AROMATIC COMPOUNDS

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Syllabus

Reactions of benzene: Structure and aromaticity; Electrophilic substitution reactions: halogenation, nitration, sulphonation, Friedel-Crafts alkylation and acylation; Effect of o-, m- and p-directing groups in monosubstituted benzenes.

Phenols: Acidity, electrophilic substitution reactions (halogenation, nitration and sulphonation); Reimer-Tieman reaction, Kolbe reaction.

Name: ____________________________  Contact No. __________________
Aromatic Compounds

Introduction

These compounds also had low hydrogen-to-carbon ratios as well as pleasant aromas, and they could be converted to benzene or related compounds. This group of compounds was called aromatic because of their pleasant odors. Other organic compounds, without these properties, were called aliphatic, meaning ‘fatlike’. As the unusual stability of aromatic compounds was investigated, the term ‘aromatic’ can to be applied to compounds with this stability, regardless of their order.

Aromatic Character: [The Hückel 4n + 2 rule]

The following three rules are useful in predicting whether a particular compound is aromatic or non-aromatic.

Rule 1. Aromatic compounds are cyclic and planer.
Rule 2. Each atom in an aromatic ring is sp² hybridised.
Rule 3. The cyclic π molecular orbital (formed by overlap of p-orbitals) must contain (4n + 2) π electrons, i.e., 2, 6, 10, 14 ....... π electrons. Where n = an integer 0, 1, 2, 3,............

Examples of Aromatic Compounds:

<table>
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<tr>
<th>n</th>
<th>π-electrons = (4n + 2)</th>
<th>Example</th>
</tr>
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<tr>
<td>0</td>
<td>2</td>
<td>cyclopropenyl cation</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>Benzene, Cyclopentadieny anion, Cycloheptatrienyl cation, Pyridine, Pyrrole, Furan, Thiophene</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>14</td>
<td>Anthracene, Phenanthrene</td>
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**Electrophilic aromatic substitution**

Like an alkene, benzene has clouds of pi electrons above and below its sigma bond framework. Although benzene's pi electrons are in a stable aromatic system they are available to attack a strong electrophile to give a carbocation. This resonance-stabilized carbocation is called a sigma complex because the electrophile is joined to the benzene ring by a new sigma bond.

The sigma complex (also called an arenium ion) is not aromatic because the sp² hybrid carbon atom interrupts the ring of p orbitals. This loss of aromaticity contributes to the highly endothermic nature of this first step. The sigma complex regains aromaticity either by a reversal of the first step (returning to the reactants) or by loss of the proton on the tetrahedral carbon atom, leading to the substitution product.

The overall reaction is the substitution of an electrophile (E) for a proton (H) on the aromatic ring: **electrophilic aromatic substitution**. This class of reactions includes substitutions by a wide variety of electrophilic reagents. Because it enables to introduce functional groups directly on to the aromatic ring, electrophilic aromatic substitution is the most important method for synthesis of substituted aromatic compound.

---

**Step 1 : Attack on the electrophile forms the sigma complex**

The sigma complex (also called an arenium ion) is not aromatic because the sp² hybrid carbon atom interrupts the ring of p orbitals. This loss of aromaticity contributes to the highly endothermic nature of this first step. The sigma complex regains aromaticity either by a reversal of the first step (returning to the reactants) or by loss of the proton on the tetrahedral carbon atom, leading to the substitution product.

**Step 2 : Loss of a proton gives the substitution product.**

**Directive Influence of Substituents In Benzene**

The first substituent may occupy any position in benzene ring i.e. one and only one monosubstituted benzene is obtained. The next group may go to ortho, meta or para position it is the group already present in the benzene nucleus that determines low readily the attack occurs and at what position of the ring it occurs. In other words, the group attached to the ring not only effects the reactivity but also determines the orientation of substitution. This is called directive influence of substituents in benzene nucleus. The substituent group is able to activate or deactivate the ring due to a number of factors like inductive effect, electromeric effect, resonance effect and hyperconjugative effect. Depending on their directive influence the substituent groups, except halogens, are of two different types.

**Activating Groups or Electron Releasing Groups**

All groups having one or more lone pair of electrons are activating groups because they release electrons towards the nucleus increasing electron density and hence energy of the system. Reaction rate is increased due to low energy of activation. Examples:

- Decreasing o- & p-directing strength
  - $-\ddot{O}H$, $-\ddot{N}H$, $-\ddot{N}HR$, $-\ddot{N}R$, $-\ddot{O}H$, $-\ddot{O}R$, $-\ddot{N}HCO$, $-R$, $-Ar$, $-X$.

Thus, all the groups which are electron donating $-\ddot{O}H$, $-\ddot{O}R$, $-\ddot{N}H$, $-\ddot{N}HR$, $-\ddot{N}R$ etc. are ortho-para directing and facilitate electrophilic substitution in the benzene ring.
Deactivating Group or Electron Withdrawing Group or Meta Directors

Such groups have tendency to withdraw π electrons from the benzene nucleus and thus decreasing its electron density are known as deactivating groups.

Due to decrease in electron density of the ring, the rate of electrophilic substitution is retarded. That’s why these group are called deactivating group.

A look on the resonating structure reveal that these groups develop positively charge at ortho and para positions leaving the meta-positions as the point of relatively high electron density and hence the electrophilic substitution occurs at m–position, not at o–and p–positions. Deactivating groups have π bonds with one more electronegative atom.

Examples:

\[ -\text{NR}_2, -\text{C}=\text{N}, -\text{Cl}, -\text{OH}, -\text{C}=\text{R}, -\text{C}=\text{OR}, -\text{C}=\text{NH}_2, -\text{NH}_3 \]

decreasing meta directing strength

Nitration

Nitration is brought about by the action of concentrated nitric acid or a mixture of concentrated nitric acid and sulphuric acid often called nitrating mixture. HNO\(_3\) alone is a weak nitrating agent where as the mixture is strong nitrating mixture.

When concentrated HNO\(_3\) and concentrated H\(_2\)SO\(_4\) is the nitrating mixture, NO\(_2^+\) (Nitronium ion) is produced as follows:

\[ \text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{H}_2\text{O}^+ + 2\text{HSO}_4^- \]

Now, the NO\(_2^+\) ion attacks the benzene nucleus and forms an intermediate cation. a benzenonium ion, which loses a proton to yields the nitro derivative.

Sulphonation

Now the electrophilic reagent, SO\(_3\), attacks the benzene ring to form the intermediate carbocation.

2H\(_2\)SO\(_4\) \rightleftharpoons SO\(_3\) + H\(_2\)O\(^+\) + HSO\(_4^-\)

Sulphonation, like iodination, is reversible and is believed to take place in concentrated sulphuric acid via the pathway.
Halogenation

Bromination of Benzene:

Bromination follows the general mechanism for electrophilic aromatic substitution. Bromine itself is not sufficiently electrophilic to react with benzene, but a strong Lewis acid such as $\text{FeBr}_3$ catalyzes the reaction.

Step 1: Formation of a stronger electrophile.

\[
\text{Br} + \text{FeBr}_3 \rightarrow \text{Br}^+ \text{FeBr}_4^- \quad \text{(a stronger electrophile than Br)}
\]

Step 2: Electrophilic attack and formation of the sigma complex.

Step 2: Loss of a proton gives the products.

formation of the sigma complex is rate limiting and the transition state leading to it occupies the highest-energy point on the energy diagram. This step is strongly endothermic because it forms a non-aromatic carbocation. The second step is exothermic because aromaticity is regained and a molecule of HBr is evolved. The overall reaction is exothermic by 10.8 kcal/mol (45 kJ/mol.)

Comparison with alkenes

Benzene is not as reactive as alkenes, which react rapidly with bromine at room temperature to give addition products. For example, cyclohexene reacts to give trans-1,2-dibromocyclohexane. This reaction is exothermic by about 29 kcal/mol (121 kJ/mol.)
The analogous addition of bromine to benzene is endothermic because it requires the loss of aromatic stability. The addition is not seen under normal circumstances. The substitution of bromine for a hydrogen atom gives an aromatic product. The substitution is exothermic, but it requires a Lewis acid catalyst to convert bromine to a stronger electrophile.

\[
\text{H} + \text{Br}_2 \rightarrow \text{H} - \text{Br} \quad \Delta H^\circ = + 2 \text{ kcal (+ 8kJ)}
\]

Chlorination of benzene
Chlorination of benzene works much like bromination, except that aluminum chloride (AlCl}_3\) is most often as the Lewis acid catalyst.

\[
\text{benzene} + \text{Cl}_2 \xrightarrow{\text{AlCl}_3} \text{chlorobenzene} + \text{HCl}
\]

Iodination of benzene
Iodination of benzene requires an acidic oxidizing agent, such as nitric acid. Nitric acid is consumed in the reaction, so it is a reagent (an oxidant) rather than a catalyst.

\[
\text{benzene} + \frac{1}{2} \text{I}_2 + \text{HNO}_3 \rightarrow \text{iodobenzene} + \text{NO}_2 + \text{H}_2\text{O}
\]

Iodination probably involves an electrophilic aromatic substitution with iodonium ion (I) acting as the electrophile. The iodonium ion results from oxidation of iodine by nitric acid.

\[
\text{H} + \text{HNO}_3 + \frac{1}{2} \text{I}_2 \rightarrow \text{iodonium} + \text{NO}_2 + \text{H}_2\text{O}
\]

Alkylation
The carbon atom of alkyl halides, R – X, is electrophile, but rarely is it sufficiently effective so, to effect the substitution of aromatic species. So, the presence of a Lewis acid catalyst is also required. Anhydrous aluminum chloride, AlCl}_3, being a Lewis acid, accepts a lone pair of electrons from halogen (Chlorine atom) of R – Cl. This makes R (alkyl) group to be sufficiently polar so as to act as an electrophile. Now, two mechanisms are possible for Friedel Craft's alkylation. both involve electrophilic substitution, but they differ as to the nature of the electrophile. One of the mechanism for Friedel Craft's reaction involves the following steps.
(i)  
\[ R\text{-Cl} + \text{AlCl}_3 \rightarrow R\text{Cl} + \text{AlCl}_3^{+} \rightarrow R^{+} + \text{AlCl}_3^{2-} \]

(ii)  
\[ \sigma\text{-complex} \]

(iii)  
\[ \text{H} + \text{AlCl}_4^{-} \rightarrow \text{HCl} + \text{AlCl}_3 \]

(iii) **Nature of Lewis acid as catalyst**  
The order of effectiveness of Lewis acid catalyst has been shown to be  
\[ \text{AlCl}_3 > \text{FeCl}_3 > \text{BF}_3 > \text{TiCl}_3 > \text{ZnCl}_2 > \text{SnCl}_4 \]

**Acylation**  
Acylation of benzene may be brought about with acid chlorides or anhydrides in presence of Lewis acids.  
e.g.  
\[ \text{O} + \text{CH}_2\text{COCl} + \text{AlCl}_3 \rightarrow \text{OCOCH}_3 + \text{HCl} \]

**Preparation of Benzene** :  
(1) By polymerisation (of Acetylene) :  
\[ 3\text{HC} = \text{CH} \xrightarrow{\text{Red hot iron tube}} \text{O} \]

(2) By decarboxylation (of Benzoic acid) :  
\[ \text{COOH} \xrightarrow{\text{NaOH}} \text{COONa} \xrightarrow{\text{NaOH} (\text{CaO})} \text{O} + \text{Na}_2\text{CO}_3 \]

(3) By catalytic reforming of n-Hexane :  
\[ \text{CH}_3 - (\text{CH}_2)_4 - \text{CH}_3 \xrightarrow{\text{Pt, 873 K, H}_2} \text{cyclohexane} \xrightarrow{\text{Pt, 873 K, 3H}_2} \text{O} \]

(4) By reduction (of Benzene diazonium Chloride) :  
\[ \text{O} + \text{H}_3\text{PO}_2 + \text{H}_2\text{O} \rightarrow \text{O} + \text{N}_2 \]
Reactions of Benzene:

Con. HNO₃ → H₂SO₄

Con. H₂SO₄ + SO₃ →

Cl₂ → FeCl₃

RCI → AlCl₃

RCOCI → AlCl₃

D⁺/D₂O

HNO₂

ArN₂⁺X⁻

Preparation of Toluene:
(1) By Friedel-Craft’s reaction:

[苯] + CH₃Cl → [苯]CH₃ + HCl

(2) By Wurtz fitting reaction:

Bromobenzene + 2Na + CH₃Br → Toluene + 2NaBr

(3) From Grignard reagents:

MgBr

+ CH₃Br → Toluene + MgBr₂
(4) By catalytic reforming of n-Heptane:

\[
\begin{align*}
\text{CH}_3 & \quad \xrightarrow{873 \text{ K}, \text{Pt}} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \xrightarrow{873 \text{ K}, \text{Pt}} \quad \text{CH}_3 \\
\end{align*}
\]

Methylcyclohexane \quad \text{Toluene}

Preparation of Xylene:

\[
\begin{align*}
\text{CH}_3 & \quad \xrightarrow{\text{CH}_3\text{X, AlCl}_3} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \xrightarrow{\text{CH}_3\text{X, AlCl}_3} \quad \text{CH}_3 \\
\end{align*}
\]

Toluene \quad \text{O-Xylene} \quad \text{p-Xylene}

**Phenols and Quinones**

1. Phenols may be prepared by fusion of sodium arylsulphonates with sodium hydroxide:
   \[
   \text{ArSO}_3^- \text{Na}^+ + 2\text{NaOH} \rightarrow \text{ArO}^- \text{Na}^+ + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}
   \]

2. When a diazonium sulphate solution is steam distilled, a phenol is produced:
   \[
   \text{ArN}_2\text{H}_2\text{SO}_4^- + \text{H}_2\text{O} \rightarrow \text{ArOH} + \text{N}_2 + \text{H}_2\text{SO}_4
   \]

3. Phenols are formed when compounds containing an activated halogen atom are heated with aqueous sodium hydroxide; e.g., p-nitrophenol from p-chloronitrobenzene:
   \[
   \text{Cl} + 2\text{NaOH} \rightarrow \text{O}^-\text{Na}^+ + \text{NaCl} + \text{H}_2\text{O}
   \]

4. Distillation of phenolic acids with soda-lime produces phenols; e.g., sodium salicylate gives phenol:
   \[
   \text{OH} + \text{NaOH (CaO)} \rightarrow \text{O}^-\text{Na}^+ + \text{Na}_2\text{CO}_3
   \]

5. Phenols may be prepared by means of a Grignard reagent:
   \[
   \text{ArMgBr} \xrightarrow{\text{ArMgBr}} 2\text{ArOMgBr} \xrightarrow{\text{H}^+} 2\text{ArOH}
   \]

**Properties of phenol -**

These are characteristic of monohydric phenols. Phenol is a colourless crystalline solid, m.p. 43°, b.p. 182°C, which turns pink on exposure to air and light. It is moderately soluble in cold water, but is readily soluble in concentrated sulphuric acid and a few the Liebermann reaction; when phenol is dissolved in concentrated sulphuric acid and a few drops of aqueous sodium nitrite added, a red colour is obtained on dilution, and turns blue when made alkaline with aqueous sodium hydroxide.

Phenol is used as an antiseptic and disinfectant, and in the preparation of dyes, drugs, bakelite, etc.
Preparation & Reactions of Phenol:

Preparation of ArOH:
- $\text{C}_6\text{H}_5\text{SO}_3\text{Na}$ → $\text{NaOH}$
- $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$ → $\text{H}_2\text{O}$
- $\text{C}_6\text{H}_5\text{MgBr}$ → $\text{O}_2/\text{H}_2\text{O}$
- $\text{C}_6\text{H}_5\text{OH}$
- $\text{C}_6\text{H}_5\text{Cl}$
- $\text{SiO}_2$
- $\text{C}_6\text{H}_5\text{Cl}$ → $\text{NaOH}$ & $\text{Na}_2\text{CO}_3$

Reactions:
- $\text{NaOH}$ & $\text{Na}_2\text{CO}_3$ → $\text{C}_6\text{H}_5\text{ONa}$
- $\text{CH}_3\text{COOH}$ & $\text{CH}_2\text{COCl}$ → $\text{CH}_3\text{COOC}_2\text{H}_5$
- $\text{CH}_2\text{COOH}$ → $\text{CH}_3\text{COOC}_2\text{H}_5$
- $\text{Zn}/\Delta$ → $\text{C}_6\text{H}_5$
- $\text{CH}_4\text{N}_2$ → $\text{C}_6\text{H}_5\text{OCH}_3$
- $\text{NH}_2\text{ZnCl}_2$ → $\text{C}_6\text{H}_5\text{NH}_2$
- $\text{NaOH}$ → $\text{C}_6\text{H}_5\text{OH}$
- $\text{PCl}_3$ → $\text{C}_6\text{H}_5\text{Cl} + \text{POCl}_3 + \text{HCl}$

- $\text{NaOH}/\text{C}_6\text{H}_5\text{I}$ → $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$
- $\text{C}_6\text{H}_5\text{SO}_3\text{Cl}$ → $\text{C}_6\text{H}_5\text{SO}_3\text{OC}_2\text{H}_5$
- $\text{Br}_2$, water → 2, 4, 6 tribromo phenol
- Dil. $\text{HNO}_3$ → o & p nitrophenol
- $\text{HNO}_2$/ $\text{H}_2\text{SO}_4$ → 2, 4, 6 trinitrophenol
- $\text{HNO}_2$/ $\text{H}_2\text{SO}_4$ → p-nitroso phenol

- $\text{CH}_2\text{COCl}$ → $\text{HO}-\text{Para product}$
- $\text{H}_2\text{SO}_4$ → $\text{SO}_2\text{H}$
- $\text{HO}-\text{Bakelite}$

- $\text{ArOH}$ → $\text{HCl}$
- $\text{HCN}/\text{HCl}$ → $\text{AlCl}_3$ → $\text{CHCl}/\text{KOH}$ → Salicylaldehyde

- $\text{Phthalic anhydride}$ → Phenothaline
- $\text{H}_2\text{SO}_4/\Delta$
- $\text{CH}_2\text{COCl}$ → $\text{AlCl}_3$
- $\text{H}_2\text{O}$ → Salicylaldehyde

- $\text{Ni}/\text{H}_2$
Aromatic Aldehyde & ketone

1. Gattermann-Koch aldehyde synthesis

Benzaldehyde may be synthesised by bubbling a mixture of carbon monoxide and hydrogen chloride through a solution of nitrobenzene or ether containing benzene and a catalyst consisting of aluminium chloride and a small amount of cuprous:

\[ \text{C}_6\text{H}_5 + \text{CO} + \text{HCl} \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5\text{CHO} + \text{HCl} \]

The mechanism of this reaction is uncertain, but it appears likely that the formyl cation is the active species:

\[ \text{CO} + \text{HCl} + \text{AlCl}_3 \xrightarrow{} [\text{H}^\circ \text{C} = \text{O} \leftrightarrow \text{HC} = \text{O}^\circ] + \text{AlCl}_4^- \]

It also appears likely that the cuprous chloride forms a complex with the carbon monoxide, thereby increasing its local concentration.

2. Gattermann aldehyde synthesis

When benzene is treated with a mixture of hydrogen cyanide and hydrogen chloride in the presence of aluminium chloride, and the complex so produced decomposed with water, benzaldehyde is produced (in low yield).

Several mechanism have been proposed for this reaction. A widely accepted one is that imidoformyl chloride is formed as an intermediate:

\[ \text{HCl} + \text{HCN} \xrightarrow{\text{AlCl}_3} \text{HN} = \text{CHCl} \]

\[ \text{C}_6\text{H}_5 + \text{HN} = \text{CHCl} \xrightarrow{\text{AlCl}_3} \text{HCl} + \text{C}_6\text{H}_5\text{CH} = \text{NH} \xrightarrow{\text{H}_2\text{O}} \text{C}_6\text{H}_5\text{CHO} + \text{NH}_3 \]

The Gattermann reaction is applicable to phenols and phenolic ethers, but not to nitrobenzene.

3. Sommelet’s reaction

Benzaldehyde is produced when benzyl chloride is refluxed with hexamethylenetetramine in aqueous ethanolic solution, followed by acidification and steam distillation.

\[ \text{C}_6\text{H}_5\text{CH}_2\text{Cl} + (\text{CH}_2)_6\text{N}_4 \xrightarrow{} \text{C}_6\text{H}_5\text{CHO} (60 – 70\%) \]

The mechanism of this reaction is uncertain.

(i) \[ \text{C}_6\text{H}_5\text{CH}_2\text{Cl} + (\text{CH}_2)_6\text{N}_4 \xrightarrow{} [\text{C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_12\text{N}_4]^- \xrightarrow{\text{Cl}^-} \text{C}_6\text{H}_5\text{CH}_2\text{N} = \text{CH}_2 \xrightarrow{\text{H}^+} \text{C}_6\text{H}_5\text{CH}_2\text{N} = \text{CH}_2 \]

(ii) \[ \text{C}_6\text{H}_5\text{CH}_2\text{NH} = \text{CH}_2 + \text{C}_6\text{H}_5\text{CH} = \text{NH}_3 \xrightarrow{\text{H}_2\text{O}} \text{C}_6\text{H}_5\text{CHO} + \text{NH}_3 \]

Methylenbenzylamine, formed by hydrolysis of the quaternary compound, adds on a proton, and the ion thus formed reacts with benzylamine (formed as an intermediate) with transfer of a hydride ion from the latter to the former.

4. Rosenmund reduction

Benzaldehyde is produced by the catalytic reduction of benzoyl chloride in the presence of a quinoline-sulphur poisson.

\[ \text{C}_6\text{H}_5\text{COCl} + \text{H}_2 \xrightarrow{\text{Pd}^+} \text{C}_6\text{H}_5\text{CHO} + \text{HCl} \]

This method may be used to prepare hydroxybenzaldehydes provided the hydroxyl group is protected, e.g., by acetylation.

5. Stephen’s method

When phenyl cyanide is reduced with stannous chloride and hydrochloric acid in ethereal solution, and then the product hydrolysed with water, benzaldehyde is formed.

\[ \text{C}_6\text{H}_5\text{CN} \xrightarrow{(i)} \text{SnCl}_2 / \text{HCl} \xrightarrow{(ii)} \text{H}_2\text{O} \xrightarrow{} \text{C}_6\text{H}_5\text{CHO} \]
6. Benzaldehyde may be prepared by the reaction between phenylmagnesium bromide and ethyl formate, or better, ethyl orthoformate

7. Benzaldehyde may be obtained from aniline via the diazonium salt and formaldoxime.

\[
\begin{align*}
\text{C}_6\text{H}_5\text{N}_2\text{Cl}^- + \text{CH}_3\text{=NOH} & \rightarrow \text{C}_6\text{H}_5\text{CH} = \text{NOH} + \text{H}_2\text{O} \\
& \rightarrow \text{C}_6\text{H}_5\text{CHO (40\%)}
\end{align*}
\]

8. Claisen reaction

Benzaldehyde, in the presence of dilute alkali, condenses with aliphatic aldehydes or ketones containing α-hydrogen; e.g., with acetaldehyde it forms cinnamaldehyde:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CHO} + \text{CH}_2\text{CHO} & \rightarrow \text{C}_6\text{H}_5\text{CH} = \text{CHCHO} + \text{H}_2\text{O} \\
\text{With acetone, benzaldehyde form benzylideneacetone.} & \\
\text{C}_6\text{H}_5\text{CHO} + \text{CH}_2\text{COCH}_3 & \rightarrow \text{C}_6\text{H}_5\text{CH} = \text{CHCOCH}_3 + \text{H}_2\text{O} \\
& (65 - 78\%)
\end{align*}
\]

If the reaction is carried out in aqueous ethanolic sodium hydroxide, dibenzylideneacetone is produced by interaction of benzylidenacetone and another molecular of benzaldehyde:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CH} = \text{CHCOCH}_3 + \text{C}_6\text{H}_5\text{CHO} & \rightarrow \text{C}_6\text{H}_5\text{CH} = \text{CHCOCH} = \text{CHC}_6\text{H}_5 + \text{H}_2\text{O} \\
& (90 - 94\%)
\end{align*}
\]

9. Perkin reaction

When benzaldehyde (or any other aromatic aldehyde) is heated with the anhydride of an aliphatic acid (containing two α-hydrogen atoms) in the presence of its sodium salt, condensation takes place to form a β-arylacrylic acid; e.g., with acetic anhydride and sodium acetate, cinnamic acid is formed.

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CHO} + (\text{CH}_3\text{CO})_2\text{O} & \rightarrow \text{C}_6\text{H}_5\text{CH} = \text{CHCO}_2\text{H}
\end{align*}
\]

Methods of preparation of nitrobenzene

(i) \[
\begin{align*}
\text{ } + \text{HNO}_3 & \text{conc.} \rightarrow \text{NO}_2 \\
\text{H}_2\text{SO}_4 \text{390K} & \rightarrow \text{H}_2\text{O} (85\%)
\end{align*}
\]

(ii) \[
\begin{align*}
\text{CH}_3 & + \text{CH}_2\text{CO} - \text{O} - \text{NO}_2 \rightarrow \text{CH}_3\text{NO}_2 + \text{CH}_3\text{COOH}
\end{align*}
\]

(iii) \[
\begin{align*}
\text{H}_3\text{C}-\text{N}_2\text{Cl}^- & \rightarrow \text{H}_2\text{C} - \text{NO}_2 + \text{HCl} + \text{N}_2
\end{align*}
\]

General properties of nitrobenzene

(i) Yellow liquid
(ii) Denser than water. Thus insoluble in water soluble in organic solvents
(iii) b.p. = 211°C
(iv) steam - volatile
Methods of preparation of benzoic acid

(1) Industrial

-$\text{air CO} - \text{Mn acetate, 340°C}$

$\text{coal-tar or petroleum}$

(coaly refining)

- $\text{toluene}$
- $\text{Cl}_2, \Delta$
- $\text{benzene trichloride}$

(i) $\text{OH}^-$

(ii) $\text{H}_2\text{O}^-$

$\text{COOH}$

(2) Oxidation of alkyl benzenes

$R \xrightarrow{\text{alkaline KMnO}_4} \text{COOH}$

($R$ is $1^\circ$ and $2^\circ$ alkyl)

(3) $\text{CH}_2\text{CH}_3\text{CH}_3 \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7, / H}_2\text{SO}_4 \text{ or } \text{Cr}_2\text{O}_3, 40\% H}_2\text{SO}_4 / 373K} \text{COOH}$

(4) Oxidation of alkyl side chair requires a benzylic hydrogen. Thus tert-butyl benzene (no benzylic hydrogen) is resistant to benzylic oxidation under vigorous conditions, benzene ring is affected

$\text{CH}_3 \xrightarrow{\text{alkaline KMnO}_4, \Delta} \text{H}_3\text{C} - \text{C} - \text{COOH}$

no $\text{H}$ at benzylic carbon.

(5) $\text{Br} \xrightarrow{\text{Mg \ ether}} \text{MgBr} \xrightarrow{(\text{i}) \text{CO}_2, (\text{ii}) \text{H}_2\text{O}^+} \text{COOH}$

(6) $\text{CN} + 2\text{H}_2\text{O} \xrightarrow{H^+} \text{COOH} + \text{NH}_4^+$

(7) $\text{benzyl chloride} \xrightarrow{\text{AlCl}_3, \text{H}_2\text{O}} \text{COOH}$

General properties of benzoic acid

(1) Slightly stronger acids than aliphatic acids
(2) Less soluble in water as compared to aliphatic acids and also less volatile
(3) m.p. of benzoic acid = 122°.
Preparation & Reactions of Aniline:

\[ \text{HCl} \rightarrow [\text{C}_6\text{H}_5\text{NH}_3]^+\text{Cl}^- \]

\[ \text{H}_2\text{SO}_4 \rightarrow [\text{C}_6\text{H}_5\text{NH}_3]^+\text{SO}_4^{2-} \]

\[ \text{HAuCl}_4 \rightarrow [\text{C}_6\text{H}_5\text{NH}_3]^+\text{AuCl}_4^- \]

\[ \text{H}_2\text{PtCl}_6 \rightarrow [\text{C}_6\text{H}_5\text{NH}_3]^+\text{PtCl}_6^{2-} \]

\[ \text{CH}_3\text{I} \rightarrow \text{C}_6\text{H}_5\text{NH}-(\text{CH}_3) \quad \text{CH}_3\text{I} \rightarrow \text{C}_6\text{H}_5\text{N}-(\text{CH}_3)_3 \text{I} \]

\[ \text{CH}_3\text{COCl} \rightarrow \text{C}_6\text{H}_5\text{NCOCH}_3 \]

\[ \text{C}_6\text{H}_5\text{COCl} \rightarrow \text{C}_6\text{H}_5\text{NCOCH}_6 \]

\[ \text{C}_6\text{H}_5\text{MgBr} \rightarrow \text{C}_6\text{H}_6 \]

\[ \text{C}_6\text{H}_5\text{SO}_2\text{Cl} \rightarrow \text{C}_6\text{H}_5-\text{SO}_2-\text{NH}-	ext{C}_6\text{H}_5 \]

\[ \text{COCl}_2 \rightarrow \text{C}_6\text{H}_5-\text{NH}-\text{C} \quad \text{NH}-	ext{C}_6\text{H}_5 \]

\[ \text{CS}_2 \rightarrow \text{C}_6\text{H}_5-\text{NH}-\text{C} \quad \text{NH}-	ext{C}_6\text{H}_5 \]

\[ \text{CS}_2/\text{HCl} \rightarrow \text{C}_6\text{H}_5-\text{N} = \text{C} = \text{S} \]

\[ \text{Na} \rightarrow \text{C}_6\text{H}_5\text{NaN} \]

\[ \text{C}_6\text{H}_5\text{CHO} \rightarrow \text{C}_6\text{H}_5\text{CH} = \text{N} - \text{C}_6\text{H}_5 \]

\[ \text{CHCl}_3/\text{KOH} \rightarrow \text{C}_6\text{H}_5\text{N}^+ = \text{C}^- \]

\[ \text{NaNO}_2/\text{HCl} \rightarrow \text{C}_6\text{H}_5\text{NCl} \]

\[ \text{O} \rightarrow 5^\circ \rightarrow \text{C}_6\text{H}_5\text{NH}_2 \]

\[ \text{Ni}/\text{H}_2 \rightarrow \text{C}_6\text{H}_5\text{NH}_2 \]

\[ \text{Na},\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4, \text{Na},\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4 \rightarrow \text{Aniline black} \]

\[ \text{Br}/\text{CS}_2 \rightarrow \text{NH}_2 + \text{NH}_3 \]

\[ \text{Br}/\text{H}_2\text{O} \rightarrow \text{O} \quad \text{m-Nitro Aniline} \]

\[ \text{HNO}_3/\text{H}_2\text{SO}_4 \rightarrow \text{O} \quad \text{o} \quad \text{p-Nitro Aniline} \]

(i) \text{CH}_3\text{COCl}

(ii) \text{HNO}_3/\text{H}_2\text{SO}_4

(iii) \text{H}_2\text{O}
Reactions of Benzenediazonium chloride:

\[ \text{H}_2\text{PO}_4 + \text{H}_2\text{O} / \text{Cu}^+ \rightarrow \text{C}_6\text{H}_5 + \text{N}_2 + \text{H}_3\text{PO}_4 + \text{HCl} \text{ (Deamination)} \]
\[ (\text{Hypophosphoric acid}) \]

\[ \text{C}_6\text{H}_6\text{OH}, \Delta \rightarrow \text{C}_6\text{H}_5 + \text{N}_2 + \text{HCl} + \text{CH}_2\text{CHO} \]
\[ (\text{Boiling dil. H}_2\text{SO}_4) \]

\[ \text{CuCl} / \text{HCl} \rightarrow \text{C}_6\text{H}_5\text{Cl} \text{ (Sandmeyer reaction)} \]

\[ \text{CuBr} / \text{HBr} \rightarrow \text{C}_6\text{H}_5\text{Br} \text{ (Sandmeyer reaction)} \]

\[ \text{Cu} / \text{HCl} \rightarrow \text{C}_6\text{H}_5\text{Cl} \text{ (Gattermann reaction)} \]

\[ \text{Cu} / \text{HBr} \rightarrow \text{C}_6\text{H}_5\text{Br} \text{ (Gattermann reaction)} \]

\[ \text{KCN} / \text{CuCN} \text{ or Cu powder} \rightarrow \text{C}_6\text{H}_5\text{CN} \]

\[ \text{Kl}, \Delta \rightarrow \text{C}_6\text{H}_5\text{I} + \text{N}_2 + \text{KCl} \]

\[ \text{HBF}_4^- \text{ or } -\text{HCl} \rightarrow \text{C}_6\text{H}_5\text{N}_2\text{BF}_4^- \text{ or } \text{HBF}_4^- \text{ or } -\text{HCl} \rightarrow \text{C}_6\text{H}_5\text{N}_2\text{BF}_4^- \text{ or } \text{HBF}_4^- \text{ or } -\text{HCl} \]
\[ \text{NaNO}_2 \text{ or Cu powder} \rightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{NaBF}_4 + \text{N}_2 \]

\[ \text{C}_6\text{H}_5\text{OH} / \text{NaOH} \rightarrow \text{C}_6\text{H}_5\text{H}_2 + \text{N}_2 + \text{NaCl} + \text{H}_2\text{O} \text{ (Gomberg reaction)} \]

\[ \text{PH } 9 \text{ to } 10, 273 \text{ to } 278 \text{ K} \text{ p–Hydroxyazobenzene} \]

\[ \text{PH } 4 \text{ to } 5, 273 \text{ to } 278 \text{ K} \text{ p–Aminoazobenzene} \text{ (yellow dye)} \]

\[ \text{SnCl}_2 / \text{HCl} \rightarrow \text{C}_6\text{H}_5\text{NHNH}_2\text{HCl} \]

\[ \text{Na}_2\text{SO}_3 / \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{NHNH}_2 \]

\[ \text{Zn} / \text{HCl} \rightarrow \text{[C}_6\text{H}_5\text{NHNH}_2], \text{Zn} / \text{HCl} \rightarrow \text{C}_6\text{H}_5\text{NH}_2 + \text{NH}_3 \]
Reduction in acidic medium with Sn and HCl → C₆H₅NH₂

+4(H) Na₂AsO₃/NaOH → C₂H₅–N=N–C₆H₅+3H₂O
Azoxybenzene

+8(H); Zn/NaOH/CH₃OH or LiAlH₄ → C₂H₅N=NO₂H₂+4H₂O
Azobenzene

+10[H]; Zn/NaOH → C₆H₅–NH–NH–C₆H₅+4H₂O
Hydrazobenzene

Electrolytic reduction (Weakly acidic medium) → C₆H₅NH₂
Aniline

Electrolytic reduction (Strongly acidic medium) → NHOH
Phenyl hydroxylamine

Rearrangement → NH₂
p-aminophenol

C₆H₅–NO₂

H₂/Ni or NiPd (Weakly acidic medium) → C₆H₅NH₃⁺ (Catalytic reduction)
Aniline

HNO₃/363 K → m-Dinitrobenzene

Br₂/Fe → m-Bromonitrobenzene

Conc. H₂SO₄ → m-Nitrosulphonic acid
PART - I: OBJECTIVE QUESTIONS

* Marked Questions are having more than one correct option.

Section (A): Aromatic Electrophilic Substitution Reaction (ArS₂)

A-1.* Which of the following species should be aromatic?

- (A) ![S₆C₆]
- (B) ![C₆⁺]
- (C) ![O₆]
- (D) ![10 Annulene]

A-2.* Using Huckel rule, predict which of the following hydrocarbons will exhibit aromatic stabilisation:

- (A) ![C₆⁺]
- (B) ![C₆⁻]
- (C) ![C₆⁺]
- (D) ![C₆⁻]

A-3. Arrange the following compounds in the order of decreasing reactivity towards electrophilic substitution reaction.

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

A-4. The correct order towards electrophilic substitution reaction is

- (A) iv > iii > ii > i
- (B) i > ii > iii > iv
- (C) iii > ii > i > iv
- (D) iii > iv > i > ii

A-5. Give the order of decreasing reactivity towards an electrophile.

- (A) 2 > 3 > 1 > 5 > 4
- (B) 3 > 1 > 2 > 5 > 4
- (C) 5 > 4 > 2 > 3 > 1
- (D) 1 > 5 > 2 > 3 > 4

A-6. Give the order of decreasing reactivity towards an electrophile.

- (A) 1 > 2 > 3 > 4
- (B) 4 > 1 > 3 > 2
- (C) 3 > 4 > 1 > 2
- (D) 3 > 2 > 4 > 1
A-7. * Friedel craft acylation is/are not observed in

(A) \( \text{ } \)  \[ \text{ } \]  \( \text{ } \)  \[ \text{ } \]
(B) \( \text{CH}_3 \) \[ \text{ } \]  \( \text{CH}_2 \) \[ \text{ } \]
(C) \( \text{NH}_2 \) \[ \text{ } \]  \( \text{NO}_2 \) \[ \text{ } \]
(D) \( \text{ } \)  \[ \text{ } \]  \( \text{ } \)  \[ \text{ } \]

A-8. Which of the following organic chlorides will not give a Friedel-Craft alkylation product when heated with benzene and \( \text{AlCl}_3 \)?

(A) \( \text{CH}_3\text{CCI} \)  \( \text{(CH}_2\text{CH}_2\text{Cl} \)  \( \text{CH}_3\text{CH}_2\text{Cl} \)  \( \text{CH}_2 = \text{CHCl} \)

A-9. The major product obtained in the following is:

\[ \text{Ph-CH-CH-Ph} \xrightarrow{\text{Br}_2/\text{Fe}} \]

(A) \( \text{Br-CH-CH-Ph} \)  \( \text{Br} \)  \( \text{Br} \)
(B) \( \text{Br-CH-CH-Ph} \)
(C) \( \text{Br-CH-CH-Ph} \)
(D) \( \text{Br-CH-CH-Ph} \)

A-10. The nitration will mainly take place at position

(A) 1  \( \text{(B) 2} \)  \( \text{(C) 3} \)

(A)  \( \text{(B) 2} \)  \( \text{(C) 3} \)

A-11. Identify P

\[ \text{Ph-C-CH}_3 \xrightarrow{\text{conc. HNO}_3/\text{H}_2\text{SO}_4} \]

(A) \( \text{Ph-C-CH}_3 \)  \( \text{NO}_2 \)
(B) \( \text{Ph-C-CH}_3 \)  \( \text{NO}_2 \)
(C) \( \text{Ph-C-CH}_3 \)  \( \text{NO}_2 \)
(D) None of these
A-12. Nitration of the following compound \( \text{CH}_3-\text{N}=\text{O} \) gives:

- (A) \( \text{CH}_3-\text{N}=\text{O} \text{NO}_2 \)
- (B) \( \text{CH}_3-\text{N}=\text{O} \text{NO}_2 \)
- (C) \( \text{CH}_3-\text{N}=\text{O} \text{NO}_2 \)
- (D) \( \text{CH}_3-\text{N}=\text{O} \text{NO}_2 \)

A-13. \( \text{CH}_2-\text{C}=\text{O} \xrightarrow{\text{Br}_2/\text{Fe}} \text{CH}_2\text{Br+HO-CH}_2\text{Br} \)

- (A) \( \text{CH}_2\text{Br+HO-CH}_2\text{Br} \)
- (B) \( \text{CH}_2\text{OH}+\text{Br}_2 \)
- (C) \( \text{CH}_2\text{OH}+\text{Br}_2 \)
- (D) \( \text{HO-CH}_2\text{CH}_2\text{Br} \)

A-14. \( \text{O} \xrightarrow{\text{Br}_2/\text{Fe}} (1 \text{ eq.)} \)

- (A) \( \text{O} \)
- (B) \( \text{O} \)
- (C) \( \text{O} \)
- (D) \( \text{O} \)

A-15. \( \text{SO}_2\text{H} \xrightarrow{(i) \text{Cl}_2/\text{Fe}} \xrightarrow{(ii) \text{H}_2\text{O, A, H}^+} \text{Identify the product} \)

- (A) \( \text{Cl} \text{SO}_2\text{H} \)
- (B) \( \text{Br} \text{Cl} \text{SO}_2\text{H} \)
- (C) \( \text{Br} \text{Cl} \text{SO}_2\text{H} \)
- (D) \( \text{Br} \text{Cl} \text{SO}_2\text{H} \)
A-16

\[
(\text{CH}_3)_2C = CH_2 + H^+ \xrightarrow{\text{HCl}} (\text{CH}_3)_2C = CH_2
\]

\[
\begin{array}{cccc}
\text{A} & \text{B} & \text{C} & \text{D} \\
\begin{array}{c}
\text{OCH}_3 \\
\text{C(CH}_3)_2 \\
\text{CH}_3 \\
\end{array} & \\
\begin{array}{c}
\text{OCH}_3 \\
\text{C(CH}_3)_2 \\
\text{CH}_3 \\
\end{array} & \\
\begin{array}{c}
\text{OCH}_3 - \text{CH(CH}_3)_2 \\
\text{CH}_3 \\
\end{array} & \\
\begin{array}{c}
\text{O} - \text{C} - \text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\end{array}
\]

A-17

\[
\begin{array}{c}
\text{C} + \text{CH}_2 = \text{CHCH}_2\text{Cl} \xrightarrow{\text{AlCl}_3} \xrightarrow{\text{BH}_3/\text{THF}} \xrightarrow{\text{HF, } \Delta} \text{P}
\end{array}
\]

The compound 'P' is:

(A) \[
\begin{array}{c}
\text{CH}_2-\text{CH}=\text{CH}_2
\end{array}
\]

(B) \[
\begin{array}{c}
\text{CH}_2-\text{CH}-\text{CH}_2-\text{OH}
\end{array}
\]

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

(D) \[
\begin{array}{c}
\text{C}
\end{array}
\]

A-18.

The end product of following reaction is

\[
\begin{array}{c}
\text{C} \xrightarrow{\text{CH}_3\text{Cl/AlCl}_3} \xrightarrow{\text{NBS}} \xrightarrow{\text{HO}^\circ} \xrightarrow{\text{MnO}_2/\Delta} \text{S}
\end{array}
\]

(A) Benzyl alcohol

(B) Benzene carbaldehyde

(C) Benzoic acid

(D) Benzenaphene

A-19.

\[
\begin{array}{c}
\text{o-HOOC} - \text{C}_6\text{H}_4 - \text{CH}_2 - \text{C}_6\text{H}_5 \xrightarrow{\text{SOCl}_2} \xrightarrow{\text{anhdyrous AlCl}_3} \xrightarrow{\text{Zn-Hg/HC}I} \text{Z}
\end{array}
\]

Identify 'Z':

(A) \[
\begin{array}{c}
\text{C}
\end{array}
\]

(B) \[
\begin{array}{c}
\text{C}
\end{array}
\]

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

(D) \[
\begin{array}{c}
\text{C}
\end{array}
\]

A-20.

\[
\begin{array}{c}
\text{C} \xrightarrow{\text{AlCl}_3} \xrightarrow{\text{Zn-Hg/Conc.HCl}} \xrightarrow{\text{AlCl}_3} \text{C}
\end{array}
\]

The product C is:

(A) \[
\begin{array}{c}
\text{C}
\end{array}
\]

(B) \[
\begin{array}{c}
\text{C}
\end{array}
\]

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

(D) \[
\begin{array}{c}
\text{C}
\end{array}
\]
A-21. \[
\begin{align*}
\text{Cl}_2 & / \text{hv} \ (\text{excess}) \rightarrow (X) \xrightarrow{(i)\text{aq. NaOH (excess)}} (Y) \\
\end{align*}
\]

The product ‘Y’ is:

(A) ![Image of product A]  
(B) ![Image of product B]  
(C) ![Image of product C]  
(D) ![Image of product D]

A-22.* Select the reactions in which the correct orientations have been mentioned in the major products.

(A) \[
\begin{align*}
\text{Cl} & \xrightarrow{\text{HNO}_3 + \text{H}_2\text{SO}_4} \text{NO}_2
\end{align*}
\]

(B) \[
\begin{align*}
\text{NHCOCH}_3 & \xrightarrow{\text{Br}_2 / \text{Fe}^{3+}} \text{Br} \xrightarrow{\text{Br}_2 / \text{Br}_2} \text{Br}
\end{align*}
\]

(C) \[
\begin{align*}
\text{CHO} & \xrightarrow{\text{Br}_2 / \text{Fe}^{3+}} \text{CHO} \xrightarrow{\text{Br}_2 / \text{Br}_2} \text{CHO}
\end{align*}
\]

(D) ![Mononitration reaction]

Section (B) : Phenol

B-1.* In which of the following reactions phenol is obtained:

(A) \[
\begin{align*}
\text{OH} & \xrightarrow{\text{NaOH/CaO}} \text{COOH}
\end{align*}
\]

(B) \[
\begin{align*}
\text{MgBr} & \xrightarrow{\text{H}_2\text{O}^+}
\end{align*}
\]

(C) \[
\begin{align*}
\text{Cl} & \xrightarrow{\text{NaOH \ 633 K, 300Atm}} \text{N}_2\text{Cl}
\end{align*}
\]

(D) \[
\begin{align*}
\text{H}_2\text{O} & \xrightarrow{\Delta}
\end{align*}
\]
B-2. The major products of the following reaction are

\[ \text{Ph} - \text{C} - \text{O} - \text{O} - \text{H} \xrightarrow{\text{H}_3\text{O}^+ / \Delta} \text{Products} \]

(A) \text{PhOH}  \hspace{1cm} (B) \text{Ph-C-CH}_3  \hspace{1cm} (C) \text{CH}_3\text{CHO}  \hspace{1cm} (D) \text{CH}_3\text{CH}_2\text{OH}

B-3. Identify the product in the following reaction.

\[ \text{O}_2\text{N-} - \text{C-} \text{C}_6\text{H}_5 - \text{O} - \text{O} - \text{H} \xrightarrow{\text{H}_3\text{O}^+} \]

(A) \text{O}_2\text{N} - \text{C-} \text{C}_6\text{H}_5 + \text{C}_6\text{H}_5\text{OH}  \hspace{1cm} (B) \text{O}_2\text{N-} - \text{C-} \text{C}_6\text{H}_5

(C) \text{O}_2\text{N} - \text{C-} \text{C}_6\text{H}_5 + \text{C}_6\text{H}_5\text{OH}  \hspace{1cm} (D) \text{C}

B-4. \text{Ph} + \text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow{\text{H}_3\text{PO}_4 / \Delta} \text{A} \xrightarrow{(1) \text{O}_2, \Delta} \text{B} + \text{C}

The products B & C are respectively

(A) Phenol & acetic acid  \hspace{1cm} (B) Phenol & acetaldehyde
(C) Benzoic acid & acetone  \hspace{1cm} (D) Phenol & acetone

B-5. Identify the product in following reaction

\[ \text{OH} \xrightarrow{\text{D}_2\text{SO}_4 / \Delta} \text{D}_2\text{O} \]

(A) \text{D}\text{-} \text{D}\text{-} \text{D}  \hspace{1cm} (B) \text{D}\text{-} \text{D}\text{-} \text{D}  \hspace{1cm} (C) \text{D}\text{-} \text{D}\text{-} \text{D}  \hspace{1cm} (D) \text{D}\text{-} \text{D}\text{-} \text{D}

B-6. \text{Ph-OH} \xrightarrow{\text{Br}_2, \text{Fe}} \text{P (Major)}

P is:

(A) \text{OH} \hspace{1cm} \text{Br} \hspace{1cm} \text{CHO}  \hspace{1cm} (B) \text{OH} \hspace{1cm} \text{Br} \hspace{1cm} \text{CHO}  \hspace{1cm} (C) \text{OH} \hspace{1cm} \text{Br} \hspace{1cm} \text{CHO}  \hspace{1cm} (D) \text{OH} \hspace{1cm} \text{Br} \hspace{1cm} \text{CHO}
B-7. The product (Y) of the following sequence of reactions would be:

\[
\begin{align*}
\text{Me} & \quad \text{OH} \\
\downarrow & \quad \downarrow \\
\text{H}_2\text{C} & \quad \text{CH} - \text{CH} = \text{CH}_2 \\
\text{H}_2\text{C} & \quad \text{OH} \\
\end{align*}
\]

\[
\begin{align*}
\text{Me} & \quad \text{CHO} \\
\downarrow & \quad \downarrow \\
\text{H}_2\text{C} & \quad \text{CH} - \text{CH} = \text{CH}_2 \\
\text{H}_2\text{C} & \quad \text{OH} \\
\end{align*}
\]

\[
\begin{align*}
\text{Me} & \quad \text{Br} \\
\downarrow & \quad \downarrow \\
\text{H}_2\text{C} & \quad \text{CHO} \\
\text{H}_2\text{C} & \quad \text{Br} \\
\end{align*}
\]

\[
\begin{align*}
\text{Me} & \quad \text{OH} \\
\downarrow & \quad \downarrow \\
\text{H}_2\text{C} & \quad \text{CHO} \\
\text{H}_2\text{C} & \quad \text{Br} \\
\end{align*}
\]

B-8. Identify 'Z' in the given sequence of reaction

\[
\begin{align*}
\text{OH} & \quad \downarrow \quad \downarrow \quad \downarrow \quad \downarrow \quad \downarrow \\
1. \text{NaOH} & \quad \text{Cl} - \text{CH}_2 - \text{COOH} \\
2. \text{Cl} - \text{CH}_2 - \text{COOH} & \quad \text{SOCl}_2 \\
\text{Y} & \quad \text{AlCl}_3 \\
\end{align*}
\]

B-9. Give the product of the following reactions

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{O} - \text{CH}_2 - \text{CH} = \text{CH}_2 \\
\Delta & \\
\text{H}_2\text{C} & \quad \text{OH} \\
\text{CH}_2 - \text{CH} = \text{CH}_2 \\
\text{H}_2\text{C} & \quad \text{OH} \\
\text{CH}_2 - \text{CH} = \text{CH}_2 \\
\text{H}_2\text{C} & \quad \text{OH} \\
\text{CH}_2 - \text{CH} = \text{CH}_2 \\
\end{align*}
\]

B-10.*

\[
\begin{align*}
\text{O} - \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_3 \\
\Delta & \quad \downarrow \\
\text{P} & \quad \text{Q} + \text{R} \\
\text{Q} & \quad \text{AlCl}_3 \\
\text{R} & \quad \text{AlCl}_3 \\
\end{align*}
\]

(A) \text{P} is

(B) \text{Q} may be

(C) \text{R} may be HCHO

(D) No reaction
Section (C) : Aniline

C-1. The product ‘X’ is:

(A) \( \text{H}_2\text{O} \) (B) \( \text{NH}_2 \) (C) \( \text{NO}_2 \) (D) \( \text{O} \) – \( \text{H} \) – \( \text{NH}_2 \)

C-2. The major product of the reaction between m-dinitrobenzene with \( \text{NH}_4\text{HS} \) is:

(A) \( \text{H}_2\text{O} \) (B) \( \text{NH}_2 \) (C) \( \text{NH}_2 \) (D) \( \text{H}_2\text{N} \cdot \text{NH}_2 \)

C-3. \( \text{H}_2\text{O} \) (A) \( \text{OH} \) (B) \( \text{N}^{+} \text{Cl}^{-} \) (C) \( \text{N}^{+} \text{Cl}^{-} \) (D) \( \text{N}^{+} \text{H}^{-} \)

C-4. The product of the following reaction is:

(A) \( \text{NO}_2 \) (B) \( \text{Cl} \) (C) \( \text{NH}_2 \) (D) \( \text{NO}_2 \)

C-5. In the reaction sequence

(A) \( \text{H}_2\text{O} \) (B) \( \text{NH}_2 \) (C) \( \text{F} \) (D) \( \text{NH} \cdot \text{NH} \)

(X) will be:

(A) \( \text{NO}_2 \) (B) \( \text{NH}_2 \) (C) \( \text{F} \) (D) \( \text{NH} \cdot \text{NH} \)
C-6. \[
\text{Ph – NH}_2 \xrightarrow{\text{HNO}_3 / 0^\circ C} A \xrightarrow{\text{HF / BF}_3} B \xrightarrow{\Delta} C, \text{ C is.}
\]

\[(A) \text{ Ph – N}^+ \equiv \text{N BF}_4^-
\]
\[(B) \text{ Ph – F}
\]
\[(C) \text{ F- Ph – F}
\]
\[(D) \text{ Ph – F}
\]

C-7. In the given reaction sequence

\[
\begin{align*}
\text{X} & \xrightarrow{\text{Br}_2 / \text{H}_2\text{O}} \text{Y} & \xrightarrow{\text{NaNO}_2 / \text{HCl}} \text{Z} & \xrightarrow{\Delta} \text{C}_2\text{H}_3\text{OH}
\end{align*}
\]

[X] will be:

\[(A) \text{ Benzoic acid} \quad (B) \text{ Salicylic acid} \quad (C) \text{ Phenol} \quad (D) \text{ Aniline}
\]

C-8. An aromatic electrophilic substitution reaction with NaNO\(_2 / \text{HCl}\) will be observed in:

\[
\begin{align*}
\text{I} & \quad \text{II} & \quad \text{III} & \quad \text{IV}
\end{align*}
\]

(A) All

(B) I, III

(C) II, III

(D) I, II, III

C-9. \[
\text{Ph}^+ - \text{N}_2 \xrightarrow{(\text{pH}=9-11)} \text{X} (\text{major product})
\]

X - will be

\[
\begin{align*}
(A) & \quad (B) & \quad (C) & \quad (D)
\end{align*}
\]

C-10. \[
\text{Ph}^+ - \text{N}_2 \xrightarrow{\text{Ph}=4-7} \text{X} (\text{major product}) \text{ X will be -}
\]

\[
\begin{align*}
(A) & \quad (B) & \quad (C) & \quad (D)
\end{align*}
\]
PART - II : MISLLANEIOUS QUESTIONS

MATCH THE COLUMN
1. Match the following :

<table>
<thead>
<tr>
<th>Group</th>
<th>Nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>–CH=CHCOOH</td>
</tr>
<tr>
<td>(B)</td>
<td>–CCl₃</td>
</tr>
<tr>
<td>(C)</td>
<td>–OH</td>
</tr>
<tr>
<td>(D)</td>
<td>–NO₂</td>
</tr>
<tr>
<td>(p)</td>
<td>Activating</td>
</tr>
<tr>
<td>(q)</td>
<td>deactivating</td>
</tr>
<tr>
<td>(r)</td>
<td>o,p-directing</td>
</tr>
<tr>
<td>(s)</td>
<td>m-directing</td>
</tr>
</tbody>
</table>

2. Match following column (I) with column (II) :

<table>
<thead>
<tr>
<th>Column-I (Reactants)</th>
<th>Column-II (Products)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) OH</td>
<td>(p) CH₃OH</td>
</tr>
<tr>
<td>(B) NH₂</td>
<td>(q) OCH₃OH</td>
</tr>
<tr>
<td>(C) OH</td>
<td>(r) OH</td>
</tr>
<tr>
<td>(D) Br</td>
<td>(s) OCH₃Br</td>
</tr>
</tbody>
</table>

(A) OH → (1) Br/CS₂ → (2) (CH₃)₂SO/OH⁻
(B) NH₂ → (1) NaNO₃/HCl(aq) → (2) Δ
(C) OH → (1) CHBr/OH⁻ → (2) H₂O → (3) NaBH₄
(D) Br → (1) Br/Fe → (2) Mg/Ether → (3) O₂ → (4) H₂O
3. Match the column – I with reaction mechanism mentioned in Column – II

<table>
<thead>
<tr>
<th>Column – I</th>
<th>Column – II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) <img src="image" alt="Reagent" /> \xrightarrow{Br_2/Fe}</td>
<td>(p) Electrophilic substitution</td>
</tr>
<tr>
<td>(B) <img src="image" alt="Reagent" /> \xrightarrow{Cl_2/Fe}</td>
<td>(q) Electrophilic addition</td>
</tr>
<tr>
<td>(C) <img src="image" alt="Reagent" /> \xrightarrow{HBr/RO_2}</td>
<td>(r) Nucleophilic substitution</td>
</tr>
<tr>
<td>(D) <img src="image" alt="Reagent" /> \xrightarrow{CH_3NH_2, \Delta}</td>
<td>(s) Free Radical reaction</td>
</tr>
</tbody>
</table>

4. Match the column:

**Column A**

- (A) ![Reagent](image) + CrO_3 in CH_3COOH \xrightarrow{?} (P) Tropylium ion
- (B) ![Reagent](image) + Ph_3C+ \xrightarrow{?} (Q) Benzaldehyde
- (C) ![Reagent](image) + n-Pr Br + ZnCl_2 \xrightarrow{?} (R) Two types of products
- (D) ![Reagent](image) + Br_2 \xrightarrow{?} (S) Cumene
5. Match the following:

<table>
<thead>
<tr>
<th>Column I</th>
<th>Column II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) CO₂↑ is evolved from</td>
<td>(P) <img src="image1.png" alt="Image" /></td>
</tr>
<tr>
<td>NaHCO₃ by the reaction</td>
<td></td>
</tr>
<tr>
<td>(B) Libermann nitroso test is given by</td>
<td>(Q) <img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>(C) Compounds gives yellow oily</td>
<td>(R) <img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>liquid on reaction with NaNO₂ + HCl</td>
<td></td>
</tr>
<tr>
<td>(D) Compounds evolve a colourless gas on reaction with active metals</td>
<td>(S) <img src="image4.png" alt="Image" /></td>
</tr>
</tbody>
</table>

6. Match the following:

<table>
<thead>
<tr>
<th>Column I</th>
<th>Column II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Compounds which on reaction with neutral FeCl₃ gives violet/Blue colour are</td>
<td>(P) <img src="image5.png" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>(B) Compounds which on reaction with NaO₂S-N₂Cl gives para red dye.</td>
<td>(Q) <img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>(C) Compounds which do not give yellow ppt. On reaction with NaOI</td>
<td>(R) <img src="image7.png" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>(D) Compound which have maximum % of enol form</td>
<td>(S) <img src="image8.png" alt="Image" /></td>
</tr>
</tbody>
</table>
7. Match the following:

<table>
<thead>
<tr>
<th>Column I</th>
<th>Column II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Compounds which gives Diels Elder's reaction in greater extent with dienophile</td>
<td>(P) <img src="image1" alt="Diagram" /></td>
</tr>
<tr>
<td>(B) Compounds which undergoes ArSN reaction are</td>
<td>(Q) <img src="image2" alt="Diagram" /></td>
</tr>
<tr>
<td>(C) Compound which has highest aromatic characters</td>
<td>(R) <img src="image3" alt="Diagram" /></td>
</tr>
<tr>
<td>(D) Strongest Base</td>
<td>(S) <img src="image4" alt="Diagram" /></td>
</tr>
</tbody>
</table>

**ASSERTION / REASONING**

**DIRECTIONS:**

Each question has 4 choices (A), (B), (C) and (D) out of which ONLY ONE is correct.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(C) Statement-1 is True, Statement-2 is False.

(D) Statement-1 is False, Statement-2 is True.

8. **Statement-1**: Cyclopentadiene reacts with Na metal and liberates hydrogen gas.

**Statement-2**: It has acidic hydrogen and cyclopentadienyl anion is aromatic in nature.

9. **Statement-1**: Nitration of benzene and hexadeuterobenzene occurs almost at the same rate.

**Statement-2**: Cleavage of C – H bond takes faster than C – D bond.

10. **Statement-1**:

    ![Diagram](image5)

**Statement-2**: Reaction ‘A’ is electrophilic substitution and reaction ‘B’ is nucleophilic substitution.

11. **Statement-1**: Phenol is more reactive than C₆H₆ towards electrophilic substitution reaction.

**Statement-2**: Phenoxide ion is more resonance stabilised.

12. **Statement-1**: Halogens are deactivating groups but have ortho-para directing nature.

**Statement-2**: Deactivating nature of halogen can be explain by – I & ortho-para directing nature can be explain by stability of intermediate by + M.

13. **Statement-1**: Nitrobenzene, gives metanitrotoluene on reaction with CH₃Cl/AlCl₃.

**Statement-2**: Nitro group is meta directing

14. **Statement-1**: Diphenyl can not be prepared by following reacton .

    ![Diagram](image6)

**Statement-2**: Phenyl chloride is very weakly ionised by AlCl₃ because Ph⁺ carbocation is very less stable.

15. **Statement-1**: Phenol decolourises bromine water

**Statement-2**: Phenol has high degree of unsaturation
TRUE I FALSE
16. Phenols predominantly exist in enolic form
17. Reaction of Br₂ water with phenol gives o- and p-bromophenols

FILL IN THE BLANKS
18. In sulphonation of benzene by cone. H₂SO₄, electrophile formed is.............
19. Benzene sulphonyl chloride is called ............ and is a reagent used in the separation of mixture of.............
20. Syndets are generally.............
21. Main constituent of sulphadrug is.............
22. Carbylation reaction is given by.............amine
23. Benzene diazonium chloride can be converted to chlorobenzene by.............
24. Benzene diazonium chloride reacts with H₃PO₄ forming .............as the main aromatic compound.
25. Arene diazonium ions act as weak.............in aromatic Sₖ.
26. Cannizzaro reaction is a.............transfer reaction.
27. Benzaldehyde reacts with aniline forming.............
28. Carbonyl group is.............and.............directing group.
29. Formation of addition product in benzene nucleus is not favourable since it leads to.............in potential energy and thus.............instability.
30. In Friedel-Crafts reaction, anhydrous AlCl₃ is a.............and helps in the formation of.............
31. Mixture of conc. HNO₃ and conc. H₂SO₄ helps in the formation of.............
32. NBS is a .............for replacement of .............or .............hydrogen.
33. Benzyl radical or carbocation is stabilised by.............
34. The cyclic system must contain (4n + 2)π-electrons used in delocalisation including lone pair. This is called.............
35. Cyclopentadienyl anion is.............and cyclobutadiene is
36. Halogen atoms are.............and.............directing.
37. Phenol is.............since deprotonation forms resonance stabilised.............ion.
PART - I : MIXED OBJECTIVE

Single Correct Answer Type

1. Benzene is a resonance hybrid mainly of two Kekule structures. Hence:
(A) Half of the molecules correspond to one structure, and half of the second structure
(B) At low temperatures benzene can be separated into two structures
(C) Two structures make equal contribution to resonance hybrid
(D) An individual benzene molecule changes back and forth between two structures

2. Which of the following is/are fitting reaction:
(A) \( \text{C}_6\text{H}_5\text{I} + 2\text{Na} + \text{ICH}_3 \rightarrow \text{C}_6\text{H}_5\text{–CH}_3 \)
(B) \( \text{C}_6\text{H}_5\text{I} + 2\text{Na} + \text{IC}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{–C}_6\text{H}_5 \)
(C) \( \text{CH}_3\text{J} + 2\text{Na} + \text{ICH}_3 \rightarrow \text{CH}_3\text{–CH}_3 \)
(D) \( \text{C}_6\text{H}_5\text{CH}_2\text{–Cl} + 2\text{Na} + \text{ClCH}_2\text{C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{–CH}_2\text{C}_6\text{H}_5 \)

3. Which of the following gives Friedel Crafts reaction?

4. Which of the following will undergo nitration slow than benzene?

5. Which of the following is ortho-para directing group?

6. Which of the following statements is true?
(A) Ortho-and para-directing groups increase electron density at ortho-and para-positions
(B) Meta-directing groups increase electron density at meta-position
(C) Meta-directing groups decrease electron density at meta-position
(D) Ortho-and para-directing groups decrease electron density at meta-position

7. Amongst the following, the moderately activating group is
(A) \( –\text{NHR} \)
(B) \( –\text{NHCOCH}_3 \)
(C) \( –\text{NR}_2 \)
(D) \( –\text{CH}_3 \)

8. If meta-nitroaniline is chlorinated, the major product is:

9. An aromatic compound of molecular formula \( \text{C}_6\text{H}_4\text{Br}_2 \) was nitrated when three isomers of formula \( \text{C}_6\text{H}_3\text{Br}_2\text{NO}_2 \) were obtained. The original compound is:
(A) \( \text{o-dibromobenzene} \)
(B) \( \text{m-dibromobenzene} \)
(C) \( \text{p-dibromobenzene} \)
(D) None of these
10. Which of the following carbocations is expected to be most stable?

(A) ![Image of carbocation A]
(B) ![Image of carbocation B]
(C) ![Image of carbocation C]
(D) ![Image of carbocation D]

11. Which of the following carbocations is expected to be most stable?

(A) ![Image of carbocation A]
(B) ![Image of carbocation B]
(C) ![Image of carbocation C]
(D) ![Image of carbocation D]

12. The number of disubstituted products of benzene is

(A) 2  (B) 3  (C) 4  (D) 5

13. Which of the following species is expected to have maximum enthalpy in an electrophilic aromatic substitution reaction?

(I) ![Image of reaction I]
(II) ![Image of reaction II]
(III) ![Image of reaction III]
(IV) ![Image of reaction IV]
(V) ![Image of reaction V]

(A) Species (II)  (B) Species (III)  (C) Species (IV)  (D) Species (V)

14. For the electrophilic substitution reaction involving nitration, which of the following sequence regarding the rate of reaction is true?

(A) \( k_{C_6H_6} > k_{C_6D_6} > k_{C_6T_6} \)
(B) \( k_{C_6H_6} < k_{C_6D_6} < k_{C_6T_6} \)
(C) \( k_{C_6H_6} = k_{C_6D_6} = k_{C_6T_6} \)
(D) \( k_{C_6H_6} > k_{C_6D_6} < k_{C_6T_6} \)

15. For the electrophilic substitution reaction involving sulphonation, which of the following sequence regarding the rate of reaction is true?

(A) \( k_{C_6H_6} > k_{C_6D_6} > k_{C_6T_6} \)
(B) \( k_{C_6H_6} < k_{C_6D_6} < k_{C_6T_6} \)
(C) \( k_{C_6H_6} = k_{C_6D_6} = k_{C_6T_6} \)
(D) \( k_{C_6H_6} > k_{C_6D_6} < k_{C_6T_6} \)

16. The order of relative reactivity of the given halides towards \( S_N^1 \) reaction is

(A) benzylchloride > p-methoxybenzylchloride > p-nitrobenzylchloride
(B) p-methoxybenzylchloride > benzylchloride > p-nitrobenzylchloride
(C) p-methoxybenzylchloride > p-nitrobenzylchloride > benzylchloride
(D) benzylchloride > p-nitrobenzylchloride > p-methoxybenzylchloride

More than one choice type

17. Which of the following will show aromatic character:

(A) ![Image of compound A]
(B) ![Image of compound B]
(C) ![Image of compound C]
(D) ![Image of compound D]

18. Which aromatic compound is obtained when n-octane undergoes catalytic hydroforming:

(A) ethyl benzene  (B) m-Xylene  (C) o-Xylene  (D) p-Xylene
19. Benzoic acid may be prepared by the oxidation of:

- (A) CH₂CH₃
- (B) CH₂OH
- (C) COCH₃
- (D) OH

30. In which of the following reaction t-butylbenzene is formed:

- (A) Benzene + iso-butyl chloride, AlCl₃
- (B) Benzene + (CH₃)₂C = CH₂ → BF₃-HF
- (C) Benzene + t-butyl alcohol → H₂SO₄
- (D) Benzene + (CH₃)₂C = CH₂ → AlCl₃

21. Cl → NaOH H₂O → Product is:

- (A) OH
- (B) OH
- (C) Cl
- (D) Cl

22. Which of the following reactions of benzene proves the presence of three carbon–carbon double bonds in it:

- (A) Formation of a triozonide
- (B) Hydrogenation of benzene to cyclohexane
- (C) Formation of C₆H₅Cl by addition of chlorine
- (D) Formation of nitrobenzene on heating benzene with a mixture of concentrated nitric acid and sulphuric acid

23. Electrophile NO₂⁺ attacks the following in which cases NO₂⁺ will be at meta position:

- (A) CCl₃
- (B) NO₂
- (C) NMe₃
- (D) O³⁻

24. The reaction of replacement of a hydrogen atom in benzene by alkyl group can be brought about with the following reagents:

- (A) Alkyl chloride and AlCl₃
- (B) Alkene and AlCl₃
- (C) Alkanol and alkali
- (D) Alkanol and acid

25. Which of the following statements is correct:

- (A) Bromination of toluene occurs faster than that of benzene
- (B) Nitration of toluene is faster than that of ethylbenzene
- (C) The bromonium ion is a good nucleophile
- (D) Effective nitrating agent is nitrate ion

26. Electrophilic substitution in cinnamic acid will take place at:

- (A) Ortho-position
- (B) Para-position
- (C) Meta-position
- (D) On side chain

27. Which of the following can be used in Friedel Crafts reaction?

- (A) Cl
- (B) CH₂=CH–Cl
- (C) CH₃CH₂Cl
- (D) CH₂=CH–CH₂–Cl
28. The good method for converting benzene into propyl benzene is:
   (A) \( \text{C}_6\text{H}_6 + \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{Anhyd. AlCl}_3 \)
   (B) \( \text{C}_6\text{H}_6 + \text{CH}_3\text{CH}_2\text{COCl} + \text{Anhyd. AlCl}_3 \) and then treatment with \( \text{Zn/Hg/HCl} \)
   (C) \( \text{C}_6\text{H}_6 + \text{CH}_3\text{CH}_2\text{COCl} + \text{Anhyd. AlCl}_3 \) and then treatment with \( \text{H}_2\text{Ni} \)
   (D) \( \text{C}_6\text{H}_6 + \text{Anhyd. AlCl}_3 + \text{cyclopropane} \)

29. Which of the following statements is/are not true?
   (A) All ortho-para directing groups activates the ring
   (B) All ortho-para directing groups except halogens activate the ring
   (C) All meta-directing groups have \( \pi \)-bond on the atom directly attached to the ring
   (D) All meta directing groups are deactivating.

30. Which of the following compounds can be classified as aromatic?
   (A) 1, 2, 3-Triphenylcyclopropenium cation
   (B) Cyclooctatetraenyl dianion
   (C) Azulene
   (D) 10-Azulene

31. The structure of the compound that gives a tribromo derivative on treatment with bromine water is:
   (A) \[
   \begin{array}{c}
   \text{CH}_3 \\
   \text{OH}
   \end{array}
   \]
   (B) \[
   \begin{array}{c}
   \text{CH}_3 \\
   \text{OH}
   \end{array}
   \]
   (C) \[
   \begin{array}{c}
   \text{SO}_2\text{H} \\
   \text{OH}
   \end{array}
   \]
   (D) \[
   \begin{array}{c}
   \text{COOH} \\
   \text{OH}
   \end{array}
   \]

32. False statement is / are:
   (A) Although benzene contains three double bonds, normally it does not undergo addition reaction.
   (B) \( \text{m-ClBrC}_6\text{H}_4\text{Br} \) is an isomer of \( \text{m-BrClC}_6\text{H}_4\text{Br} \).
   (C) In benzene, carbon uses all the three \( p \) orbitals for hybridization.
   (D) An electron donating substituent in benzene orients the incoming electrophilic group to the meta position.

33. Of the species \( \text{PhSH}, \text{PhSR}, \text{PhS}^- \text{OR} \) the meta-substituted product is obtained from:
   (A) \( \text{PhSR} \)
   (B) \( \text{PhSR} \)
   (C) \( \text{PhSR} \)
   (D) \( \text{PhS}^- \text{OR} \)

---

**PART - II : SUBJECTIVE QUESTIONS**

1. Arrange the following in descending order of their reactivity with an electrophile.
   (I) (II) (III) (IV)
   (a) \[
   \begin{array}{c}
   \text{Cl} \\
   \text{(I)}
   \end{array}
   \]
   (b) \[
   \begin{array}{c}
   \text{NO}_2 \\
   \text{(II)}
   \end{array}
   \]
   \[
   \begin{array}{c}
   \text{OH} \\
   \text{(III)}
   \end{array}
   \]
   (c) \[
   \begin{array}{c}
   \text{OC}_2\text{H}_5 \\
   \text{(IV)}
   \end{array}
   \]
   (d) \[
   \begin{array}{c}
   \text{O\text{C-CH}_3} \\
   \text{(IV)}
   \end{array}
   \]
   (e) \[
   \begin{array}{c}
   \text{CN} \\
   \text{(IV)}
   \end{array}
   \]
   (f) \[
   \begin{array}{c}
   \text{Br} \\
   \text{(IV)}
   \end{array}
   \]
   (g) \[
   \begin{array}{c}
   \text{Ph} \\
   \text{(IV)}
   \end{array}
   \]
2. Arrange the following in decreasing order of their reactivity with an electrophile.

(I) \( \emptyset \text{NMe}_3 \)  (II) \( \text{ONa} \)  (III) \( \text{F} \)

(a) \( \emptyset \text{NMe}_3 \)  (b) \( \text{ONa} \)  (c) \( \text{OMe} \)  (d) \( \text{OMe} \)  (e) \( \text{NH}_2 \)  (f) \( \text{NO}_2 \)

3. Complete the following reactions:

\( \begin{align*}
\text{(A)} &: \quad \text{CH}_3 + \text{H}_2\text{C} = \text{CH}_2 \quad \text{H}^+ \\
\text{(B)} &: \quad \text{+ CH}_3\text{CH}_2\text{CH}_2\text{OH} \quad \text{H}^+ \\
\end{align*} \)

4. Complete the following reaction:

\( \text{OH} \quad \text{Br}_2 / \text{H}_2\text{O} \)

5. \( \text{OH} \quad \text{conc. HNO}_3 + \text{H}_2\text{SO}_4 \)

6. \( \text{OH} \quad \text{conc. H}_2\text{SO}_4 \quad \text{NaOH} \quad \text{H}^+ \quad \text{fusion} \)

7. \( \text{H}_2\text{C} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{OH} \quad \text{CHCH}_3 + \text{NaOH} + \Delta \)
8. Complete the reaction equation:

\[ \text{MeOH} \xrightarrow{\text{MeI, NaOH}} ? \]

9. Complete the reaction equations:

\[ \text{OH} \xrightarrow{\text{H}_2\text{SO}_4, 100^\circ} \xrightarrow{\text{NaOH, Fusion}} X \]

\[ \text{OH} \xrightarrow{\text{H}_2\text{SO}_4, 15^\circ} \xrightarrow{\text{NaOH, Fusion}} Y \]

10. Complete the reaction equations:

\[ \text{NO}_2 \xrightarrow{?} \text{NH}_2 \xrightarrow{(i) \text{NaNO}_2/\text{H}_2\text{SO}_4, (ii) \text{H}_2\text{O, boil}} ? \]

11. Convert the following:

\[ \text{NH}_2 \]

\[ \text{C}_6\text{H}_5 \]

12. Convert the following:

\[ \text{CH(CH}_3)_2 \xrightarrow{?} \text{NH}_2\text{Br} \]

\[ \text{CH(CH}_3)_2 \]

13. Convert the following:

\[ \text{NH}_2 \]

\[ \text{Cl} \]
14. Convert the following:

\[
\begin{align*}
&\text{苯} \rightarrow \text{氯苯} \\
&\text{苯} \rightarrow \text{氨基苯}
\end{align*}
\]

15. \[
\text{苯} \text{Me} + \text{H}_2\text{SO}_4 \xrightarrow{\Delta} ?
\]

16. Complete the equations:

\[
\text{(CH}_3\text{)}_2\text{CH}_3 \xrightarrow{\text{KMnO}_4 / \text{OH}^+ / \Delta} ?
\]

17. Write the possible isomers of the aromatic compounds of molecular formula C\(_7\)H\(_7\)Cl. What is the oxidation product of each isomers?

18. How will you prepare the following from benzene?

\[
\begin{align*}
&\text{(i) } \text{苯} \rightarrow \text{溴苯} \\
&(ii) \text{苯} \rightarrow \text{溴苯} \\
&(iii) \text{苯} \rightarrow \text{溴苯}
\end{align*}
\]

---

**EXERCISE # 3**

**PART - I : IIT-JEE PROBLEMS (PREVIOUS YEARS)**

*Marked Questions are having more than one correct option.*

1. \[
\text{苯} \xrightarrow{\text{(liq.) Br}_2 / \text{Fe}} \text{F}
\]  
*[JEE 2000, 1/100]*

2. Convert

(a) \[
\text{苯} \rightarrow \text{溴苯} (\text{in not more than 3 steps})
\]

(b) \[
\text{OH} \rightarrow \text{Aspirin}
\]  
*[JEE-2003, 4/60]*
3. Convert:

\[ \text{in not more than four steps, indicating all the reagents used and the reaction conditions.} \]

4. Explain why 7-bromo-1, 3, 5-cycloheptatriene exist as an ion while 5-Bromo-1, 3-cyclopentadiene does not form any ion even in the presence of Ag\(^+\). Explain why?

5. Following compound reacts with Br\(_2\)/Fe to produce:

6. Explain the following observations

(A)

\[ \text{No release of } F^- \]

(B)

\[ \text{but not} \]

(C)

\[ \text{conc. } H_2SO_4 + \text{conc. HNO}_3 \]

7. Identify A, B, C, D and write the balanced chemical equation of formation of A to B and A to C.
8. \[ \text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{Cl} / \text{AlCl}_3 \rightarrow \text{P} \xrightarrow{\text{O}_2, \text{H}_2\text{O}^\circ} \text{Q} + \text{Phenol} \] [JEE 2006, 5/184]

What are P & Q?

(A) \[ \text{CH}_3 - \text{CH}_2 - \text{CH}_3 + \text{CH}_3 - \text{C} - \text{CH}_3 \]

(B) \[ \text{CH}_3 - \text{CH}_2 - \text{CH}_3 + \text{CH}_3 - \text{CH}_2 - \text{C} - \text{H} \]

(C) \[ \text{CH}_3 + \text{CH}_3 - \text{C} - \text{H} \]

(D) \[ \text{CH}_3 + \text{CH}_3 - \text{C} - \text{CH}_3 \]

9. IUPAC name of \[ \text{C} - \text{Cl} \] is:

(A) Benzoyl chloride

(B) Chlorophenyl ketone

(C) Chloroacetobenzene

(D) Benzenecarbonyl Chloride

Comprehension (Q. No. 10 to 12)

Riemer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, ortho to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehydes as depicted below.

10. Which one of the following reagents is used in the above reaction? [JEE 2007, 4/162]

(A) aq. NaOH + CHCl

(B) aq. NaOH + CHCl

(C) aq. NaOH + CHCl

(D) aq. NaOH + CCl

11. The electrophile in this reaction is:

(A) :CHCl

(B) :CHCl

(C) :CCl

(D) :CCl

12. The structure of the intermediate I is:

(A) \[ \text{O}^\circ\text{Na}^+ \text{CHCl} \]

(B) \[ \text{O}^\circ\text{Na}^+ \text{CHCl} \]

(C) \[ \text{O}^\circ\text{Na}^+ \text{CCl}_3 \]

(D) \[ \text{O}^\circ\text{Na}^+ \text{CHOH} \]
13. In the following reaction,

\[ \text{Ph}_2C=NOH + \text{HNO}_3 \rightarrow X \]

the structure of the major product ‘X’ is [JEE 2007, 3/162]

(A) ![Structure A](image)

(B) ![Structure B](image)

(C) ![Structure C](image)

(D) ![Structure D](image)

14. The major product of the following reaction is: [JEE 2008, 3/163]

![Reaction](image)

(A) ![Structure A](image)

(B) ![Structure B](image)

(C) ![Structure C](image)

(D) ![Structure D](image)

15. STATEMENT-1: Bromobenzene upon reaction with Br₂/Fe gives 1,4-dibromobenzene as the major product.
STATEMENT-2: In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile. [JEE 2008, 3/163]

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(C) Statement-1 is True, Statement-2 is False.
(D) Statement-1 is False, Statement-2 is True.

16. STATEMENT-1: Aniline on reaction with NaNO₂ / HCl at 0°C followed by coupling with β-naphthol gives a dark blue precipitate. [JEE 2008, 3/163]
STATEMENT-2: The colour of the compound formed in the reaction of aniline with NaNO₂/HCl at 0°C followed by coupling with β-naphthol is due to the extended conjugation.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(C) Statement-1 is True, Statement-2 is False.
(D) Statement-1 is False, Statement-2 is True.
17.* In the reaction\[\text{NaOH (aq)}\] the intermediate(s) is (are): 

(A) \(\text{Br} \quad \text{Br}\)  
(B) \(\text{O} \quad \text{Br} \quad \text{Br} \quad \text{Br}\)  
(C) \(\text{O} \quad \text{Br}\)  
(D) \(\text{O} \quad \text{Br} \quad \text{Br}\)

18. The compounds P, Q and S were separately subjected to nitration using HNO\(_3\) / H\(_2\)SO\(_4\) mixture. The major product formed in each case respectively, is:

(A) \(\text{COOH} \quad \text{OCH}_3 \quad \text{O}_2\text{N}\)
(B) \(\text{COOH} \quad \text{OCH}_3 \quad \text{O}_2\text{N}\)
(C) \(\text{COOH} \quad \text{OCH}_3 \quad \text{O}_2\text{N}\)
(D) \(\text{COOH} \quad \text{OCH}_3 \quad \text{O}_2\text{N}\)
19. Match the reactions in Column I with appropriate options in Column II.  

**Column I**

(A) \[ \text{Ph-NCl} + \text{Ph-OH} \xrightarrow{\text{NaOH/H}_2\text{O}} \text{Ph-N-N-Ph} \]

(B) \[ \text{H}_3\text{C}\xrightarrow{\text{H}_2\text{SO}_4} \text{H}_3\text{C} \]

(C) \[ \text{Ph-C-CH_3} \xrightarrow{1. \text{LiAlH}_4, 2. \text{H}_2\text{O}^-} \text{Ph-CH_2-CH_3} \]

(D) \[ \text{HS-Ph-Cl} \xrightarrow{\text{Base}} \text{S} \]

**Column II**

(p) Racemic mixture

(q) Addition reaction

(r) Substitution reaction

(s) Coupling reaction

(t) Carbocation intermediate

20. The major product of the following reaction is:

\[ \text{Ph-CON} \xrightarrow{(i) \text{KOH}} \]

\[ \text{Br-Ph-CH_2Cl} \xrightarrow{(ii) \text{Br-Ph-CH_2Cl}} \]

(A) \[ \text{Ph-CON-CH_2-Ph-Br} \]

(B) \[ \text{Ph-CON-Ph-CH_2Cl} \]

(C) \[ \text{Ph-CON-CH_3-Ph-Br} \]

(D) \[ \text{Ph-CON-Ph-CH_2Cl} \]
21. Among the compounds given, the one that would form a brilliant colored dye on treatment with NaNO$_2$ in dill. HCl followed by addition to an alkaline solution of $\beta$-naphthol is:

\[ \text{[JEE-2011, 3/160]} \]

- (A) $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$
- (B) $\text{C}_6\text{H}_5\text{NHCH}_3$
- (C) $\text{C}_6\text{H}_5\text{NH}_2$
- (D) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

22. The carboxyl functional group (–COOH) is present in

- (A) picric acid
- (B) barbituric acid
- (C) ascorbic acid
- (D) aspirin

\[ \text{[JEE-2012, 3/136]} \]

23. Among P, Q, R and S, the aromatic compound(s) is/are:

\[ \text{[JEE-2013_Advanced-P-1]} \]

- (A) P
- (B) Q
- (C) R
- (D) S

24. The major product(s) of the following reaction is(are)

\[ \text{[JEE-2013_Advanced-P-2]} \]

- (A) P
- (B) Q
- (C) R
- (D) S
25.* In the following reaction, the product(s) formed is(are)

\[
\begin{array}{c}
\text{OH} \\
\text{CH}_3
\end{array}
\xrightarrow{\text{CHCl}_3, \text{OH}^+}?
\]

\[
\begin{array}{c}
\text{OH} \\
\text{CH}_3
\end{array}
\quad \begin{array}{c}
\text{OH} \\
\text{CH}_3
\end{array}
\quad \begin{array}{c}
\text{O} \\
\text{H}_2\text{C} \\
\text{CHCl}_2 \\
\text{CH}_3
\end{array}
\quad \begin{array}{c}
\text{OH} \\
\text{CHO} \\
\text{CH}_3
\end{array}
\]

(A) P (major)  (B) Q (minor)  (C) R (minor)  (D) S (major)

**PART - II : AIEEE PROBLEMS (PREVIOUS YEARS)**

1. Picric acid is :

   (1) \( \begin{array}{c}
   \text{COOH} \\
   \text{NO}_2
   \end{array} \)
   (2) \( \begin{array}{c}
   \text{COOH} \\
   \text{OH}
   \end{array} \)
   (3) \( \begin{array}{c}
   \text{NO}_2 \\
   \text{OH} \\
   \text{NO}_2
   \end{array} \)
   (4) \( \begin{array}{c}
   \text{COOH} \\
   \text{NO}_2 \\
   \text{O}_2
   \end{array} \)

2. The reaction of chloroform with alcoholic KOH and p-toluidine forms :

   (1) \( \begin{array}{c}
   \text{H}_3\text{C} \\
   \text{CN}
   \end{array} \)
   (2) \( \begin{array}{c}
   \text{H}_3\text{C} \\
   \text{N}_2\text{Cl}
   \end{array} \)
   (3) \( \begin{array}{c}
   \text{H}_3\text{C} \\
   \text{NHCHCl}
   \end{array} \)
   (4) \( \begin{array}{c}
   \text{H}_3\text{C} \\
   \text{NC}
   \end{array} \)

3. Fluorobenzene (C\(_6\)H\(_5\)F) can be synthesized in the laboratory
   (1) from aniline by diazotisation followed by heating the diazonium salt with HBF\(_4\)
   (2) by direct fluorination of benzene with F\(_2\) gas
   (3) by reacting bromobenzene with NaF solution
   (4) by heating phenol with HF and KF

4. The structure of the compound that gives a tribromo derivative on treatment with bromine water is :

   (1) \( \begin{array}{c}
   \text{CH}_3\text{OH}
   \end{array} \)
   (2) \( \begin{array}{c}
   \text{CH}_3
   \text{OH}
   \end{array} \)
   (3) \( \begin{array}{c}
   \text{CH}_3
   \text{OH}
   \end{array} \)
   (4) \( \begin{array}{c}
   \text{CH}_3
   \text{OH}
   \end{array} \)

5. In the chemical reaction,

   \( \text{CH}_3\text{CH}_2\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow (A) + (B) + 3\text{H}_2\text{O} \), the compounds (A) and (B) are respectively :

   (1) C\(_2\)H\(_5\)CN and 3KCl
   (2) CH\(_3\)CH\(_2\)CONH\(_2\) and 3KCl
   (3) C\(_2\)H\(_5\)NC and K\(_2\)CO\(_3\)
   (4) C\(_2\)H\(_5\)NC and 3KCl
6. The reaction of toluene with Cl₂ in presence of FeCl₃ gives predominantly:
(A) Benzoyl chloride (B) Benzyl chloride (C) o-and p-Chlorotoluene (D) m-Chlorotoluene

7. Presence of a nitro group in a benzene ring:
(A) activates the ring towards electrophilic substitution.
(B) renders the ring basic.
(C) deactivates the ring towards nucleophilic substitution.
(D) deactivates the ring towards electrophilic substitution.

8. Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated with cuprous bromide. The reaction mixture so formed contains:
(A) mixture of o- and p-dibromobenzenes (B) mixture of o- and p-bromoanilines
(C) mixture of o- and m-bromotoluenes (D) mixture of o- and p-bromotoluenes

9. The electrophile, E⁺, attacks the benzene ring to generate the intermediate σ-complex. Of the following, which s-complex is of lowest energy?

10. The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is:
(A) salicylaldehyde (B) salicylic acid (C) phthalic acid (D) benzoic acid

11. In the chemical reaction:
\[ \text{NH}_2 \quad \text{K}_2\text{CO}_3 \quad \text{HCl} \quad \text{NaNO}_2 \rightarrow A \quad \text{HBF}_4 \rightarrow B \]
the compounds ‘A’ and ‘B’ respectively are:
(A) nitrobenzene and fluorobenzene
(B) phenol and benzene
(C) benzene diazonium chloride and fluorobenzene
(D) nitrobenzene and chlorobenzene

12. Phenol is heated with a solution of mixture of KBr and KBrO₃. The major product obtained in this reaction is:
(A) 2-Bromophenol (B) 3-Bromophenol (C) 4-Bromophenol (D) 2,4,6-Tribromophenol

13. Which of the following reagents may be used to distinguish between phenol and benzoic acid?
(A) Aqueous NaOH (B) Tollen's reagent (C) Molisch reagent (D) Neutral FeCl₃

14. Aspirin is known as:
(A) Acetyl salicylic acid (B) Phenyl salicylate (C) Acetyl salicylate (D) Methyl salicylic acid

15. Ortho-Nitrophenol is less soluble in water than p- and m-Nitrophenols because:
(A) o-Nitrophenol is more volatile in steam than those of m- and p-isomers.
(B) o-Nitrophenol shows o-intramolecular H-bonding
(C) o-Nitrophenol shows Intermolecular H-bonding
(D) Melting point of o-Nitrophenol is lower than those of m- and p-isomers.
NCERT QUESTIONS

1. Why is benzene extra ordinarily stable though it contains three double bonds?

2. What are the necessary conditions for any system to be aromatic?

3. Explain why the following systems are not aromatic?
   (i) [Diagram]
   (ii) [Diagram]
   (iii) [Diagram]

4. How will you convert benzene into
   (i) p-nitrobromobenzene
   (ii) m-nitrochlorobenzene
   (iii) p-nitrotoluene
   (iv) acetophenone?

5. Arrange benzene, n-hexane and ethyne in decreasing order of acidic behaviour. Also give reason for
   this behaviour.

6. Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions
   with difficulty?

7. How would you convert the following compounds into benzene?
   (i) Ethyne
   (ii) Ethene
   (iii) Hexane

8. Write structures of all the alkenes which on hydrogenation give 2-methylbutane.

9. Arrange the following set of compounds in order of their decreasing relative reactivity with an
   electrophile, E⁺:
   (a) Chlorobenzene, 2,4-dinitrochlorobenzene, p-nitrochlorobenzene
   (b) Toluene, p-H₃C – C₆H₄ – NO₂, p-O₂N – C₆H₄ – NO₂.

10. Out of benzene, m–dinitrobenzene and toluene which will undergo nitration most easily and why?

11. Suggest the name of a Lewis acid other than anhydrous aluminium chloride which can be used
    during ethylation of benzene.

12. Write the structure of the major organic product.
    CH₃CH₂CH₂OH + SOCl₂ \rightarrow

13. Out of C₆H₅CH₂Cl and C₆H₅CHClC₆H₅, which is more easily hydrolysed by aqueous KOH.

14. p-Dichlorobenzene has higher m.p. and solubility than those of o- and m-isomers. Discuss.

15. How the following conversions can be carried out?
   (i) Toluene to benzyl alcohol
   (ii) Benzene to 4-bromonitrobenzene
   (iii) Benzyl alcohol to 2-phenylethanoic acid
   (iv) Ethanol to propanenitrile
   (v) Aniline to chlorobenzene
   (vi) Chlorobenzene to p-nitrophenol
   (vii) Benzene to diphenyl
   (viii) Aniline to phenylisocyanide
16. What happens when
(i) bromobenzene is treated with Mg in the presence of dry ether,
(ii) chlorobenzene is subjected to hydrolysis.

17. While separating a mixture of ortho and para nitrophenols by steam distillation, name the isomer
which will be steam volatile. Give reason.

18. Give the equations of reactions for the preparation of phenol from cumene.

19. Write chemical reaction for the preparation of phenol from chlorobenzene.

20. You are given benzene, conc. H$_2$SO$_4$ and NaOH. Write the equations for the preparation of phenol
using these reagents.

21. Show how will you synthesise :
(i) 1-phenylethanol from a suitable alkene.
(ii) cyclohexylmethanol using an alkyl halide by an S$_{N}$2 reaction.

22. Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of
ethanol.

23. Explain why is ortho nitrophenol more acidic than ortho methoxyphenol ?

24. Explain how does the –OH group attached to a carbon of benzene ring activate it towards electrophilic
substitution?

25. Give equations of the following reactions :
(i) Bromine in CS$_2$ with phenol.
(ii) Dilute HNO$_3$ with phenol.
(iii) Treating phenol with chloroform in presence of aqueous NaOH.

26. How are the following conversions carried out?
Benzyl chloride $\rightarrow$ Benzyl alcohol.

27. Name the reagents used in the following reactions :
(i) Bromination of phenol to 2,4,6-tribromophenol.
(ii) Benzyl alcohol to benzoic acid.

28. Write the equation of the reaction of hydrogen iodide with :
methoxybenzene

29. Explain the fact that in aryl alkyl ethers
(i) the alkoxy group activates the benzene ring towards electrophilic substitution and
(ii) it directs the incoming substituents to ortho and para positions in benzene ring.

30. Write equations of the following reactions :
(i) Friedel-Crafts reaction – alkylation of anisole.
(ii) Nitration of anisole.
(iii) Bromination of anisole in ethanoic acid medium.
(iv) Friedel-Craft's acetylation of anisole.

31. Give one chemical test to distinguish between the following pairs of compounds.
(i) Ethylamine and aniline  (ii) Aniline and benzylamine  (iii) Aniline and N-methylaniline.

32. Account for the following:
(i) pK$_a$ of aniline is more than that of methylamine.
(ii) Ethylamine is soluble in water whereas aniline is not.
(iii) Aniline does not undergo Friedel-Crafts reaction.
(iv) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
(v) Gabriel phthalimide synthesis is preferred for synthesising primary amines.
33. Arrange the following:
   (i) In decreasing order of the pK_b values:
       C_6H_5NH_2, C_6H_5NHCH_3, (C_2H_5)2NH and C_6H_5NH_2
   (ii) In increasing order of basic strength:
       C_6H_5NH_2, C_6H_5N(CH_3)2, (C_2H_5)2NH and CH_3NH_2
   (iii) In increasing order of basic strength:
       (a) Aniline, p-nitroaniline and p-toluidine
       (b) C_6H_5NH_2, C_6H_5NHCH_3, C_6H_5CH_2NH_2.
   (vi) In increasing order of solubility in water:
       C_6H_5NH_2, (C_2H_5)2NH, C_2H_5NH_2.

34. Write short notes on the following:
   (i) Diazotisation
   (ii) Coupling reaction

35. Accomplish the following conversions:
   (i) Nitrobenzene to benzoic acid
   (ii) Benzene to m-bromophenol
   (iii) Benzoic acid to aniline
   (iv) Aniline to 2,4,6-tribromofluorobenzene
   (v) Benzyl chloride to 2-phenylethanamine
   (vi) Chlorobenzene to p-chloroaniline
   (vii) Aniline to p-bromoaniline
   (viii) Benzamide to toluene
   (ix) Aniline to benzyl alcohol.

36. Give the structures of A, B and C in the following reactions:
   (i) C_6H_5N_2Cl + CuCN → A → H_2O/\Delta → B → NH_2 → C
   (ii) C_6H_5NO_2 + Fe/HCl → A → NaNO_2+HCl/273K → B → H_2O/\Delta → C
   (iii) C_6H_5NO_2 + Fe/HCl → A → HNO_2/273K → B → C_6H_5OH → C

37. Complete the following reactions:
   (i) C_6H_5NH_2 + CHCl_3 + alc. KOH →
   (ii) C_6H_5N_2Cl + H_3PO_2 + H_2O →
   (iii) C_6H_5NH_2 + H_2SO_4 (conc.) →
   (iv) C_6H_5N_2Cl + C_2H_5OH →
   (v) C_6H_5NH_2 + Br_2 (aq) →
   (vi) C_6H_5NH_2 + (CH_3CO)_2 O →
   (vii) C_6H_5N_2Cl + (i)HBF_4

38. Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

39. Write the reactions of aromatic and aliphatic primary amines with nitrous acid.

40. Give plausible explanation for each of the following:
    Why are aliphatic amines stronger bases than aromatic amines?
ANSWERS

Exercise # 1

PART - I

1. (ABC)  2. (AC)  3. (B)  4. (D)  5. (A)  6. (C)  7. (CD)  8. (D)  9. (B)  10. (D)  11. (A)  12. (C)  13. (A)  14. (B)

PART - II

1. A → q, r ; B → q, s ; C → p, r ; D → q, s  2. A → s, B → q, C → p, D → r

Exercise # 2

PART - I

1. (C)  2. (B)  3. (A)  4. (C)  5. (C)  6. (A)  7. (B)  8. (B)  9. (B)  10. (B)  11. (D)  12. (B)  13. (A)  14. (C)

PART - II

1. (a) (II) > (III) > (IV) > (I)  (b) (IV) > (III) > (II) > (I)  2. (a) (I) > (II) > (III)  (b) (II) > (III) > (I)  (c) (II) > (I) > (III)  (d) (III) > (I) > (II)
The o-isomer is formed at low temperatures, and the p-isomer at high temperatures.

**Reason:** Sulfonation is reversible. At higher temperatures the rate controlled ortho product reverts to phenol which then reacts to give the thermodynamically controlled para product.

10. \[ \text{NH}_2\text{HS and } \text{OH} \]

11. \[ \text{CH}_3\text{CH}_2\text{Cl} \quad \stackrel{\text{AlCl}_3}{\longrightarrow} \quad \text{HNO}_3 \quad \stackrel{\text{Sn/HCl}}{\longrightarrow} \quad \text{CH}_2\text{CH}_3 \]

12. \[ \text{CH(CH}_3)_2 \quad \stackrel{\text{HNO}_3}{\longrightarrow} \quad \text{CHCH}_2\text{CH}_3 \quad \stackrel{\text{Sn/HCl}}{\longrightarrow} \quad \text{CH}_2\text{CH}_3 \]

13. \[ \text{CH(NO}_2)_2 \quad \stackrel{\text{HNO}_3}{\longrightarrow} \quad \text{Cl}_2/\text{Fe} \quad \stackrel{\text{Sn/HCl}}{\longrightarrow} \quad \text{Cl} \]

14. \[ \text{Br}_2/\text{Fe} \quad \stackrel{\text{HNO}_3}{\longrightarrow} \quad \text{Cl}_2/\text{Fe} \quad \stackrel{\text{Sn/HCl}}{\longrightarrow} \quad \text{Cl} \]

15. \[ \text{NH}_2\text{Me} + \text{H}_2\text{SO}_4 \quad \Delta \quad \text{NH}_2\text{Me} \quad \text{SO}_4\text{H} \]

16. \[ \text{COOH} \]
17. 

\[
\begin{align*}
\text{CH}_2\text{Cl} & \quad \text{CH}_3\text{Cl} & \quad \text{CH}_3\text{Cl} & \quad \text{CH}_3 \\
(\text{I}) & \quad \text{(II)} & \quad \text{(III)} & \quad \text{(IV)} \\
\end{align*}
\]

Oxidation

\[
\begin{align*}
\text{COOH} & \quad \text{COOH} & \quad \text{COOH} & \quad \text{COOH} \\
\end{align*}
\]

18. 

\[
\begin{align*}
(1) \quad \text{C}_6\text{H}_5\text{CH}_3 & \quad \text{C}_6\text{H}_5\text{CH}_3 & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
(\text{i}) \quad \text{CH}_3\text{Cl} & \quad \text{AlCl}_3 & \quad \text{H}_2\text{SO}_4 & \quad \text{Br}_2 & \quad \text{Fe} & \quad \text{Br}_2 & \quad \text{KMnO}_4 \\
(\text{ii}) \quad \text{C}_6\text{H}_5\text{CH}_3 & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} \\
(\text{iii}) \quad \text{C}_6\text{H}_5\text{CH}_3 & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} \\
\end{align*}
\]

\[
\begin{align*}
\text{COOH} & \quad \text{COOH} & \quad \text{COOH} & \quad \text{COOH} \\
\end{align*}
\]

\[
\begin{align*}
\text{COOH} & \quad \text{COOH} & \quad \text{COOH} & \quad \text{COOH} \\
\end{align*}
\]

Exercise # 3

PART - I

1.

2. 

(a) 

(i) Conc. H$_2$SO$_4$  
(ii) KHF$_2$/\(\Delta\)  
(iii) Sn + HCl

(b) 

(i) NaOH + CO$_2$  
(ii) $\text{H}^+$  
(iii) (CH$_3$CO)$_2$O

3. 

\[
\begin{align*}
\text{NO}_3 & \quad \text{NO}_2 & \quad \text{NO}_2 & \quad \text{NO}_2 \\
\text{C}_6\text{H}_5\text{NO}_2 & \quad \text{HNO}_3 & \quad \text{NH}_3\text{HS} & \quad \text{NH}_2\text{NH}_2 & \quad \text{NaNO}_2 & \quad \text{HNO}_3\text{HCl} & \quad \text{H}_2\text{O} \\
\end{align*}
\]

4. 

7-bromo-1, 3, 5-cycloheptatriene on ionisation gives tropylium ion which is aromatic & highly stable, but ionisation of 5-bromo-1, 3-cyclopentadiene gives 1, 3-cyclopentadienyl cation which is anti aromatic & unstable. (non existent)

5. 

(A)
6. (A) Due to presence of p-NO₂ group, (– I, -m group) the SN² Ar reaction is accelerated (due to stabilization of intermediate carbanion. In the second case NO₂ can not exert its – m effect to stabilize the carbanion.

(B) In the formation of first product the antiaromaticity due to the presence of three “ ” rings of the reactant is finished and the product becomes more stable. While in 2nd case the product is thermodynamically less stable.

\[ \text{SN}_2 \]

The – NO group exerts +m effect at ortho and para-positions and increases electron density so gives o and p electrophilic substitution product.

\[ \text{etc.} \]

– NO₂ exerts -m effect, so has more electron density at meta position.

7. (A) H₂SO₄ (conc.) , (B) Br₂ , (C) NO₂⁻ , (D) (T.N.T. = Trinitrotoluene)

Part - II

1. Due to resonance
2. Planar, conjugated ring system with delocalisation of \((4n + 2) \) \(\pi\) electrons, where, \(n\) is an integer
3. Lack of delocalisation of \((4n + 2) \) \(\pi\) electrons in the cyclic system.

Exercise # 4

1. Due to resonance
2. Planar, conjugated ring system with delocalisation of \((4n + 2) \) \(\pi\) electrons, where, \(n\) is an integer
3. Lack of delocalisation of \((4n + 2) \) \(\pi\) electrons in the cyclic system.
5. \( H - C \equiv C - H > C_6H_5 > C_6H_{14} \). Due to maximum s orbital character in ethyne (50 per cent) as compared to 33 per cent in benzene and 25 per cent in \( n \)-hexane.

6. Due to the presence of 6 \( \delta \) electrons, benzene behaves as a rich source of electrons thus being easily attacked by reagents deficient in electrons.

7. (i) \( 3 \text{CH} \equiv \text{CH} \xrightarrow{\text{Red hot iron tube}} \xrightarrow{873K} \)

(ii) \( \text{C}_2\text{H}_4 \xrightarrow{\text{Br}} \text{CH}_2 \xrightarrow{\text{Br}} \xrightarrow{\text{alc KOH}} \xrightarrow{\text{CH}_2 - \text{CHBr}} \xrightarrow{\text{NaOH}} \xrightarrow{\text{HC} = \text{HC}} \xrightarrow{\text{Red hot iron tube}} \xrightarrow{873K} \)

(iii) \( \text{C}_6\text{H}_{14} \xrightarrow{\text{Cr}_2\text{O}_3 / \text{V}_2\text{O}_5 / \text{MoO}_3} \xrightarrow{773K, 10-20 \text{ atom}} \)

8. \( \text{CH}_3 \quad \text{CH}_3 \quad \text{2-Methylbut-1-ene} \)

9. \( \text{CH}_3 \quad \text{CH}_3 \quad \text{2-Methylbut-2-ene} \)

10. \( \text{CH}_3 \quad \text{CH}_3 \quad \text{3-Methylbut-1-ene} \)

9. (a) Chlorobenzene \( > \) p-nitrochlorobenzene \( > \) 2,4 – dinitrochlorobenzene

(b) Toluene \( > \) p-\( \text{CH}_3\text{C}_6\text{H}_4\text{-NO}_2 \) \( > \) p-\( \text{O}_2\text{N-C}_6\text{H}_4\text{-NO}_2 \)

10. Toluene undergoes nitration most easily due to electron releasing nature of the methyl group.

11. \( \text{FeCl}_3 \)

20. (i) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{CH}_3\text{Br} \)

(ii) \( \text{HO} + \text{C}_6\text{H}_5\text{Br} \)

(iii) \( \text{NO}_2 + \text{OC}_6\text{H}_5 \)

(iv) \( (\text{CH}_3)_n \text{C} - \text{I} + \text{C}_6\text{H}_5\text{OH} \)