# **HYDROCARBONS**

#### **ALKANES**

Alkanes are the simplest organic compounds. They are also known as paraffins. The general formula of alkanes is  $C_nH_{2n+2}$ . Each carbon atom of alkane is  $sp^3$  hybridized and its shape is tetrahedral. The bond lengths between C–H and C–C bonds are 1.12  $\stackrel{\circ}{A}$  and 1.54  $\stackrel{\circ}{A}$  respectively. The simplest member of alkane series is methane (CH<sub>4</sub>).

## **Methods of Preparation**

Acetylene

## 1. By catalytic hydrogenation of unsaturated hydrocarbons:

Hydrogenation takes place in the presence of finely divided nickel as catalyst at 200°C. This reaction is known as Sabatier and Sanderson's reaction.

$$\begin{split} \text{CH}_2 &= \text{CH}_2 + \text{H}_2 \xrightarrow{\phantom{0}\text{Ni}\phantom{0}\phantom{0}} \text{CH}_3 - \text{CH}_3 \\ \text{Ethylene} & \text{Ethane} \\ \text{CH} &= \text{CH} + 2\text{H}_2 \xrightarrow{\phantom{0}\text{Ni}\phantom{0}\phantom{0}} \text{CH}_3 - \text{CH}_3 \end{split}$$

Hydrogenation is possible at room temperature when platinum or palladium is used as a catalyst in place of Ni. Methane cannot be obtained by this method as no unsaturated hydrocarbon contains a single carbon atom.

# 2. By the reduction of alkyl halides:

Alkyl halide can be reduced with Zn + CH<sub>3</sub>COOH, Zn + HCl, Zn + NaOH, Zn–Cu couple in  $C_2H_5OH$ , aluminium amalgam in  $C_2H_5OH$  or LiAlH<sub>4</sub>.

$$R - X + 2H \longrightarrow R - H + HX$$

Alkyl halides can also be conveniently reduced by heating with HI and red phosphorous in a sealed tube.

$$R - I + HI \xrightarrow{P} RH + I_2$$

The function of red phosphorous is to remove iodine.

## 3. By the reduction of alcohols, aldehydes, ketones and fatty acids:

The above compounds and their derivatives can be reduced with hot hydroiodic acid and red phosphorous at 150°C in a sealed tube to give alkanes.

$$\begin{array}{c} \text{ROH} + 2\text{HI} & \xrightarrow{\text{Red P}} \text{RH} + \text{H}_2\text{O} + \text{I}_2 \\ \text{RCHO} + 4\text{HI} & \xrightarrow{\text{Red P}} \text{RCH}_3 + 2\text{I}_2 + \text{H}_2\text{O} \\ \text{R-COR} + 4\text{HI} & \xrightarrow{\text{Red P}} \text{R-CH}_2\text{-R} + \text{H}_2\text{O} + 2\text{I}_2 \\ \text{R-COOH} + 6\text{HI} & \xrightarrow{\text{Red P}} \text{RCH}_3 + 2\text{H}_2\text{O} + 3\text{I}_2 \end{array}$$

Aldehydes and ketones can also be reduced to alkanes by amalgamated zinc and conc. HCl. The reaction is known as Clemmensen reduction.

$$R-CHO+2H_2 \xrightarrow{\quad \quad Zn-Hg \quad \quad } R-CH_3+H_2O$$

Aldehydes can be reduced to alkanes with hydrazine and KOH at 150–200°C. This reaction is known as Wolff–Kishner reduction.

$$\mathsf{CH_3CHO} + \mathsf{NH_2NH_2} \longrightarrow \mathsf{CH_3CH=NNH_2} \xrightarrow{\phantom{\mathsf{KOH}\phantom{\mathsf{KOH}\phantom{\mathsf{M}}}}} \mathsf{CH_3CH_3} + \mathsf{N_2}$$

#### 4. By condensing two molecules of alkyl halides:

Two molecules of alkyl halides when treated with sodium metal in presence of dry ether coupled to form alkane. This reaction is known as Wurtz synthesis.

$$R - Br + 2Na + R - Br \xrightarrow{Dry \text{ ether}} R - R + 2NaBr$$

5. **By decarboxylation of carboxylic acid:** The sodium salt of carboxylic acid is strongly heated with soda lime to give alkane by elimination of CO<sub>2</sub> as carbonate.

$$R-COONa+NaOH \xrightarrow{\quad \text{Heat} \quad \atop \text{CaO} \quad} RH+Na_2CO_3$$

- 6. **Kolbe's electrolysis:** Sodium or potassium salts of fatty acids are electrolyzed to give higher alkanes at node. 2CH₃COONa + 2H₂O → CH₃ − CH₃ + 2CO₂ + 2NaOH + H₂ Methane can't be prepared by this method.
- 7. By action of water on aluminium carbide or beryllium carbide:

$$AI_4C_3 + 12H_2O \longrightarrow 4AI(OH)_3 + 3CH_4$$
 Aluminium carbide  
 $Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$  Beryllium carbide

# **Physical Properties**

- State: Due to weak forces, the alkanes upto four carbon atoms are colourless, odourless gases, the next thirteen members are colourless, odourless liquids. Alkanes from C<sub>18</sub> onwards are colourless and odourless solids.
  - In alkenes, except ethene, all are odourless and follow some trend as alkanes. Ethene has a pleasant odour. All are colourless. Alkynes also follow the same trend as alkanes.
- 2. **Density:** The density of alkanes increases very slowly with the rise of molecular mass until it becomes constant at 0.8.
- 3. **Solubility:** They are generally insoluble in polar solvents such as water but insoluble in non-polar solvents like ether, CCl<sub>4</sub>, benzene etc.
- 4. **Boiling and melting points:** The boiling point of straight chain alkanes increase regularly with increasing number of carbon atoms. The melting points of alkanes do not follow a very smooth gradation with the increase of molecular size. Alkenes and alkynes also show a gradual increase in boiling and melting points with the increase of molecular mass in homologous series. They are less volatile than alkanes, i.e., their boiling point and melting point are higher than corresponding alkanes.

#### **Chemical Properties**

Alkanes are extremely stable and inert substance due to presence of non-polar C – C and C – H bonds. Alkanes are saturated compounds with strong sigma bonds which doesn't break under ordinary conditions. Alkanes react at high temperature by free radical mechanism.

1. Halogenation (free radical substitution):

Alkanes react with halogens (Cl<sub>2</sub>, Br<sub>2</sub>) in presence of light or in dark at high temperature to form corresponding substituted products.

$$\begin{array}{c} \operatorname{CH}_4 & \xrightarrow{\operatorname{Cl}_2} & \operatorname{CH}_3 \operatorname{Cl} & \xrightarrow{\operatorname{Cl}_2} & \operatorname{CH}_2 \operatorname{Cl}_2 & \xrightarrow{\operatorname{Cl}_2} & \operatorname{CHCl}_3 & \xrightarrow{\operatorname{Cl}_2} & \operatorname{CCl}_4 \\ \operatorname{methene} & \operatorname{chloroform} & \operatorname{carbon} \end{array}$$

The relative reactivity of halogens and alkanes follows this order,

$$F_2 > Cl_2 > Br_2 > l_2$$
 and  $3^{\circ} > 2^{\circ} > 1^{\circ} > CH_3$ 

2. **Nitration:** Nitration is possible for alkanes having three or more carbon atoms. Nitration of propane yields mixture of nitro products.

$$\begin{array}{c} NO_2 \\ \text{CH}_3\text{CH}_2\text{CH}_3 \xrightarrow{\text{HNO}_3} \text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2 + \text{CH}_3 + \text{CH}_3\text{CH}_2\text{NO}_2 + \text{CH}_3\text{NO}_2 \end{array}$$

## 3. Sulphonation:

Higher alkanes (hexane onwards) undergo sulphonation when treated with fuming H<sub>2</sub>SO<sub>4</sub>.

$$\begin{array}{ccc} n-C_6H_{14}+HOSO_3H & \longrightarrow & C_6H_{13}SO_3H+H_2O \\ Hexane & & Hexane \ sulphonic \ acid \end{array}$$

#### 4. Oxidation or combustion:

Alkanes burn in presence of O<sub>2</sub> to form CO<sub>2</sub> and H<sub>2</sub>O with evolution of heat.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$
  
 $2C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 6H_2O$ 

Illustration 1: The order of reactivity of halogens towards halogenation of alkane is

(A) 
$$F_2 > Br_2 > Cl_2$$
 (B)  $F_2 > Cl_2 > Br_2$  (C)  $Cl_2 > F_2 > Br_2$  (D)  $Cl_2 > Br_2 > F_2$ 

**Solution:** (B). In a group, electronegativity of the atom decreases. So, the reactivity of halogen also decreases in a group. Thus, the order of reactivity is  $F_2 > Cl_2 > Br_2$ .

# Illustration 2: Consider the following reaction:

$$\begin{array}{c} \text{H}_{3}\text{C} & \text{CH}_{3} \\ \\ \text{D} & \text{CH}_{3} \end{array} + \quad \text{Br}^{\bullet} \longrightarrow \text{'X'} + \text{HBr}$$

Identify the structure of the major product 'X'.

(A) 
$$H_3C$$
  $CH_2$   $CH_3$   $CH_$ 

**Solution:** (B). Br• is less reactive and more selective and so the most stable free radical (3°) will be the major product.

Exercise 1

(1) The compound with the highest boiling point is

(A) n- hexane

(B) n- pentane

(C) 2,2- dimethyl propane

(D) 2- methyl butane

(2) Relative reactivity of halogens on alkanes follow the order

(A)  $F_2 > Cl_2 > Br_2 > l_2$ 

(B)  $CI_2 > Br_2 > I_2 > F_2$ 

(C)  $F_2 > I_2 > Br_2 > CI_2$ 

(D)  $I_2 > Br_2 > CI_2 > F_2$ 

(3) Propane is obtained from propene by which of the following method?

(A) Wurtz reaction

(B) Dehydration

(C) Frankland reaction

(D) Catalytic hydrogenation

#### **ALKENES**

Alkenes are characterized by the presence of a double bond between two carbon atoms. Alkenes have the general formula  $C_nH_{2n}$ .

## **Methods of Preparation**

## 1. By dehydration of alcohols:

Dehydration of alcohols in presence of acids forms alkene. This is elimination reaction.

$$R-CH_2-CH_2-OH \xrightarrow{\quad H^+\quad \atop \Delta} R-CH=CH_2+H_2O$$

# 2. By the dehydrohalogenation of alkyl halides:

$$CH_3CH_2CH_2Br \xrightarrow{alc. KOH} CH_3CH=CH_2 + HBr$$

If dehydrogenation of alkyl halide gives two products, the major product will be according to Saytzeff's rule, i.e. the alkene which is most substituted is the major product.

The ease of dehydrohalogenation follows the order,

Tertiary alkyl halide > secondary alkyl halide > primary alkyl halide.

Among the different halides, the order is alkyl iodide > alkyl bromide > alkyl chloride.

#### 3. By the dehalogenation of vicinal dihalides:

Dehydrohalogenation of vicinal dihalides in presence of Zn dust in alcoholic solution yields pure alkene.

$$Br \rightarrow Br +Zn \longrightarrow H_2C = CH_2 +ZnBr_2$$

#### 4. Kolbe's electrolysis method:

The electrolysis of sodium or potassium salts of dicarboxylic acid gives alkene at anode.

NaOOC COONa 
$$+2H_2O \xrightarrow{\text{electrolysis}} CH_2 \atop CH_2 + 2CO_2 + H_2 + 2NaOH$$

However, if Na/ liq NH₃ is used, trans alkene is formed, and in presence of Ni cis alkene is formed.

#### **Chemical Properties**

Alkenes are reactive due to the presence of double bonds. Due to presence of  $\pi$  bonds alkenes give electrophilic addition reaction. Alkenes also give free radical addition reaction.

- 1. Addition reactions:
- (i) Addition of hydrogen (catalytic hydrogenation)

$$CH_2 = CH_2 + H_2 \xrightarrow{N_1} CH_3 - CH_3$$

(ii) Addition of halogens (Cl<sub>2</sub> or Br<sub>2</sub>)

$$CH_2 = CH_2 + Br_2 \longrightarrow BrCH_2 - CH_2Br$$

Ethylene dibromide (colourless)

Addition of bromine is used as a test for detecting the presence of a carbon– carbon double bond or triple bond.

(iii) Addition of hydrogen halides

$$CH_2 = CH_2 + HX \longrightarrow CH_3CH_2X$$

The order of reactivity among hydrogen halides is

In case of unsymmetrical alkenes addition occurs according to Markonikov's rule. This reaction takes place through an ionic mechanism. Electrophilic addition to a carbon–carbon double bond involves the formation of an intermediate, i.e. more stable carbocation.

#### Deviation from Markonikov's rule:

It has been observed that addition of HBr to unsymmetrical alkenes like propene in presence of air, peroxide or light yields n-propyl bromide by anti-Markonikov's rule. The effect is called peroxide effect or Kharasch effect.

$$\begin{array}{c} \text{Br} \\ \mid \\ \text{H}_{3}\text{C} - \text{CH} - \text{CH}_{3} \\ \text{isopropylbromide} \\ \text{(Markonikov's)} \end{array} \xrightarrow{\text{HBr} \\ \text{no peroxide}} \text{CH}_{3}\text{CH} = \text{CH}_{2} \xrightarrow{\text{HBr} \\ \text{peroxide}} \text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{Br} \\ \text{(Anti-Markonikov's)} \\ \text{Addition} \end{array}$$

(iv) Addition of hypochlorous acid

$$\label{eq:ch2} \begin{aligned} \mathbf{CH}_2 &= \mathbf{CH}_2 \ + \ \mathbf{HOCl} \\ & \text{Ethylene} \end{aligned} + \begin{aligned} \mathbf{HOCl} \\ & \text{Hypochlorous acid} \end{aligned} \\ & \text{ethylene chlorohydrin} \end{aligned}$$

(v) Addition of sulphuric acid

$$H_3C$$
 $CH_2$ 
 $+$ 
 $H_2SO_4$ 
 $H_3C$ 
 $CH_3$ 
 $CH_3$ 
isopropyl hydrogen sulphate

Alkyl hydrogen sulphates are water soluble, when heated at about 160°C, they give olefins. On reaction with water they give alcohol.

$$CH_3 - CH_2 - OH + H_2SO_4 \xleftarrow{H_2O, boil} CH_3 - CH_2 - OSO_3H \xrightarrow{160^{\circ}C} CH_2 = CH_2 + H_2SO_4$$

(vi) Addition of water

$$CH_3 - CH = CH_2 + H_2O \xrightarrow{H^+} CH_3 - CH - CH_3$$

(vii) Addition of alkanes (alkylation)

(viii) Addition of diborane (hydroboration)

In case of unsymmetrical alkenes, addition follows the Anti Markonikov's rule.

$$6\mathrm{CH_3CH_2CH} = \mathrm{CH_2} + \mathrm{B_2H_6} \longrightarrow 2(\mathrm{CH_3CH_2CH_2CH_2})_3\,\mathrm{B}$$

tributyl borane

Trialkyl borane on oxidation (H<sub>2</sub>O<sub>2</sub>/OH<sup>-</sup>) gives alcohol and on reduction (LiAlH<sub>4</sub>) gives alkane.

# (ix) Oxymercuration – demurcuration

$$+ H_2O + Hg(OAc)_2 \xrightarrow{-AcOH} OH HgOAc$$

$$+ AcOH + Hg$$

$$OH H$$

## (x) Addition of oxygen

$$H_2C \longrightarrow CH_2 + \frac{1}{2}O_2 \xrightarrow{Ag}$$
 ethylene oxide

#### 2. Oxidation:

(i) Oxidation by cold alkaline KMnO<sub>4</sub> (Bayer's reagent)

$$\begin{array}{c} \text{H}_2\text{C} \longrightarrow \text{OH} \\ \text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O} + \text{O} \longrightarrow \begin{array}{c} \text{H}_2\text{C} \longrightarrow \text{OH} \\ \text{ethylene glyco} \end{array}$$

It is a test for detecting double bonds in alkene. Hydroxylation by KMnO<sub>4</sub> is always syn addition. The *cis* alkene on hydroxylation gives meso compound and *trans* alkene gives racemic mixture. Like Bayer's reagent OsO<sub>4</sub> also gives glycol and the hydroxylation is syn addition.

$$\text{RCH=CH}_2 + \text{OsO}_4 \longrightarrow \qquad \text{R} \qquad \text{OH}$$
 glycol

## (ii) Oxidation by per acids (RCO<sub>3</sub>H)

meso - compound

This addition occurs in *trans* manner. The *cis* alkene gives racemic mixture and *trans* alkenes give meso compound.

# (iii) Ozonolysis

(a)

$$RCH = CH_2 + O_3 \xrightarrow{CCl_4} RCH \xrightarrow{O} CH_2 \xrightarrow{Zn} RCHO + CH_2CO$$
ozonide

(iv) Oxidation by hot concentrated alkaline KMnO<sub>4</sub>

$$RCH = CH2 + KMnO4 \longrightarrow RCOOH + CO2 + H2O$$
(conc.)

## 3. Substitution reaction:

$$\begin{array}{c|c} H_3C & & H_3C \\ & \leftarrow & Cl_{4,low \ temp.} \\ \hline & liq.phase & & Cl_2 + Cl_2 & \xrightarrow{500-600^{\circ}C} & Cl_2 \\ \end{array}$$

However, allylic bromination (bromination at allylic carbon atom) is very easily achieved by treating the alkene having hydrogen atom at the allylic carbon atom with N-bromosuccinimde (NBS).

Illustration 3: Which of the following alkene has the lowest heat of hydrogenation?

$$(A) \qquad H \qquad H \qquad (B) \qquad CH_2 \qquad CH_3 \qquad (B) \qquad H \qquad H \qquad H \qquad CH_3 \qquad (C) \qquad H_3C \qquad H \qquad (D) \qquad (D)$$

Solution:

(B). Higher the stability of alkene, lower the heat of hydrogenation.

#### Illustration 4:

$$H_3C$$
 $CH_3$ 
 $\xrightarrow{alkaline \ KMnO_4}$ 
 $(A)$ 

Which is true about this reaction?

- (A) A is meso 1, 2-butan-di-ol formed by syn addition.
- (B) A is meso 1, 2-butan-di-ol formed by anti addition.
- (C) A is a racemic mixture of d and I, 1, 2-butan-di-ol formed by anti addition.
- (D) A is a racemic mixture of d and I, 1, 2-butan-di-ol formed by syn addition.

Solution: (A).

On *cis* alkene there is syn addition of two –OH groups forming meso compound.

Exercise 2

(1) 
$$CH_3 - CH - CH = CH_2 + HBr \longrightarrow A$$
 (predominant), A is

$$CH_3$$

$$H_3C$$

$$CH_3$$

$$(B)$$

$$H_3C$$

$$CH_3$$

$$(C) Br$$

$$CH_3$$

$$(C) Br$$

$$CH_3$$

$$(D) None of the above$$

(2)  $CH_2 = CH - CH = CH_2$ 

$$\frac{H_2/Pt}{1 \text{ equiv.}} \times X \xrightarrow{0_3/H_2O} Y$$

X and Y are

(A)  $CH_3 - CH_2 - CH = CH_2$ , ( $CH_3CH_2COOH + CO_2$ )
(B)  $CH_3 - CH = CH - CH_3$ ,  $CH_3COOH (2 \text{ moles})$ 
(C)  $CH_3 - CH = CH - CH_3$ ,  $CH_3CH_2COOH + CO_2$ )
(B)  $CH_3 - CH = CH - CH_3$ ,  $CH_3CH_2COOH (2 \text{ moles})$ 
(D)  $CH_3 - CH_2 - CH = CH_2$ , ( $CH_3CH_2CHO + HCHO$ )
(3) The reaction of propene with HOCI proceeds via the addition of (A)  $H^*$  in the first step
(B)  $CT^*$  in the first step
(C)  $CT^*$  and  $CT^*$  of  $T^*$  in the first step

#### **ALKYNES**

Alkynes are characterized by the presence of a triple bond between two carbon atoms. The general formula of alkyne is  $C_nH_{2n-2}$ .

# **Methods of Preparation**

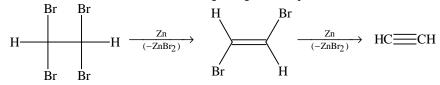
1. By the dehydrohalogenation of vicinal dihalides:

$$CH_2 = CH_2 \xrightarrow{Br_2} Br - CH_2 - CH_2 - Br + KOH \text{ (alc.)} \xrightarrow{NaNH_2} Br - CH = CH_2 \xrightarrow{NaNH_2} CH \equiv CH$$

$$CH_3 - CHBr_2 + KOH \text{ (alc.)} \xrightarrow{CH_2} CH_2 = CH - Br \xrightarrow{NaNH_2} CH \equiv CH$$

2. By dehalogenation of vicinal tetrahalides:

Reaction with active metals like Zn, Mg etc. gives acetylene.



1,1,2,2 — tetrabromoethane

3. By Kolbe electrolysis method:

KOOC 
$$+ 2H_2O \xrightarrow{\text{electrolysis}} HC \longrightarrow CH + 2KOH + H_2 + CO_2$$
Potassium fumarate

4. By heating iodoform or chloroform with silver powder or zinc:

This method can be used for the preparation of only acetylene.

$$CHI_3 + 6Ag + CHI_3 \longrightarrow CH \equiv CH + 6AgI$$

5. From acetylene:

Higher alkynes can be prepared from acetylene when treated with sodium metal in liquid ammonia.

$$\label{eq:charge_constraints} \begin{split} \text{CH} &\equiv \text{CH} + \text{Na} & \xrightarrow{-\text{liq.NH}_3} \text{CH} \\ &= \text{CNa} + \text{CH}_3 \\ \text{Br} & \longrightarrow \text{CH} \\ &= \text{C} - \text{CH}_3 + \text{NaBr} \\ \text{Sodium acetylide} & \text{propyne} \\ \\ \text{Similarly, CH} &\equiv \text{CH} & \xrightarrow{-\text{2Na} \\ -\text{liq.NH}_3} & \text{NaC} \\ &= \text{CNa} & \xrightarrow{-\text{2CH}_3 \\ \text{Br}} & \text{CH}_3 \\ \\ &= \text{CH}_3 \\ \end{split}$$

#### **Chemical Properties**

Alkyne gives electrophilic addition reaction due to the presence of loosely held  $\pi$  electrons, but electrophilic addition reactions in alkyne are slower than that of alkenes.

Terminal hydrogen present in alkynes is acidic in nature. Since, s electrons are closer to nucleus than p electrons, the electrons present in bond having more s character will be more closer to the nucleus. The amount of s character in various types of C – H bond are as follows

Type of C-H bond	Hybrid orbital	Percentage of s character
≡ C-H	sp	50.0
= C – H	sp <sup>2</sup>	33.3
- C – H	sp <sup>3</sup>	25.0

Relative acidities:  $HOH \approx HOR > CH \equiv CR > NH_3 > CH_2 = CH_2 > CH_3 - CH_3$ 

Relative basicities:  $OH^- \approx OR^- < C^- \equiv C - R < NH_2^- < CH^- \equiv CH_2 < CH_2^- - CH_3$ 

## 1. Addition of hydrogen:

$$CH \equiv CH + H_2 \xrightarrow{\text{Ni}} CH_2 = CH_2 \xrightarrow{\text{H2}} CH_3 - CH_3$$
 acetylene ethane

In case of alkynes where triple bond is not present at the end of the chain, on reduction gives *cis* or *trans* alkene, which depends upon the choice of reducing agent. With sodium in liquid ammonia the alkene is *trans* form and on catalytic reduction the alkene is *cis* form.

## 2. Electrophilic addition:

# (i) Addition of halogens

$$\begin{array}{c} \text{CH} & \text{Cl} & \text{Cl} & \text{Cl} \\ & \text{CH} & \text{Cl}_2 & \text{Cl} & \text{Cl} \\ \text{acetylene} & \text{cotylene} \\ & \text{dichloride} & \text{acetylene} \\ & \text{tetrachloride} \end{array}$$

The order of reactivity of halogens is  $Cl_2 > Br_2 > l_2$ 

# (ii) Addition of halogen acid

The order of reactivity of halogen acids is HI > HBr > HCl.

$$\begin{array}{c} \text{CH} \\ \text{CH}_3 \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{CH}_3 \\ \text{CH}_2 \\ \text{CH}_3 \\$$

In presence of peroxide, anti Markonikov's product is obtained.

$$\begin{array}{c|c} CH_3 & & & Br \\ \hline & + & HBr & \xrightarrow{peroxide} & & & H_3C \\ \hline & & & & & Br \\ \hline & & & & Br \\$$

(iii)Addition of hypohalous acids

HC 
$$\longrightarrow$$
 CH + HOCl  $\longrightarrow$  HOCl  $\longrightarrow$ 

## 3. Nucleophilic addition reaction:

In these reactions, the addition is initiated by a nucleophile and are generally catalysed by salt of heavy metals (e.g.  $Hg^{2+}$ ,  $Pb^{2+}$ ,  $Ba^{2+}$ ) which are found to form  $\pi$  compound with multiple bonds.

(i) Addition of water

$$H_3C$$
 —  $CH_3$   $H_3C$  —  $CH_3$   $H_3C$  —  $CH_3$   $CH_2$   $CH_3$  acetone

(ii) Addition of hydrogen cyanide

$$HC \longrightarrow CH + HCN \xrightarrow{Ba(CN)_2} CH_2 = CHCN$$
 vinyl cyanide

(iii) Addition of acetic acid

(iv) Addition of alcohol

HC CH + 
$$C_2H_5OH$$
  $\xrightarrow{HgSO_4}$   $CH_2 = CHOC_2H_5 \xrightarrow{H_2O}$   $CH_3CHO + C_2H_5OH$  vinyl ethyl ether

(v) Addition of ozone and ozonolysis

$$HC \longrightarrow CH + O_3 \longrightarrow O \xrightarrow{CH \longrightarrow O} OHC \longrightarrow CHO + H_2O_2$$
 $CH \longrightarrow O \longrightarrow OHC \longrightarrow CHO + H_2O_2$ 

$$H_3C \xrightarrow{\qquad \qquad } CH + O_3 \xrightarrow{\qquad \qquad } \bigcup_{O \xrightarrow{\qquad \qquad } O} C \xrightarrow{\qquad \qquad } CH_3COCHO + H_2O_2 \xrightarrow{\qquad \qquad } CH_3COOH + HCOOH$$
 methylglyoxal acetic acid formic acid

## 4. Oxidation:

(i) Oxidation with alkaline KMnO<sub>4</sub>

$$\begin{array}{ccc} HC & & +4[O] & \xrightarrow{alk.KMnO_4} & HOOC & \hline & COOH \\ acetylene & & Oxalic acid \end{array}$$

$$H_3C$$
 CH  $+4[O]$   $\xrightarrow{alk.KMnO_4}$   $CH_3COOH + HCOOH or  $CO_2 + H_2$$ 

(ii) Oxidation with acidic K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> or KMnO<sub>4</sub>

#### 5. Formation of metallic derivatives:

The group −C≡C−H in alkynes is slightly acidic in nature and hence its hydrogen atom can be easily replaced by certain metals to give metallic derivatives called acetylides or alkynides.

$$H = H$$

acetylene

 $H_3C$ 
 $H_3C$ 

(i) Formation of sodium acetylides

HC CH + Na 
$$\xrightarrow{\text{liq. NH}_3}$$
 HC C-Na + Na  $\xrightarrow{\text{NaNH}_2}$  NaC = CNa

Mono sodium acetylide

H<sub>3</sub>C H  $\xrightarrow{\text{NaNH}_2}$  H<sub>3</sub>C Na sodium propynide

(ii) Formation of copper and silver acetylides

HC CH + 
$$2 \text{ CuCl}_2 + 2 \text{NH}_4 \text{OH} \longrightarrow \text{Cu} - \text{C} \equiv \text{C} - \text{Cu} \downarrow + 2 \text{NH}_4 \text{Cl} + 2 \text{H}_2 \text{O}$$

Ammoniacal cuprous chloride copper acetylide (red ppt.)

HC 
$$\longrightarrow$$
 CH + 2AgNO<sub>3</sub> + 2NH<sub>4</sub>OH  $\longrightarrow$  AgC  $\equiv$  CAg  $\downarrow$  + 2NH<sub>4</sub>NO<sub>3</sub> + 2H<sub>2</sub>O  
Ammoniacal silver nitrate silver acetylide (white ppt.)

These reactions are used for detecting the presence of acetylinic hydrogen atom.

Illustration 4: The products obtained via oxymercuration (HgSO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub>) of 1-butyne would be

(A) 
$$H_3C$$
  $COOH + HCOOH$ 

Solution: (A).
$$H_3C \longrightarrow CH \xrightarrow{H_2SO_4} H_3C \longrightarrow CH_2 \longrightarrow CH_2$$

$$H_3C \longrightarrow CH_2 \longrightarrow CH_2$$