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

$$n(CH_2=CH_2) \xrightarrow[\text{Catalyst}]{\text{High temp./pressure}} -\!\!\left(CH_2-CH_2\right)_n$$
Polythene

(13.53)

$$n(CH_3-CH=CH_2) \xrightarrow[\text{Catalyst}]{\text{High temp./pressure}} -\!\!\left(CH-CH_2\right)_n$$
$$|$$
$$CH_3$$
Polypropene

(13.54)
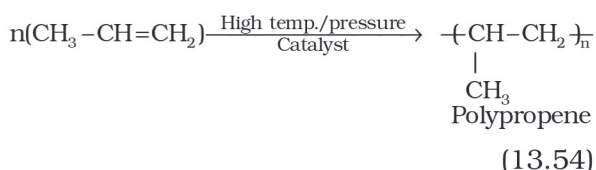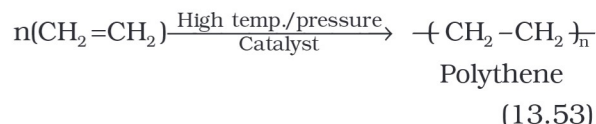
Polymers are used for the manufacture of plastic bags, squeeze bottles, refrigerator dishes, toys, pipes, radio and T.V. cabinets etc. Polypropene is used for the manufacture of milk crates, plastic buckets and other moulded articles. Though these materials have now become common, excessive use of polythene 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}.
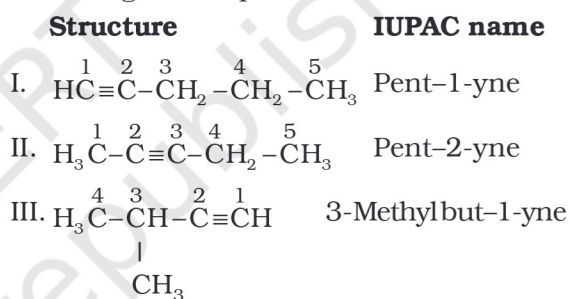
The first stable member of alkyne series is ethyne which is popularly known as acetylene. Acetylene is used for arc welding purposes in the form of oxyacetylene flame obtained by mixing acetylene with oxygen gas. Alkynes are starting materials for a large number of organic compounds. Hence, it is interesting 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. $\overset{1}{H}C\equiv\overset{2}{C}-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H_3$	Pent–1-yne
II. $H_3\overset{1}{C}-\overset{2}{C}\equiv\overset{3}{C}-\overset{4}{C}H_2-\overset{5}{C}H_3$	Pent–2-yne
III. $H_3\overset{4}{C}-\overset{3}{C}H-\overset{2}{C}\equiv\overset{1}{C}H$ $\quad\quad\ |$ $\quad\quad CH_3$	3-Methyl but–1-yne

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

Problem 13.13

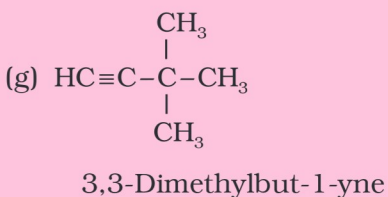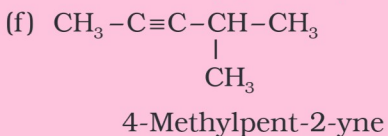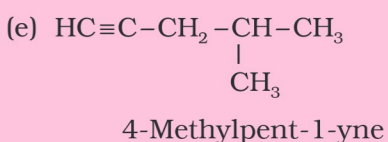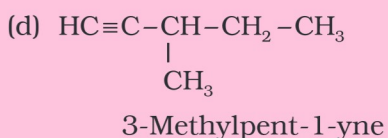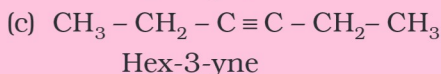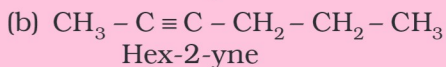Write structures of different isomers corresponding to the 5th member of alkyne series. Also write IUPAC names of all the isomers. What type of isomerism is exhibited by different pairs of isomers?

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≡CH	Acetylene	Ethyne
3	C_3H_4	CH_3-C≡CH	Methylacetylene	Propyne
4	C_4H_6	CH_3CH_2-C≡CH	Ethylacetylene	But-1-yne
4	C_4H_6	CH_3-C≡C-CH_3	Dimethylacetylene	But-2-yne

(a) HC ≡ C – CH$_2$ – CH$_2$ – CH$_2$ – CH$_3$

      Hex-1-yne

(b) CH$_3$ – C ≡ C – CH$_2$ – CH$_2$ – CH$_3$

      Hex-2-yne

(c) CH$_3$ – CH$_2$ – C ≡ C – CH$_2$– CH$_3$

      Hex-3-yne

(d) HC≡C–CH–CH$_2$–CH$_3$

           |

          CH$_3$

      3-Methylpent-1-yne

(e) HC≡C–CH$_2$–CH–CH$_3$

             |

           CH$_3$

      4-Methylpent-1-yne

(f) CH$_3$ –C≡C–CH–CH$_3$

            |

         CH$_3$

      4-Methylpent-2-yne

         CH$_3$

          |

(g) HC≡C–C–CH$_3$

          |

         CH$_3$

      3,3-Dimethylbut-1-yne
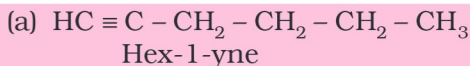
Position and chain isomerism shown by different pairs.

13.4.2 Structure of Triple Bond

Ethyne is the simplest molecule of alkyne series. Structure of ethyne is shown in Fig. 13.6.

Each carbon atom of ethyne has two *sp* hybridised orbitals. Carbon-carbon sigma (σ) bond is obtained by the head-on overlapping of the two *sp* hybridised orbitals of the two carbon atoms. The remaining *sp* hybridised orbital of each carbon atom undergoes overlapping along the internuclear axis with the 1*s* orbital of each of the two hydrogen atoms forming two C-H sigma bonds. H-C-C bond angle is of 180°. Each carbon has two unhybridised *p* orbitals which are perpendicular to each other as well as to the plane of the C-C sigma bond. The 2*p* orbitals of one carbon atom are parallel to the 2*p*
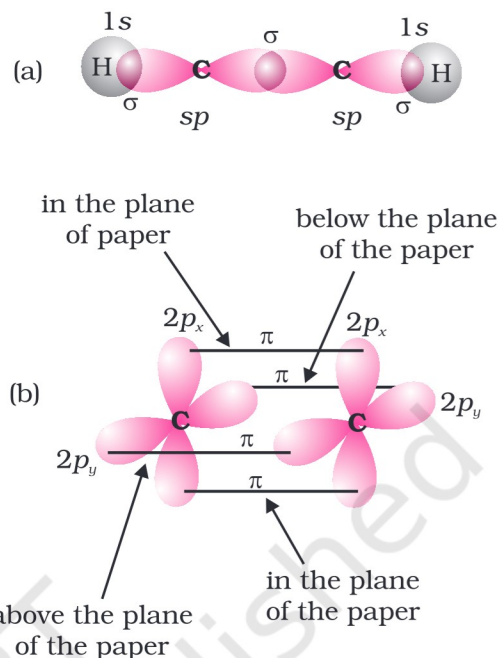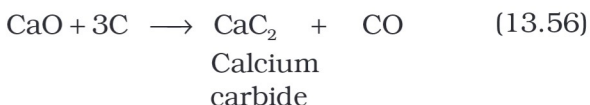

Fig. 13.6 Orbital picture of ethyne showing (a) sigma overlaps (b) pi overlaps.

orbitals of the other carbon atom, which undergo lateral or sideways overlapping to form two pi (π) bonds between two carbon atoms. Thus ethyne molecule consists of one C–C σ bond, two C–H σ bonds and two C–C π bonds. The strength of C≡C bond (bond enthalpy 823 kJ mol^{-1}) is more than those of C=C bond (bond enthalpy 681 kJ mol^{-1}) and C–C bond (bond enthalpy 348 kJ mol^{-1}). The C≡C bond length is shorter (120 pm) than those of C=C (133 pm) and C–C (154 pm). Electron cloud between two carbon atoms is cylindrically symmetrical about the internuclear axis. Thus, ethyne is a linear molecule.
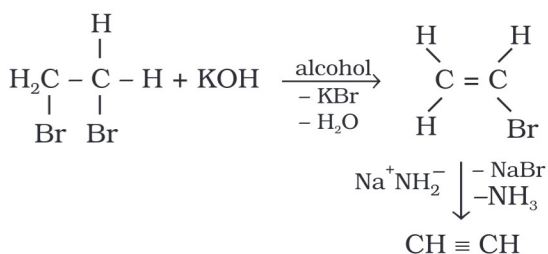
13.4.3 Preparation

1. *From calcium carbide:* On industrial scale, ethyne is prepared by treating calcium carbide with water. Calcium carbide is prepared by heating quick lime with coke. Quick lime can be obtained by heating limestone as shown in the following reactions:

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \qquad (13.55)$$

$$CaO + 3C \longrightarrow CaC_2 + CO \qquad (13.56)$$
$$\text{Calcium}$$
$$\text{carbide}$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2 \qquad (13.57)$$

2. From vicinal dihalides : Vicinal dihalides on treatment with alcoholic *potassium hydroxide* undergo dehydrohalogenation. One molecule of hydrogen halide is eliminated to form alkenyl halide which on treatment with sodamide gives alkyne.

$$
\begin{array}{c}
\underset{\substack{|\\ \text{Br} \quad \text{Br}}}{\overset{\text{H}}{\underset{|}{\text{H}_2\text{C} - \text{C} - \text{H}}}} + \text{KOH} \xrightarrow[\substack{-\text{KBr}\\-\text{H}_2\text{O}}]{\text{alcohol}}
\underset{\text{H} \qquad \text{Br}}{\overset{\text{H} \qquad \text{H}}{\text{C} = \text{C}}}
\end{array}
$$

$$Na^+NH_2^- \downarrow \begin{array}{l} -NaBr \\ -NH_3 \end{array}$$

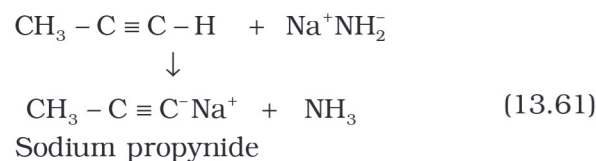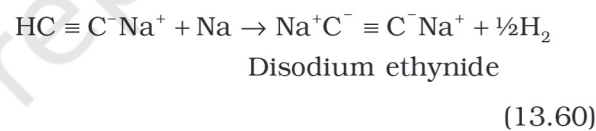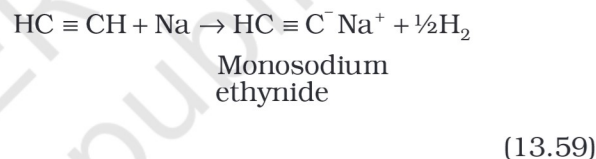$$CH \equiv CH$$

13.4.4 Properties

Physical properties

Physical properties of alkynes follow the same trend of alkenes and alkanes. First three members are gases, the next eight are liquids and the higher ones are solids. All alkynes are colourless. Ethyene has characteristic odour. Other members are odourless. Alkynes are weakly polar in nature. They are lighter than water and immiscible with water but soluble in organic solvents like ethers, carbon tetrachloride and benzene. Their melting point, boiling point and density increase with increase in molar mass.

Chemical properties

Alkynes show acidic nature, addition reactions and polymerisation reactions as follows :

A. Acidic character of alkyne: Sodium metal and sodamide ($NaNH_2$) are strong bases. They react with ethyne to form sodium acetylide with the liberation of dihydrogen gas. These reactions have not been observed in case of ethene and ethane thus indicating that ethyne is acidic in nature in comparison to ethene and ethane. Why is it so ? Has it something to do with their structures and the hybridisation ? You have read that hydrogen

atoms in ethyne are attached to the sp hybridised carbon atoms whereas they are attached to sp^2 hybridised carbon atoms in ethene and sp^3 hybridised carbons in ethane. Due to the maximum percentage of s character (50%), the sp hybridised orbitals of carbon atoms in ethyne molecules have highest electronegativity; hence, these attract the shared electron pair of the C-H bond of ethyne to a greater extent than that of the sp^2 hybridised orbitals of carbon in ethene and the sp^3 hybridised orbital of carbon in ethane. Thus in ethyne, hydrogen atoms can be liberated as protons more easily as compared to ethene and ethane. Hence, hydrogen atoms of ethyne attached to triply bonded carbon atom are acidic in nature. You may note that the hydrogen atoms attached to the triply bonded carbons are acidic but not all the hydrogen atoms of alkynes.

$$HC \equiv CH + Na \rightarrow HC \equiv C^- Na^+ + \tfrac{1}{2}H_2$$
$$\text{Monosodium}$$
$$\text{ethynide}$$

$$(13.59)$$

$$HC \equiv C^- Na^+ + Na \rightarrow Na^+ C^- \equiv C^- Na^+ + \tfrac{1}{2}H_2$$
$$\text{Disodium ethynide}$$

$$(13.60)$$

$$CH_3 - C \equiv C - H + Na^+NH_2^-$$
$$\downarrow$$
$$CH_3 - C \equiv C^- Na^+ + NH_3 \qquad (13.61)$$
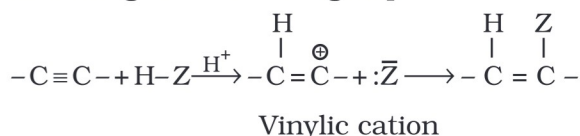$$\text{Sodium propynide}$$

These reactions are not shown by alkenes and alkanes, hence used for distinction between alkynes, alkenes and alkanes. What about the above reactions with but-1-yne and but-2-yne ? Alkanes, alkenes and alkynes follow the following trend in their acidic behaviour :

i) $HC \equiv CH > H_2C = CH_2 > CH_3 - CH_3$

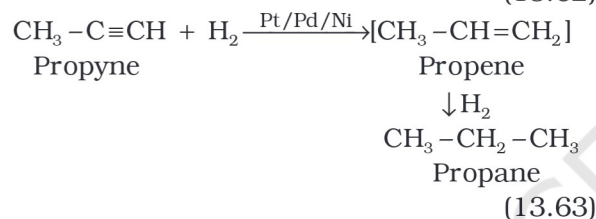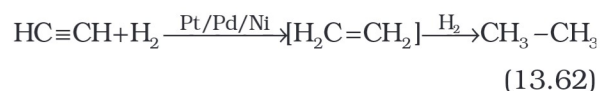ii) $HC \equiv CH > CH_3 - C \equiv CH >> CH_3 - C \equiv C - CH_3$

B. Addition reactions: Alkynes contain a triple bond, so they add up, two molecules of dihydrogen, halogen, hydrogen halides etc.

Formation of the addition product takes place according to the following steps.

$$-C\equiv C-+H-Z\xrightarrow{H^+}\overset{\overset{\displaystyle H}{\mid}}{-C}=\overset{\oplus}{C}-+:\bar{Z}\longrightarrow\overset{\overset{\displaystyle H}{\mid}}{-C}=\overset{\overset{\displaystyle Z}{\mid}}{C}-$$
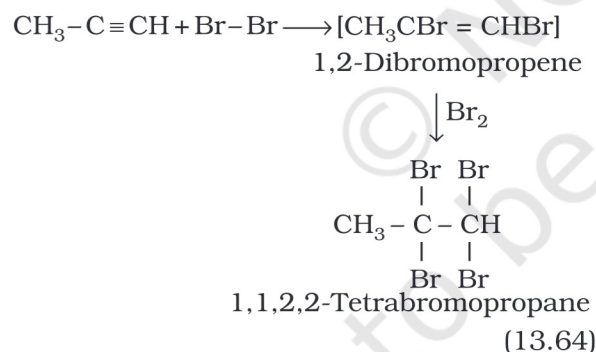
Vinylic cation

The addition product formed depends upon stability of vinylic cation. Addition in unsymmetrical alkynes takes place according to Markovnikov rule. Majority of the reactions of alkynes are the examples of electrophilic addition reactions. A few addition reactions are given below:
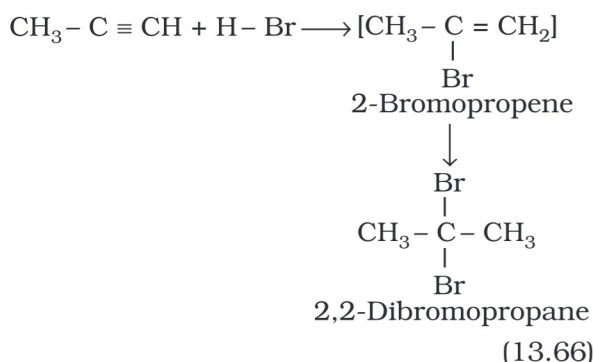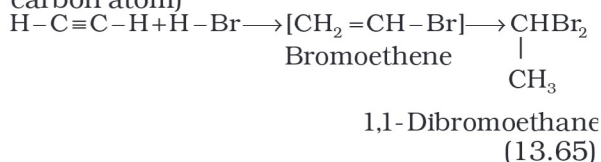
(i) *Addition of dihydrogen*

$$HC\equiv CH+H_2\xrightarrow{Pt/Pd/Ni}[H_2C=CH_2]\xrightarrow{H_2}CH_3-CH_3 \tag{13.62}$$

$$\underset{\text{Propyne}}{CH_3-C\equiv CH}+H_2\xrightarrow{Pt/Pd/Ni}\underset{\text{Propene}}{[CH_3-CH=CH_2]}$$
$$\downarrow H_2$$
$$\underset{\text{Propane}}{CH_3-CH_2-CH_3} \tag{13.63}$$

(ii) Addition of halogens

$$CH_3-C\equiv CH+Br-Br\longrightarrow\underset{\text{1,2-Dibromopropene}}{[CH_3CBr=CHBr]}$$
$$\downarrow Br_2$$
$$\underset{\underset{\text{1,1,2,2-Tetrabromopropane}}{Br\ \ Br}}{\overset{\overset{Br\ \ Br}{\mid\ \ \mid}}{CH_3-C-CH}} \tag{13.64}$$

Reddish orange colour of the solution of bromine in carbon tetrachloride is decolourised. This is used as a test for unsaturation.
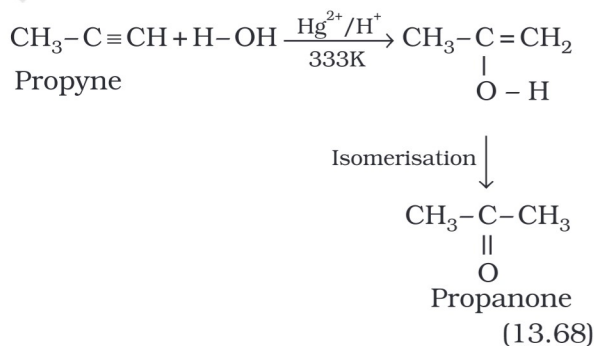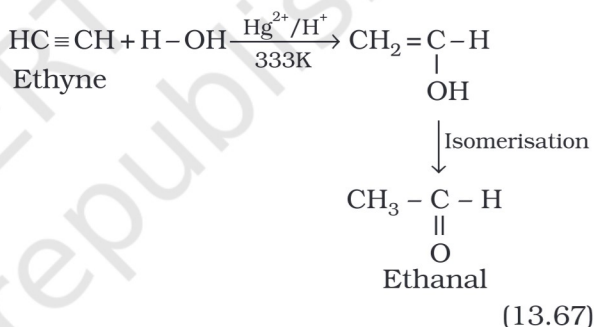
(iii) Addition of hydrogen halides

Two molecules of hydrogen halides (HCl, HBr, HI) add to alkynes to form *gem* dihalides (in which two halogens are attached to the same carbon atom)

$$H-C\equiv C-H+H-Br\longrightarrow\underset{\text{Bromoethene}}{[CH_2=CH-Br]}\longrightarrow\underset{\underset{\text{1,1-Dibromoethane}}{CH_3}}{\overset{CHBr_2}{\mid}} \tag{13.65}$$

$$CH_3-C\equiv CH+H-Br\longrightarrow\underset{\underset{\text{2-Bromopropene}}{Br}}{[CH_3-\overset{\mid}{C}=CH_2]}$$
$$\downarrow$$
$$\underset{\underset{\text{2,2-Dibromopropane}}{Br}}{\overset{\overset{Br}{\mid}}{CH_3-\overset{\mid}{C}-CH_3}} \tag{13.66}$$

(iv) Addition of water

Like alkanes and alkenes, alkynes are also immiscible and do not react with water. However, one molecule of water adds to alkynes on warming with mercuric sulphate and dilute sulphuric acid at 333 K to form carbonyl compounds.

$$\underset{\text{Ethyne}}{HC\equiv CH}+H-OH\xrightarrow[333K]{Hg^{2+}/H^+}\underset{\underset{OH}{\mid}}{CH_2=C-H}$$
$$\downarrow\text{Isomerisation}$$
$$\underset{\underset{\underset{\text{Ethanal}}{O}}{\parallel}}{CH_3-C-H} \tag{13.67}$$

$$\underset{\text{Propyne}}{CH_3-C\equiv CH}+H-OH\xrightarrow[333K]{Hg^{2+}/H^+}\underset{\underset{O-H}{\mid}}{CH_3-C=CH_2}$$
$$\text{Isomerisation}\downarrow$$
$$\underset{\underset{\underset{\text{Propanone}}{O}}{\parallel}}{CH_3-C-CH_3} \tag{13.68}$$

(v) Polymerisation

(a) *Linear polymerisation*: Under suitable conditions, linear polymerisation of ethyne takes place to produce polyacetylene or polyethyne which is a high molecular weight polyene containing repeating units of $(CH=CH-CH=CH)$ and can be represented as $-(CH=CH-CH=CH)_n-$ Under special conditions, this polymer conducts electricity.

Thin film of polyacetylene can be used as electrodes in batteries. These films are good conductors, lighter and cheaper than the metal conductors.

(b) *Cyclic polymerisation:* Ethyne on passing through red hot iron tube at 873K undergoes cyclic polymerization. Three molecules polymerise to form benzene, which is the starting molecule for the preparation of derivatives of benzene, dyes, drugs and large number of other organic compounds. This is the best route for entering from aliphatic to aromatic compounds as discussed below:

(13.69)
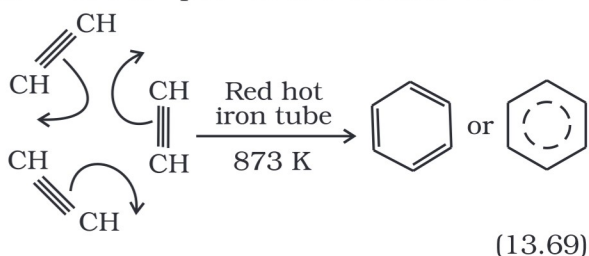
Problem 13.14

How will you convert ethanoic acid into benzene?

Solution
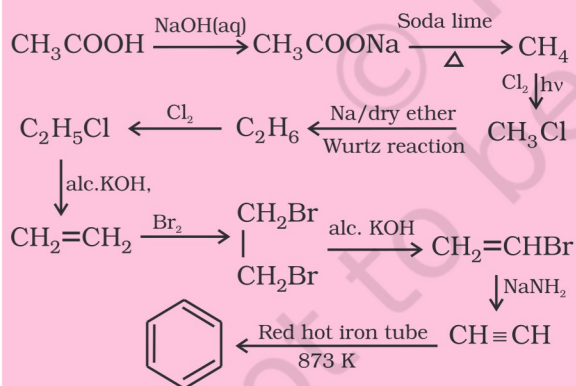
13.5 AROMATIC HYDROCARBON

These hydrocarbons are also known as '**arenes**'. Since most of them possess pleasant odour (*Greek; aroma meaning pleasant smelling*), the class of compounds was named as '*aromatic compounds*'. Most of such compounds were found to contain benzene ring. Benzene ring is highly unsaturated but

in a majority of reactions of aromatic compounds, the unsaturation of benzene ring is retained. However, there are examples of aromatic hydrocarbons which do not contain a benzene ring but instead contain other highly unsaturated ring. Aromatic compounds containing benzene ring are known as **benzenoids** and those not containing a benzene ring are known as **non-benzenoids**. Some examples of arenes are given below:

Benzene   Toluene   Naphthalene

Biphenyl
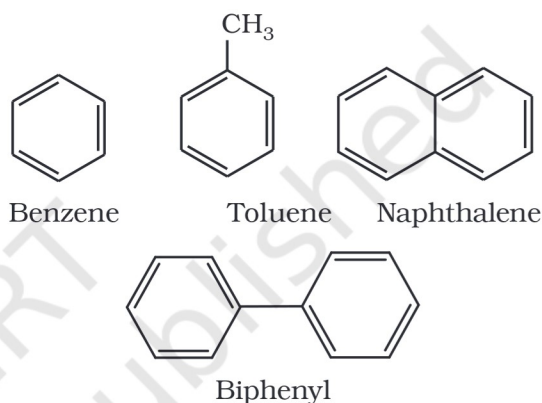
13.5.1 Nomenclature and Isomerism

The nomenclature and isomerism of aromatic hydrocarbons has already been discussed in Unit 12. All six hydrogen atoms in benzene are equivalent; so it forms one and only one type of monosubstituted product. When two hydrogen atoms in benzene are replaced by two similar or different monovalent atoms or groups, three different position isomers are possible. The 1, 2 or 1, 6 is known as the *ortho* (*o*–), the 1, 3 or 1, 5 *as meta* (*m*–) and the 1, 4 as *para* (*p*–) disubstituted compounds. A few examples of derivatives of benzene are given below:

Methylbenzene   1,2-Dimethylbenzene
(Toluene)   (*o*-Xylene)