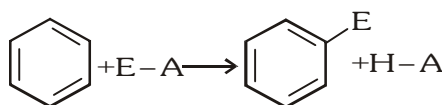
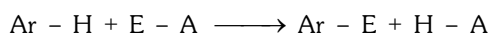


# ELECTROPHILIC AROMATIC SUBSTITUTION REACTION

## Introduction :

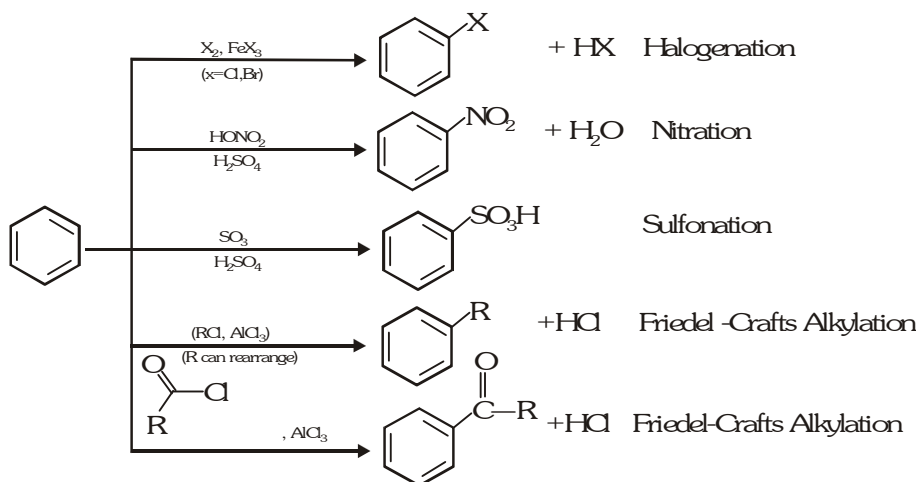
Aromatic hydrocarbons are known generally as arenes. An aryl group is one derived from an arene by removal of a hydrogen atom and its symbol is Ar—. Thus, arenes are designated ArH just as alkanes are designated RH.

The most characteristic reactions of benzenoid arenes are the substitution reactions that occur when they react with electrophilic reagents. These reactions are of the general type shown below.



The electrophiles are either a positive ion ( $\text{E}^+$ ) or some other electron-deficient species with a large partial positive charge. For example, benzene can be brominated when it reacts with bromine in the presence of  $\text{FeBr}_3$ . Bromine and  $\text{FeBr}_3$  react to produce positive bromine ions,  $\text{Br}^+$ . These positive bromine ions act as electrophiles and attack the benzene ring, replacing one of the hydrogen atoms in a reaction that is called an electrophilic aromatic substitution (EAS).

Electrophilic aromatic substitutions allow the direct introduction of a wide variety of groups into an aromatic ring, and because of this they provide synthetic routes to many important compounds. The five electrophilic aromatic substitutions that we shall study in this chapter are outlined in figure.



Electrophilic Aromatic Substitution Reactions

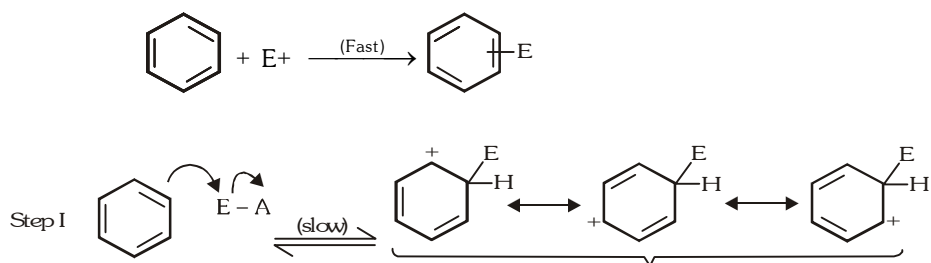
## (1) A GENERAL MECHANISM FOR ELECTROPHILIC AROMATIC SUBSTITUTION :

Benzene is susceptible to electrophilic attack primarily because of its exposed  $\pi$ -electrons. In this respect benzene resembles an alkene, for in the reaction of an alkene with an electrophile the site of attack is the exposed  $\pi$  bond.

We saw in however, that benzene differs from an alkene in a very significant way. Benzene's closed shell of six  $\pi$  electrons gives it a special stability. So although benzene is susceptible to electrophilic attack, it undergoes substitution reactions rather than addition reactions. Substitution reactions allow the aromatic sextet of  $\pi$  electrons to be regenerated after attack by the electrophile was occurred. We can see how this happens if we examine a general mechanism for electrophilic aromatic substitution.

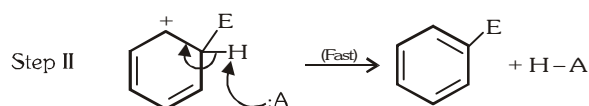
Once the electrophile,  $\text{E}^+$  is generated in the reaction, it enters into some kind of a weak interaction with the  $\pi$  cloud of benzene ring leading to the formation of a  $\pi$  - complex. This  $\pi$  - complex is a donor-acceptor type of a complex, benzene being the donor and electrophile, the acceptor. These adducts are known as charge

transfer complexes. In the complex that benzene forms with bromine, it has been shown that the halogen molecule is located centrally and at right angles to the plane of the benzene ring.



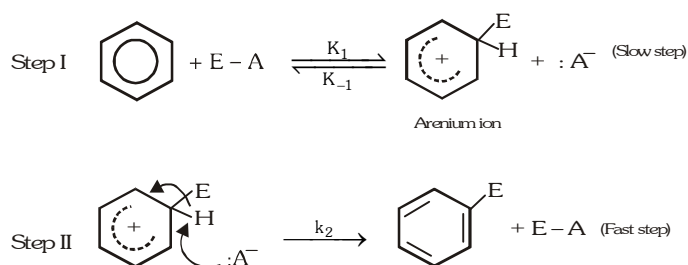
In step 1 the electrophile takes two electrons of the six- electron  $\pi$  system to form a  $\sigma$  bond to one carbon atom of the benzene ring. Formation of this bond interrupts the cyclic system of  $\pi$  - electrons, because in the formation of the arenium ion the carbon that forms a bond to the electrophile becomes  $sp^3$  hybridized and therefore, no longer has an available p-orbital. Now only five carbon atoms of the ring are still  $sp^2$  hybridized and still have p-orbitals. A calculated electrostatic potential map for the arenium ion formed by electrophilic addition of bromine to benzene indicates that positive charge is distributed in the arenium ion ring (figure) just as was shown in the contributing resonance structures.

In step 2 a proton is removed from the carbon atom of the arenium ion that bears the electrophile. The two electrons that bonded this proton to carbon becomes a part of the  $\pi$  system. The carbon atom that bears the electrophile becomes  $sp^2$  hybridized again and a benzene derivative with six fully delocalized  $\pi$  electrons is formed. We can represent step 2 with any one of the resonance structures for the arenium ion.



(The proton is removed by any of the bases present, for example, by the anion derived from the electrophile).

Kekul'e structure are more appropriate for writing mechanisms such as electrophilic aromatic substitution because they permit the use of resonance theory, it can be described however, using the modern formula for benzene in the following way.



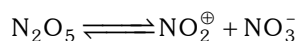
Where  $k_1$  and  $k_{-1}$  is the rate constant of the forward and backward reactions in step-I,  $k_2$  is the rate constant of the step-II.

There is firm experimental evidence that the arenium ion is a true intermediate in electrophilic substitution reactions. It is not a transition state. This means that in a free energy diagram (figure shown below) the arenium ion lies in an energy valley between two transition states.

The free energy of activation,  $\Delta G_{(1)}^\ddagger$ , for the reaction leading from benzene and the electrophile,  $E^+$ , to the arenium ion has been shown to be much greater than the free energy of activation,  $\Delta G_{(2)}^\ddagger$ , leading from the arenium ion to the final product. This is consistent with what we would expect. The reaction leading from benzene and an electrophile to the arenium ion is high endothermic, because the benzene ring loses its resonance energy. The reaction leading from the arenium ion to the substituted benzene, by contrast, is highly exothermic because in it the benzene ring regains its resonance energy.



(b)  $\text{N}_2\text{O}_5$  in  $\text{CCl}_4$  when used, results in a spontaneous dissociation reaction.



(c) With concentrated  $\text{HNO}_3$  alone

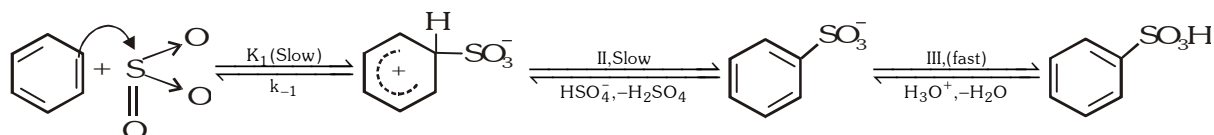


The electrophile generated in this case is obtained by the behaviour of one nitric acid as the base and other molecule as the acid, but the equilibrium lies in the reactant side.

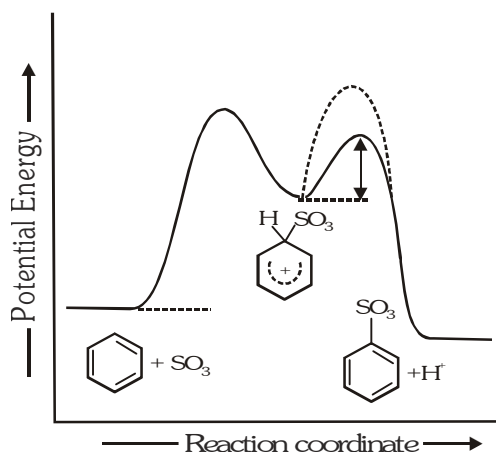
### (3) Sulphonation :

Sulphonation is another synthetically important reaction. It is often accomplished with concentrated sulphuric acid or fuming sulphuric acid containing excess of  $\text{SO}_3$  or chlorosulphonic acid,  $\text{ClSO}_2\text{OH}$ .

It is believed that the electrophile varies with the reagent, though in all cases  $\text{SO}_3$ , is involved either free or along with a carrier, like in  $\text{H}_2\text{SO}_4$  ( $\text{SO}_3 + \text{H}_3\text{O}^+$ ) or  $\text{H}^2\text{S}_2\text{O}_7$ . Sulphur trioxide is generated from sulphuric acid as follows  $2\text{H}_2\text{SO}_4 \rightleftharpoons \text{HSO}_4^{-} + \text{H}_3\text{O}^{+} + \text{SO}_3$ . The mechanism of sulphonation of benzene is given below :



Sulphonation is different from other aromatic electrophilic substitution reactions. Firstly, it is reversible and secondly, it shows some amount of isotope effect which is totally absent in other cases. Let us have a look at the potential energy diagram, Fig. of sulphonation reaction to understand these anomalies.

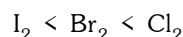


We see that once the  $\sigma$ -complexed benzenium intermediate is formed ; the energy barriers on either side of the intermediate are roughly of the same magnitude. This means that the intermediate can cross over to the product and can also come back to the reactant. This accounts for a reversible nature. Now, if we have the deuterated substrate, then the potential energy diagram gets slightly modified (dotted curve). The barrier to step II becomes higher as it now involves the cleavage of C–D bond. The barrier for step I, on the other hand, remains the same as it pertains to  $\sigma$ -complex formation. The rate of its reverting back to reactants is higher than its crossover to the product. Therefore, there is a net decrease in the overall rate of sulphonation for deuterated substrate—it shows a kinetic isotope effect. The loss of proton (Step II) is the slowest step (rds). The equilibrium in step III lies to the left as aryl sulphonic acids are strong acids.

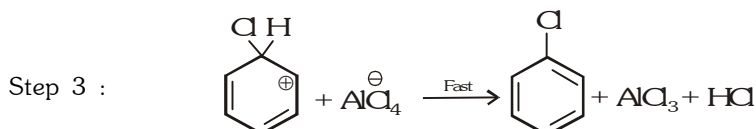
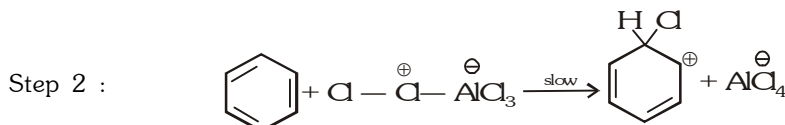
In the case of other electrophilic substitutions, in contrast, energy barrier for the first step is much higher than that for the second step even for a deuterated substrate.

#### (4) Halogenation :

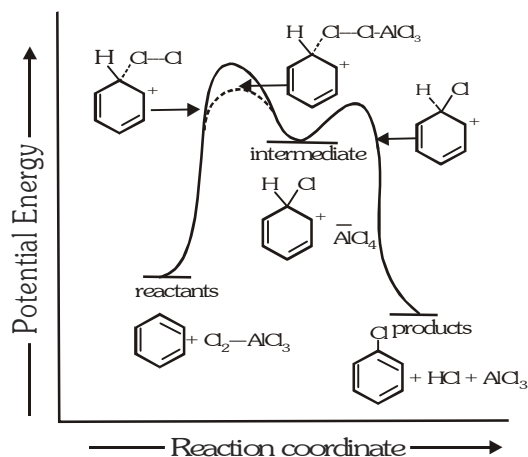
Halogenation of an aromatic ring is a synthetically important reaction. It takes place in the presence of varied reaction condition depending on the reactivity of the aromatic ring. For very reactive aromatic compounds in polar solvents, the molecular halogens themselves may act as electrophiles. In the case of nonpolar solvents, halogenation is catalysed by a Lewis acid like  $\text{AlCl}_3$ , or  $\text{FeCl}_3$ . Reactivity of halogens has the following order,



Let us take chlorination as a representative reaction to understand the mechanism of halogenation. Chlorine, in the presence of  $\text{AlCl}_3$  or  $\text{FeCl}_3$  forms a complex,  $\text{Cl}_2\text{--AlCl}_3$ . This complex can itself be the reactive electrophile or it may dissociate to give  $\text{Cl}^+$ .



However, there is no significant evidence for the involvement of  $\text{Cl}^+$  as an electrophile and it is likely that the complex itself attacks the substrate. In the  $\text{Cl}_2\text{--AlCl}_3$  complex, role of the Lewis acid is to polarize the halogen molecule and weaken the  $\text{Cl--Cl}$  bond. This lowers the activation energy for the formation of  $\sigma$ -complex.

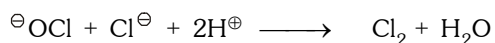


Schematic potential energy diagram for chlorination of benzene with  $\text{Cl}_2$ (---) and  $\text{Cl}_2\text{AlCl}_3$  (—) as the electrophile

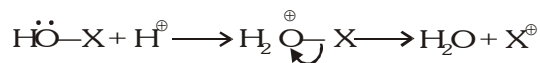
Bromination follows a similar mechanism. As said above, Iodine is weakest of the three halogens and even in the presence of a Lewis acid, it can halogenate reactive aromatics only. Therefore, in most other cases iodine-monochloride is used in the presence of Lewis acid,  $\text{ZnCl}_2$ .

Halogenation may be effected by hypohalous acids,  $\text{HO--}\overset{\delta-}{\text{X}}\overset{\delta+}{\text{X}}$ , also. This is markedly slower than with molecular

halogens as  $\text{HO--}\overset{\delta-}{\text{X}}\overset{\delta+}{\text{X}}$  is a poorer leaving group from  $\text{HO--}\overset{\delta-}{\text{X}}\overset{\delta+}{\text{X}}$ , than,  $\text{X--}\overset{\delta+}{\text{X}}\overset{\delta-}{\text{X}}$ . The reaction is speeded in the presence of  $\text{X}^-$ , however, as  $\text{HO--X}$  is then converted into the more reactive  $\text{X}_2$ , e.g. :



In the presence of strong acid, however,  $\text{HO--Hal}$  becomes a very powerful halogenating agent due to the formation of a highly polarized complex :

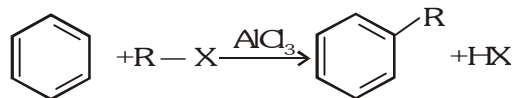


The evidence is that this species is the effective electrophile under these conditions and does not support the further conversion of complex into  $\text{Hal}^{\oplus}$ , i.e. unlike the case with  $\text{H}_2\text{O}^{\oplus} - \text{NO}_2$ .  $\text{F}_2$  reacts vigorously with benzene, but C—C bond breaking occurs and the reaction is of no preparative significance.

#### (5) Friedel-Crafts Alkylation :

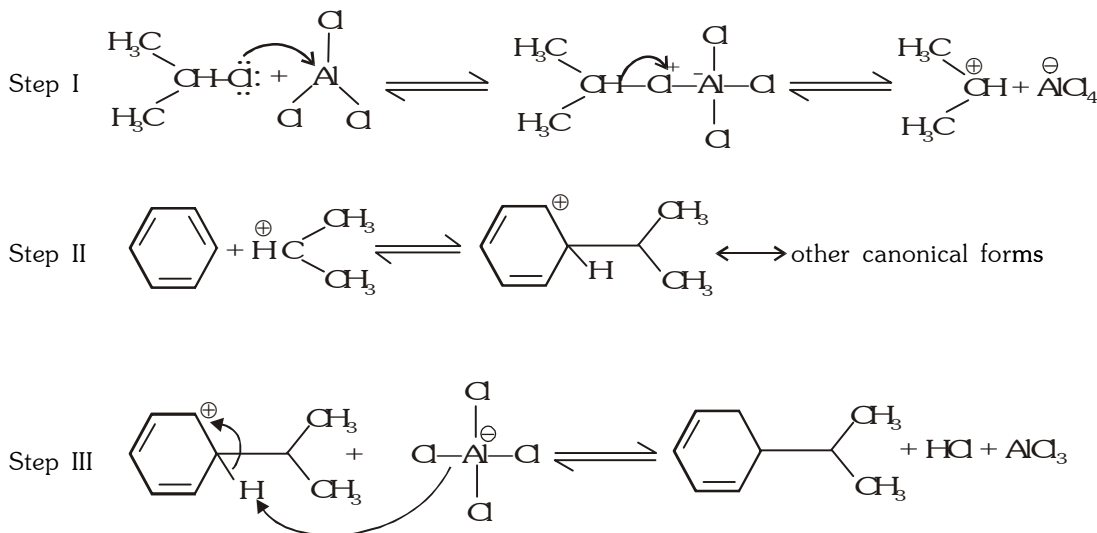
Alkyl halides react with benzene in presence of aluminium chloride to yield alkyl benzenes. Alkylation of benzene with alkyl halides in the presence of aluminium chloride was discovered by Charles Friedel and James. M. Crafts in 1877.

A general equation for a Friedel-Crafts alkylation reaction is the following



Alkyl halides by themselves are insufficiently electrophilic to react with benzene.  $\text{AlCl}_3$  serves as a Lewis acid catalyst to enhance the electrophilicity of the alkylating agent. The mechanism for the reaction (shown in the following steps, with isopropyl chloride as  $\text{R}-\text{X}$ ) starts with the formation of carbocation (step I). The carbocation then acts as an electrophile (step II) and attacks the benzene ring to form an arenium ion. The arenium ion (Step III) then loses a proton to generate isopropyl benzene. Some times carbocation rearrange to a more stable carbocation.

Mechanism for the Reaction :

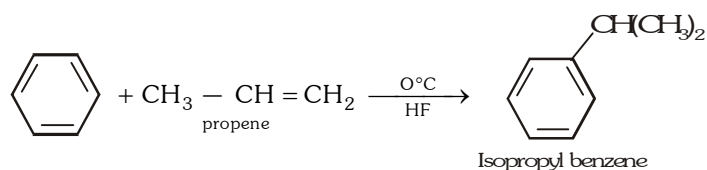


With  $\text{R}-\text{X}$  is a primary halide, a simple carbocation probably does not form. Instead, the  $\text{AlCl}_3$  forms a complex with the alkyl halide and this complex acts as the electrophile. In the complex the carbon halogen bond is nearly broken and one in which the carbon atom has a considerable +ve charge.

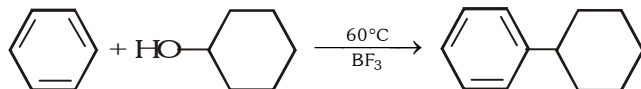


These complexes are so carbocation like that they also undergo typical carbocation rearrangements.

Friedel-Crafts alkylations are not restricted to the use of alkyl halides and  $\text{AlCl}_3$ . Many other pairs of reagents that form carbocations (or carbocation like species) may be used as well. These possibilities include the use of a mixture of an alkene and an acid.



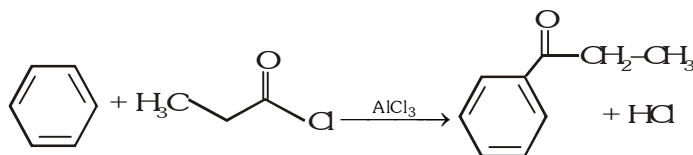
A mixture of an alcohol and an acid may also be used.



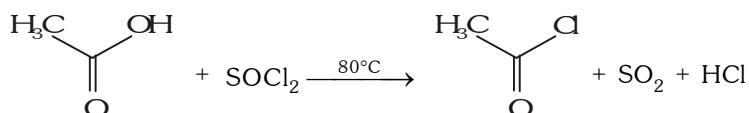
#### (6) Friedel-Crafts Acylation :

The group is called an acyl group and a reaction whereby an acyl group is introduced into a compound is called an acylation reaction.

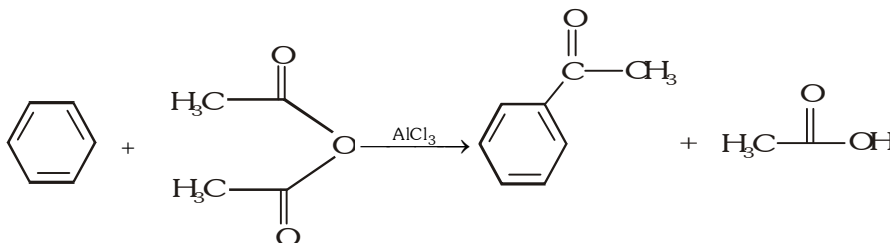
The Friedel-Crafts acylation reaction is an effective means of introducing an acyl group into an aromatic ring. The reaction is often carried out by treating the aromatic compound with an acyl halide.



Acyl chlorides (also called acid chlorides) are easily prepared by treating carboxylic acids with thionyl chloride ( $\text{SOCl}_2$ ) or phosphorous pentachloride ( $\text{PCl}_5$ ).

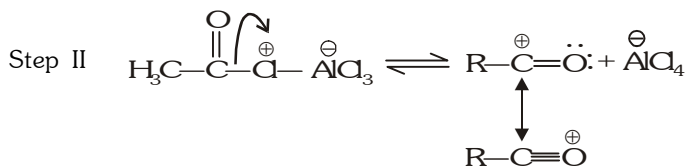


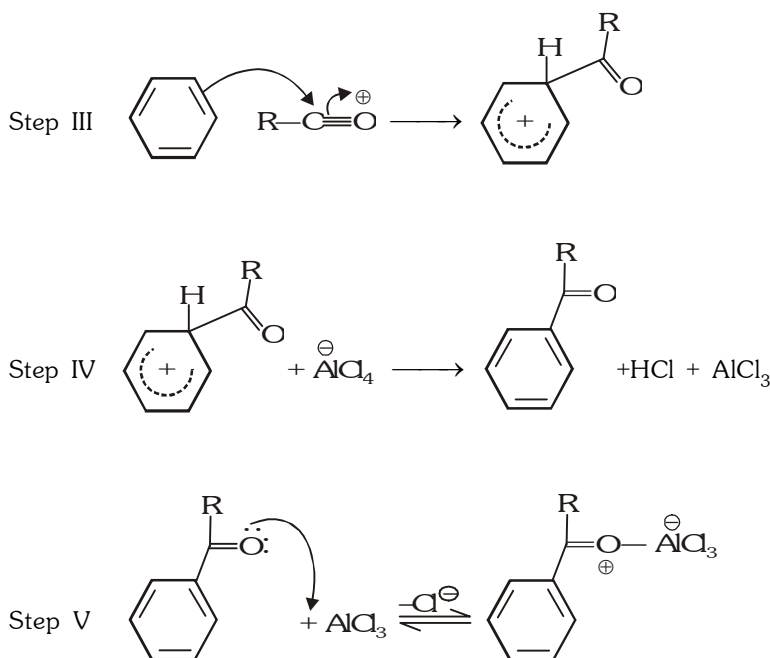
Friedel-Crafts acylations can also be carried out using carboxylic acid anhydrides. eg.



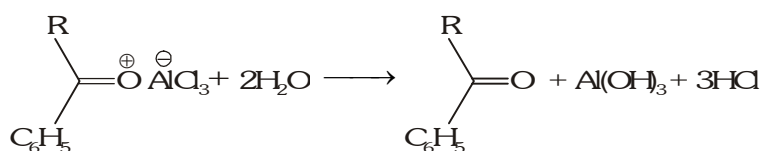
#### □ Mechanism of the Reaction :

In most Friedel-Crafts acylation reactions the electrophile appears to be an acylium ion formed from an acyl halide in the following way.





In the last step,  $\text{AlCl}_3$  (a Lewis acid) forms a complex with the ketone (a Lewis base). After the reaction is over, treating the complex with water liberates the ketone.

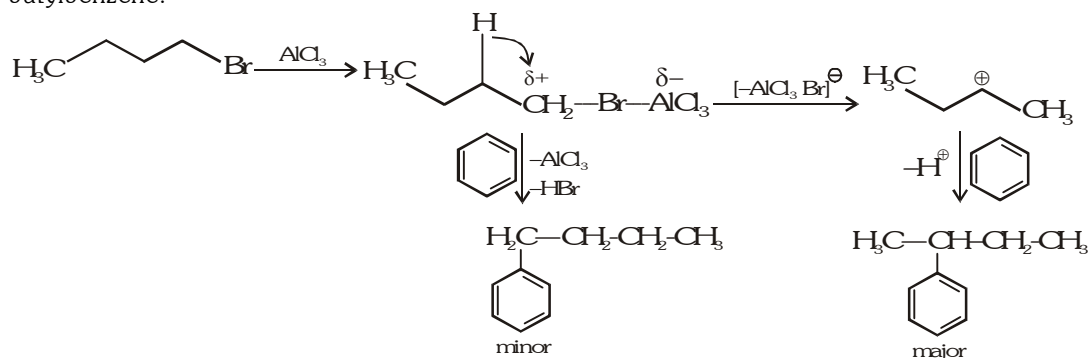


### ❑ Limitations of Friedel - Crafts Reactions :

Several restrictions limit the usefulness of Friedel- Crafts reactions.

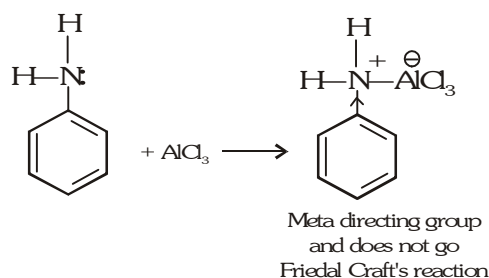
- (a) When the carbocation formed from an alkyl halide, alkene, or alcohol can rearrange to a more stable carbocation, it usually does so and the major product obtained from the reaction is usually the one from the more stable carbocation.

When benzene is alkylated with butyl bromide, for example, some of the developing butyl cations rearrange by a hydride shift-some developing 1° carbocations (see following reactions) become more stable 2° carbocations. The benzene reacts with both kinds of carbocations to form both butylbenzene and sec-butylbenzene.

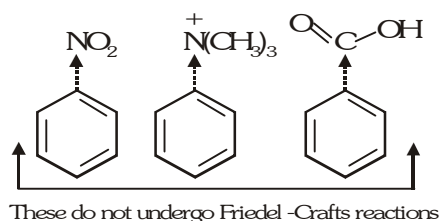


- (b) An aromatic ring less reactive than that of halobenzene don't undergo Friedel Craft's reaction. Aromatic ring containing  $-\text{NH}_2$ ,  $-\text{NHR}$ ,  $-\text{NR}_2$ , groups does not undergo friedal craft's alkylation due to formation of anilinum complex which is meta directing and has more electron withdrawing power than halogen in benzene ring.

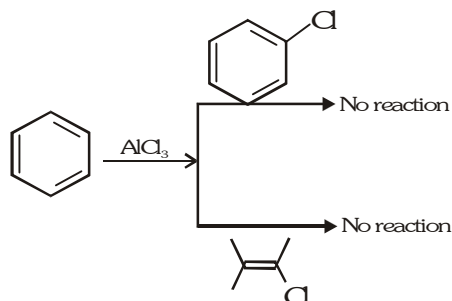




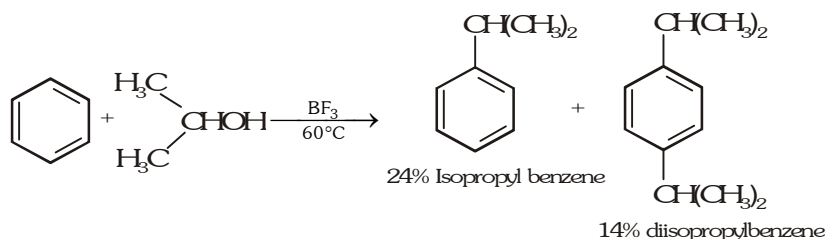
- (c) Friedel-Crafts reactions do not occur when powerful electron-withdrawing groups are present on the aromatic ring or when the ring bears an  $\text{-NH}_2$ ,  $\text{-NHR}$  or  $\text{-NR}_2$  group. This applies to both alkylations and acylations.



- (d) Aryl and vinylic halides cannot be used as the halide component because they do not form carbocations readily.



- (e) Polyalkylations often occur - Alkyl groups are electron releasing groups, and once one is introduced into the benzene ring it activates the ring towards further substitution.

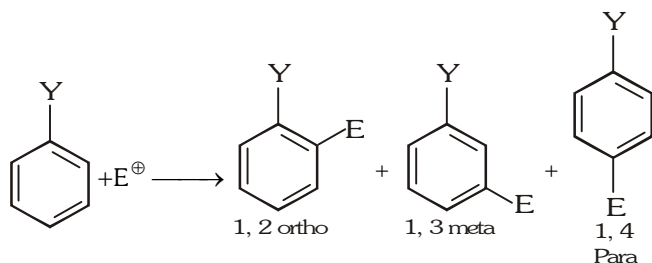


Polyacylations are not a problem in Friedel-Crafts acylations however. The acyl group ( $\text{RCO-}$ ) by itself is an electron-withdrawing group, and when it forms a complex with  $\text{AlCl}_3$  in the last step of the reaction, it is made even more electron withdrawing. This strongly inhibits further substitution and makes monoacylation easy.

## (7) Orientation and reactivity in electrophilic aromatic substitution :

In the case of benzene we get just one monosubstituted product in electrophilic aromatic substitution as all the positions are equivalent. However, for substitution in a compound which already has a group attached to the

ring, three disubstituted products, (1, 2), (1, 3) (1, 4) commonly called ortho, meta and para meaning next to, between and opposite respectively are possible. These are abbreviated as o, m and P.



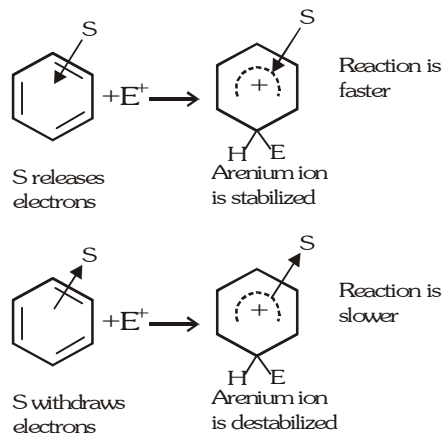
## □ Reactivity :

We have now seen that certain groups activate the benzene ring toward electrophilic substitutions, while other groups deactivate the ring. We mean that an aromatic compound with an activating group reacts faster in electrophilic substitutions than benzene. When we say that a group deactivates the ring, we mean that an aromatic compound with a deactivating group reacts slower than benzene.

We have also seen that we can account for relative reaction rates by examining the transition state for the rate-determining steps. Any factor that increases the energy of the transition state relative to that of the reactants decreases the relative rate of the reaction. It does this because it increases the free energy of activation of the reaction. In the same way, any factor that decreases the energy of the transition state relative to that of activation and increases the relative rate of the reaction.

The rate-determining step in electrophilic substitutions of substituted benzene compounds is the step that results in the formation of arenium ion. We can write the formula for a substituted benzene in a generalized way if we use the letter S to represent any ring substituent including hydrogen, (if S is hydrogen, the compound is benzene). We can also write the structure for the arenium ion in the way shown here. By this formula we mean that S can be in any position -ortho, meta or para - relative to the electrophile, E. Using these conventions, we can write the rate-determining step for electrophilic aromatic substitution in the following way.

When we examine this step for a large number of reactions, we find that the relative rates of the reactions depend on whether S withdraws or releases electrons. If S is an electron-releasing group (relative to hydrogen), the reaction occurs faster than the corresponding reaction of benzene. If S is an electron withdrawing group, the reaction occurs slower than that of benzene.



It appears, that the substituent (S) must affect stability of the transition state relative to that of the reactants. Electron-releasing groups apparently make the transition state more stable, while electron withdrawing groups make it less stable. That is entirely reasonable, because the transition state resembles the arenium ion, and the arenium ion is a delocalized carbocation.

**The effects of substituents on the reactivity of a benzene ring toward electrophilic substitution:**

Strong activating groups :  $-\text{NH}_2$ ,  $-\text{NHR}$ ,  $-\text{NR}_2$ ,  $-\text{OH}$ ,  $-\text{OR}$ .

Moderately activating groups :  $-\text{NHCO}\text{R}$ ,  $-\text{OCOR}$ ,

Weakly activating groups :  $-\text{R}$ ,  $-\text{Ar}$ ,  $-\text{CH}=\text{CR}_2$

Weakly deactivating groups :  $-\text{F}$ ,  $-\text{Cl}$ ,  $-\text{Br}$ ,  $-\text{I}$

Ortho/para  
directing

Moderately deactivating groups :  $-\text{CHO}$ ,  $-\text{COR}$ ,  $-\text{COOR}$ ,  
 $-\text{COOH}$ ,  $-\text{COCl}$

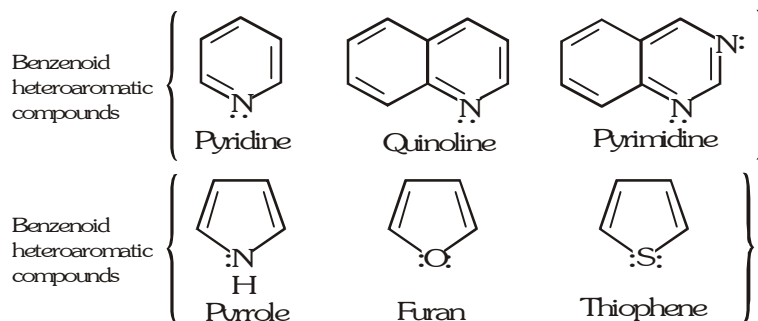
Strong deactivating groups :  $-\text{C}\equiv\text{N}$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{NH}_3^+$ ,  $-\text{NH}_2\text{R}^+$ ,

$-\text{NHR}_2^+$ ,  $-\text{NR}_3^+$ ,  $-\text{NO}_2$

Meta  
directing

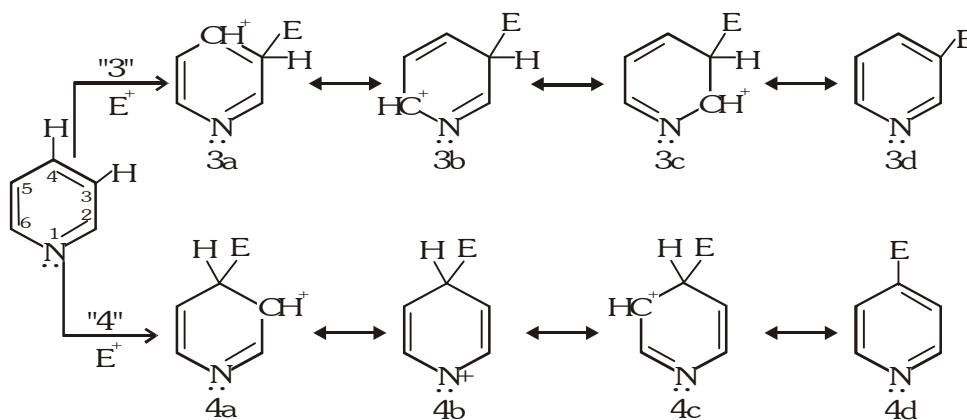
## (8) HETEROCYCLIC AROMATIC COMPOUND :

This is a class of compounds with aromatic properties, in which one or more of the ring carbons has been replaced by a heteroatom (an atom other than carbon) such as nitrogen, oxygen or sulphur. Some of these compounds preserve the six-membered ring and are therefore called benzenoid aromatic. In other, the  $(4n + 2)$   $\pi$ -electron reside in a five- membered ring, so these are called non-benzenoid. A key difference between these two classes of aromatic compounds is that in non-benzenoid heteroaromatic compounds a formally non-bonding pair of electrons on the heteroatom becomes part of the  $(4n + 2)$   $\pi$ -electron of the aromatic  $\pi$ -system, whereas in benzenoid aromatic compounds, the non-bonding pairs on heteroatoms are normally separated from the aromatic system. Here are a few examples :



### Electrophilic Substitution in Pyridine :

In pyridine the attack may take place at "3" or "4" position in general.

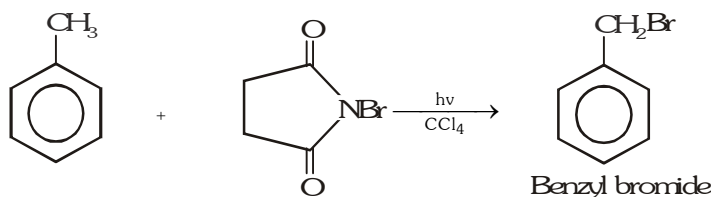


At first glance the two sets of resonance structures look quite similar. But notice how in 4b (one of the resonance structure of the intermediate that results from attack at the 4th position) the valence of nitrogen is left unfilled, an unfavourable situation not encountered in the intermediate formed by attack at the 3<sup>rd</sup> position. Again, it is the electronegativity of the nitrogen that reduces the reactivity of pyridine (relative to benzene) toward electrophiles.

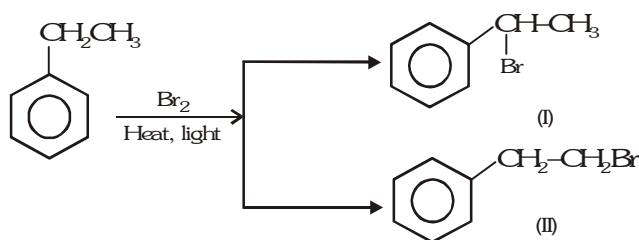
## (9) REACTIONS OF ALKYL BENZENES :

### Halogenation of the side chain :

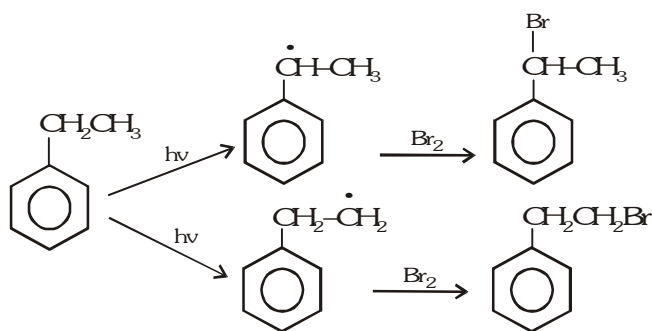
The side chain halogenation of alkyl benzenes takes place in the presence of light or high temperatures. Side chain halogenation is mostly carried out by using the reagent N-bromosuccinimide (NBS) in the presence of light.



An alkyl benzene with side chain other than methyl may lead to the formation of more than one products



Product (I) is the only product obtained, and formation of such product can be attributed to mechanism governing this reaction. Side chain halogenation has a similar mechanism as that of alkanes. It involves the formation of free radical intermediates. Now if we observe the free radicals formed by attack of bromine free radical on ethyl benzene, we will find that product (I) involves formation of benzyl free radical and (II) involves formation of primary free radical.



The benzyl free radical is more stable than primary free radical because its bond dissociation energy is 19 kcal/mole less than that of primary free radical.

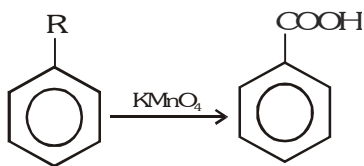
Order of stability of free-radicals.

Benzyl > allyl > 3° > 2° > 1° > CH<sub>3</sub> ≈ vinyl (from bond dissociation energy data)

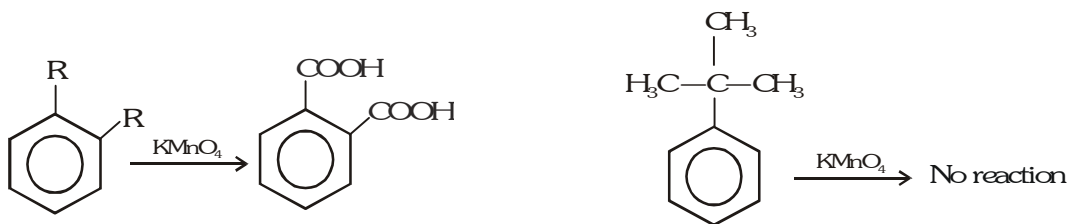
### Oxidation of side chain :

Although benzene itself is not susceptible to oxidation but side chain attached to the benzene ring undergoes

oxidation and converts itself into a  $\text{—COOH}$  group. Oxidation of side chain takes place after substance is heated for a long time with  $\text{KMnO}_4$ .



The above reaction can be used for identifying substitution pattern in aromatic compound. If any compound gives phthalic acid on heating with  $\text{KMnO}_4$ , then we can infer that it is ortho disubstituted benzene.



There is no reaction because of the absence of a benzylic hydrogen.

## SOLVED EXAMPLES

**Ex.1** Which of the following is not correctly matched :

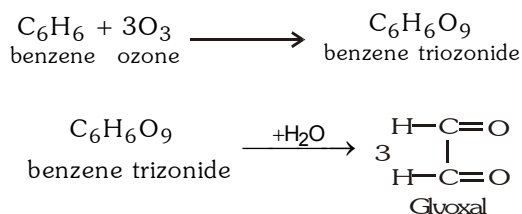
- (A) Hydrolysis of phenyl magnesium iodide – benzene  
 (B)  $\gamma$ -Isomer of BHC – lindane  
 (C)  $(2n + 4)\pi$  Rule – aromaticity  
 (D) Trimerisation of propyne – mesitylene

**Sol.** (C) The Huckel rule to account for aromaticity is closed ring of  $(4n + 2)\pi$  electrons.

**Ex.2** Ozonolysis of benzene in vigorous condition yields :

- (A) Glyoxal (B) Glycerine (C) Glycol (D) Glycerol

**Sol.**(A) Ozonolysis of benzene yields glyoxal. Benzene adds three molecules of ozone and forms benzene triozone which on decomposition with water gives three molecules of glyoxal.



**Ex.3** Benzene undergoes substitution reaction more easily than addition because :

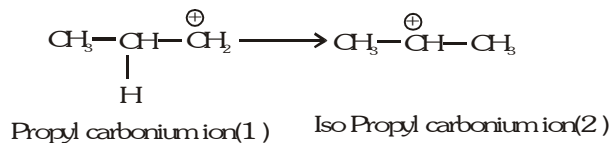
- (A) It has cyclic structure (B) It has three double bonds  
 (C) It has six hydrogen atoms (D) Of resonance

**Sol.** (D) If there were no resonance in benzene,  $\pi$  electrons would have not been delocalised and hence easily available to undergo addition reactions as in ethylene. Further the substituted benzene is stable due to resonance.

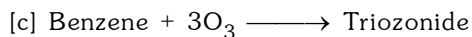
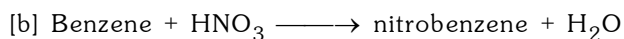
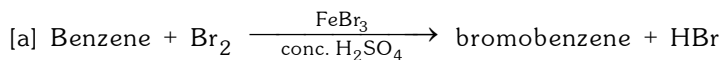
**Ex.4** Benzene reacts with n-propyl chloride in the presence of anhydrous  $\text{AlCl}_3$  to give predominantly :

- (A) n-Propylbenzene (B) Isopropylbenzene  
 (C) 3-Propyl-1-chlorobenzene (D) No reaction

**Sol.** (B) Propyl carbonium ion,  $\text{CH}_3\text{CH}_2\overset{+}{\text{C}}\text{H}_2$  is primary carbonium ion, it rearranges to the more stable secondary carbonium ion  $\text{CH}_3\overset{+}{\text{C}}\text{HCH}_3$ , which then reacts to form isopropylbenzene.



**Ex.5** Which of the following reactions of benzene does not account for the three 'C = C' bonds in the molecule-

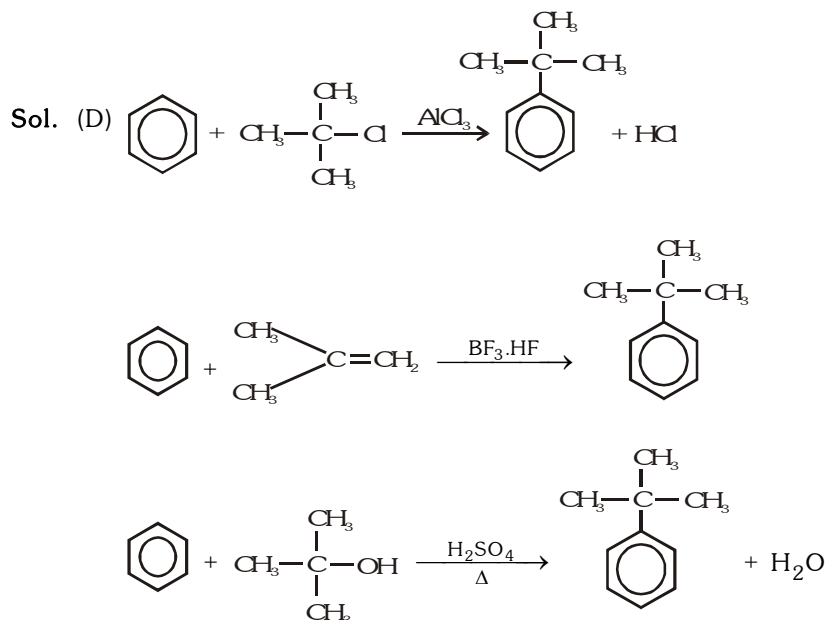


- (A) a, c (B) b, d (C) b, c, d (D) a, b

**Sol.** (D) a and b are the electrophilic substitution reactions and do not account for the C = C bond reaction.

**Ex.6** In which of the following reaction t-butylbenzene is formed :

- (A) Benzene + t-butyl chloride  $\xrightarrow{\text{AlCl}_3}$  (B) Benzene +  $(\text{CH}_3)_2\text{C} = \text{CH}_2 \xrightarrow{\text{BF}_3 \cdot \text{HF}}$   
 (C) Benzene + t-butyl alcohol  $\xrightarrow{\text{H}_2\text{SO}_4}$  (D) All of these



**Ex.7** The order of reactivity of :

$\phi\text{-CH}_3$  (I),  $\phi\text{-CH}_2\text{-CH}_3$  (II),  $\phi\text{-CH}(\text{CH}_3)_2$  (III) and  $\phi\text{-C}(\text{CH}_3)_3$  (IV)

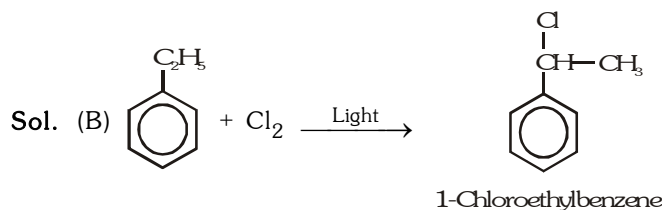
Where  $\phi = \text{C}_6\text{H}_5$

- (A) I > II > III > IV (B) IV > III > II > I (C) II > I > III > IV (D) III > II > I > IV

**Sol. (A)** More are the number of  $\alpha$ -hydrogen present in the alkyl group attached to the benzene ring more pronounced will be the hyperconjugation and the benzene ring will be more electron rich and easily be attacked by an electrophile.  $\alpha$ -hydrogen in  $-\text{CH}_3$ ,  $-\text{CH}_2-\text{CH}_3$ ,  $-\text{CH}(\text{CH}_3)_2$  and  $-\text{C}(\text{CH}_3)_3$  respectively are three, two one and zero.

**Ex.8** Ethylbenzene +  $\text{Cl}_2 \xrightarrow{\text{Light}}$  (main) compound is :

- (A) o- & p- Chloroethylbenzene (B) 1-Chloroethylbenzene  
 (C) 2-Chloroethylbenzene (D) m-Chloroethylbenzene



**Ex.9**  $\phi\text{-CH}_3 \xrightarrow[\Delta]{\text{KMnO}_4} \text{A} \xrightarrow[\Delta]{\text{Soda Lime}} \text{B}$

Compound B is :

- (A) Toluene (B) Benzene (C) Cresol (D) Benzaldehyde

**Sol. (B)**

**Ex.10** Formation of which of the following compound confirms the unsaturation character of benzene :

- (A) Cyclohexane      (B) Gammexane      (C) Triozonide      (D) All the above

**Sol.** (D) Formation of all the three compounds are the result of addition reaction. Hence confirm the unsaturation nature of benzene.

**Ex.11** Toluene may be prepared by :

- (A) Toluic acid      (B) Cresol  
(C) Toluene sulphonic acid      (D) All the above

**Sol.** (D) Toluene may be prepared by all the above compounds described earlier.

**Ex. 12** Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives :

- (A) o-Cresol      (B) p-Cresol      (C) 2,4-Dihydroxy toluene      (D) Benzoic acid

