**ELECTROPHILIC AROMATIC SUBSTITUTION**

**INTRODUCTION**

The most characteristic reactions of arenes are substitution reactions. Benzene ring has electron density above and below its plane and it is of suitable size for electrophilic attack. The electrophile displaces hydrogen atom and gets attached directly to the benzene ring. This is known as electrophilic aromatic substitution.

\[
\text{Ar} - \text{H} + \text{E}^+ \rightarrow \text{Ar} - \text{E} + \text{H}^+
\]

The electrophiles which take part in these substitution reactions can be of following types,

(i) +vely charged ions
(ii) electron deficient species with a partial +ve charge
(iii) neutral molecules such as SO₃.

In this chapter we will study five types of reaction which comes under the category of electrophilic aromatic substitution. They are,

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Products</th>
<th>Electrophiles</th>
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<tbody>
<tr>
<td>( \text{Fe/X}_2 ) (Hxegation)</td>
<td>( \text{X} )</td>
<td>( \text{X}^+ )</td>
</tr>
<tr>
<td>( \text{HNO}_2 )</td>
<td>( \text{NO}_2 )</td>
<td>( \text{NO}_2^+ )</td>
</tr>
<tr>
<td>( \text{H}_2\text{SO}_4 ) (Nitrntion)</td>
<td>( \text{SO}_3 \text{H} )</td>
<td>( \text{SO}_3 )</td>
</tr>
<tr>
<td>( \text{RCl,AlCl}_3 )</td>
<td>( \text{R} )</td>
<td>( \text{R}^+ )</td>
</tr>
<tr>
<td>( \text{R} - \text{C} - \text{Cl, AlCl}_3 ) (acylation)</td>
<td>( \text{R} - \text{C} = \text{O} )</td>
<td>( \text{R} - \text{C}^+ = \text{O} )</td>
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</table>

**GENERAL MECHANISM**

Benzene undergoes electrophilic substitution because of its exposed \( \pi \) electrons. In case of electrophilic substitution, benzene resembles alkene as the site of electrophilic attack in alkene is \( \pi \) bond only. But benzene also differs from alkene as the latter undergoes addition reaction and benzene prefers substitution rather than addition.

In step 1, the electrophile attacks the \( \pi \) system of benzene to form a non-aromatic cyclohexadienyl carbocation or arenium ion.

\[
\begin{align*}
\text{E} - \text{A} & \rightarrow \text{E}^+ \text{H}^- \\
\text{E}^+ \text{H}^+ & \rightarrow \text{E}^+ \text{H} \\
\text{E}^+ \text{H}^- & \rightarrow \text{E}^+ \text{H}^+ \\
\end{align*}
\]

Now, the carbon atom attached to electrophile E is sp³ hybridized, so it does not have p-orbital available for delocalization. As a result, aromatic character is lost. The four \( \pi \) electrons are delocalized over 5 p-orbitals (delocalization is there but aromaticity is not there).

In step 2, a proton is removed from the carbon atom to which electrophile is attached. \( \text{H}^+ \) leaves the ion leaving behind the shared pair of electron, which now forms a double bond and aromaticity is regained.
The following diagram gives the kinetic description of electrophilic aromatic substitution.

Step 1 is highly endothermic because benzene ring loses its resonance energy. Step 2 is exothermic because in this step benzene ring regains its resonance energy. So, step 1 is slow and rate-determining step.

**Halogenation**

Direct halogenation of benzene is not possible and it does not decolourize bromine solution as there is no reaction. Benzene readily reacts with Br₂ or Cl₂ in presence of Lewis acids such as FeCl₃, FeBr₃, anhydrous AlCl₃ etc.

**Nitration**

Benzene reacts slowly with hot conc. HNO₃ to yield nitrobenzene. The reaction is much faster if it is carried out in the presence of conc. H₂SO₄.

Here, H₂SO₄ acts as an acid and HNO₃ as a base.
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Step 1: $\text{HSO}_3^- + \text{H}^+ \rightarrow \text{SO}_3^- + \text{H}_2\text{O}$

Step 2: $\text{C}_6\text{H}_5\text{NO}_2^+ + \text{H}_2\text{O}^+ \rightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_3\text{O}^+$

Step 3: $\text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}^+$

**Sulphonation**

Sulphonating agent is fuming $\text{H}_2\text{SO}_4 + \text{SO}_3$ or conc. $\text{H}_2\text{SO}_4$.

Step 1: $2\text{H}_2\text{SO}_4 \rightleftharpoons \text{SO}_3 + \text{H}_3\text{O}^+ + \text{HSO}_4^-$ (In fuming sulphuric acid $\text{SO}_3$ attacks directly)

Step 2: $\text{C}_6\text{H}_5 + \text{SO}_3^- \rightarrow \text{C}_6\text{H}_5\text{SO}_3^-$

Step 3: $\text{C}_6\text{H}_5\text{SO}_3^- + \text{H}_2\text{SO}_4 \rightarrow \text{C}_6\text{H}_5\text{SO}_3 + \text{H}_2\text{SO}_4$

In sulphonation, all the steps are reversible. To sulphonate benzene, concentrated $\text{H}_2\text{SO}_4$ acid is used (under these conditions position of equilibrium lies at the right). To desulphonate benzene, dilute $\text{H}_2\text{SO}_4$ is used and steam is passed into the reaction mixture. Now the reaction equilibrium is shifted to left.

**Isotope effects.** Suppose, benzene is labelled with D (i.e. H atom is replaced by deuterium atom) and electrophilic substitution is performed on it, the rate will not be affected because $\text{C} - \text{H}$ bond is not broken in the rate-determining step of electrophilic aromatic substitution. But in sulphonation, the isotope effect is observed. In sulphonation unlabelled benzene is twice as reactive as D labelled benzene. Isotopic effects are also observed in iodination of benzene.

**Friedel–Crafts Alkylation**
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\[
\text{C}_{6}\text{H}_{5} + R - X \xrightleftharpoons[\text{AlCl}_3]{\text{AlCl}_3} \rightarrow \text{C}_{6}\text{H}_{5}R + HX
\]

**Step 1**
\[
\text{H}_3\text{C} - \text{Cl} \xunderleftarrow[\text{AlCl}_3]{\text{AlCl}_3} \rightarrow \text{CH}_3^+ + \text{AlCl}_4^-
\]

**Step 2**
\[
\text{H}_3\text{C} - \text{CH}_3 \xrightarrow[\text{HCl}]{\text{AlCl}_3} \rightarrow \text{CH}_3\text{CH}_3
\]

**Step 3**
\[
\text{H}_3\text{C} - \text{CH}_3 \xrightarrow[\text{Cl} - \text{AlCl}_3]{\text{AlCl}_3} \rightarrow \text{CH}_3\text{CH}_3 + \text{AlCl}_3 + \text{HCl}
\]

**Other examples of alkylation:**

(a) \[
\text{C}_{6}\text{H}_{5} + \text{H}_3\text{C} - \text{CH}_2 \xrightarrow{0^\circ\text{C}} \text{HF or H}_2\text{SO}_4 \rightarrow \text{C}_{6}\text{H}_{5}\text{CH}_3
\]

(b) \[
\text{C}_{6}\text{H}_{5} + \text{C}_{6}\text{H}_{12} \xrightarrow{0^\circ\text{C}} \text{HF or H}_2\text{SO}_4 \rightarrow \text{C}_{6}\text{H}_{5}\text{C}_{6}\text{H}_{12}
\]

cyclohexylbenzene

(c) \[
\text{C}_{6}\text{H}_{5} + \text{HO} - \text{C}_{6}\text{H}_{12} \xrightarrow{0^\circ\text{C}} \text{BF}_3 \rightarrow \text{C}_{6}\text{H}_{5}\text{C}_{6}\text{H}_{12}
\]

(d) \[
\text{C}_{6}\text{H}_{5} + \text{CH}_3 - \text{C} \xrightarrow{\text{AlCl}_3} \rightarrow \text{C}_{6}\text{H}_{5}\text{CH}_3
\]

**Friedel–Crafts Acylation**
Introduction of acyl group is called acylation (acyl group = RCO).
ELECTROPHILIC AROMATIC SUBSTITUTION

\[ \text{Cyclohexane} + \text{HCCl} \xrightarrow{\text{AlCl}_3} \text{Acetophenone} \]

\[ \text{Step - 1} \]

\[ \text{R} \xrightarrow{\text{Cl}} \text{O} \xrightarrow{\text{Al-CH}_3} \text{R} \xrightarrow{\text{C=O}} \text{AlCl}_4^- \]

\[ \text{Step - 2} \]

\[ \text{Acetophenone} + \text{R-C=O} \xrightarrow{\text{Cl-AlCl}_3} \text{Phenylacetate} + \text{HCl + AlCl}_3 \]

Limitations of Friedel–Crafts Reactions

1. In alkylation carbocation can rearrange to more stable form (irrespective of whether it is formed from alkyl halide, alkene or alcohol).

\[ \text{R} \xrightarrow{\text{CH}_2\text{Cl}} \text{Cl} \xrightarrow{\text{AlCl}_3} \text{No reaction} \]

Rearrangements do not occur in Friedel–Crafts acylations. The acylium ion is resonance stabilized, so there is no need for it to rearrange.

2. If the groups present are – NH_2, –NHR, –NR_2 or – OH, Friedel–Crafts reactions give very poor yields.

3. Aryl and vinylic halides can’t be used as halide component because of the difficulty in producing the corresponding carbocations.

\[ \text{No reaction} \]

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4. Polyalkylations take place frequently during alkylation reactions but in case of acylation no such difficulty arises.

Synthetic applications of Friedel–Crafts reactions:

(a) \[ \text{CH}_3\text{Br} \xrightarrow{\text{AlCl}_3} \text{CH}_3\text{CH}_3 \]

(b) \[ \text{CH}_3\text{Cl} \xrightarrow{\text{AlCl}_3} \text{Zn(Hg)/HCl} \xrightarrow{\text{NH}_2\text{NH}_2/\text{NaOH}} \text{CH}_3 \]

(c) \[ \text{SOCl}_2 \xrightarrow{\text{Cl}} \text{AlCl}_3 \xrightarrow{\text{SO}_3\text{H}} \text{Zn(Hg)/HCl} \xrightarrow{\text{HCl}} \text{OH} \]

**ORIENTATION AND REACTIVITY**

Like benzene, toluene also undergoes electrophilic substitution.

\[ \text{H}_2\text{SO}_4(\text{SO}_3) \xrightarrow{25^\circ\text{C}} \text{CH}_3\text{SO}_3\text{H} \]

Electrophilic substitution of toluene is much faster in comparison to benzene. Sulphonation of benzene takes 20 to 30 minutes to complete whereas in case of toluene it is one minute only. Same results are obtained with nitration, halogenation and Friedel–Crafts reactions. From the above observation we can conclude that CH\textsubscript{3} group activates the benzene ring towards electrophilic aromatic substitution. Like benzene nitrobenzene also undergoes electrophilic substitution. Aniline is 10\textsuperscript{6} times as reactive as benzene and nitro benzene is 1/10\textsuperscript{6} as reactive as benzene.

\[ \text{NO}_2\text{SO}_3\text{H} \xrightarrow{150^\circ\text{C}} \]

So, NO\textsubscript{2} group deactivates the benzene ring towards electrophilic aromatic substitution. When the substituent is CH\textsubscript{3} the products predominantly are p and o isomers. When the substituent is NO\textsubscript{2}, the major product is meta isomer. The groups
which activate the benzene ring are called activating groups and those which deactivate the benzene ring are called deactivating groups.

Groups which direct the incoming group predominantly to o and p positions are called as o and p directors and those which direct predominantly to meta position are called meta directors.

Generally, activating groups are o and p directors and deactivating groups are m directors. But there is an exception, i.e. halogens. Halogens are deactivating groups but o and p directors.

<table>
<thead>
<tr>
<th>o and p directors</th>
<th>m directors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strongly activating</td>
<td>Moderately deactivating</td>
</tr>
<tr>
<td>(-\text{NH}_2, -\text{NH}_R, -\text{NR}_2, -\text{OH}, -\text{O}^\equiv)</td>
<td>(-\text{C=N}, -\text{SO}_2\text{H}, -\text{COOH}, -\text{CHO}, -\text{COR})</td>
</tr>
<tr>
<td>Moderately activating</td>
<td>Strongly deactivating</td>
</tr>
<tr>
<td>(-\text{NHCOCH}_3, -\text{NHCOR} -\text{OCH}_3, -\text{OR})</td>
<td>(-\text{NO}_2, -\text{NR}_3^+)</td>
</tr>
<tr>
<td>Weakly activating</td>
<td></td>
</tr>
<tr>
<td>(-\text{CH}_3, -\text{C}_2\text{H}_5 -\text{C}_6\text{H}_5)</td>
<td></td>
</tr>
<tr>
<td>Weakly deactivating</td>
<td></td>
</tr>
<tr>
<td>(-\text{X}^+:\text{..}..)</td>
<td></td>
</tr>
</tbody>
</table>

We must remember that reactivity and orientation are both influences the relative rates of reaction. Methyl group activates the benzene ring because its presence makes the benzene ring react faster than benzene. It is o and p director because it makes ortho and para positions react faster than the meta position.

Transition state is structurally similar to the arenium ion rather than to the benzene ring (because they are energetically comparable). Any factor that increases the stability of the arenium ion also increases the stability of transition state and vice versa. If the energy of transition state is increased then it increases \(E_a\) (activation energy) and consequently the reaction is slowed down. So, any factor that increases the stability of arenium ion makes the reaction fast.

**Theory of Orientation (Effect of Substitution)**

Aniline and its derivatives are extremely reactive in electrophilic aromatic substitution. The \(-\text{NH}_2\) group is strongly activating and ortho and para directing.
Resonance hybrid structures resulting from the o and p attack is more stable than the meta attack. So, o and p attacks are faster than meta attack.

In case of nitrobenzene, the substituent NO₂ is strongly deactivating and meta directing.

Ortho attack

Meta attack

The resonance hybrid structures resulting from meta attack is more stable and structures in case of o and p attack is highly unstable. In case of toluene, CH₃ group is activating and o and p directing.

Ortho attack

Meta attack

(Tertiary carbocation)

(All three resonance form are secondary carbocation)
The resonance hybrid structures from the ortho and para attack are more stable due to formation of tertiary carbocation character. So, ortho and para substitution is more stable and formed faster. In case of halogens, their electron withdrawing inductive effect influences the reactivity and electron donating resonance effect influences the orientation. In halogens resonance and inductive effects are almost balanced. But during electrophilic substitution, Cl stabilizes arenium ion more in o and p attack than from meta attack. The Cl does this in the same way as – NH₂ and – OH will do by donating unshared pair electrons.

Ortho attack

<table>
<thead>
<tr>
<th>Cl</th>
<th>E</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<tr>
<td>←→</td>
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Meta attack

<table>
<thead>
<tr>
<th>Cl</th>
<th>E</th>
<th>H</th>
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So, hybrids resulting from o and p attacks are more stable than that from meta attack. So, halogens deactivate the benzene ring (electron withdrawing I effect). Similarly, OH and NH₂ also deactivates but their electron releasing +R effect is more pronounced which results in net activation of benzene ring. +R effect is not effective in case of halogens as overlapping of 2p orbital of carbon and 3p orbital of halogen (chlorine) is not effective.

USE OF PROTECTING AND BLOCKING GROUPS

Very powerful activating groups such as amino and hydroxyl groups, make benzene ring so reactive that unwanted reactions take place. Some reagents used in electrophilic aromatic substitution such as HNO₃ are also strong oxidizing agents. Both electrophilic and oxidizing agents seek electrons, so – OH and – NH₂ group activates the ring not only towards electrophilic aromatic substitution but also towards oxidation.

To avoid the oxidation of the substrate, blocking or protecting groups are used, like treating aniline with acetyl chloride or acetic anhydride converts aniline to acetanilide. Acetamide group is moderately activating and on nitration no oxidation takes place. After nitration is complete desired product can be obtained by removing the blocking group by hydrolysis. Suppose, we want to prepare o-nitro aniline then we should follow the following procedure.
ORIENTATION (TWO SUBSTITUENTS)

(a) If one group is activating and the other group is deactivating, then the group which is activating in nature determines the orientation.

\[
\begin{align*}
\text{OH} & \quad \xrightarrow{\text{Cl}_2/\text{AlCl}_3} \quad \text{OH} \quad \xrightarrow{} \quad \text{OH} \\
\text{NO}_2 & \quad \quad \quad \text{Cl} \\
\end{align*}
\]

(b) If both are activating, the more activating group determines the orientation.

\[
\begin{align*}
\text{NH}_2 & \quad \xrightarrow{\text{conc. HNO}_3/\text{conc. H}_2\text{SO}_4} \quad \text{NH}_2 \quad \xrightarrow{} \quad \text{NH}_2 \\
\text{CH}_3 & \quad \quad \quad \text{O}_2\text{N} \quad \text{CH}_3 \\
\end{align*}
\]

(c) If both are deactivating, less deactivating group determines the orientation.

\[
\begin{align*}
\text{NHCOCH}_3 & \quad \xrightarrow{\text{Cl}_2} \quad \text{NHCOCH}_3 \quad \xrightarrow{} \quad \text{NHCOCH}_3 \\
\text{CH}_3 & \quad \quad \quad \text{Cl} \\
\end{align*}
\]

(d) If both groups are activating and reinforce at the same position, then there is no problem.

\[
\begin{align*}
\text{OH} & \quad \xrightarrow{\text{Cl}_2/\text{FeCl}_3} \quad \text{OH} \quad \xrightarrow{} \quad \text{OH} \\
\text{Cl} & \quad \quad \quad \text{CH}_3 \\
\end{align*}
\]

SOLVED EXAMPLES

Multiple Choice Questions

1. When nitrobenzene is treated with Br\(_2\) in presence of FeBr\(_3\), the major product formed is m-bromonitro benzene. Statements which are related to obtain m-isomer are:
   (A) The electron density on meta carbon is more than that on ortho and para positions.
   (B) The intermediate carbonium ion formed after initial attack of Br\(^+\) at the meta position is least destabilized.
   (C) Loss of aromaticity when Br\(^+\) attacks at the ortho and para positions not at meta position.
   (D) Easier loss of H\(^+\) to regain aromaticity from the meta position than from ortho and para positions.

Sol. (B).
2. Terephthalic acid is obtained by oxidation of which of the following compounds?

(A) \[ \text{CH}_3 \]

(B) \[ \text{CH}_3 \]

(C) \[ \text{CH}_3 \]

(D) \[ \text{CH}_3 \]

**Sol.** (C). Terephthalic acid is a para dicarboxylic acid.

3. Which of the following species is most stable?

(A) \[ p-\text{O}_2\text{NC}_6\text{H}_4^+ \text{CH}_2^- \]

(B) \[ C_6\text{H}_5^+ \text{CH}_2^- \]

(C) \[ p-\text{ClC}_6\text{H}_4^+ \text{CH}_2^- \]

(D) \[ p-\text{CH}_3\text{O}_2\text{C}_6\text{H}_4^+ \text{CH}_2^- \]

**Sol.** (D). Positive charge on \[ \text{CH}_2^- \] is dispersed due to electron repelling nature of methoxy group.

4. The most basic compound among the following is

(A) benzylamine

(B) aniline

(C) acetanilide

(D) p-nitroaniline

**Sol.** (A). Rest all show less tendency to donate electron pair due to resonance.

5. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4. In the nitrating mixture HNO_3 acts as a

(A) base

(B) acid

(C) reducing agent

(D) catalyst

**Sol.** (A). HNO_3 accepts a proton from H_2SO_4

\[ \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^- \]

\[ \text{HNO}_3 + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{NO}_2^+ \]

6. In the reaction of p-chlorotoluene with KNH_2 in liq. NH_3, the major product is

(A) o-toluidine

(B) p-toluidine

(C) p-chloroaniline

(D) m-toluidine

**Sol.** (D). It follows benzyne mechanism.

7. Which one of the following compounds will be most easily attacked by electrophile?

(A) \[ \text{Cl} \]

(B) \[ \text{CH}_3 \]

(C) \[ \text{CH}_3 \]

(D) \[ \text{OH} \]
1. In phenol –OH group has more +M effect than –I effect so the ring becomes activated and easily attacked by an electrophile.

8. Main product formed when benzene is alkylated with n-propyl chloride in the presence of anhydrous AlCl₃.
   (A) Ethyl and methyl benzene  (B) n-propyl benzene
   (C) Isopropyl benzene   (D) Chlorobenzene

   Sol. (C). Friedel–Crafts reaction involves the formation of carbonium ion. When n-propyl chloride is used then the n-propyl carbonium ion converts to stable isopropyl carbonium ion and cumene (isopropyl benzene) is the product.

9. Toluene on oxidation with alkaline KMnO₄ forms benzoic acid. What is the product formed when n-propyl benzene is oxidized with KMnO₄?
   (A) C₆H₅CH₂COOH  (B) C₆H₅CH₂CH₂COOH
   (C) C₆H₅COOH  (D) C₆H₅CHO

   Sol. (C). When any type of alkyl group (with benzylic hydrogen) is attached with benzene ring then this chain will be oxidized to carboxylic group.

10. Benzene diazonium chloride when treated with dilute H₂SO₄ and strongly heated gives
   (A) benzene sulphonyl chloride  (B) benzene sulphonyl chloride
   (C) benzene   (D) phenol

   Sol. (D).

11. Friedel–Crafts reaction using CH₃COCl/AlCl₃ takes place at the slowest rate in
   (A) C₆H₆  (B) C₆H₅OH
   (C) C₆H₅CHO  (D) C₆H₅CH₃

   Sol. (C). CHO group deactivates benzene ring.

12. –CH₂Cl group is an example of
   (A) strongly deactivating group  (B) strongly activating group
   (C) weakly activating group (D) weakly deactivating group

   Sol. (C).

13. Which of the following alcohols is dehydrated most readily with conc. H₂SO₄?
   (A) p-NO₂C₆H₄CH(OH)CH₃  (B) p-CH₃O C₆H₄CH(OH)CH₃
   (C) p-Cl C₆H₄CH(OH)CH₃  (D) C₆H₄CH(OH)CH₃

   Sol. (A).

14. The correct order of reactivity towards electrophilic substitution is
   (A) benzoic acid > chlorobenzene > benzene > phenol
   (B) benzoic acid > phenol > benzene > chlorobenzene
   (C) phenol > benzene > chlorobenzene > benzoic acid
   (D) phenol > chlorobenzene > benzene > benzoic acid

   Sol. (D).

15. C₆H₆ + HNO₃/H₂SO₄ → A  A + Zn/HCl → B → C → D

   The product D is
Fill in the Blanks

1. Benzene reacts with ________ in presence of AlCl₃ to form benzophenone. (benzoyl chloride)
2. The bond dissociation energy needed to form the benzyl radical from toluene is ________ than the formation of methyl radical from methane. (less)
3. The presence of nitrogen in pyridine ring makes it ________ active than benzene towards EAS as nitrogen is more electronegative than carbon atoms. (less)
4. Cyclopropene is an example of ________ compound. (non-aromatic)
5. The cleavage of C–H bond is the rate-determining step in two electrophilic aromatic substitution namely ________ and ________. (sulphonation, iodination)
6. Toluene is nitrated ________ than benzene. (faster)
7. It is ________ to carry out nitration of benzene than that of nitrobenzene. (easy)
8. Benzene has ________ H atoms less than the corresponding alkane. (8)
9. Toluene is converted to benzaldehyde by reaction with ________ (Chromyl chloride)
10. The reaction between phenol and alkaline chloroform is known as ________. (Riemer–Tiemann)

Short Answer Type Questions
Prob.1. Benzene is highly unsaturated but it does not undergo addition reactions. Explain.

Sol. π electrons of benzene ring are delocalized throughout the molecule. This makes the molecule very stable. The addition reactions would result in the breaking of this delocalization, i.e. molecule will get destabilized.

Prob.2. Show by an arrow the preferred product of reaction with E⁺ in each of the three isomeric
(a) nitrotoluenes
(b) methoxy toluene's
(c) methoxy acetanilides. Explain your choices in each case.

Sol. (a) 

\[
\begin{array}{c}
\text{Ortho (A)} \\
\text{Meta (B)} \\
\text{Para (C)}
\end{array}
\]

In (A), CH₃ directs E⁺ to ortho and para positions which are also meta to NO₂, i.e. substituents reinforce each other. In (B), the orientation is in opposition. The o, p-director controls the orientation, i.e. E⁺ enters para to CH₃ and ortho to NO₂. In (C), both groups are reinforcing, i.e. ortho to CH₃ and meta to NO₂.

(b) 

\[
\begin{array}{c}
\text{Ortho (A)} \\
\text{Meta (B)} \\
\text{Para (C)}
\end{array}
\]

Both groups are o and p-directing. In (B), the substituents reinforce each other very little substitution occurs between the groups due to steric hindrance. In (A) and (C), the two groups are in opposition. The more strongly activating - OCH₃ controls the orientation.

(c) 

\[
\begin{array}{c}
\text{Ortho (A)} \\
\text{Meta (B)} \\
\text{Para (C)}
\end{array}
\]

Both the substituents are o and p-directing and equally moderately strong activating groups. In (B), both the groups are reinforcing and a mixture of two isomers is obtained. In (A) and (C), two groups are in opposition. In (A), substantial amounts of all isomers are obtained while in (C) substitution occurs ortho to both the groups.

Prob.3. Aniline undergoes bromination in ortho and para position but in presence of strong acid it gives m-bromo aniline.

Sol. NH₂ group is o and p-directing. However, in the presence of strong acid, aniline combines with proton to form C₅H₅⁺H₂N⁺ and H₂N⁺ group is m-directing. Thus, m-bromo product is formed in the presence of strong acid.

Prob.4. Why fluoroarenes cannot be prepared by direct reaction of fluorine with benzene?

Sol. Fluorine is too reactive in nature. Both addition and polysubstitution occur.
Prob.5. Compound (A) $C_7H_8O$, is insoluble in $NaHCO_3$ solution but dissolves in sodium hydroxide and gives a characteristic colour with aqueous ferric chloride. When treated with bromine, (A) forms a compound (B) $C_7H_5OBr_3$.

(i) Give structural formula of (A) and (B).

(ii) What would be the structure of (A) if it neither dissolves in sodium hydroxide solution nor gives a characteristic colour with $FeCl_3$?

Sol. (i) (A) gives characteristic colour with $FeCl_3$ solution, so it is a phenol. (A) forms tribromo product, thus it is meta cresol.

(ii) If the compound dose not dissolve in aqueous $NaOH$ and does not give characteristic colour with $FeCl_3$, it should be a neutral compound, i.e. either anisole ($C_6H_5-O-CH_3$) or benzyl alcohol ($C_6H_5CH_2OH$).

True or False Type Questions

1. In benzene, carbon uses all the three p-orbitals for hybridization.
   Sol. False

2. Chlorobenzene is more reactive than benzene as chlorine is ortho–para directing group.
   Sol. False

3. Nitrobenzene does not undergo Friedel–Crafts alkylation.
   Sol. True

4. The electron donating group in benzene directs the incoming electrophilic group to the meta position.
   Sol. False

5. Electrophilic substitution in naphthalene takes place with difficulty in comparison with benzene.
   Sol. False

6. Aniline is soluble in $HCl$.
   Sol. True

7. Phenol can get oxidized readily than ethanol.
   Sol. True

8. Aniline is weaker base than ammonia.
   Sol. True

9. Cyclooctatetraene is aromatic compound.
   Sol. False

10. Resonance effect of chloro group deactivates benzene ring.
    Sol. False
Subjective Problem

Prob. 1. (i) \( \text{C}_6\text{H}_6 + (\text{CH}_3)_2\text{CHCH}_2\text{OH} \rightleftharpoons \text{H}_2\text{SO}_4 \rightarrow ? \)
   (ii) \( \text{C}_6\text{H}_6 + (\text{CH}_3)_2\text{CHCH}_2\text{Cl} \rightleftharpoons \text{AlCl}_3 \rightarrow ? \)

Sol. (i) \( \text{C}(\text{CH}_3)_3 \)
   (ii) \( \text{C}(\text{CH}_3)_3 \)

Prob. 2. Convert benzene into m-bromonitrobenzene.

Sol.

Prob. 3. Arrange the following substances in order of activating a benzene ring. Phenylacetate, Acetophenone, Phenol

Sol.

Prob. 4. Convert benzene into benzoic acid

Sol.

Prob. 5. \( \text{CH}_3 - \text{CH} = \text{CH}_2 \rightarrow \text{A} \)

Identify A and also the electrophile involved in the reaction.
**Sol.**

\[ \text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow{H^+} \text{CH}_3 - \text{CH} - \text{CH}_3 \]

\[ \text{CH}_3 - \text{CH} - \text{CH}_2 + \text{A} \rightarrow \text{A} \]

(A) is isopropyl benzene or cumene and electrophile involved is \( \text{CH}_3 - \text{CH}_3 \) (isopropyl carbocation). Rearrangements are also possible in Friedel–Crafts reactions when benzene is treated with n-butyl chloride and Lewis acid, the product obtained is isobutyl benzene.

**Prob.6.** How will you synthesize \( \text{CH}_2\text{CH}_2\text{CH}_3 \) from benzene?

**Sol.**

\[ \text{CH}_3\text{O} \xrightarrow{\text{Cl}^{-}} \text{Zn(Hg)} / \text{HCl (Clemmensen reduction)} \]

**Prob.7.** Give the structures and names of the principal products expected from the ring monobromination of each of the following compounds. In each case tell whether bromination will occur slower or faster than with benzene itself.

(a) Acetanilide
(b) Iodobenzene
(c) sec-Butylbenzene
(d) N-Methylaniline
(e) Ethylbenzoate
(f) Acetophenone
(g) Phenetole \((C_6\text{H}_5-O-\text{CH}_2\text{CH}_3)\)
(h) Diphenylmethane \((C_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_5)\)
(i) Benzonitrile \((C_6\text{H}_5\text{CN})\)
(j) Benzotrifluoride \((C_6\text{H}_5\text{CF}_3)\)
(k) Biphenyl \((C_6\text{H}_5-C_6\text{H}_5)\)

**Sol.**

(a) faster (very little o-isomer)
(b) slower, \( \overline{\text{Br}} \)
(c) faster, \( \overline{\text{Bu-sec}} \)
(d) faster, very little o-isomers.
(e) slower, \( \overline{\text{Br}} \)
(f) slower, \( \overline{\text{OC}} \)
(g) faster, \( \text{OEt} \) + \( \text{Br} \)

(h) faster, \( \text{CH} \) + \( \text{Br} \)

(i) slower, \( \text{CN} \)

(j) slower, \( \text{CF}_3 \)

(k) faster, \( \text{Br} + (\text{o-isomer}) \)

Prob.8. \( \text{C}_7\text{H}_7\text{Cl} \) has four isomers \( A_1, A_2, A_3 \) and \( A_4 \).

\[ A_4 \xrightarrow{(i) \text{KMnO}_4} \text{Benzene}, \text{Identify } A_1, A_2, A_3 \text{ and } A_4. \]

Sol.

\[
\begin{align*}
(A_1) & \quad \text{CH}_3 \quad \text{Cl} \\
(A_2) & \quad \text{CH}_3 \quad \text{Cl} \\
(A_3) & \quad \text{CH}_3 \quad \text{Cl} \\
(A_4) & \quad \text{Cl} \end{align*}
\]

Prob.9. Prepare \( p \)-chlorobenzoic acid from \( p \)-chloronitrobenzene.

Sol.

\[
\begin{align*}
\text{NH}_2 \quad \text{Cl} & \quad \text{NO}_2 \quad \text{Cl} \\
\text{Sn/HCl} & \xrightarrow{} \text{NaNO}_2 + \text{HCl} \\
\text{CuCN} & \xrightarrow{} \text{CN} \\
\text{HO}_2 & \xrightarrow{} \text{COOH}
\end{align*}
\]

Prob.10. Find the product in the following reaction:

Sol. No reaction, as there is no \( \alpha \) hydrogen atom along with chloride group.

Prob.11. Nitrobenzene, but not benzene, is used as a solvent for the Friedel–Crafts alkylation of bromobenzene. Explain.

Sol. Benzene is more reactive than bromobenzene and hence would preferentially undergo alkylation. On the other hand, nitrobenzene is very much less reactive than bromobenzene (due to deactivating effect of the \( \text{NO}_2 \) group) and hence will not undergo Friedel–Crafts reaction.

Prob.12. What happens when benzene is treated with methyl chloride in presence of anhydrous \( \text{AlCl}_3 \) and the product is treated with excess of chlorine in presence of UV light?

Sol. \( \text{C}_6\text{H}_6 + \text{CH}_3\text{Cl} \xrightarrow{\text{anhy. } \text{AlCl}_3} \text{C}_6\text{H}_5\text{CH}_3 \xrightarrow{\text{Cl}_2, \text{UV light}} \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \xrightarrow{\text{Cl}_2} \text{C}_6\text{H}_5\text{CHCl}_2 \xrightarrow{\text{Cl}_2} \text{C}_6\text{H}_5\text{CCl}_3 \)
Prob.13. Friedel–Crafts acylation requires an excess of the catalyst but Friedel–Crafts alkylation requires only a catalytic amount. Explain.

Sol. The product of acylation co-ordinates with the catalyst and removes the latter from the reactant side and thereby stops further acylation. For this reason, Friedel–Crafts acylation requires an excess of the catalyst. The product of alkylation does not co-ordinate with the catalyst. So, the catalyst can form complex with the alkylation agent and the catalyst propagates the reaction.

Prob.14. During reaction of benzene with neopentyl chloride, with benzene in the presence of AlCl₃, the major product is 2-methyl-2-phenylbutane and not neopentylbenzene. Explain.

Sol. The initially formed primary carbocation rearranges by methyl migration to form a more stable tertiary carbocation which acts as an electrophile and attacks the benzene to give the major product:

![Chemical structure](image)

Prob.15. The $\text{N(CH}_3\text{)}_3$ and CN substituents are both meta directors. Still nitration of the corresponding benzene derivative does give a minor amount of the ortho and para isomers of the product. Which of the two substituents should lead to a greater ortho/para ratio? Why?

Sol. The CN group, being a linear two-atom group, is much less sterically demanding than the t- butyl $\text{N(CH}_3\text{)}_3$ group. So, the CN group should give the greater ortho/para ratio. In fact, here are the actual data:

<table>
<thead>
<tr>
<th>Group</th>
<th>% meta</th>
<th>% ortho</th>
<th>% para</th>
<th>ortho/para ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N(CH}_3\text{)}_3$</td>
<td>87</td>
<td>2</td>
<td>11</td>
<td>0.18</td>
</tr>
<tr>
<td>-CN</td>
<td>81</td>
<td>17</td>
<td>2</td>
<td>8.5</td>
</tr>
</tbody>
</table>
ASSIGNMENT PROBLEMS

SECTION - A

Multiple Choice Questions

1. For the reaction
   
   O
   \( \text{major} \quad \text{mononitration} \rightarrow P \) (major)
   
   What is the product \( P \)?
   
   \( \text{(A)} \)
   
   \( \text{(B)} \)
   
   \( \text{(C)} \)
   
   \( \text{(D)} \)

2. \( \text{H} + \quad \text{OH} \quad \text{H}_2\text{C} - \text{OH} \quad \text{H} \rightarrow (A) \)

   The structure of \( (A) \) should be
   
   \( \text{(A)} \)
   
   \( \text{(B)} \)
   
   \( \text{(C)} \)
   
   \( \text{(D)} \)

3. \( \text{NO}_2 \rightarrow A \)

   The structure of \( A \) should be
4. \( \text{CH}_2\text{Cl}_2 \rightarrow \text{AlCl}_3 \rightarrow \text{CH}_2\text{Cl} \) (excess)

5. Conc. HNO\(_3\) + H\(_2\)SO\(_4\) mixture gives
   - (A) NO\(_2^+\)
   - (B) NO\(^+\)
   - (C) NH\(_4^+\)
   - (D) NO\(_3^-\)

6. \( \begin{array}{c} \text{H}_3\text{C} = \text{CH} \text{CH} \text{CH} \text{A} \\ \text{HClO}_4 \end{array} \rightarrow \text{A} \)

   (A) is
   - (A) n-propyl benzene
   - (B) cumene
   - (C) diethyl benzene
   - (D) none of the above

7. For sulphonation of benzene effective electrophile is
   - (A) SO\(_3^-\)
   - (B) SO\(_3^+\)
   - (C) SO\(_3\)
   - (D) SO\(_2^-\)

8. \( \text{Hg(OCOCH}_3)_2 \rightarrow \text{A} \)

   A may be...
9.  
\[ \text{A} \stackrel{+}{\text{CH}_3\text{OCOCl}} \rightarrow \text{A} \]  
A is:
(A) \( \text{CH}_3\text{COOH} \)  
(B) \( \text{CH}_3\text{OCOCH}_3 \)  
(C) \( \text{CH}_3\text{COCH}_3 \)  
(D) \( \text{CH}_3\text{COCH}_3 \)  

10. The decreasing order of reactivity of the following compounds towards electrophilic substitution is:

- \( \text{NH}_2 \)  
- \( \text{NHCOC}_2\text{H}_3 \)  
- \( \text{CO}_2\text{H}_3 \)  

(A) \( \text{I} > \text{II} > \text{III} > \text{IV} \)  
(B) \( \text{II} > \text{I} > \text{IV} > \text{III} \)  
(C) \( \text{II} > \text{I} > \text{III} > \text{IV} \)  
(D) \( \text{I} > \text{II} > \text{IV} > \text{III} \)  

11. Predict the product in the below mentioned reaction.

\[ \text{OH} \stackrel{\text{HNO}_3, \text{H}_2\text{SO}_4}{\rightarrow} \]  
(A)  
(B)
12. Arrange the following in the decreasing order of reactivity towards electrophilic substitution is

\[ \text{CH}_3 \text{OH} \quad \text{CH}_3 \quad \text{NO}_2 \quad \text{OH} \]

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

13. The halide which will not react with benzene in the presence of anhydrous AlCl$_3$ is

(A) CH$_3$CHClCH$_3$  (B) C$_6$H$_5$CH$_2$Cl  (C) C$_6$H$_5$Cl  (D) CH$_3$ CH$_2$CH$_2$Cl

14. Which of the following structures correspond to the product expected, when excess of C$_6$H$_6$ reacts with CH$_2$Cl$_2$ in the presence of anhydrous AlCl$_3$?

(A)  (B)  (C)  (D) 

15. Which of the following will be most reactive towards electrophilic substitution?

(A)  (B)  (C)  (D) 

16. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds:
17. Which of the following substituted benzene derivatives would furnish three isomers when one more substituent is introduced?

(A) Cl
(B) Cl
(C) Cl
(D) Cl

18. X will be
(A) p-isomer
(B) o-isomer
(C) m-isomer
(D) A and B both

19. The product will be
(A) OH
(B) OH
(C) SO₃H
(D) SO₃H

20. Which of the following compound will show Friedel–Crafts alkylation?
Fill in the Blanks

1. \( \text{F} + \text{Br}_2 \rightarrow \) ____________

2. When phenol reacts with nitrous acid, electrophile involved is ____________.

3. The -CN and - CF\(_3\) groups are both ____________ directors.

4. Among nitration, sulphonation, and halogenation, most reversible reaction is ____________.

5. The conversion of methyl benzene into benzyl chloride can be carried out by using chlorine and ____________.

6. Aniline when treated with alkaline chloroform gives ____________.

7. Picric acid is an ____________.

8. Pure aniline is ____________ liquid.

9. ____________ and ____________ have better almond smell.

10. Toluidine are ____________ basic than aniline.

Short Answer Type Questions

1. Nitrobenzene does not undergo Friedel–Crafts alkylation.

2. Explain why electrophilic substitution in naphthalene exclusively occurs at the \( \alpha \)-position.

3. Explain why pyridine does not undergo Friedel–Crafts reaction?

4. Pyridine is more basic than aniline, explain.

5. A hydrocarbon, \( \text{C}_8\text{H}_{10} \), gives two monobromo derivatives. On oxidation, it forms an acid, isomeric with the oxidation product of naphthalene. What is the structure of the original hydrocarbon?

True or False Type Questions

1. Each ring of \( \text{biphenyl} \) is more reactive than benzene towards electrophilic substitution and the chief products are ortho and para isomers.

2. Planar conjugated cyclic polyenes whose stability is comparable to their open chain analogues are called non-aromatic.

3. Rate of nitration of benzene and hexadeuterobenzene is same under same set of experimental conditions.

4. The role of sulphuric acid in nitrating mixture is to absorb the water formed in the initiation process and so prevents the reverse reaction from proceeding.

\[
\text{C}_6\text{H}_5 + \text{HNO}_3 \rightarrow \text{C}_6\text{H}_2\text{NO}_2 + \text{H}_2\text{O}
\]

5. Pyrrole is more reactive than pyridine towards electrophilic substitution.

6. –CCl\(_3\) or –CF\(_3\) is o- and p-directing group.
7. Aniline with concentrated \((\text{HNO}_3 + \text{H}_2\text{SO}_4)\) forms \(o\) and \(p\)-nitroaniline.

8. Benzamide on treatment with \(\text{Br}_2\) and \(\text{KOH}\) gives aniline.

9. Acetophenone and benzophenone can be distinguished by iodoform test.

10. Aniline on standing in air darkens its colour due oxidation.
SECTION - B

Subjective Problems

1. Give the structure of the principal product:
   (a) [Structure image with O mononitration]
   (b) [Structure image with O₂N mononitration]
   (c) [Structure image with NO₂ mononitration]

2. Convert:
   (i) [Structure image with NH₂ to CO₂H conversion]
   (ii) [Structure image with CH₃ and Cl conversion]
   (iii) [Structure image with CH₃ and Br conversion]
   (iv) [Structure image with CH₃ and OH conversion]

3. Predict the products for the following reactions.
(a) Write structures of the products A, B and C in the following scheme.

(b) Complete the reactions:

4. Predict the product

(i) 

(ii) 

5. Complete the following reaction with appropriate reagents:

6. How can you synthesise the following compounds from benzene or toluene by using any inorganic reagents or aliphatic compounds having maximum of three carbons?

(i) 

(ii) 

(iii) 

7. Arrange the following in decreasing order of reactivity towards ring nitration.

(a) benzene, mesitylene \((1,3,5\text{-C}_6\text{H}_3\text{(CH}_3)_3\text{)}\), toluene, m-xylene, p-xylene.

(b) benzene, bromobenzene, nitrobenzene, toluene.

(c) acetonilide, acetophenone, aniline, benzene.

(d) terephthalic acid, toluene, p-toluic acid, p-xylene.

9. Give the structural formula and name for the major alkylation product:

(a) \(\text{C}_6\text{H}_5\text{CH}_3 + (\text{CH}_3)_2\text{CC}H\text{OH} \xrightarrow{\text{BF}_3} \)?
(b) \( \text{C}_6\text{H}_6 + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{AlCl}_3, 100^\circ\text{C}} ? \)

10. What product (or products) would you expect to obtain when the following compounds undergo ring bromination with \( \text{Br}_2 \) and \( \text{FeBr}_3 \)?

(a) \[
\begin{array}{c}
\text{CH}_2 - \text{C} - \text{O} \\
\text{CH}_2
\end{array}
\]

(b) \[
\begin{array}{c}
\text{C} - \text{O} \\
\text{C}
\end{array}
\]

11. An organic compound (A) \( \text{C}_8\text{H}_6 \), on treatment with dil. \( \text{H}_2\text{SO}_4 \) containing mercuric sulphate gives a compound (B), which can also be obtained from benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound (B) when treated with iodine in aqueous KOH, yields (C) and a yellow compound (D). Identify (A), (B), (C) and (D).

12. The sodium salt of sulphanilic acid can be readily acetylated with acetic anhydride but not the free acid. Explain.

13. Complete the equations and comment:

(i) \( \text{PhBr} + \text{Ac}_2\text{O} \xrightarrow{\text{AlCl}_3} ? \)

(ii) \( \text{PhCH}_2\text{CN} \xrightarrow{\text{HNO}_3} ? \)

(iii) \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{CH}_3
\end{array}
\]

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{CH}_3
\end{array}
\xrightarrow{\text{HNO}_3, \text{H}_2\text{SO}_4} ?
\]

(iv) \[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array}
\xrightarrow{\text{AlCl}_3} \text{CH}_3\text{COCl}
\]

(v) \( \text{Ph(CH}_2\text{)}\text{Me} \xrightarrow{\text{KMnO}_4} ? \)

(vi) \( \text{PhNO}_2 + \text{EtCl} \xrightarrow{\text{AlCl}_3} ? \)

14. Suggest oxidizing agents for the conversions:

(i) \[
\begin{array}{c}
\text{Me} \\
\text{Me}
\end{array}
\]

\[
\begin{array}{c}
\text{Me} \\
\text{Me}
\end{array}
\xrightarrow{\text{CO}_2\text{H}} \text{Me}
\]

(ii) \[
\begin{array}{c}
\text{NO}_2 \\
\text{Me}
\end{array}
\]

\[
\begin{array}{c}
\text{NO}_2 \\
\text{Me}
\end{array}
\xrightarrow{\text{Cl}} \text{Me}
\]

15. Predict the products in the following reactions:

(a) \[
\begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array}
\xrightarrow{\text{KNH}_2, \text{NH}_3} A
\]
(b) \[ \text{Cl} \quad \text{Cl} \quad \text{B} \]

\[ \frac{\text{KNH}_2}{\text{NH}_3} \]

(c) \[ \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{C} \]

\[ \frac{\text{KNH}_2}{\text{NH}_3} \]
Multiple Choice Questions

1. (A) 2. (D) 3. (A) 4. (B)
5. (A) 6. (B) 7. (C) 8. (B)
9. (B) 10. (D) 11. (C) 12. (A)
13. (C) 14. (D) 15. (A) 16. (C)
17. (B) 18. (D) 19. (C) 20. (C)

Fill in the Blanks

1. \( \text{Br} \)
2. nitrosonium ion
3. meta
4. sulphonation
5. heat or light
6. phenyl isocyanide
7. explosive
8. colourless
9. Nitrobenzene, benzaldehyde
10. more

Short Answer Type Questions

1. The nitro group in nitrobenzene strongly deactivates the benzene ring. This decreases the reactivity of benzene towards Friedel–Crafts alkylation.

2. This can be explained on the basis of intermediate carbonium ion. Two resonance structures can be written for the carbonium ion obtained from attack at \( \alpha \) - position (without involving the other ring), whereas only one such structure is possible for substitution at \( \beta \) - position.

Attack at \( \alpha \) - position

Attack at \( \beta \) - position
The transitory carbonium ion formed as a result of attack at α - position is comparatively more stable than the transitory carbonium ion formed by attack at β- position.

3. The Lewis acids AlCl₃ or FeCl₃, used as catalyst in Friedel–Crafts reaction coordinate with nitrogen of the pyridine through lone pair of electrons and form a complex. The +ve charge on N greatly reduces the reactivity towards electrophilic substitution.

4. In pyridine lone pair of electron on nitrogen atom is not delocalized, so is more available for protonation. In aniline lone pair of electron on nitrogen is delocalized thus less available for protonation.

5. The oxidation product of naphthalene is phthalic acid. C₈H₁₀[ oxid ] → Phthalic acid. Hence, C₈H₁₀ is o-xylene as it gives two monobromo derivatives

**True or False Type Questions**

1. True  
2. True  
3. True  
4. False  
5. True  
6. False  
7. False  
8. True  
9. True  
10. True
SECTION – B

Subjective Problems

1. (a) 

![Diagram](image)

Deactivated
Ring
Activated Ring

Substitution is faster in the ring that is activated by nitrogen. The other ring is actually deactivated by -COOAr.

(b) 

![Diagram](image)

Deactivated
Ring

Substitution is faster in the ring that is not deactivated by –NO₂. Orientation is o, p to the other ring.

(c) 

![Diagram](image)

Activated ring

Substitution is faster in the ring that is not deactivated by —NO₂. Orientation is o, p to the substituent, CH₂Ar.

3. 

![Chemical Structures](image)

(b) 

![Chemical Structures](image)

4. (i) 

![Chemical Structures](image)

(ii) 

![Chemical Structures](image)
5.


8. (a) mesitylene > m-xylene > p-xylene > toluene > benzene
   (the two - CH_3 groups in m-xylene activate the same positions, but the two -CH_3 groups in p-xylene activate different positions.
   (b) toluene > benzene > bromobenzene > nitrobenzene.
   (c) aniline > acetanilide > benzene > acetophenone.
   (d) p-xylene > toluene > p-toluic acid > terephthalic acid.

9. (a) 

10. (a) 

11. (A) (B) (C) (D)
There is no availability of lone pair of electrons on the nitrogen atom in case of acid (A), hence the ring is deactivated. In sodium salt of the acid, i.e. (B) the lone pair is available hence the ring can be easily acetylated.

13. (i) \[
\text{Br} \quad \text{MeOC} \quad \text{→} \quad 3\text{AlCl}_3 + \text{Ac}_2\text{O}
\]
Two molecules of aluminium chloride must be used, since the acetylating species is acetic anhydride. The formation of the para-product is probably due to steric effects.

(ii) \[
\text{CN} \quad \text{CN} \quad \text{O}_2\text{N} \quad \text{→} \quad 3\text{HNO}_3
\]
The cyano group directly attached to the benzene ring has a very strong -R effect and so is m-orienting. When 'isolated' from the benzene ring, it exerts only a -I effect on the ring. This effect must be weak, otherwise m-substitution would have occurred. At the same time, the CH$_2$ group exerts hyperconjugation, which favours o, p substitution. Presumably the steric effect largely decides p-substitution rather than ortho.

(iii) \[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{NO}_2 & \quad \text{HNO}_3/\text{H}_2\text{SO}_4
\end{align*}
\]
Both alkyl groups have a +I effect, Me$_2$CH $>$ Me. Both also have a hyperconjugative effect, Me $>$ Me$_2$CH. Since these effects are in opposition, it is not easy to predict the orientation. However, steric effects due to Me$_2$CH are far larger than those due to Me, and this decides (presumably) in favour of substitution at ortho to Me.

(iv) \[
\begin{align*}
\text{CH}_3 & \quad \text{H}_3\text{C} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{H}_3\text{C} \quad \text{CH}_3 \\
+\text{CH}_3\text{COCl} & \quad \text{AlCl}_3 \quad \text{→}
\end{align*}
\]
The explanation is similar to that given for (iii).

(v) \[
\text{Ph(CH}_2)_3\text{Me} \quad \xrightarrow{\text{KMnO}_4} \quad \text{PhCO}_2\text{H}
\]
Matter how long the side-chain is, oxidation with strong oxidizing reagents results in benzoic acid.

(vi) \[
\text{PhNO}_2 + \text{EtCl} \quad \xrightarrow{\text{AlCl}_3} \quad \text{No reaction}
\]
14. (i) $$\text{Me} \quad \text{NO}_2 \quad \text{CO}_2\text{H}$$

(ii) $$\text{Me} \quad \text{Cl} \quad \text{CO}_2\text{H}$$

The presence of an -I group at ortho to the side-chain usually require the use of alkaline permanganate.

15. (a) $$\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{NH}_2$$

(b) $$\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{NH}_2$$

(c) $$\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{NH}_2$$