

Position and chain isomerism shown by different pairs.

9.4.2 Structure of Triple Bond

Ethyne is the simplest molecule of alkyne series. Structure of ethyne is shown in Fig. 9.6.

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 $1s$ orbital of each of the two hydrogen atoms forming two C-H sigma bonds. The remaining sp hybridised orbital of each carbon atom undergoes overlapping along the internuclear axis with the $1s$ orbital of each of the two hydrogen atoms forming two C-H sigma bonds. The remaining sp hybridised orbital of each carbon atom undergoes overlapping along the internuclear axis with the $1s$ 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 $2p$ orbitals of one carbon atom are parallel to the $2p$

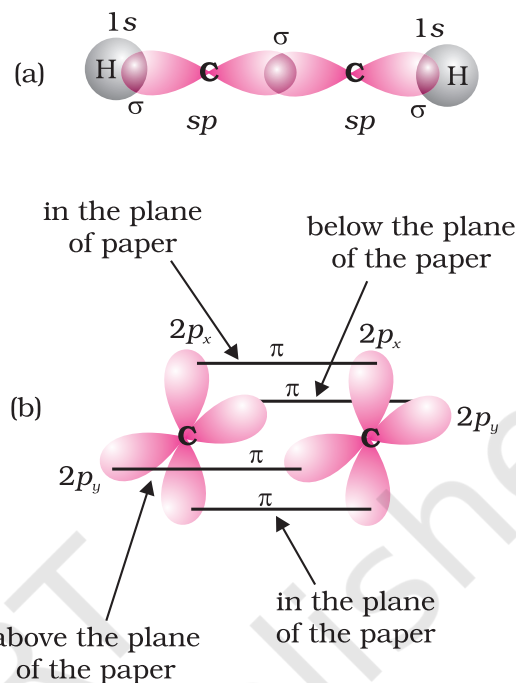


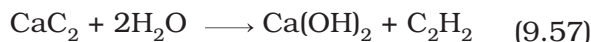
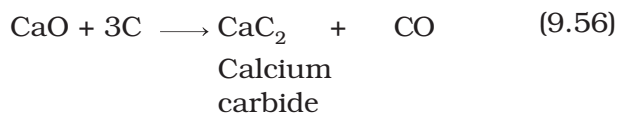
Fig. 9.6 Orbital picture of ethyne showing (a) sigma overlaps (b) pi overlaps.

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 \equiv 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 \equiv 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.

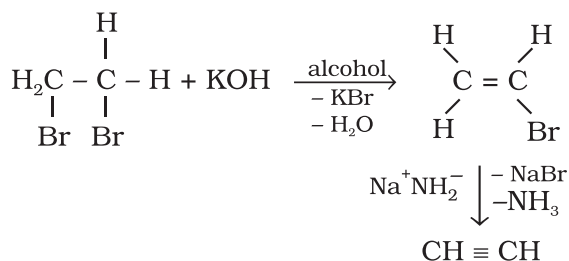
9.4.3 Preparation

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:





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.



9.4.4 Properties

Physical properties

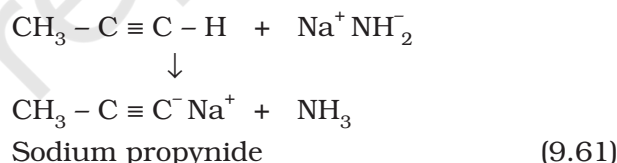
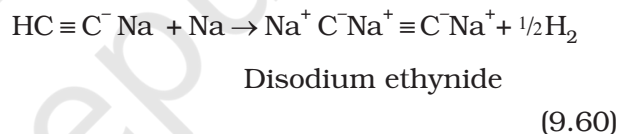
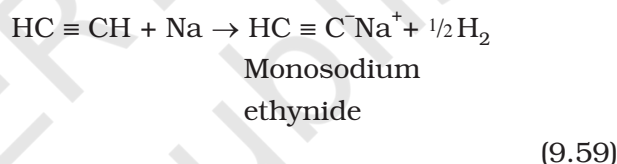
Physical properties of alkynes follow the same trend of alkenes and alkanes. First three members are gases, the next eight are liquids and the higher ones are solids. All alkynes are colourless. Ethyne has characteristic odour. Other members are odourless. Alkynes are weakly polar in nature. They are 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

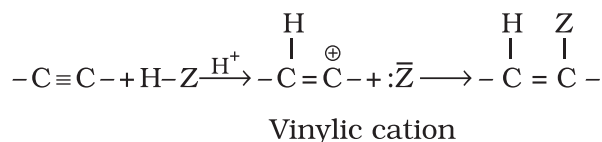
the sp hybridised carbon atoms whereas they are attached to sp^2 hybridised carbon atoms in ethene and sp^3 hybridised carbons in ethane. Due to the maximum percentage of s character (50%), the sp hybridised orbitals of carbon atoms in ethyne molecules have highest electronegativity; hence, these attract 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.



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 :

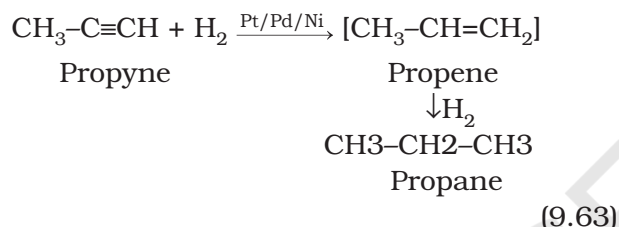
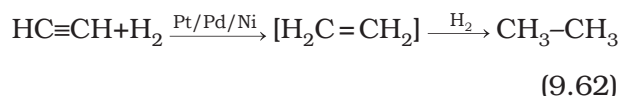
- i) $\text{CH} \equiv \text{CH} > \text{H}_2\text{C} = \text{CH}_2 > \text{CH}_3 - \text{CH}_3$
- ii) $\text{HC} \equiv \text{CH} > \text{CH}_3 - \text{C} \equiv \text{CH} >> \text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3$

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.

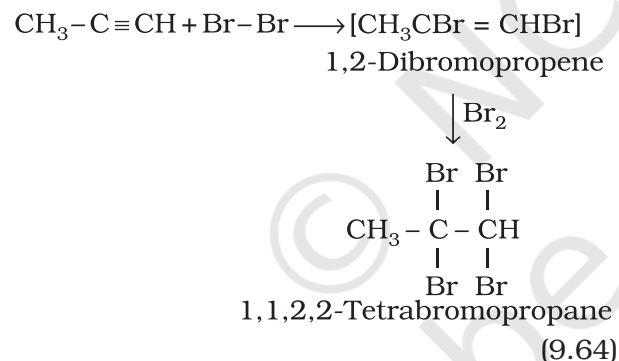


The addition product formed depends upon stability of vinyl cation. Addition in unsymmetrical alkynes takes place according to Markovnikov rule. Majority of the reactions of alkynes are the examples of electrophilic addition reactions. A few addition reactions are given below:

(i) Addition of dihydrogen



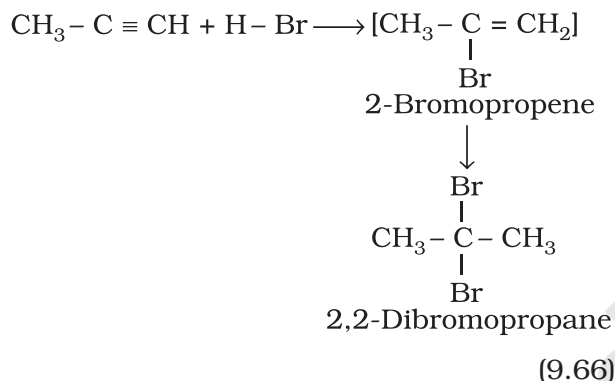
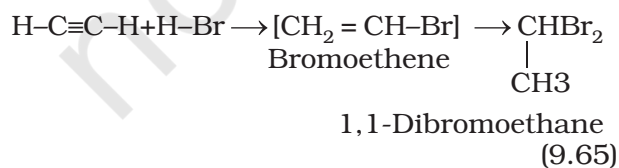
(ii) Addition of halogens



Reddish orange colour of the solution of bromine in carbon tetrachloride is decolourised. This is used as a test for unsaturation.

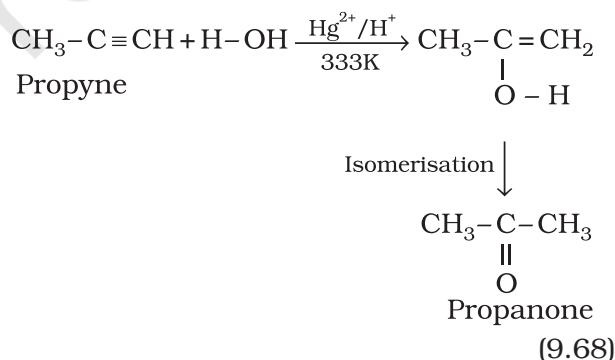
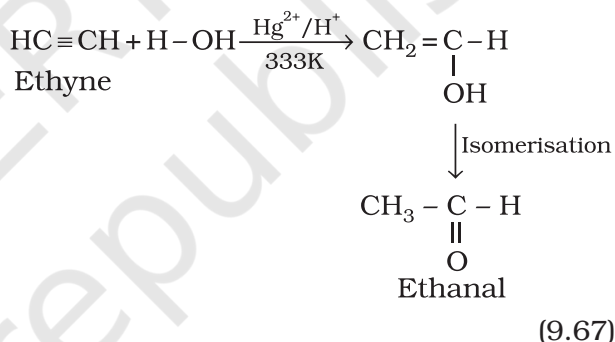
(iii) Addition of hydrogen halides

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)



(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.

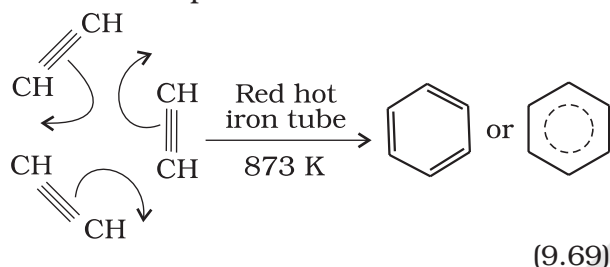


(v) Polymerisation

(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.

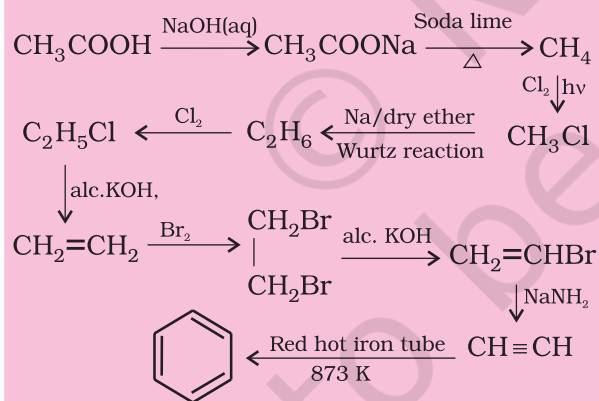
(b) Cyclic polymerisation: Ethyne on passing through red hot iron tube at 873K undergoes cyclic polymerization. Three molecules polymerise to form benzene, which is the starting molecule for the preparation of derivatives of benzene, dyes, drugs and large number of other organic compounds. This is the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



Problem 9.14

How will you convert ethanoic acid into benzene?

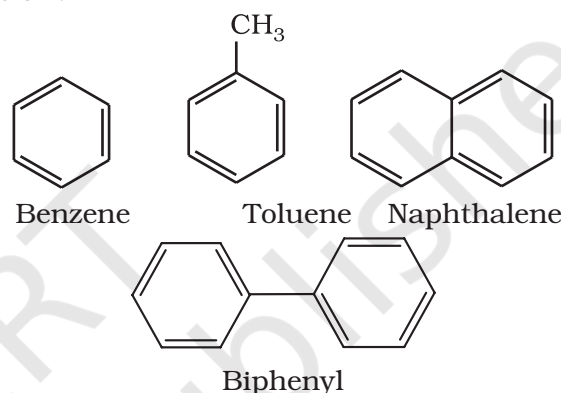
Solution



9.5 AROMATIC HYDROCARBON

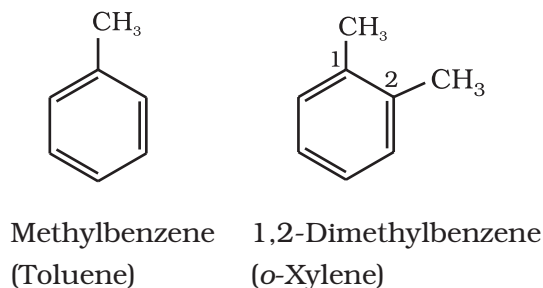
These hydrocarbons are also known as '**arenes**'. Since most of them possess pleasant odour (Greek; *aroma* meaning pleasant smelling), the class of compounds was named as '*aromatic compounds*'. Most of such compounds were found to contain benzene ring. Benzene ring is highly unsaturated

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:



9.5.1 Nomenclature and Isomerism

The nomenclature and isomerism of aromatic hydrocarbons has already been discussed in Unit 8. 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:



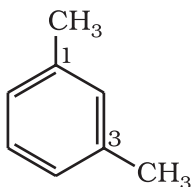
Friedrich August Kekulé, a German chemist was born in 1829 at Darmsdt in Germany. He became Professor in 1856 and Fellow of Royal Society in 1875. He made major contribution to structural organic chemistry by proposing in 1858 that carbon atoms can join to one another to form chains and later in 1865, he found an answer to the challenging problem of benzene structure by suggesting that these chains can close to form rings. He gave the dynamic structural formula to benzene which forms the basis for its modern electronic structure. He described the discovery of benzene structure later as:

"I was sitting writing at my textbook, but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire, and dozed. Again the atoms were gambolling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of this kind, could now distinguish larger structures of manifold conformations; long rows, sometimes more closely fitted together; all twisting and turning in snake like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I woke;.... I spent the rest of the night working out the consequences of the hypothesis. Let us learn to dream, gentlemen, and then perhaps we shall learn the truth but let us beware of making our dreams public before they have been approved by the waking mind." (1890).

One hundred years later, on the occasion of Kekulé's centenary celebrations a group of compounds having polybenzenoid structures have been named as Kekulenes.



**FRIEDRICH
AUGUST KEKULÉ**
(7th September
1829–13th July
1896)

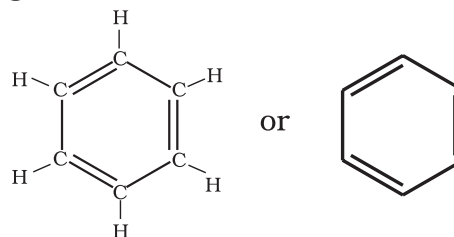


1,3 Dimethylbenzene (m-Xylene)



1,4-Dimethylbenzene (p-Xylene)

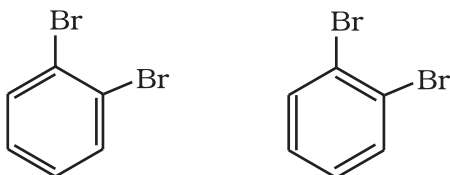
was further found to produce one and only one monosubstituted derivative which indicated that all the six carbon and six hydrogen atoms of benzene are identical. On the basis of this observation August Kekulé in 1865 proposed the following structure for benzene having cyclic arrangement of six carbon atoms with alternate single and double bonds and one hydrogen atom attached to each carbon atom.



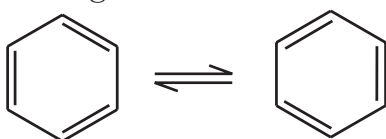
The Kekulé structure indicates the possibility of two isomeric 1,2-dibromobenzenes. In one of the isomers, the bromine atoms are attached to the doubly bonded carbon atoms whereas in the other, they are attached to the singly bonded carbons.

9.5.2 Structure of Benzene

Benzene was isolated by Michael Faraday in 1825. The molecular formula of benzene, C_6H_6 , indicates a high degree of unsaturation. This molecular formula did not account for its relationship to corresponding alkanes, alkenes and alkynes which you have studied in earlier sections of this unit. What do you think about its possible structure? Due to its unique properties and unusual stability, it took several years to assign its structure. Benzene was found to be a stable molecule and found to form a triozone which indicates the presence of three double bonds. Benzene



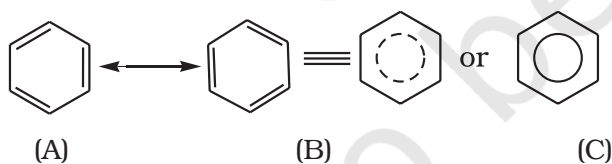
However, benzene was found to form only one ortho disubstituted product. This problem was overcome by Kekulé by suggesting the concept of oscillating nature of double bonds in benzene as given below.



Even with this modification, Kekulé structure of benzene fails to explain unusual stability and preference to substitution reactions than addition reactions, which could later on be explained by resonance.

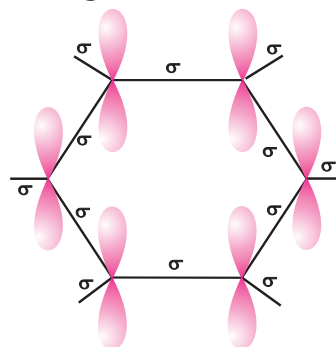
Resonance and stability of benzene

According to Valence Bond Theory, the concept of oscillating double bonds in benzene is now explained by resonance. Benzene is a hybrid of various resonating structures. The two structures, A and B given by Kekulé are the main contributing structures. The hybrid structure is represented by inserting a circle or a dotted circle in the hexagon as shown in (C). The circle represents the six electrons which are delocalised between the six carbon atoms of the benzene ring.



The orbital overlapping gives us better picture about the structure of benzene. All the six carbon atoms in benzene are sp^2 hybridized. Two sp^2 hybrid orbitals of each carbon atom overlap with sp^2 hybrid orbitals of adjacent carbon atoms to form six C—C sigma bonds which are in the hexagonal plane. The remaining sp^2 hybrid orbital of each carbon atom overlaps with s orbital of a hydrogen atom to form six C—H sigma bonds. Each carbon atom is now left with one

unhybridised p orbital perpendicular to the plane of the ring as shown below:



The unhybridised p orbital of carbon atoms are close enough to form a π bond by lateral overlap. There are two equal possibilities of forming three π bonds by overlap of p orbitals of $C_1 - C_2$, $C_3 - C_4$, $C_5 - C_6$ or $C_2 - C_3$, $C_4 - C_5$, $C_6 - C_1$ respectively as shown in the following figures.

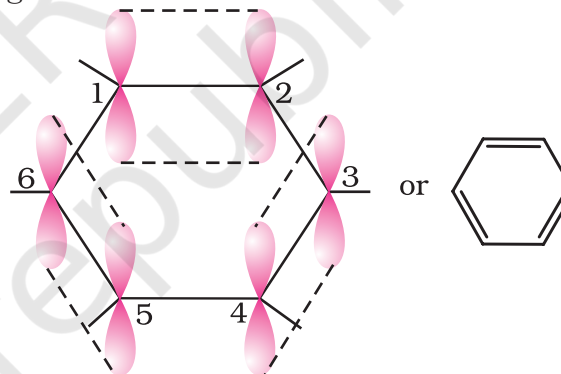


Fig. 9.7 (a)

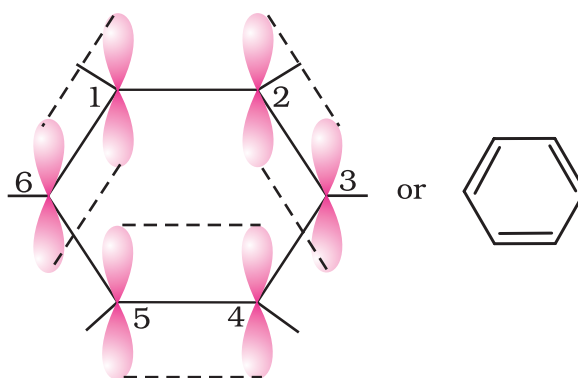


Fig. 9.7 (b)

Structures shown in Fig. 9.7(a) and (b) correspond to two Kekulé's structure with localised π bonds. The internuclear distance

between all the carbon atoms in the ring has been determined by the X-ray diffraction to be the same; there is equal probability for the p orbital of each carbon atom to overlap with the p orbitals of adjacent carbon atoms [Fig. 9.7 (c)]. This can be represented in the form of two doughnuts (rings) of electron clouds [Fig. 9.7 (d)], one above and one below the plane of the hexagonal ring as shown below:

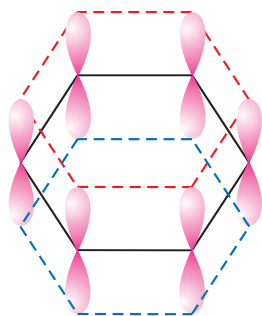


Fig. 9.7 (c)

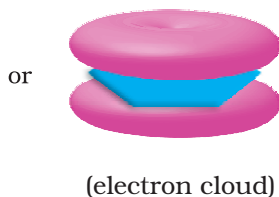


Fig. 9.7 (d)

The six π electrons are thus delocalised and can move freely about the six carbon nuclei, instead of any two as shown in Fig. 9.6 (a) or (b). The delocalised π electron cloud is attracted more strongly by the nuclei of the carbon atoms than the electron cloud localised between two carbon atoms. Therefore, presence of delocalised π electrons in benzene makes it more stable than the hypothetical cyclohexatriene.

X-Ray diffraction data reveals that benzene is a planar molecule. Had any one of the above structures of benzene (A or B) been correct, two types of C—C bond lengths were expected. However, X-ray data indicates that all the six C—C bond lengths are of the same order (139 pm) which is intermediate between C—C single bond (154 pm) and C—C double bond (133 pm). Thus the absence of pure double bond in benzene accounts for the reluctance of benzene to show addition reactions under normal conditions, thus explaining the unusual behaviour of benzene.

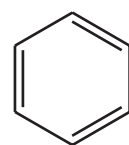
9.5.3 Aromaticity

Benzene was considered as parent 'aromatic' compound. Now, the name is applied to all the ring systems whether or not having benzene ring, possessing following characteristics.

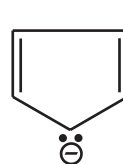
- Planarity
- Complete delocalisation of the π electrons in the ring
- Presence of $(4n + 2)$ π electrons in the ring where n is an integer ($n = 0, 1, 2, \dots$).

This is often referred to as **Hückel Rule**.

Some examples of aromatic compounds are given below:



Benzene

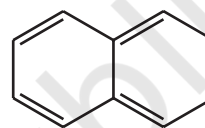


Cyclopentadienyl anion



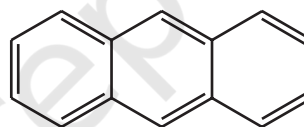
Cycloheptatrienyl cation

($n=1$, 6π electrons)

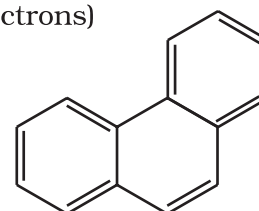


Naphthalene

($n = 2$, 10π electrons)



Anthracene



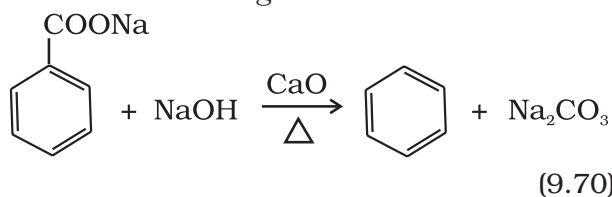
Phenanthrene

($n=3$, 14π electrons)

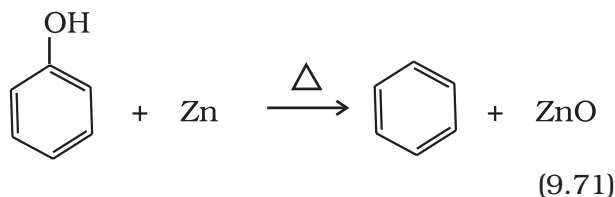
9.5.4 Preparation of Benzene

Benzene is commercially isolated from coal tar. However, it may be prepared in the laboratory by the following methods.

- Cyclic polymerisation of ethyne:** (Section 9.4.4)
- Decarboxylation of aromatic acids:** Sodium salt of benzoic acid on heating with sodalime gives benzene.



(iii) **Reduction of phenol:** Phenol is reduced to benzene by passing its vapours over heated zinc dust



9.5.5 Properties

Physical properties

Aromatic hydrocarbons are non-polar molecules and are usually colourless liquids or solids with a characteristic aroma. You are also familiar with naphthalene balls which are used in toilets and for preservation of clothes because of unique smell of the compound and the moth repellent property. Aromatic hydrocarbons are immiscible with water but are readily miscible with organic solvents. They burn with sooty flame.

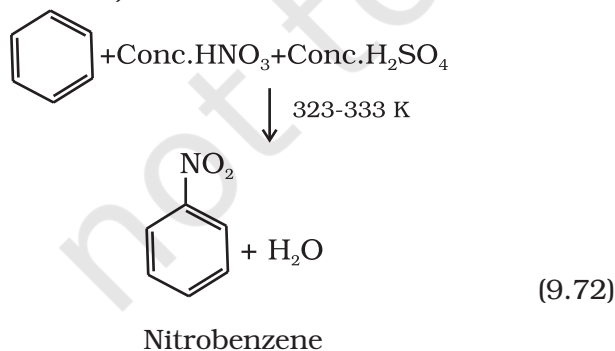
Chemical properties

Arenes are characterised by electrophilic substitution reactions. However, under special conditions they can also undergo addition and oxidation reactions.

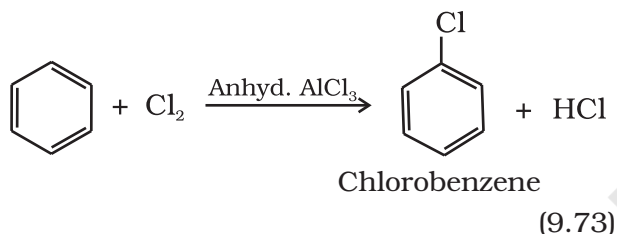
Electrophilic substitution reactions

The common electrophilic substitution reactions of arenes are nitration, halogenation, sulphonation, Friedel Craft's alkylation and acylation reactions in which attacking reagent is an electrophile (E^+)

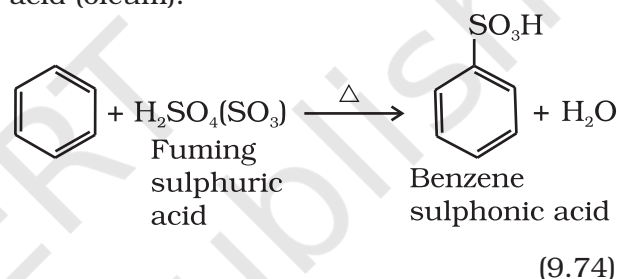
(i) **Nitration:** A nitro group is introduced into benzene ring when benzene is heated with a mixture of concentrated nitric acid and concentrated sulphuric acid (nitrating mixture).



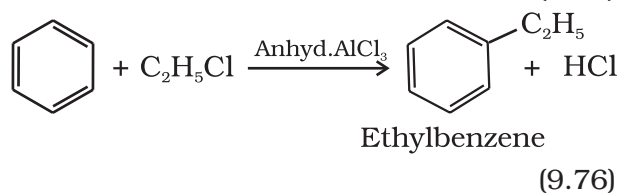
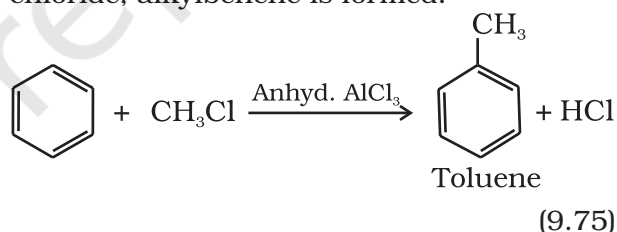
(ii) **Halogenation:** Arenes react with halogens in the presence of a Lewis acid like anhydrous FeCl_3 , FeBr_3 or AlCl_3 to yield haloarenes.



(iii) **Sulphonation:** The replacement of a hydrogen atom by a sulphonic acid group in a ring is called sulphonation. It is carried out by heating benzene with fuming sulphuric acid (oleum).

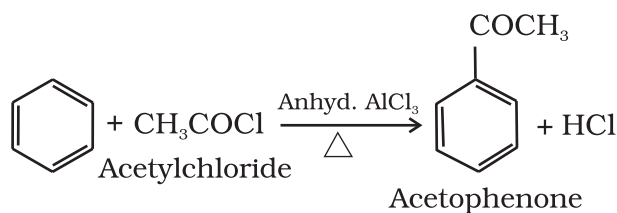


(iv) **Friedel-Crafts alkylation reaction:** When benzene is treated with an alkyl halide in the presence of anhydrous aluminium chloride, alkylbenzene is formed.

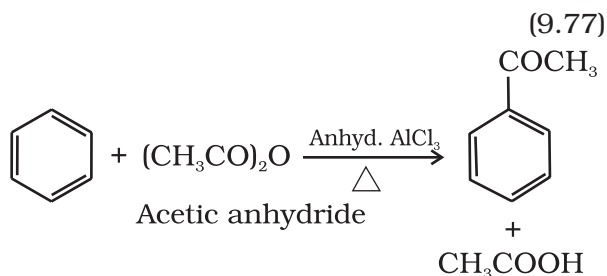


Why do we get isopropyl benzene on treating benzene with 1-chloropropane instead of *n*-propyl benzene?

(v) **Friedel-Crafts acylation reaction:** The reaction of benzene with an acyl halide or acid anhydride in the presence of Lewis acids (AlCl_3) yields acyl benzene.

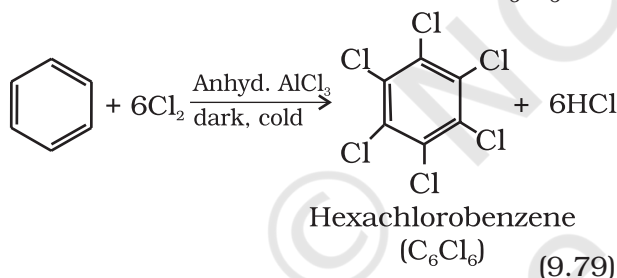


(9.77)



(9.78)

If excess of electrophilic reagent is used, further substitution reaction may take place in which other hydrogen atoms of benzene ring may also be successively replaced by the electrophile. For example, benzene on treatment with excess of chlorine in the presence of anhydrous AlCl_3 can be chlorinated to hexachlorobenzene (C_6Cl_6)



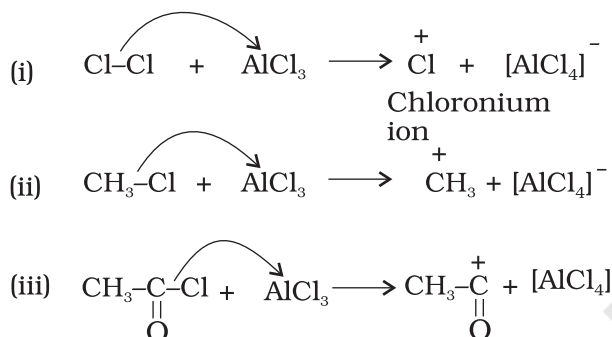
(9.79)

Mechanism of electrophilic substitution reactions:

According to experimental evidences, S_E (S = substitution; E = electrophilic) reactions are supposed to proceed via the following three steps:

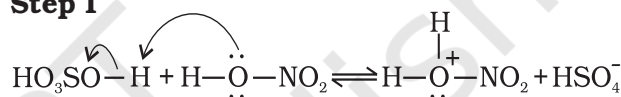
- Generation of the electrophile
- Formation of carbocation intermediate
- Removal of proton from the carbocation intermediate

(a) Generation of electrophile E^\oplus : During chlorination, alkylation and acylation of benzene, anhydrous AlCl_3 , being a Lewis acid helps in generation of the electrophile Cl^\oplus , R^\oplus , RC^\oplusO (acylium ion) respectively by combining with the attacking reagent.



In the case of nitration, the electrophile, nitronium ion, NO_2^\oplus is produced by transfer of a proton (from sulphuric acid) to nitric acid in the following manner:

Step I



Step II

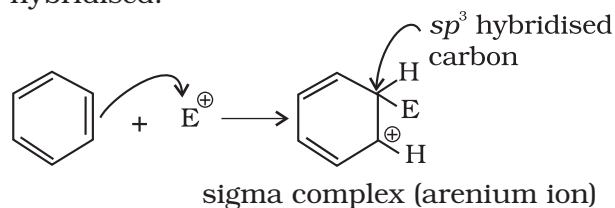


Protonated
nitric acid

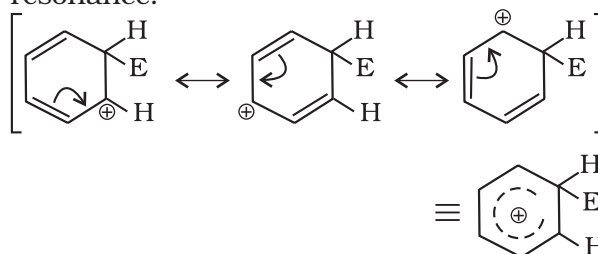
Nitronium
ion

It is interesting to note that in the process of generation of nitronium ion, sulphuric acid serves as an acid and nitric acid as a base. Thus, it is a simple acid-base equilibrium.

(b) Formation of Carbocation (arenium ion): Attack of electrophile results in the formation of σ -complex or arenium ion in which one of the carbon is sp^3 hybridised.

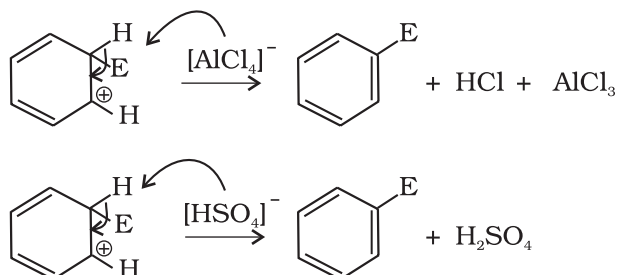


The arenium ion gets stabilised by resonance:



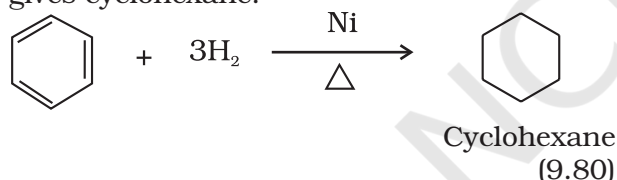
Sigma complex or arenium ion loses its aromatic character because delocalisation of electrons stops at sp^3 hybridised carbon.

(c) Removal of proton: To restore the aromatic character, σ -complex releases proton from sp^3 hybridised carbon on attack by $[AlCl_4]^-$ (in case of halogenation, alkylation and acylation) and $[HSO_4]^-$ (in case of nitration).

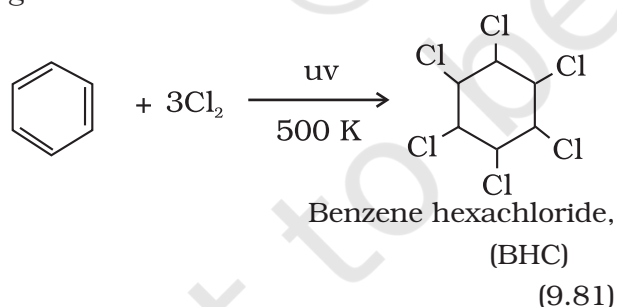


Addition reactions

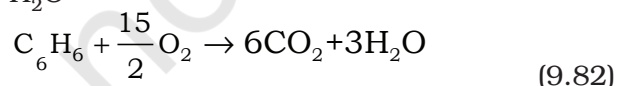
Under vigorous conditions, i.e., at high temperature and/ or pressure in the presence of nickel catalyst, hydrogenation of benzene gives cyclohexane.



Under ultra-violet light, three chlorine molecules add to benzene to produce benzene hexachloride, $C_6H_6Cl_6$ which is also called gammmaxane.

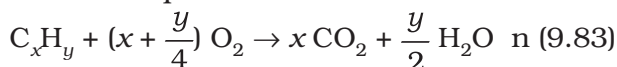


Combustion: When heated in air, benzene burns with sooty flame producing CO_2 and H_2O



General combustion reaction for any hydrocarbon may be given by the following

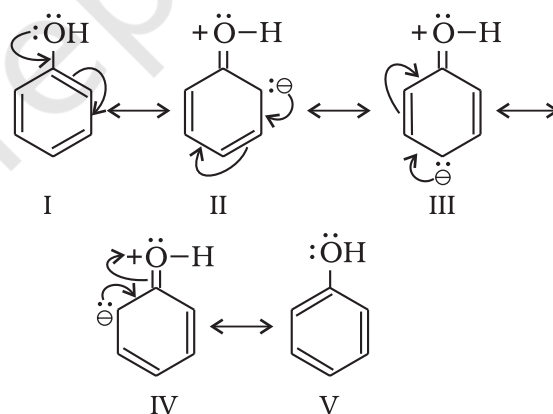
chemical equation:



9.5.6 Directive influence of a functional group in monosubstituted benzene

When monosubstituted benzene is subjected to further substitution, three possible disubstituted products are not formed in equal amounts. Two types of behaviour are observed. Either *ortho* and *para* products or *meta* product is predominantly formed. It has also been observed that this behaviour depends on the nature of the substituent already present in the benzene ring and not on the nature of the entering group. This is known as directive influence of substituents. Reasons for *ortho/para* or *meta* directive nature of groups are discussed below:

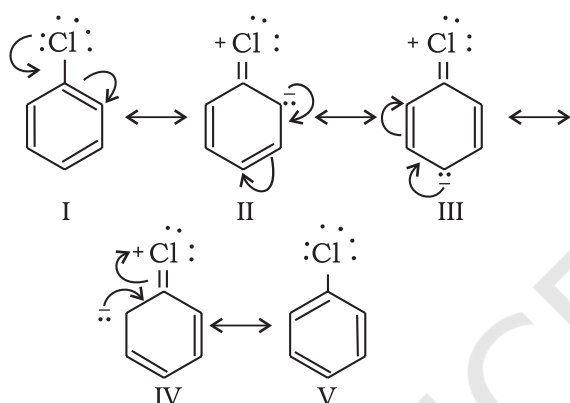
Ortho and para directing groups: The groups which direct the incoming group to *ortho* and *para* positions are called *ortho* and *para* directing groups. As an example, let us discuss the directive influence of phenolic ($-OH$) group. Phenol is resonance hybrid of following structures:



It is clear from the above resonating structures that the electron density is more on *o*- and *p*- positions. Hence, the substitution takes place mainly at these positions. However, it may be noted that $-I$ effect of $-OH$ group also operates due to which the electron density on *ortho* and *para* positions of the benzene ring is slightly reduced. But the overall electron density increases at these positions of the ring due to resonance. Therefore, $-OH$ group **activates** the benzene ring for the attack by

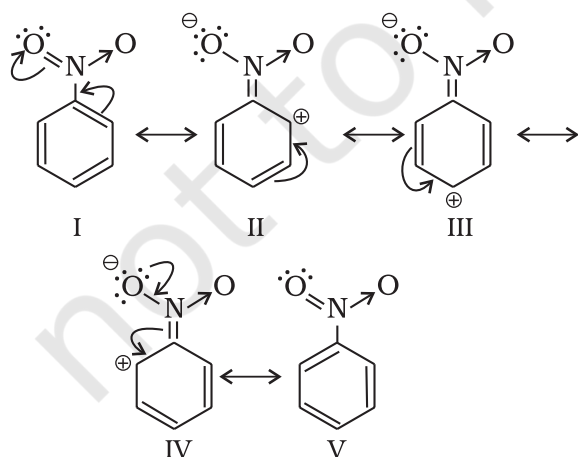
an electrophile. Other examples of **activating** groups are $-\text{NH}_2$, $-\text{NHR}$, $-\text{NHCOCH}_3$, $-\text{OCH}_3$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, etc.

In the case of aryl halides, halogens are moderately **deactivating**. Because of their strong $-I$ effect, overall electron density on benzene ring decreases. It makes further substitution difficult. However, due to resonance the electron density on o - and p - positions is greater than that at the m -position. Hence, they are also o - and p -directing groups. Resonance structures of chlorobenzene are given below:



Meta directing group: The groups which direct the incoming group to *meta* position are called *meta* directing groups. Some examples of *meta* directing groups are $-\text{NO}_2$, $-\text{CN}$, $-\text{CHO}$, $-\text{COR}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{SO}_3\text{H}$, etc.

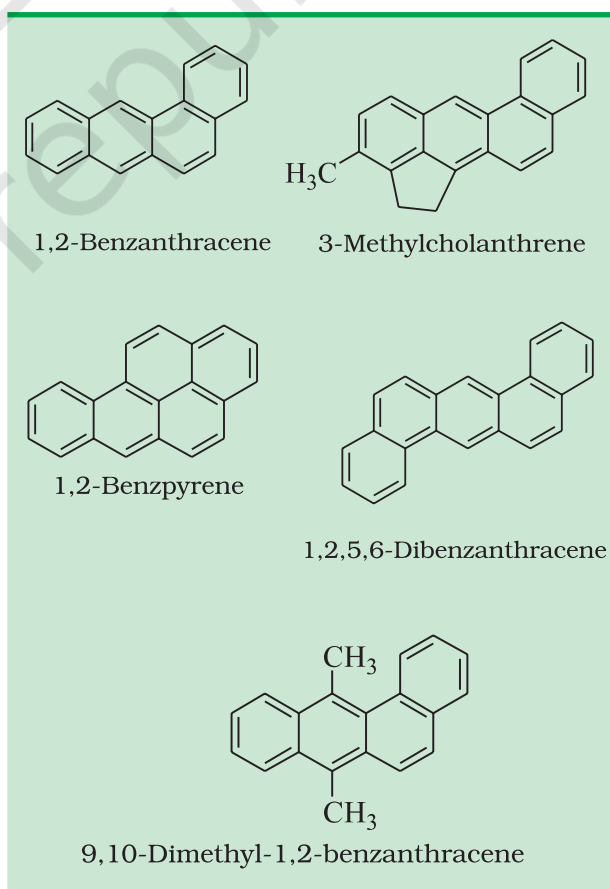
Let us take the example of nitro group. Nitro group reduces the electron density in the benzene ring due to its strong $-I$ effect. Nitrobenzene is a resonance hybrid of the following structures.



In this case, the overall electron density on benzene ring decreases making further substitution difficult, therefore these groups are also called '**deactivating groups**'. The electron density on o - and p - position is comparatively less than that at *meta* position. Hence, the electrophile attacks on comparatively electron rich *meta* position resulting in *meta* substitution.

9.6 CARCINOGENICITY AND TOXICITY

Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and said to possess cancer producing (carcinogenic) property. Such polynuclear hydrocarbons are formed on incomplete combustion of organic materials like tobacco, coal and petroleum. They enter into human body and undergo various biochemical reactions and finally damage DNA and cause cancer. Some of the carcinogenic hydrocarbons are given below (see box).



SUMMARY

Hydrocarbons are the compounds of carbon and hydrogen only. Hydrocarbons are mainly obtained from coal and petroleum, which are the major **sources of energy**. **Petrochemicals** are the prominent starting materials used for the manufacture of a large number of commercially important products. LPG (liquefied petroleum gas) and CNG (compressed natural gas), the main sources of energy for domestic fuels and the automobile industry, are obtained from petroleum. Hydrocarbons are classified as **open chain saturated** (alkanes) and **unsaturated** (alkenes and alkynes), **cyclic** (alicyclic) and **aromatic**, according to their structure.

The important reactions of alkanes are **free radical substitution**, **combustion**, **oxidation** and **aromatization**. Alkenes and alkynes undergo addition reactions, which are mainly **electrophilic additions**. Aromatic hydrocarbons, despite having unsaturation, undergo mainly **electrophilic substitution** reactions. These undergo addition reactions only under special conditions.

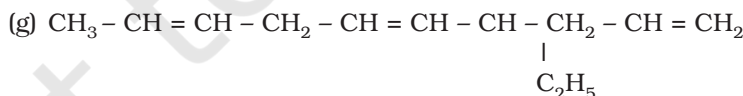
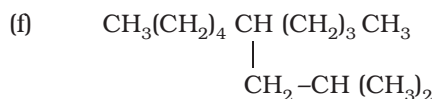
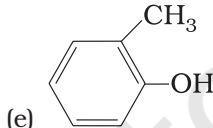
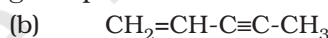
Alkanes show conformational isomerism due to free rotation along the C-C sigma bonds. Out of **staggered** and the **eclipsed** conformations of ethane, staggered conformation is more stable as hydrogen atoms are farthest apart. Alkenes exhibit **geometrical (cis-trans) isomerism** due to restricted rotation around the carbon-carbon double bond.

Benzene and **benzenoid** compounds show aromatic character. Aromaticity, the property of being aromatic is possessed by compounds having specific electronic structure characterised by Hückel $(4n+2)\pi$ electron rule. The nature of groups or substituents attached to benzene ring is responsible for activation or deactivation of the benzene ring towards further electrophilic substitution and also for orientation of the incoming group. Some of the polynuclear hydrocarbons having fused benzene ring system have carcinogenic property.

EXERCISES

9.1 How do you account for the formation of ethane during chlorination of methane ?

9.2 Write IUPAC names of the following compounds :



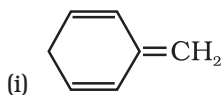
9.3 For the following compounds, write structural formulas and IUPAC names for all possible isomers having the number of double or triple bond as indicated :



9.4 Write IUPAC names of the products obtained by the ozonolysis of the following compounds :



- 9.5 An alkene 'A' on ozonolysis gives a mixture of ethanal and pentan-3-one. Write structure and IUPAC name of 'A'.
- 9.6 An alkene 'A' contains three C – C, eight C – H σ bonds and one C – C π bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Write IUPAC name of 'A'.
- 9.7 Propanal and pentan-3-one are the ozonolysis products of an alkene? What is the structural formula of the alkene?
- 9.8 Write chemical equations for combustion reaction of the following hydrocarbons:
- (i) Butane (ii) Pentene
(iii) Hexyne (iv) Toluene
- 9.9 Draw the *cis* and *trans* structures of hex-2-ene. Which isomer will have higher b.p. and why?
- 9.10 Why is benzene extra ordinarily stable though it contains three double bonds?
- 9.11 What are the necessary conditions for any system to be aromatic?
- 9.12 Explain why the following systems are not aromatic?



- 9.13 How will you convert benzene into
- (i) *p*-nitrobromobenzene (ii) *m*-nitrochlorobenzene
(iii) *p*-nitrotoluene (iv) acetophenone?
- 9.14 In the alkane $\text{H}_3\text{C}-\text{CH}_2-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{CH}(\text{CH}_3)_2$, identify 1, 2, 3 carbon atoms and give the number of H atoms bonded to each one of these.
- 9.15 What effect does branching of an alkane chain has on its boiling point?
- 9.16 Addition of HBr to propene yields 2-bromopropane, while in the presence of benzoyl peroxide, the same reaction yields 1-bromopropane. Explain and give mechanism.
- 9.17 Write down the products of ozonolysis of 1,2-dimethylbenzene (*o*-xylene). How does the result support Kekulé structure for benzene?
- 9.18 Arrange benzene, *n*-hexane and ethyne in decreasing order of acidic behaviour. Also give reason for this behaviour.
- 9.19 Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty?
- 9.20 How would you convert the following compounds into benzene?
- (i) Ethyne (ii) Ethene (iii) Hexane
- 9.21 Write structures of all the alkenes which on hydrogenation give 2-methylbutane.
- 9.22 Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile, E^+
- (a) Chlorobenzene, 2,4-dinitrochlorobenzene, *p*-nitrochlorobenzene
(b) Toluene, *p*- $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{NO}_2$, *p*- $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{NO}_2$.
- 9.23 Out of benzene, *m*-dinitrobenzene and toluene which will undergo nitration most easily and why?
- 9.24 Suggest the name of a Lewis acid other than anhydrous aluminium chloride which can be used during ethylation of benzene.
- 9.25 Why is Wurtz reaction not preferred for the preparation of alkanes containing odd number of carbon atoms? Illustrate your answer by taking one example.

Answer to Some Selected Problems

UNIT 7

7.25 15 g

UNIT 8

8.32 Mass of carbon dioxide formed = 0.505 g

Mass of water formed = 0.0864 g

8.33 % of nitrogen = 56

8.34 % of chlorine = 37.57

8.35 % of sulphur = 19.66

UNIT 9

9.1 Due to the side reaction in termination step by the combination of two $\dot{\text{C}}\text{H}_3$ free radicals.

- | | |
|---------------------------------|-------------------------------|
| 9.2 (a) 2-Methyl-but-2-ene | (b) Pent-1-ene-3-yne |
| (c) Buta-1, 3-diene | (d) 4-Phenylbut-1-ene |
| (e) 2-Methylphenol | (f) 5-(2-Methylpropyl)-decane |
| (g) 4-Ethyldeca -1,5,8- triene | |

- | | |
|--|-----------------|
| 9.3 (a) (i) $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_3$ | But-1-ene |
| (ii) $\text{CH}_3 - \text{CH}_2 = \text{CH} - \text{CH}_3$ | But-2-ene |
| (iii) $\text{CH}_2 = \underset{\text{CH}_3}{\text{C}} - \text{CH}_3$ | 2-Methylpropene |

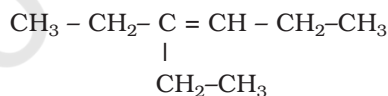
- | | |
|---|-------------------|
| (b) (i) $\text{HC} \equiv \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$ | Pent-1-yne |
| (ii) $\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_2 - \text{CH}_3$ | Pent-2-yne |
| (iii) $\text{CH}_3 - \text{CH} - \underset{\text{CH}_3}{\text{C}} \equiv \text{CH}$ | 3-Methylbut-1-yne |

- | | |
|-----------------------------------|-----------------------------------|
| 9.4 (i) Ethanal and propanal | (ii) Butan-2-one and pentan-2-one |
| (iii) Methanal and pentan-3-one | (iv) Propanal and benzaldehyde |

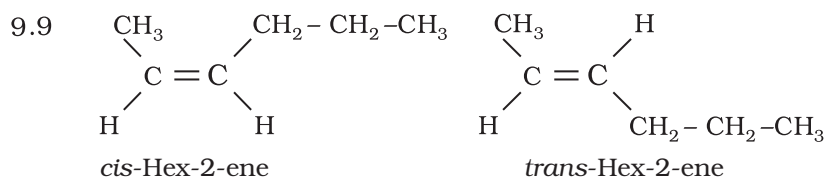
9.5 3-Ethylpent-2-ene

9.6 But-2-ene

9.7 4-Ethylhex-3-ene

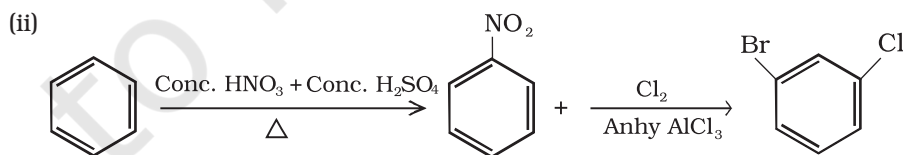
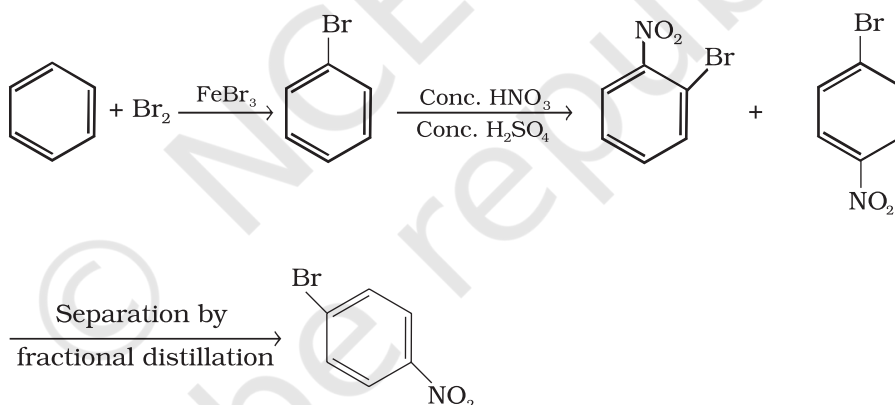


- 9.8 (a) $\text{C}_4\text{H}_{10}(\text{g}) + 13/20_2(\text{g}) \xrightarrow{\Delta} 4\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{g})$
 (b) $\text{C}_5\text{H}_{10}(\text{g}) + 15/20_2(\text{g}) \xrightarrow{\Delta} 5\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{g})$
 (c) $\text{C}_5\text{H}_{10}(\text{g}) + 17/2 \text{O}_2(\text{g}) \xrightarrow{\Delta} 6\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{g})$
 (d) $\text{C}_7\text{H}_8(\text{g}) + 9\text{O}_2(\text{g}) \xrightarrow{\Delta} 7\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$

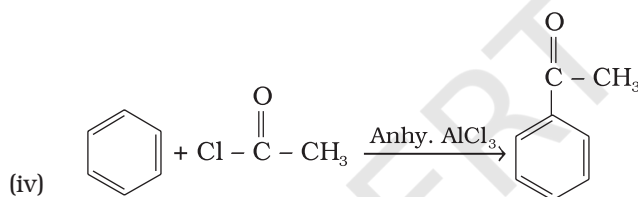
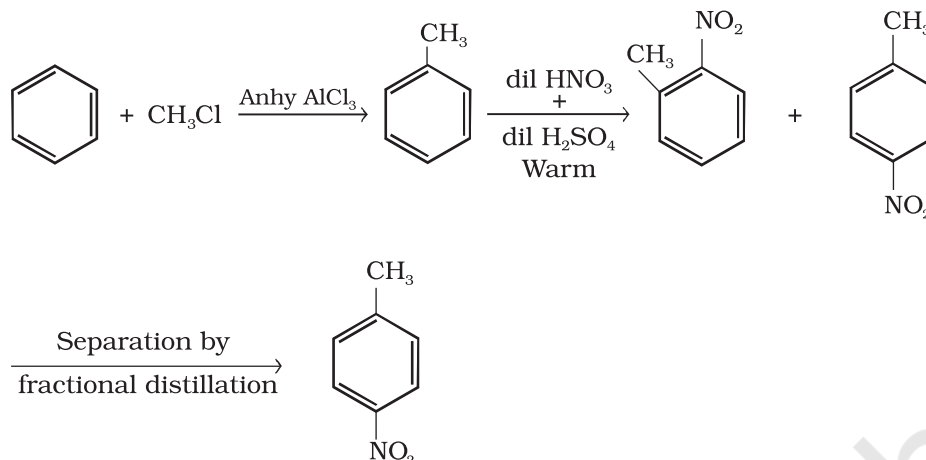


The cis form will have higher boiling point due to more polar nature leading to stronger intermolecular dipole-dipole interaction, thus requiring more heat energy to separate them.

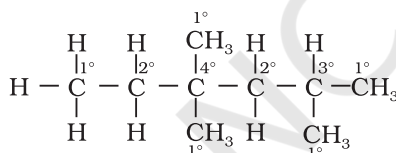
- 9.10 Due to resonance
 9.11 Planar, conjugated ring system with delocalisation of $(4n+2)$ electrons, where, n is an integer
 9.12 Lack of delocalisation of $(4n+2)$ π electrons in the cyclic system.
 9.13 (i)



(iii)



9.14



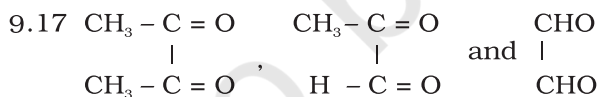
15 H attached to 1 carbons

4 H attached to 2 carbons

1 H attached to 3 carbons

9.15 More the branching in alkane, lower will be the boiling point.

9.16 Refer to addition reaction of HBr to unsymmetrical alkenes in the text.



All the three products cannot be obtained by any one of the Kekulé's structures. This shows that benzene is a resonance hybrid of the two resonating structures.

9.18 $H - C \equiv C - H > C_6H_6 > C_6H_{14}$. Due to maximum s orbital character in ethyne (50 per cent) as compared to 33 per cent in benzene and 25 per cent in n-hexane.

9.19 Due to the presence of 6 π electrons, benzene behaves as a rich source of electrons thus being easily attacked by reagents deficient in electrons.

- 9.20 (i) $3 \text{ CH} \equiv \text{CH} \xrightarrow[873\text{K}]{\text{Red hot Iron tube}} \text{C}_6\text{H}_6$
- (ii) $\text{C}_2\text{H}_4 \xrightarrow{\text{Br}_2} \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ | \quad | \\ \text{Br} \quad \text{BR} \end{array} \xrightarrow{\text{alc. KOH}} \text{CH}_2 = \text{CHN}r \xrightarrow{\text{NaNH}_2} \text{HC} \equiv \text{HC} \xrightarrow[873\text{k}]{\text{Red hot Iron tube}} \text{C}_6\text{H}_6$
- (iii) $\text{C}_6\text{H}_{14} \xrightarrow[773\text{ K, 10-20 atom}]{\text{Cr}_2\text{O}_3 / \text{V}_2\text{O}_5 / \text{Mo}_2\text{O}_3} \text{C}_6\text{H}_6$
- 9.21 $\text{CH}_2 = \text{C}(\text{CH}_3) - \text{CH}_2 - \text{CH}_3$ 2-Methylbut-1-ene
- $\text{CH}_3 - \text{C}(\text{CH}_3) = \text{CH} - \text{CH}_3$ 2-Methylbut-2-ene
- $\text{CH}_3 - \text{CH}(\text{CH}_3) - \text{CH} = \text{CH}_2$ 3-Methylbut-1-ene
- 9.22 (a) Chlorobenzene > *p*-nitrochlorobenzene > 2,4-dinitrochlorobenzene
 (b) Toluene > *p*-CH₃-C₆H₄-NO₂ > *p*-O₂N-C₆H₄-NO₂
- 9.23 Toluene undergoes nitration most easily due to electron releasing nature of the methyl group.
- 9.24 FeCl₃
- 9.25 Due to the formation of side products. For example, by starting with 1-bromopropane and 1-bromobutane, hexane and octane are the side products besides heptane.

NOTES

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