

1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 01 (Class XI, Semester - 2)
Module Name/Title	Hydrocarbons: Part 4
Module Id	kech_21304
Pre-requisites	Knowledge about hybridization and orbital overlap, sigma and pi bonds, concept of resonance, electrophilic substitution reactions, addition reactions, inductive effect
Objectives	<p>After going through this lesson, the learners will be able to:</p> <ul style="list-style-type: none">• Name aromatic hydrocarbons according to IUPAC system of nomenclature.• Recognise and write structures of various position isomers of aromatic compounds.• Understand the different methods of preparation of benzene.• Comprehend the structure of benzene, explain aromaticity and understand mechanism of electrophilic substitution reactions of benzene.• Predict the directive influence of substituents in monosubstituted benzene ring.• Learn about carcinogenicity and toxicity.
keywords	Covalent bond, sigma and pi bond, Kekule structure, Aromaticity, decarboxylation, electrophile, arenium ion, directive influence, activating and deactivating groups, carcinogenicity

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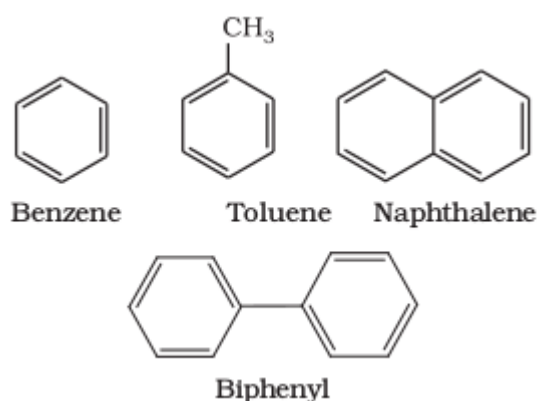
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1. Introduction: Aromatic Hydrocarbons

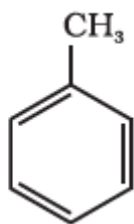
You know that hydrocarbons are classified into saturated, unsaturated and aromatic hydrocarbons. The aromatic hydrocarbons are also known as '**arenes**'. Since most of them possess pleasant odour (*Greek; aroma meaning pleasant smelling*), the class of compounds was named as '*aromatic compounds*'. 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:



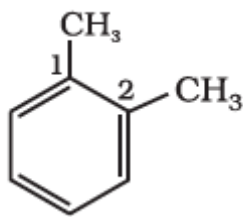
2. Nomenclature and Isomerism

You have already learned about the nomenclature and isomerism of aromatic hydrocarbons. All six hydrogen atoms in benzene are equivalent; so it forms one and only one type of

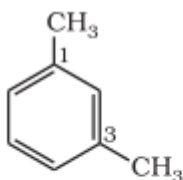
monosubstituted product. When two hydrogen atoms in benzene are replaced by two similar or different monovalent atoms or groups, three different position isomers are possible. The 1, 2 or 1, 6 is known as the *ortho* (*o*–), the 1, 3 or 1, 5 as *meta* (*m*–) and the 1, 4 as *para* (*p*–) disubstituted compounds. A few examples of derivatives of benzene are given below:



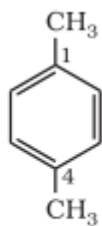
Methylbenzene
(Toluene)



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



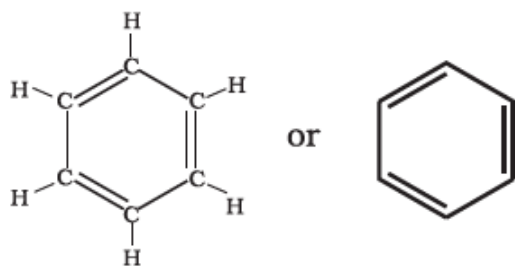
1,3 Dimethylbenzene
(*m*-Xylene)



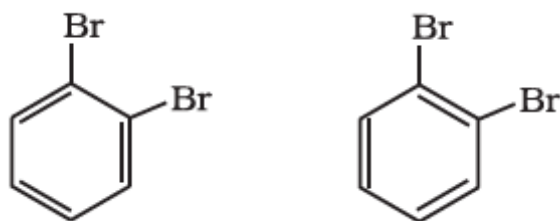
1,4-Dimethylbenzene
(*p*-Xylene)

3. 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 the earlier modules. 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 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.



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:

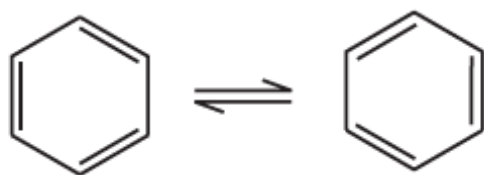
“I was sitting writing at my text book, but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire, and dozed. Again the atoms were gambolling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions 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 it’s 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.

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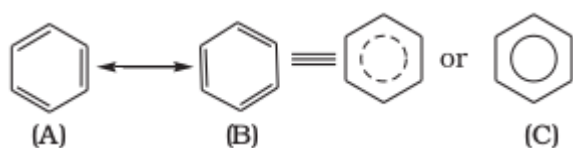
However, benzene was found to form only one ortho disubstituted product. This problem was overcome by Kekulé by suggesting the concept of oscillating nature of double bonds in benzene as given below.



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 in (Fig.1):

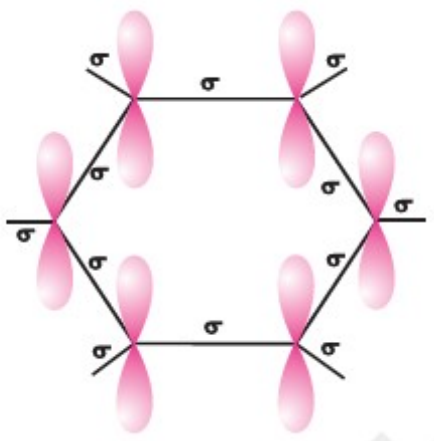


Fig. 1

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.

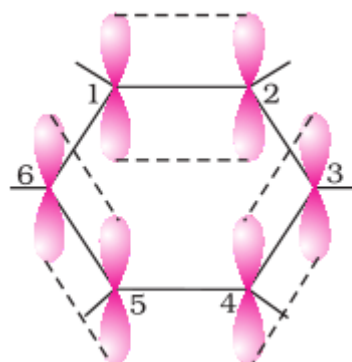


Fig. 2(a)

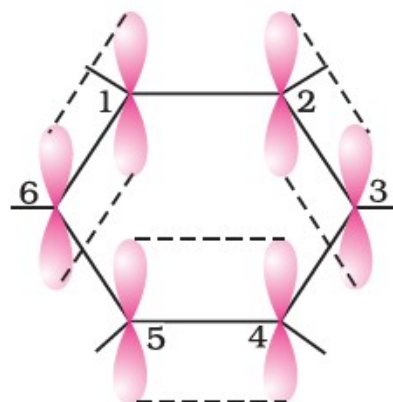
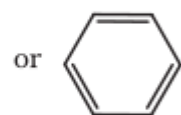
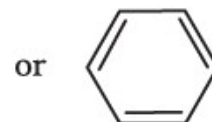


Fig. 2(b)



Structures shown in Fig. 2(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. 2 (c)]. This can be represented in the form of two doughnuts (rings) of electron clouds [Fig. 2(d)], one above and one below the plane of the hexagonal ring as shown below:

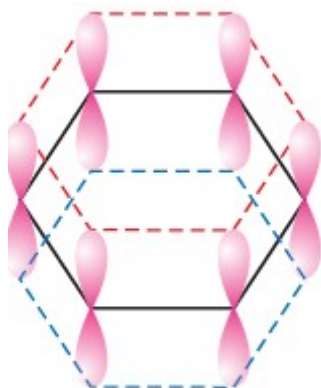


Fig.2 (c)

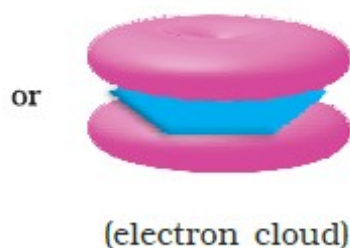


Fig.2 (d)

The six π electrons are thus delocalised and can move freely about the six carbon nuclei, instead of any two as shown in Fig. 2 (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.

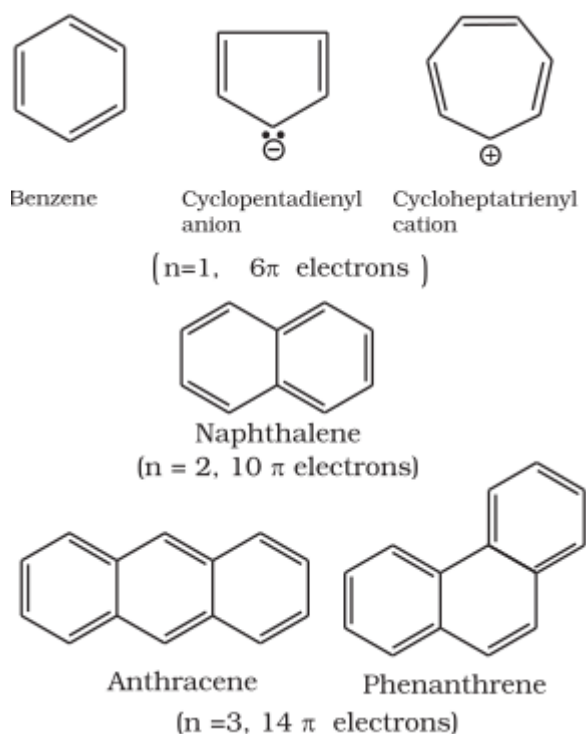
4. Aromaticity

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

- (i) Planarity
 - (ii) Complete delocalisation of the π electrons in the ring
 - (iii) 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:

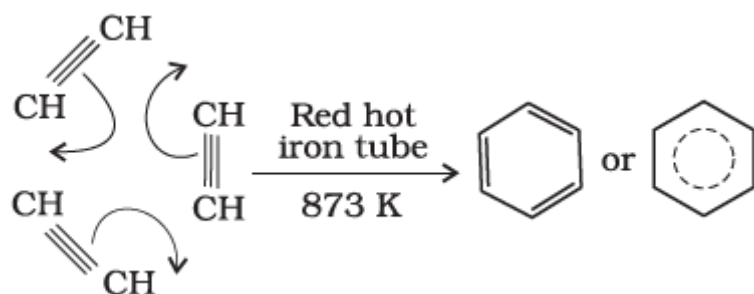


5. Preparation of Benzene

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

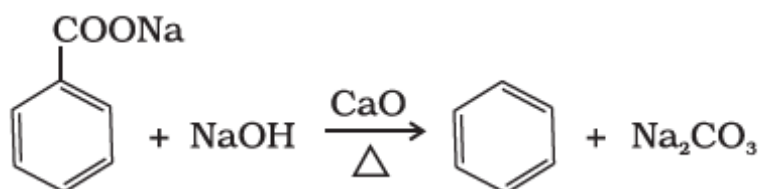
- (i) *Cyclic polymerisation of ethyne:*

Ethyne on passing through red hot iron tube at 873K undergoes cyclic polymerization. Three molecules polymerise to form benzene. This is the best route for entering from aliphatic to aromatic compounds.

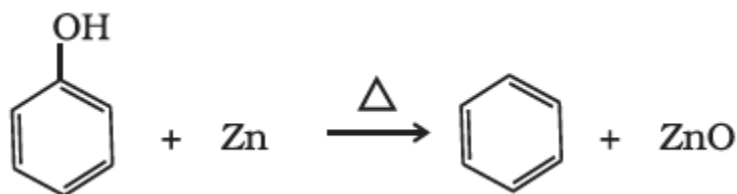


(ii) **Decarboxylation of aromatic acids:**

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.



6. 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.

7. Chemical Properties

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

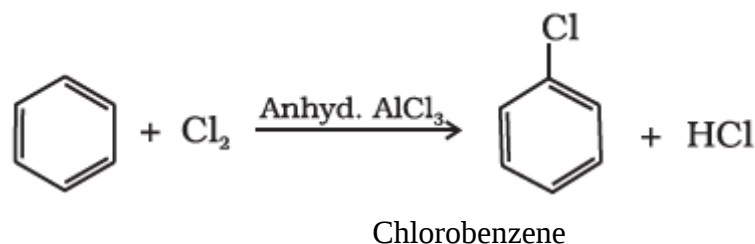
Electrophilic substitution reactions

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^+)

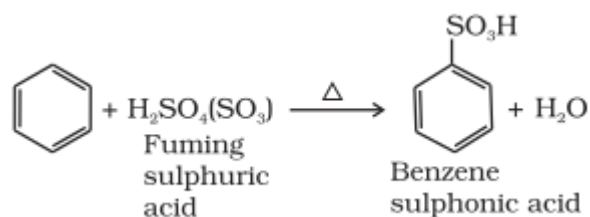
(i) **Nitration:** A nitro group is introduced into benzene ring when benzene is heated with a mixture of concentrated nitric acid and concentrated sulphuric acid (nitrating mixture).



(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.

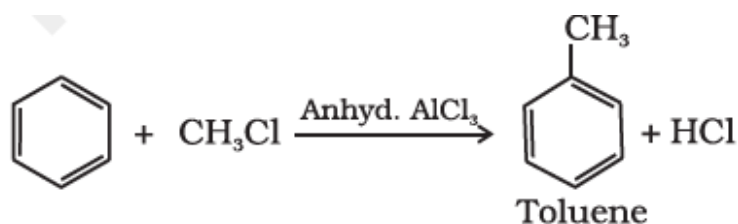


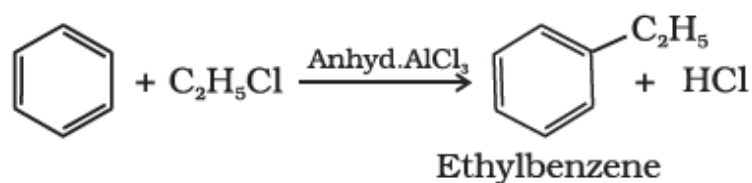
(iii) **Sulphonation:** The replacement of a hydrogen atom by a sulphonic acid group in a ring is called sulphonation. It is carried out by heating benzene with fuming sulphuric acid (oleum).



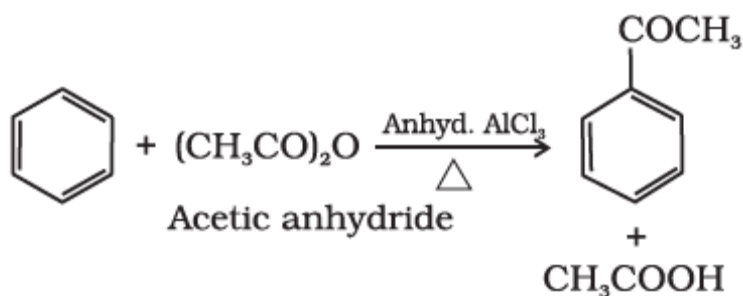
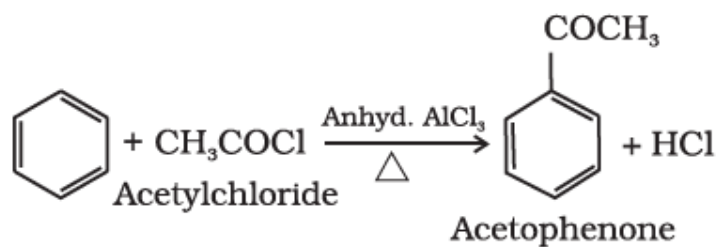
(iv) **Friedel-Crafts alkylation reaction:**

When benzene is treated with an alkyl halide in the presence of anhydrous aluminium chloride, alkylbenzene is formed.

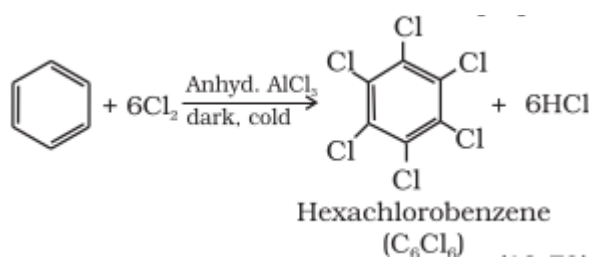




(v) **Friedel-Crafts acylation reaction:** The reaction of benzene with an acyl halide or acid anhydride in the presence of Lewis acids (AlCl_3) yields acyl benzene.



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)

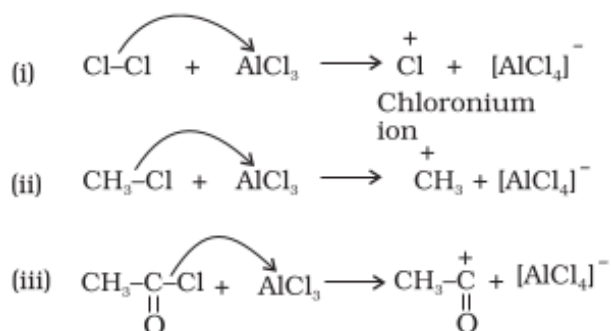


Mechanism of electrophilic substitution reactions:

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

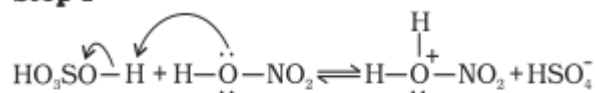
- (a) Generation of the electrophile
- (b) Formation of carbocation intermediate
- (c) Removal of proton from the carbocation intermediate

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

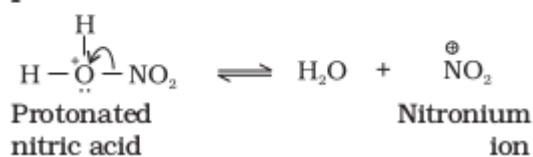


In the case of nitration, the electrophile, nitronium ion, NO_2^+ is produced by transfer of a proton (from sulphuric acid) to nitric acid in the following manner:

Step I



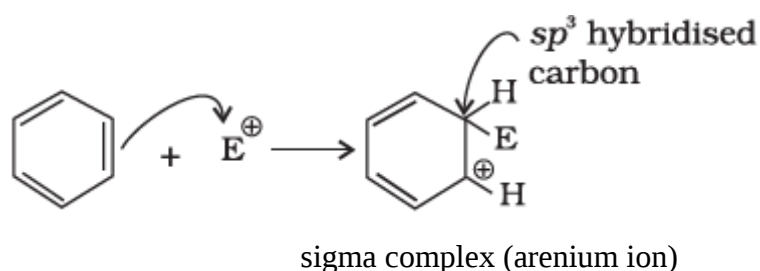
Step II



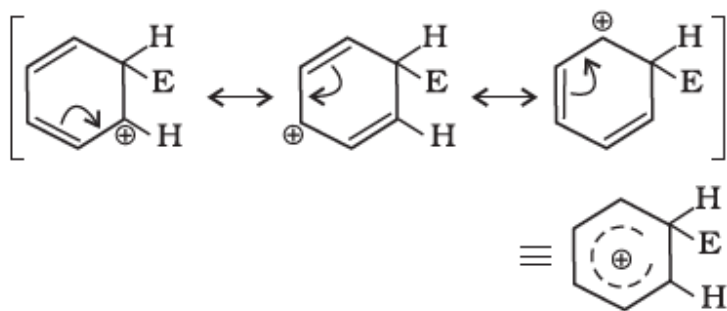
It is interesting to note that in the process of generation of nitronium ion, sulphuric acid serves as an acid and nitric acid as a base. Thus, it is a simple acid-base equilibrium.

(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.

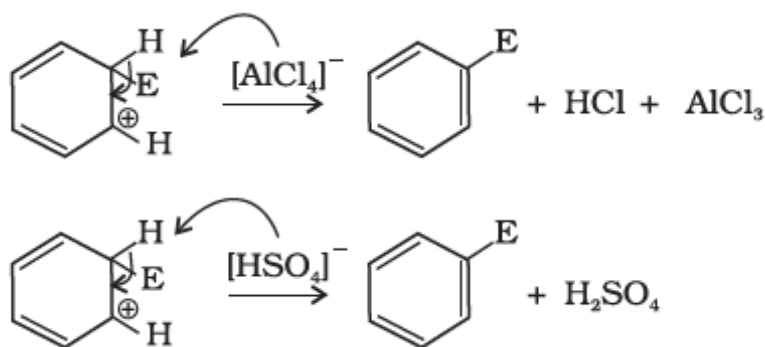


The arenium ion gets stabilised by resonance:



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 $[\text{AlCl}_4]^-$ (in case of halogenation, alkylation and acylation) and $[\text{HSO}_4]^-$ (in case of nitration).

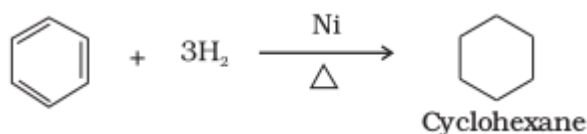


Problem : Why do we get isopropyl benzene on treating benzene with 1-chloropropane instead of *n*-propyl benzene?

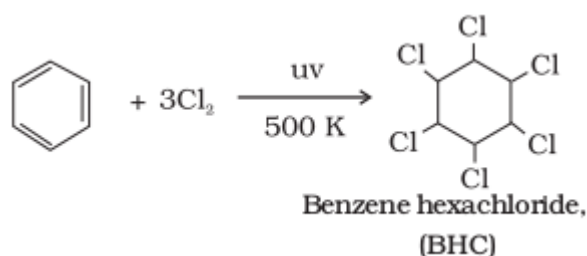
Solution: In this reaction the electrophile initially formed is propyl cation which is a primary carbocation. It rearranges to more stable isopropyl cation because it is a secondary carbocation. Then the isopropyl cation reacts with benzene to give isopropyl benzene.

Addition reactions

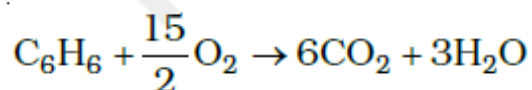
Under vigorous conditions, *i.e.*, at high temperature and/ or pressure in the presence of nickel catalyst, hydrogenation of benzene gives cyclohexane.



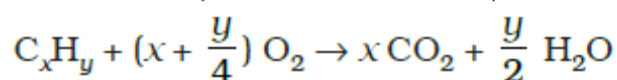
Under ultra-violet light, three chlorine molecules add to benzene to produce benzene hexachloride (BHC), $\text{C}_6\text{H}_6\text{Cl}_6$ which is also called gammaxane.



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



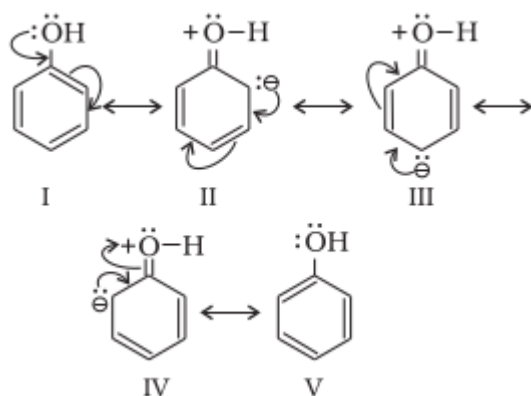
General combustion reaction for any hydrocarbon may be given by the following chemical equation:



8. Directive Influence of a Functional Group

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 ($-\text{OH}$) group. Phenol is a resonance hybrid of the following structures:



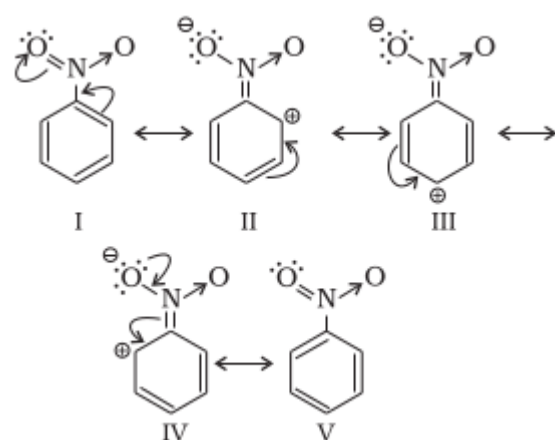
It is clear from the above resonating structures that the electron density is more on *o* – and *p* – positions. Hence, the substitution takes place mainly at these positions. However, it may be noted

that $-I$ effect of $-OH$ group also operates due to which the electron density on all positions of the benzene ring is slightly reduced. But the overall electron density increases at *ortho* and *para* 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 $-NH_2$, $-NHR$, $-NHCOCH_3$, $-OCH_3$, $-CH_3$, $-C_2H_5$, 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.

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 $-NO_2$, $-CN$, $-CHO$, $-COR$, $-COOH$, $-COOR$, $-SO_3H$, etc.

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

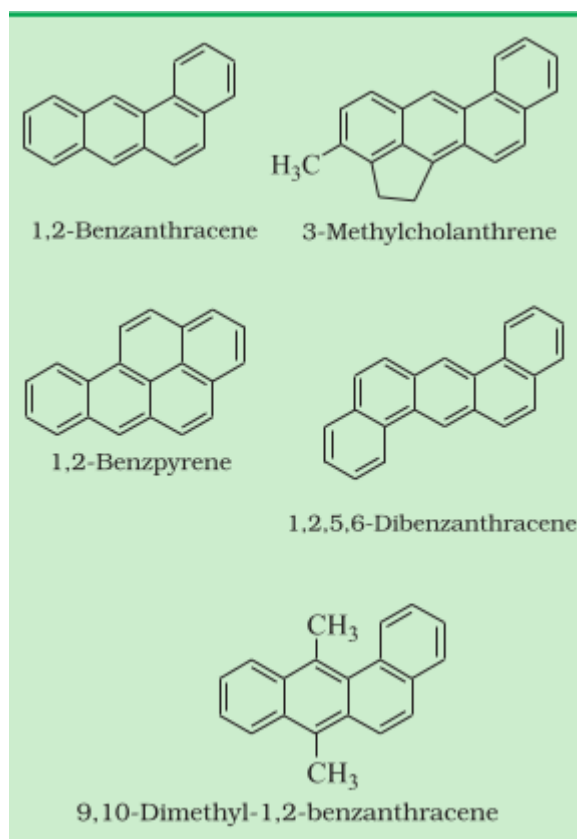


In this case, the overall electron density on benzene ring decreases making further substitution difficult. Therefore these groups are also called '**deactivating groups**'. Though the electron density on *o*- and *p*- position is comparatively less than that at *meta* position due to resonance. Hence,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

9. 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.



10. Summary

Aromatic hydrocarbons are also known as arenes. Benzene and benzenoid compounds show aromatic character. Aromaticity, the property of being aromatic is possessed by compounds having specific electronic structure characterised by **Hückel** ($4n + 2$) π electron rule. Aromatic hydrocarbons, despite having unsaturation, undergo mainly electrophilic substitution reactions. They undergo addition reactions only under special conditions. 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.