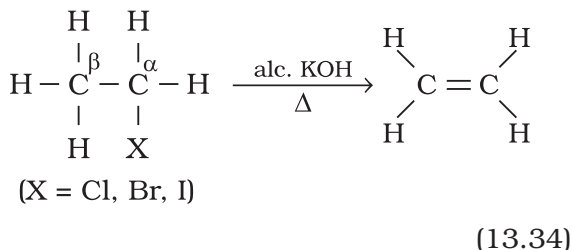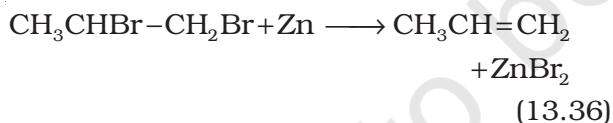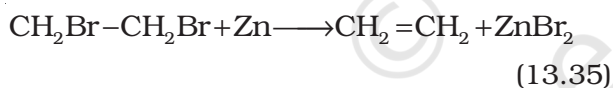say, ethanol) eliminate one molecule of halogen acid to form alkenes. This reaction is known as **dehydrohalogenation** i.e., removal of halogen acid. This is example of **β-elimination reaction**, since hydrogen atom is eliminated from the β carbon atom (carbon atom next to the carbon to which halogen is attached).

$$H - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{}^{\beta} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}{}^{\alpha} - H \xrightarrow[\Delta]{\text{alc. KOH}} \overset{\displaystyle H}{\underset{\displaystyle H}{}}C = C\overset{\displaystyle H}{\underset{\displaystyle H}{}}$$
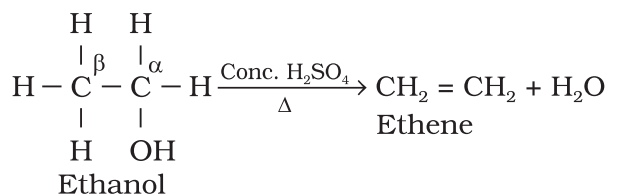
(X = Cl, Br, I)

(13.34)

Nature of halogen atom and the alkyl group determine rate of the reaction. It is observed that for halogens, the rate is: iodine > bromine > chlorine, while for alkyl groups it is : tert > secondary > primary.

3. *From vicinal dihalides:* Dihalides in which two halogen atoms are attached to two adjacent carbon atoms are known as *vicinal dihalides*. Vicinal dihalides on treatment with zinc metal lose a molecule of ZnX_2 to form an alkene. This reaction is known as **dehalogenation**.

$$CH_2Br - CH_2Br + Zn \longrightarrow CH_2 = CH_2 + ZnBr_2$$

(13.35)

$$CH_3CHBr - CH_2Br + Zn \longrightarrow CH_3CH = CH_2 + ZnBr_2$$

(13.36)

4. *From alcohols by acidic dehydration:* You have read during nomenclature of different homologous series in Unit 12 that alcohols are the hydroxy derivatives of alkanes. They are represented by R–OH where, R is C_nH_{2n+1}. Alcohols on heating with concentrated sulphuric acid form alkenes with the elimination of one water molecule. Since a water molecule is eliminated from the alcohol molecule in the presence of an acid, this reaction is known as **acidic dehydration of alcohols**. This reaction is also the example of β-elimination reaction since –OH group

takes out one hydrogen atom from the β-carbon atom.

$$H - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{}^{\beta} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}{}^{\alpha} - H \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} CH_2 = CH_2 + H_2O$$

Ethanol   Ethene

(13.37)

13.3.5 Properties

Physical properties

Alkenes as a class resemble alkanes in physical properties, except in types of isomerism and difference in polar nature. The first three members are gases, the next fourteen are liquids and the higher ones are solids. Ethene is a colourless gas with a faint sweet smell. All other alkenes are colourless and odourless, insoluble in water but fairly soluble in non-polar solvents like benzene, petroleum ether. They show a regular increase in boiling point with increase in size *i.e.,* every – CH_2 group added increases boiling point by 20–30 K. Like alkanes, straight chain alkenes have higher boiling point than isomeric branched chain compounds.
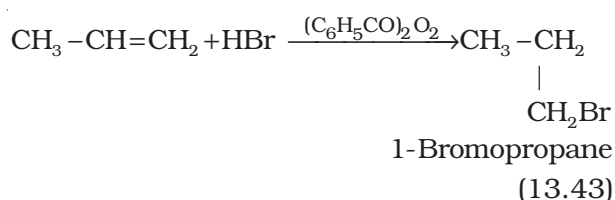
Chemical properties

Alkenes are the rich source of loosely held pi (π) electrons, due to which they show addition reactions in which the electrophiles add on to the carbon-carbon double bond to form the addition products. Some reagents also add by free radical mechanism. There are cases when under special conditions, alkenes also undergo free radical substitution reactions. Oxidation and ozonolysis reactions are also quite prominent in alkenes. A brief description of different reactions of alkenes is given below:

1. *Addition of dihydrogen:* Alkenes add up one molecule of dihydrogen gas in the presence of finely divided nickel, palladium or platinum to form alkanes (Section 13.2.2)

2. *Addition of halogens :* Halogens like bromine or chlorine add up to alkene to form vicinal dihalides. However, iodine does not show addition reaction under
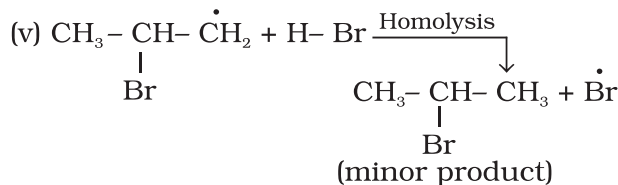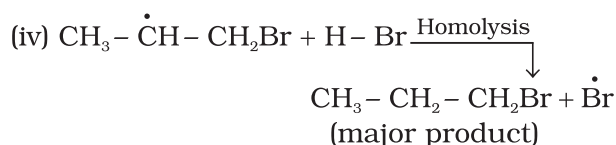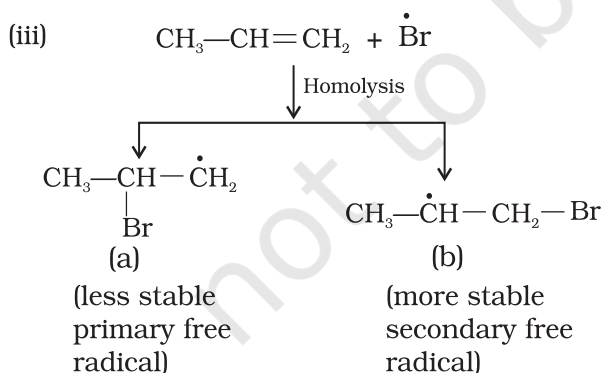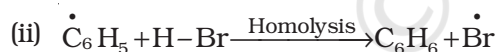
normal conditions. The reddish orange colour of bromine solution in carbon tetrachloride is discharged when bromine adds up to an unsaturation site. This reaction is used as a test for unsaturation. Addition of halogens to alkenes is an example of electrophilic addition reaction involving cyclic halonium ion formation which you will study in higher classes.

(i) $\underset{\text{Ethene}}{CH_2 = CH_2} + Br-Br \xrightarrow{CCl_4} \underset{\substack{| \quad | \\ Br \quad Br \\ \text{1,2 Dibromoethane}}}{CH_2 - CH_2}$

(13.38)

(ii) $\underset{\text{Propene}}{CH_3-CH=CH_2} + Cl-Cl \longrightarrow \underset{\substack{| \quad | \\ Cl \quad Cl \\ \text{1,2-Dichloropropane}}}{CH_3-CH-CH_2}$

(13.39)

3. *Addition of hydrogen halides:* Hydrogen halides (HCl, HBr,HI) add up to alkenes to form alkyl halides. The order of reactivity of the hydrogen halides is HI > HBr > HCl. Like addition of halogens to alkenes, addition of hydrogen halides is also an example of electrophilic addition reaction. Let us illustrate this by taking addition of HBr to symmetrical and unsymmetrical alkenes

Addition reaction of HBr to symmetrical alkenes
Addition reactions of HBr to symmetrical alkenes (similar groups attached to double bond) take place by electrophilic addition mechanism.

$CH_2 = CH_2 + H-Br \longrightarrow CH_3-CH_2-Br$ (13.40)

$CH_3-CH=CH-CH_3 + HBr \longrightarrow \underset{\substack{| \\ Br}}{CH_3-CH_2-CHCH_3}$

(13.41)

Addition reaction of HBr to unsymmetrical alkenes (Markovnikov Rule)
How will H – Br add to propene ? The two possible products are I and II.

$CH_3-CH=CH_2 + H-Br \longrightarrow$
I $\begin{array}{l} CH_3-CH-CH_3 \\ \quad\quad | \\ \quad\quad Br \\ \text{2-Bromopropane} \end{array}$
II $\begin{array}{l} CH_3-CH_2-CH_2-Br \\ \text{1-Bromopropane} \end{array}$

(13.42)

Markovnikov, a Russian chemist made a generalisation in 1869 after studying such reactions in detail. These generalisations led Markovnikov to frame a rule called **Markovnikov rule.** The rule states that negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms. Thus according to this rule, product I *i.e.,* 2-bromopropane is expected. In actual practice, this is the principal product of the reaction. This generalisation of Markovnikov rule can be better understood in terms of mechanism of the reaction.

Mechanism
Hydrogen bromide provides an electrophile, H^+, which attacks the double bond to form carbocation as shown below :

$$\overset{3}{H_3C}-\overset{2}{CH}=\overset{1}{CH_2} + H-Br$$

$\downarrow H^+$

$\underset{\substack{\text{(a) less stable} \\ \text{primary carbocation}}}{H_3C-CH_2-\overset{+}{CH_2} + Br^-} \quad \underset{\substack{\text{(b) more stable} \\ \text{secondary carbocation}}}{H_3C-\overset{+}{CH}-CH_3 + Br^-}$

(i) The secondary carbocation (b) is more stable than the primary carbocation (a), therefore, the former predominates because it is formed at a faster rate.

(ii) The carbocation (b) is attacked by Br^- ion to form the product as follows :

$\underset{Br^-}{\overset{+}{H_3C-CH-CH_3}} \longrightarrow \underset{\substack{| \\ Br \\ \text{2-Bromopropane} \\ \text{(major product)}}}{H_3C-CH-CH_3}$
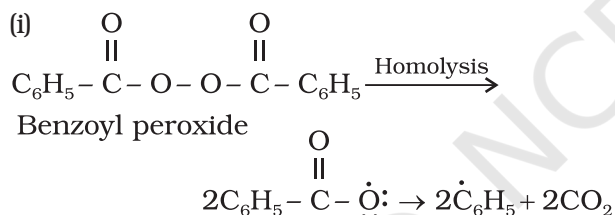
Anti Markovnikov addition or peroxide effect or Kharash effect

In the presence of peroxide, addition of HBr to unsymmetrical alkenes like propene takes place contrary to the Markovnikov rule. This happens only with HBr but not with HCl and Hl. This addition reaction was observed by M.S. Kharash and F.R. Mayo in 1933 at the University of Chicago. This reaction is known as *peroxide* or *Kharash* effect or addition reaction anti to Markovnikov rule.

$$CH_3-CH=CH_2+HBr \xrightarrow{(C_6H_5CO)_2O_2} CH_3-CH_2$$
$$\hspace{5cm} |$$
$$\hspace{5cm} CH_2Br$$
$$\hspace{4cm} \text{1-Bromopropane}$$
$$\hspace{5cm} (13.43)$$

Mechanism : Peroxide effect proceeds via free radical chain mechanism as given below:

(i)
$$\underset{\text{Benzoyl peroxide}}{C_6H_5-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-C_6H_5} \xrightarrow{\text{Homolysis}}$$

$$2C_6H_5-\overset{\overset{O}{\|}}{C}-\overset{..}{\underset{..}{O}}: \rightarrow 2\dot{C}_6H_5+2CO_2$$

(ii) $\dot{C}_6H_5+H-Br \xrightarrow{\text{Homolysis}} C_6H_6+\dot{Br}$

(iii)
$$CH_3{-}CH{=}CH_2 \ + \ \dot{Br}$$
$$\downarrow \text{Homolysis}$$

$$\underset{\substack{\text{(a)}\\ \text{(less stable}\\ \text{primary free}\\ \text{radical)}}}{CH_3{-}\underset{\underset{Br}{|}}{CH}{-}\dot{CH_2}} \hspace{2cm} \underset{\substack{\text{(b)}\\ \text{(more stable}\\ \text{secondary free}\\ \text{radical)}}}{CH_3{-}\dot{CH}{-}CH_2{-}Br}$$

(iv) $CH_3-\dot{CH}-CH_2Br + H-Br \xrightarrow{\text{Homolysis}}$
$$\underset{\text{(major product)}}{CH_3-CH_2-CH_2Br+\dot{Br}}$$

(v) $CH_3-\underset{\underset{Br}{|}}{CH}-\dot{CH_2} + H-Br \xrightarrow{\text{Homolysis}}$
$$\underset{\underset{\underset{\text{(minor product)}}{Br}}{|}}{CH_3-CH-CH_3} + \dot{Br}$$
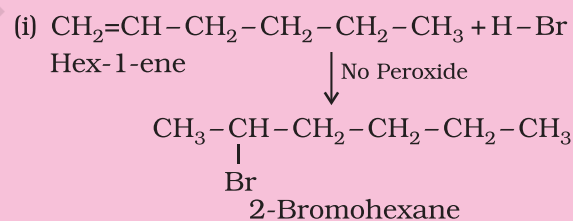
The secondary free radical obtained in the above mechanism (step iii) is more stable than the primary. This explains the formation of 1-bromopropane as the major product. It may be noted that the peroxide effect is not observed in addition of HCl and HI. This may be due to the fact that the H–Cl bond being stronger (430.5 kJ mol^{-1}) than H–Br bond (363.7 kJ mol^{-1}), is not cleaved by the free radical, whereas the H–I bond is weaker (296.8 kJ mol^{-1}) and iodine free radicals combine to form iodine molecules instead of adding to the double bond.
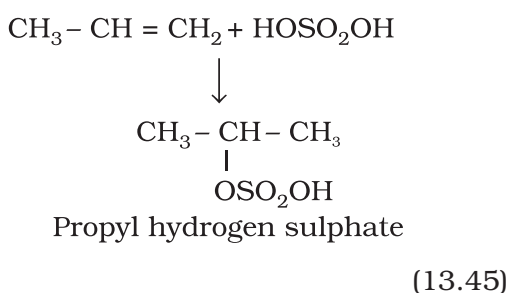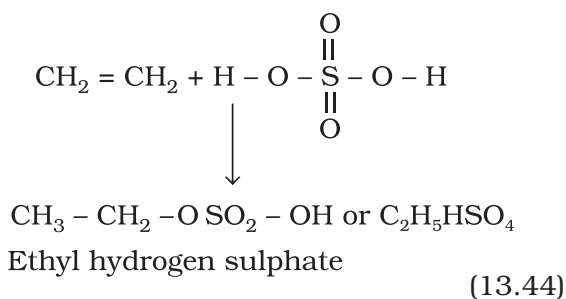
Problem 13.12

Write IUPAC names of the products obtained by addition reactions of HBr to hex-1-ene

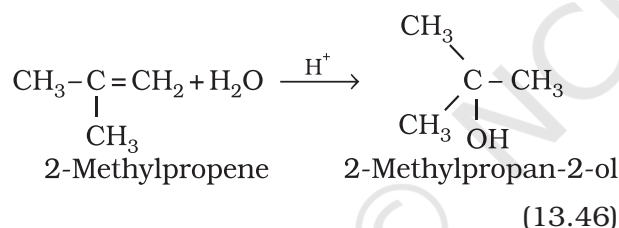(i)   in the absence of peroxide and
(ii) in the presence of peroxide.

Solution

(i) $CH_2{=}CH-CH_2-CH_2-CH_2-CH_3+H-Br$
$\underset{\text{Hex-1-ene}}{}$ $\downarrow\text{No Peroxide}$

$$\underset{\text{2-Bromohexane}}{CH_3-\underset{\underset{Br}{|}}{CH}-CH_2-CH_2-CH_2-CH_3}$$

(ii) $CH_2{=}CH-CH_2-CH_2-CH_2-CH_3 + H-Br$
$\downarrow\text{Peroxide}$

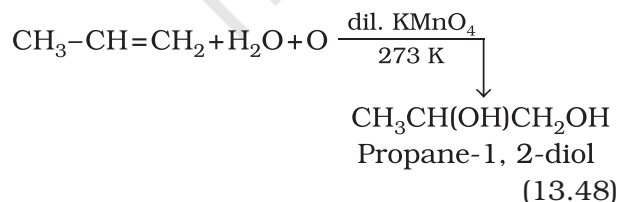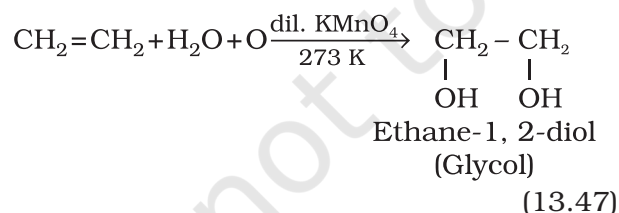$$\underset{\text{1-Bromohexane}}{\underset{\underset{Br}{|}}{CH_2}-CH_2-CH_2-CH_2-CH_2-CH_3}$$
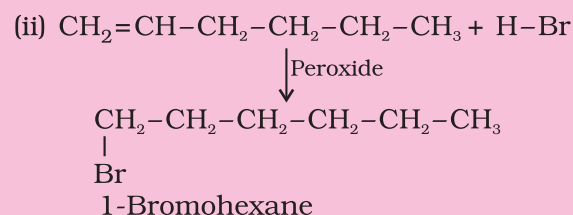
4. **Addition of sulphuric acid :** Cold concentrated sulphuric acid adds to alkenes in accordance with Markovnikov rule to form alkyl hydrogen sulphate by the electrophilic addition reaction.

$$CH_2 = CH_2 + H - O - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - O - H$$

$$\downarrow$$

$$CH_3 - CH_2 - O\,SO_2 - OH \text{ or } C_2H_5HSO_4$$
Ethyl hydrogen sulphate

(13.44)

$$CH_3 - CH = CH_2 + HOSO_2OH$$

$$\downarrow$$

$$CH_3 - \underset{\underset{OSO_2OH}{|}}{CH} - CH_3$$

Propyl hydrogen sulphate

(13.45)

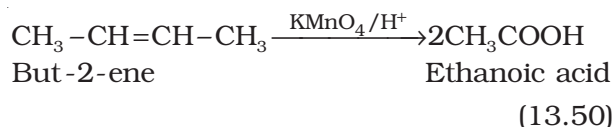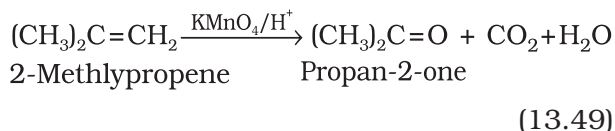5. *Addition of water :* In the presence of a few drops of concentrated sulphuric acid alkenes react with water to form alcohols, in accordance with the Markovnikov rule.

$$CH_3 - \underset{\underset{CH_3}{|}}{C} = CH_2 + H_2O \xrightarrow{H^+} \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\quad OH$$

2-Methylpropene   2-Methylpropan-2-ol

(13.46)

6. *Oxidation:* Alkenes on reaction with cold, dilute, aqueous solution of potassium permanganate (Baeyer's reagent) produce vicinal glycols. Decolorisation of $KMnO_4$ solution is used as a test for unsaturation.

$$CH_2 = CH_2 + H_2O + O \xrightarrow[273\ K]{dil.\ KMnO_4} \underset{\underset{OH}{|}}{CH_2} - \underset{\underset{OH}{|}}{CH_2}$$

Ethane-1, 2-diol
(Glycol)

(13.47)

$$CH_3 - CH = CH_2 + H_2O + O \xrightarrow[273\ K]{dil.\ KMnO_4}$$

$$\downarrow$$
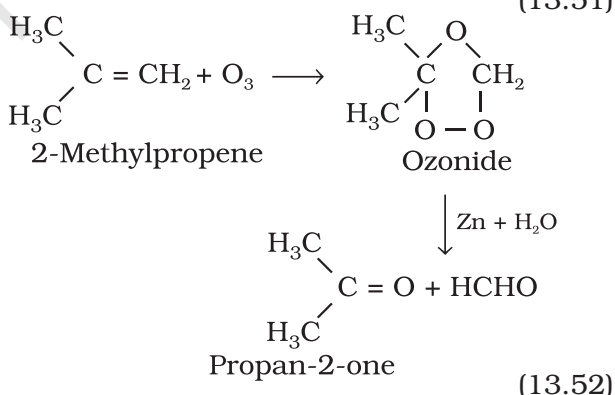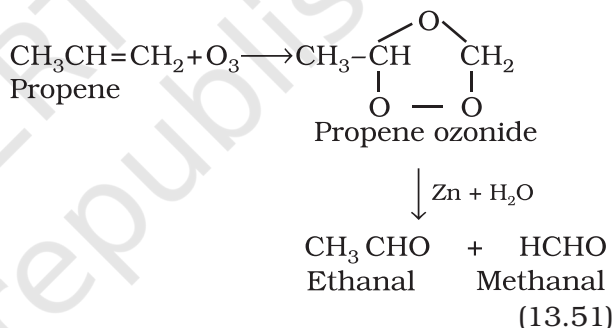
$$CH_3CH(OH)CH_2OH$$
Propane-1, 2-diol

(13.48)

b) Acidic potassium permanganate or acidic potassium dichromate oxidises alkenes to

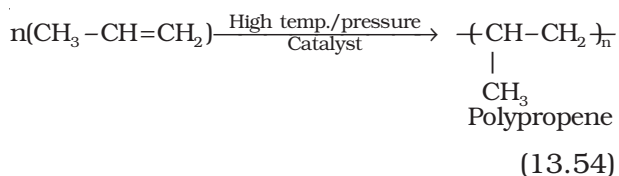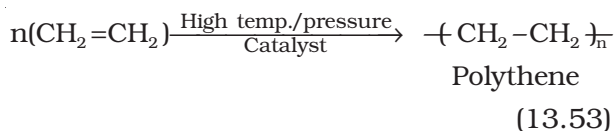ketones and/or acids depending upon the nature of the alkene and the experimental conditions

$$(CH_3)_2C = CH_2 \xrightarrow{KMnO_4/H^+} (CH_3)_2C = O + CO_2 + H_2O$$
2-Methlypropene   Propan-2-one

(13.49)

$$CH_3 - CH = CH - CH_3 \xrightarrow{KMnO_4/H^+} 2CH_3COOH$$
But-2-ene   Ethanoic acid

(13.50)

7. *Ozonolysis :* Ozonolysis of alkenes involves the addition of ozone molecule to alkene to form ozonide, and then cleavage of the ozonide by Zn-H_2O to smaller molecules. This reaction is highly useful in detecting the position of the double bond in alkenes or other unsaturated compounds.

$$CH_3CH = CH_2 + O_3 \longrightarrow \underset{\underset{O}{|}}{CH_3 - CH} \overset{O}{\underset{\underset{O}{}}{\diagdown}} CH_2$$
Propene

Propene ozonide

$$\downarrow Zn + H_2O$$

$$CH_3\,CHO \quad + \quad HCHO$$
Ethanal   Methanal

(13.51)

$$\underset{H_3C}{\overset{H_3C}{\diagdown}} C = CH_2 + O_3 \longrightarrow \underset{H_3C}{\overset{H_3C}{\diagdown}} \underset{\underset{O}{|}}{C} \overset{O}{\underset{\underset{O}{}}{\diagdown}} CH_2$$
2-Methylpropene   Ozonide

$$\downarrow Zn + H_2O$$

$$\underset{H_3C}{\overset{H_3C}{\diagdown}} C = O + HCHO$$
Propan-2-one

(13.52)

8. *Polymerisation:* You are familiar with polythene bags and polythene sheets. Polythene is obtained by the combination of large number of ethene molecules at high temperature, high pressure and in the presence of a catalyst. The large molecules thus obtained are called polymers. This reaction is known as **polymerisation.** The simple compounds from which polymers

are made are called **monomers**. Other alkenes also undergo polymerisation.

$$n(CH_2=CH_2) \xrightarrow[\text{Catalyst}]{\text{High temp./pressure}} \begin{array}{c}(CH_2-CH_2)_n\end{array}$$
Polythene
(13.53)

$$n(CH_3-CH=CH_2) \xrightarrow[\text{Catalyst}]{\text{High temp./pressure}} \begin{array}{c}(CH-CH_2)_n \\ | \\ CH_3\end{array}$$
Polypropene
(13.54)

Polymers are used for the manufacture of plastic bags, squeeze bottles, refrigerator dishes, toys, pipes, radio and T.V. cabinets etc. Polypropene is used for the manufacture of milk crates, plastic buckets and other moulded articles. Though these materials have now become common, excessive use of polythene and polypropylene is a matter of great concern for all of us.

13.4 ALKYNES

Like alkenes, alkynes are also unsaturated hydrocarbons. They contain at least one triple bond between two carbon atoms. The number of hydrogen atoms is still less in alkynes as compared to alkenes or alkanes. Their general formula is C_nH_{2n-2}.
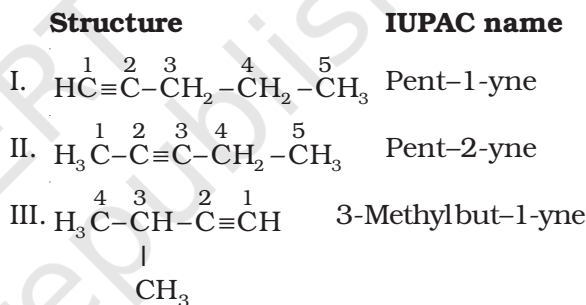
The first stable member of alkyne series is ethyne which is popularly known as acetylene. Acetylene is used for arc welding purposes in the form of oxyacetylene flame obtained by mixing acetylene with oxygen gas. Alkynes are starting materials for a large number of organic compounds. Hence, it is interesting to study this class of organic compounds.

13.4.1 Nomenclature and Isomerism

In common system, alkynes are named as derivatives of acetylene. In IUPAC system, they are named as derivatives of the corresponding alkanes replacing '*ane*' by the suffix '*yne*'. The position of the triple bond is indicated by the first triply bonded carbon. Common and IUPAC names of a few members of alkyne series are given in Table 13.2.

You have already learnt that ethyne and propyne have got only one structure but there are two possible structures for butyne – (i) but-1-yne and (ii) but-2-yne. Since these two compounds differ in their structures due to the position of the triple bond, they are known as **position isomers**. In how many ways, you can construct the structure for the next homologue i.e., the next alkyne with molecular formula C_5H_8? Let us try to arrange five carbon atoms with a continuous chain and with a side chain. Following are the possible structures :

Structure	IUPAC name
I. $\overset{1}{HC}\equiv\overset{2}{C}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_3}$	Pent–1-yne
II. $\overset{1}{H_3C}-\overset{2}{C}\equiv\overset{3}{C}-\overset{4}{CH_2}-\overset{5}{CH_3}$	Pent–2-yne
III. $\overset{4}{H_3C}-\overset{3}{CH}-\overset{2}{C}\equiv\overset{1}{CH}$ $\quad\quad\;\;	$ $\quad\quad\; CH_3$	3-Methylbut–1-yne

Structures I and II are position isomers and structures I and III or II and III are chain isomers.

> **Problem 13.13**
>
> Write structures of different isomers corresponding to the 5th member of alkyne series. Also write IUPAC names of all the isomers. What type of isomerism is exhibited by different pairs of isomers?
>
> **Solution**
>
> 5th member of alkyne has the molecular formula C_6H_{10}. The possible isomers are:

Table 13.2 Common and IUPAC Names of Alkynes (C_nH_{2n-2})

Value of n	Formula	Structure	Common name	IUPAC name
2	C_2H_2	$H-C\equiv CH$	Acetylene	Ethyne
3	C_3H_4	$CH_3-C\equiv CH$	Methylacetylene	Propyne
4	C_4H_6	$CH_3CH_2-C\equiv CH$	Ethylacetylene	But-1-yne
4	C_4H_6	$CH_3-C\equiv C-CH_3$	Dimethylacetylene	But-2-yne