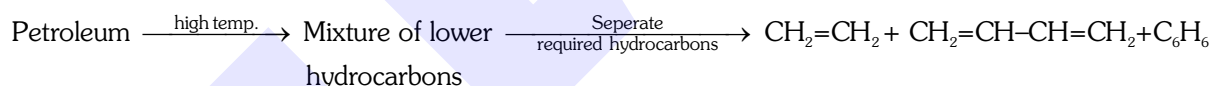
**HC0033****5.4 AROMATIC HYDROCARBONS [ARENES]****5.4.1 Introduction of Arenes**

- Arenes are cyclic, planar and follow Huckel's rule.
- There should be cyclic resonance in Arenes.
- General formula of Arenes are  $\text{C}_n\text{H}_{2n-6y}$  where  $n$  = Number of carbons  
 $y$  = Number of rings

## Pre-Medical

- Characteristic reaction of arenes is Electrophilic substitution reaction (ESR).
- Arenes are cyclic unsaturated compounds but do not give test of unsaturation with  $\text{Br}_2/\text{CCl}_4$  or alk.  $\text{KMnO}_4$ .
- Main source of Arenes is coal tar.
- They have higher percentage of carbon so burn with smoky flame.

**5.4.2 General Methods of Preparation**
**(i) From alkanes (By cyclisation or Aromatisation) Hydroforming or catalytic reforming**

**(ii) From alkyne (By cyclic polymerisation)** When acetylene is passed through red hot metallic tube cyclic polymerisation takes place and benzene is formed.

**(iii) From Phenolic compounds (By deoxygenation) :**

**(iv) From carbonyl compounds (By reduction) :**

**(v) From carboxylic acids (By decarboxylation) :**

**(vi) From sulphonic acids (By hydrolysis) :**


**(vii) By diazonium salts :****(viii) By Grignard reagent :****(ix) By Wurtz fittig reaction :****(x) From petroleum :****5.4.3 Physical & Chemical Properties of Arenes****Physical properties :**

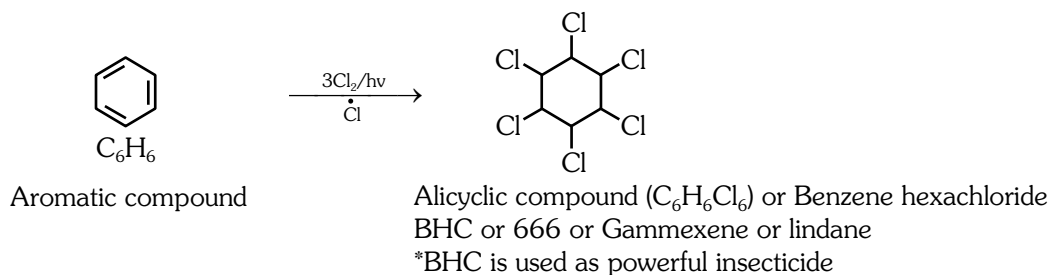
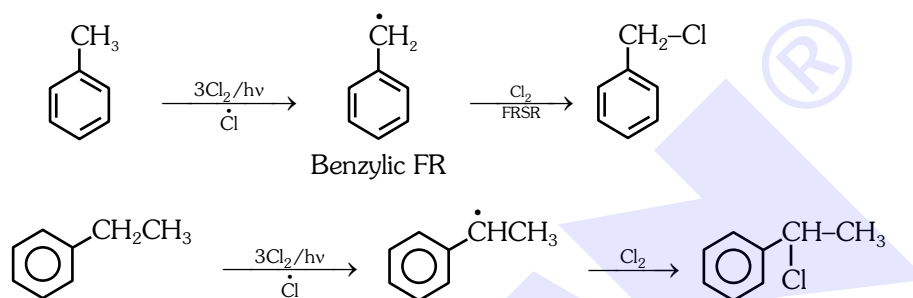
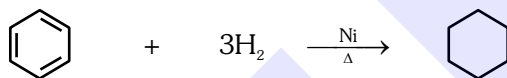
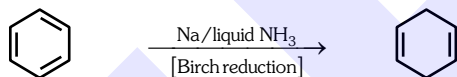
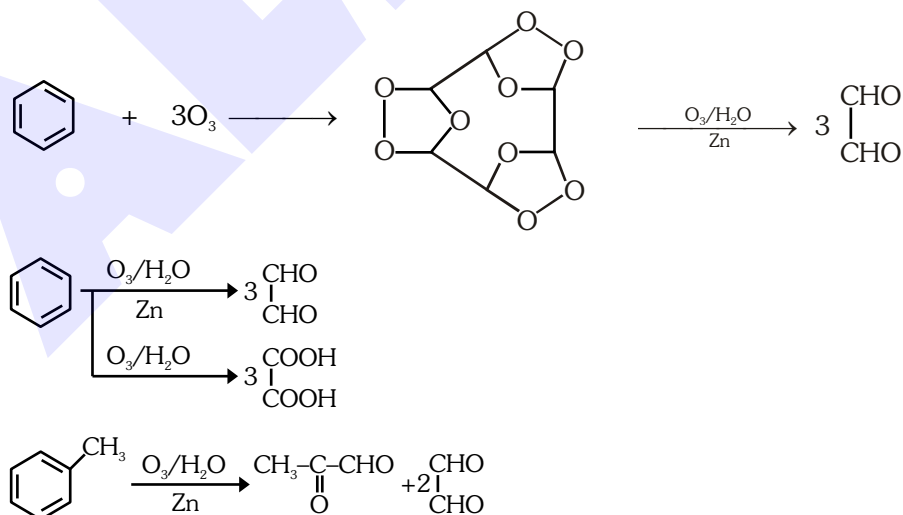
- Benzene is colourless liquid [B.P. is 80°C]
- Benzene is insoluble in  $\text{H}_2\text{O}$  and density less than  $\text{H}_2\text{O}$
- Benzene is used as a solvent and it is soluble in organic solvents.
- It is highly inflammable and burns with smoky flame.

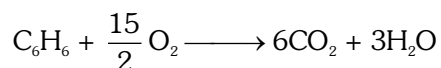
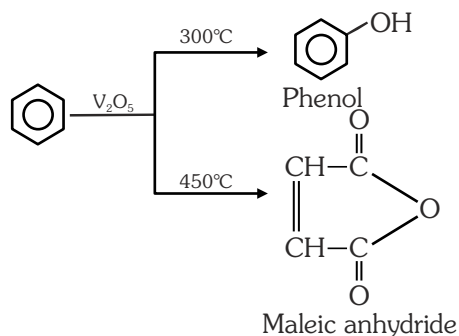
**Chemical properties :** Benzene show following types of reaction –

- (A) Addition reactions      (B) Electrophilic substitution reactions      (C) Oxidation reactions

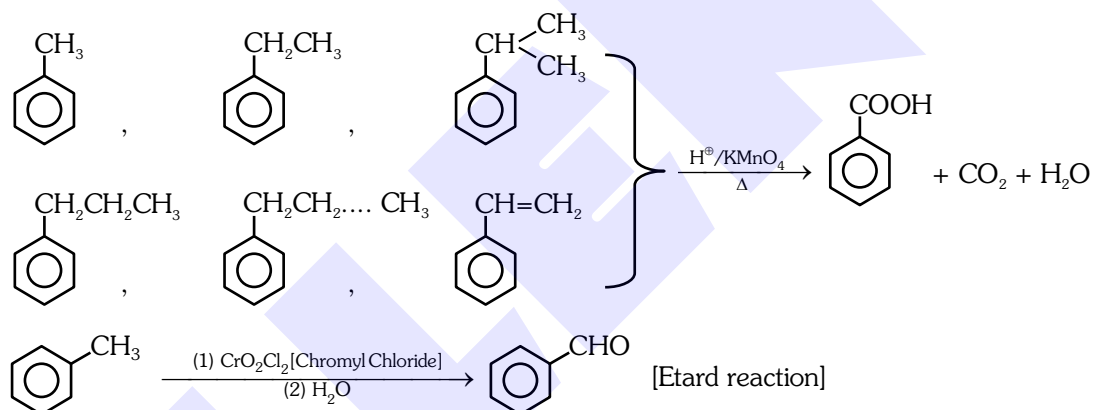


Pre-Medical

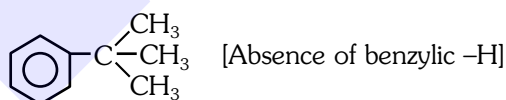
**(A) Addition reaction :**
**(i) Addition of  $X_2$** 

 Formation of BHC from  $C_6H_6$  is an example of free radical addition reaction.

**(ii) Addition of  $H_2$  :**
**(a) Complete hydrogenation :**

**(b) Partial hydrogenation :**

**(iii) Addition of  $O_3$  :**

 Addition of 3 mole  $Cl_2$  or 3 mole  $H_2$  or 3 mole  $O_3$  on benzene show presence of 3 double bonds in benzene. Benzene does not give addition reaction with  $Br_2/CCl_4$  or alkaline  $KMnO_4$

**(C) Oxidation reactions :****(i) Combustion :****(ii) Catalytic Oxidation :**

**(iii) Side chain Oxidation :** At least one benzylic -H containing alkyl benzene gives benzoic acid in presence of strong oxidising agent.



**Note :** t-butyl benzene does not give benzoic acid in presence of  $\text{H}^+/\text{KMnO}_4$ , since t-butyl benzene does not contain benzylic-H

**ANSWER'S KEY**

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6	7	
	Ans.	2	4	3	2	3	2	1	
BEGINNER'S BOX-2	Que.	1	2	3	4	5	6		
	Ans.	4	1	1	3	3	1		
BEGINNER'S BOX-3	Que.	1	2	3	4	5			
	Ans.	1	3	4	4	2			
BEGINNER'S BOX-4	Que.	1	2	3	4	5			
	Ans.	4	3	4	4	3			