CHAPTER

9

Amines

CLASS 12TH

NCERT EXERCISE AND SOLUTIONS - CHEMISTRY

Q. 1. **Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines.**

(i) $(CH_3)_2CHNH_2$

(ii) $CH_3(CH_2)_2NH_2$

(iii) $CH_3NHCH(CH_3)_2$

(iv) $(CH_3)_3CNH_2$

(v) $C_6H_5NHCH_3$

(vi) $(CH_3CH_2)_2NH_3$

(vii) m–$BrC_6H_4NH_2$

ANSWER:-

Compound	IUPAC Name	Classification
(i) $(CH_3)_2CHNH_2$	Propan-2-amine	Secondary amine
(ii) $CH_3(CH_2)_2NH_2$	Propan-1-amine	Primary amine
(iii) $CH_3NHCH(CH_3)_2$	N-Methylpropan-2-amine	Secondary amine
(iv) $(CH_3)_3CNH_2$	Trimethylamine	Tertiary amine
(v) $C_6H_5NHCH_3$	N-Methylphenylamine (Aniline derivative)	Secondary amine
(vi) $(CH_3CH_2)_2NCH_3$	N-Ethyl-N-methylamine	Tertiary amine
(vii) m–$BrC_6H_4NH_2$	3-Bromoaniline	Primary amine

Q. 2. **Give one chemical test to distinguish between the following pairs of compounds**

(i) **Methylamine and dimethylamine**

(ii) **Secondary and tertiary amines**

(iii) **Ethylamine and aniline**

(iv) **Aniline and benzylamine**

(v) **Aniline and N-methylaniline.**

ANSWER:-

(i) Methylamine and dimethylamine

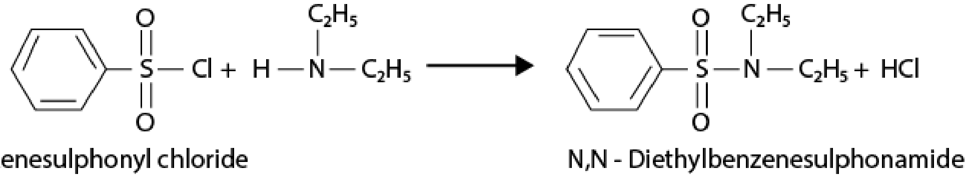
The carbylamine test can be used to distinguish between dimethylamine and methylamine. In this test, a foul-smelling isocyanide or carbylamine is produced when aliphatic and aromatic primary amines are heated with chloroform, ethanol, and potassium hydroxide. While methylamine (an aliphatic primary amine) gives a positive carbylamine test, dimethylamine does not.

$$\underset{\text{Methylamine}(1^\circ)}{CH_3-NH_2}+CHCl_3+3KOH\xrightarrow{\text{Methylisocyanide}}\underset{\text{(foul smell)}}{CH_3-NC}+3KCl+3H_2O$$

$$(CH_3)_2NH + CHCl_3 + 3KOH \xrightarrow{\text{Ä}} \text{No reaction}$$

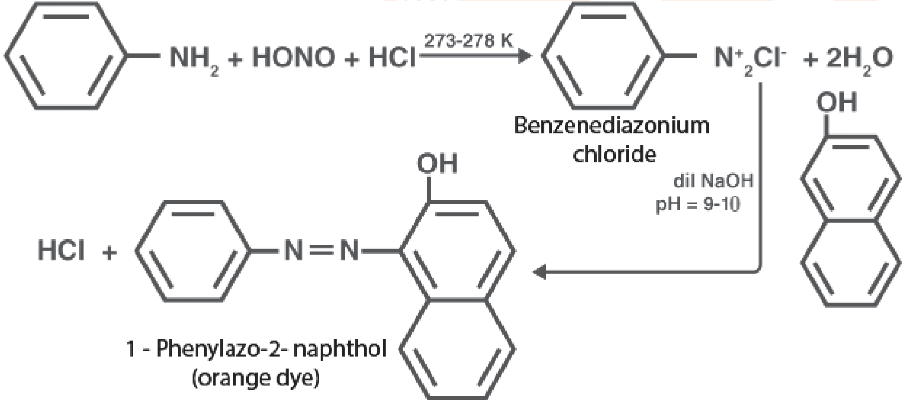
(ii) Secondary and tertiary amines

Tertiary and secondary amines can be distinguished by their reactions with Hinsberg's reagent (benzene sulphonyl chloride, $C_6H_5SO_2Cl$). When secondary amines react with Hinsberg's reagent, they form a product that is insoluble in alkali. For instance, N,N-diethylamine reacts with Hinsberg's reagent to produce N,N-diethylbenzene sulphonamide, which is insoluble in alkali. On the other hand, tertiary amines do not react with Hinsberg's reagent.



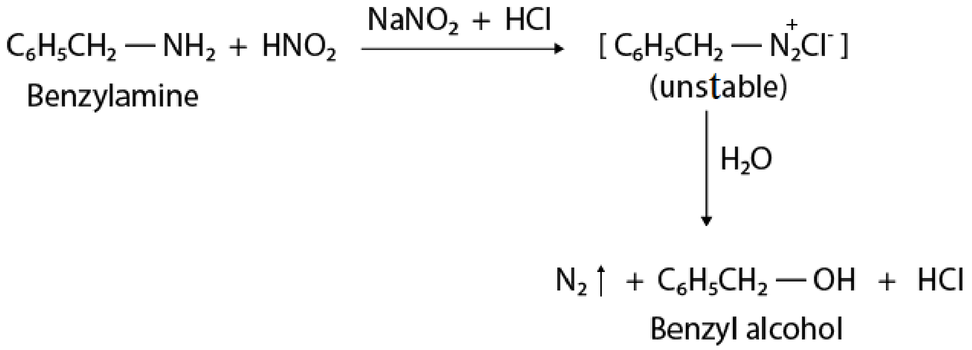
(iii) Ethylamine and aniline

The azo-dye test distinguishes aniline from ethylamine. Aromatic amines react with nitrous acid ($NaNO_2$ + dilute HCl) at 0–5°C to form an orange dye with an alkaline 2-naphthol solution. In contrast, aliphatic amines release N_2 gas, causing brisk effervescence.



(iv) Aniline and benzylamine

Benzylamine and Aniline react with nitrous acid (prepared from sodium nitrite and a mineral acid) to form unstable diazonium salts. When nitrous acid reacts with Benzylamine, it produces a by-product alcohol and releases N_2 gas.



HNO_2 reacts with aniline at a very low temperature which in turn forms stable diazonium salt. Hence, the evolution of nitrogen gas does not happen.

$$C_6H_5NH_2 \xrightarrow[273-278K]{NaNO_2+HCl} C_6H_5 - N_2^+Cl + NaCl + 2H_2O$$

(v) Aniline and N-methylaniline.

Aniline and N-methylaniline can be distinguished using the Carbylamine test.

When primary amines are heated with ethanolic chloroform and potassium hydroxide, foul-smelling isocyanides (carbylamines) are produced. Since aniline is a primary aromatic amine, it gives a positive Carbylamine test. In contrast, N-methylaniline, being a secondary amine, does not produce a positive result in the test.

$$\underset{\text{Benzylamine }(1^o)}{C_6H_5-NH_2}+CHCl_3+3KOH\xrightarrow{\text{Ä}}\underset{\text{Benzylisocyanide(foul smell)}}{C_6H_5-NC}+3KCl_3+3H_2O$$

$$\underset{\text{N - Methylaniline}}{C_6H_5NHCH_3}+CHCl_3+3KOH\xrightarrow{\text{Ä}}\text{No reaction}$$

Q. 3. **Account for the following.**

(i) **pK_b of aniline is more than that of methylamine.**

(ii) **Ethylamine is soluble in water, whereas aniline is not.**

(iii) **Methylamine in the water, when made to react with ferric chloride, precipitates hydrated ferric oxide.**

(iv) **Although the amino group is o– and p– directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.**

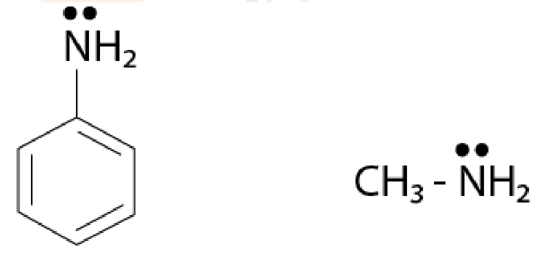
(v) **Aniline does not undergo Friedel-Crafts reaction.**

(vi) **Diazonium salts of aromatic amines are more stable than those of aliphatic amines.**

(vii) **Gabriel phthalimide synthesis is preferred for synthesising primary amines.**

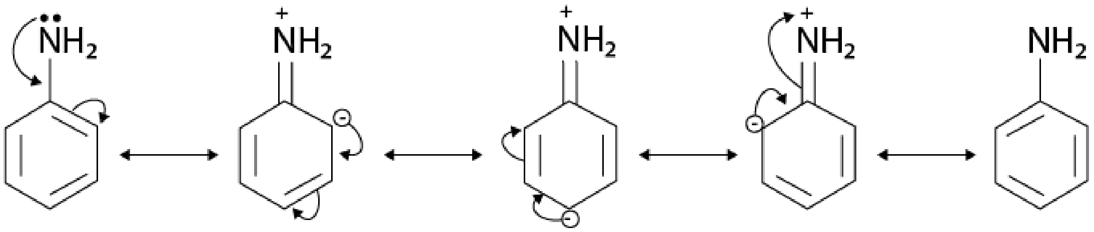
ANSWER:-

(i)



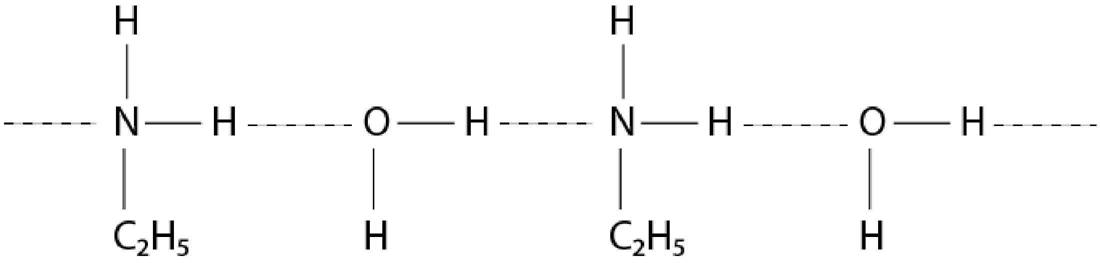
Aniline Methylamine

When aniline undergoes resonance, the electrons on the nitrogen atom become delocalized over the benzene ring. As a result, the nitrogen atom has fewer electrons available to donate.



The methyl group in methylamine exerts an inductive electron-donating (+I) effect, which increases the electron density on the nitrogen atom. This enhancement in electron density makes the nitrogen more available to accept a proton, thereby increasing the basicity of methylamine compared to aniline.

(ii) When ethylamine is dissolved in water, it forms intermolecular hydrogen bonds with water molecules. This interaction increases its solubility in water.



Ethylamine

Aniline forms hydrogen bonding with water to a significant extent due to the presence of the large hydrophobic $-C_6H_5$ group. As a result, aniline is not very soluble in water.

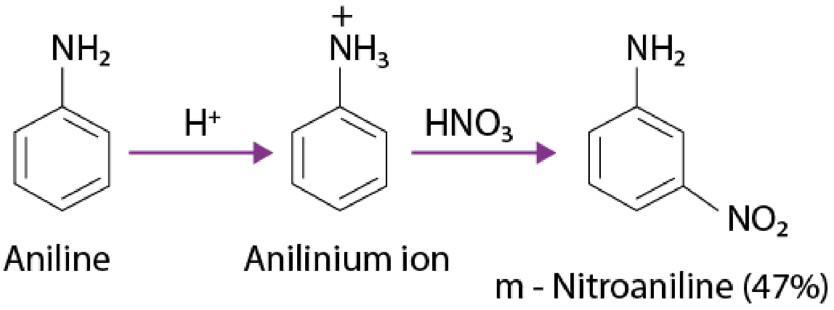
(iii) Due to the presence of $-CH_3$ group & $+I$ effect, water is less basic than methylamine. In water, thus, methylamine gives out OH^- ions by gaining H^+ ions from water.

$$CH_3-NH_2+H-OH \longrightarrow CH_3-\overset{+}{N}H_3+OH^-$$

In the above process, Ferric chloride ($FeCl_3$) splits, forming Fe^{3+} & Cl^- ions in water. OH^- ion then combines with Fe^{3+} ion and forms an impulse of hydrated ferric oxide.

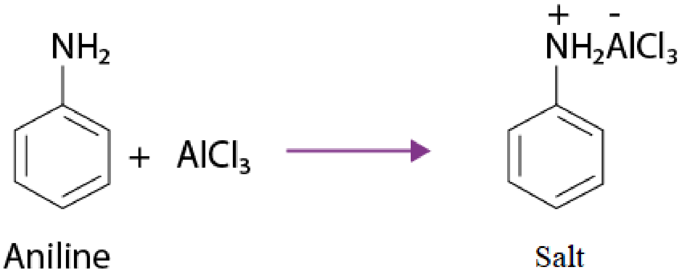
$$2Fe^{3+}+6OH^- \longrightarrow \underset{\substack{\text{Hydrated}\\ \text{ferric oxide}}}{Fe_2O_3\cdot 3H_2O}$$

(iv) Nitration is performed in an acidic medium. Under these conditions, aniline gets protonated to form the anilinium ion, which is meta-directing.



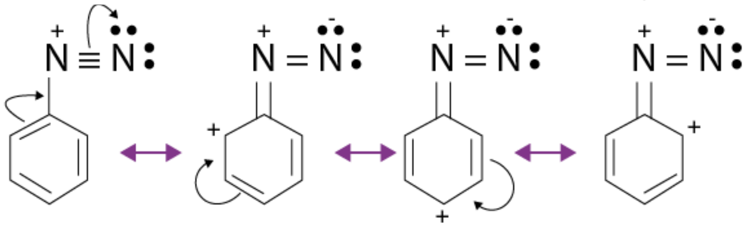
Due to the above reason, nitration aniline gives a considerable amount of m-nitroaniline.

(v) The Friedel-Crafts reaction is carried out in the presence of $AlCl_3$. However, while $AlCl_3$ is acidic, aniline is basic in nature. As a result, when aniline reacts with $AlCl_3$, a salt is formed, as shown in the equation below.



The electrophilic substitution in the benzene ring is inhibited due to the positive charge on the nitrogen atom, which is why aniline does not undergo the Friedel-Crafts reaction.

(vi) Resonance occurs in the diazonium ion, as shown in the figure below.



The stability of the diazonium ion is explained by its resonance structure. As a result, diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(vii) Gabriel phthalimide synthesis is preferred because it exclusively produces primary amines. This method does not generate secondary or tertiary amines, ensuring the formation of a pure primary amine. As a result, Gabriel phthalimide synthesis is ideal for synthesizing primary amines.

Q. 4. **Arrange the following.**

(i) **In decreasing order of the pK_b values, $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5N_2$**

(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)** **$C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$.**

(iv) **In decreasing order of basic strength in the gas phase,**
$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3

(v) **In increasing order of boiling point,**
C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

ANSWER:-

(i) The order of pKb values, from highest to lowest (weakest base to strongest base), is:

$(C_2H_5)_2NH$ (secondary amine with two electron-donating ethyl groups)

$C_2H_5NH_2$ (primary amine with one electron-donating ethyl group)

$C_6H_5NHCH_3$ (amine with a phenyl group, slightly less basic due to electron-withdrawing phenyl)

$C_6H_5N_2$ (strongly electron-withdrawing phenyl and $-N_2$ groups, making it the weakest base)

Thus, the correct order is:

$(C_2H_5)_2NH > C_2H_5NH_2 > C_6H_5NHCH_3 > C_6H_5N_2$.

(ii) $C_6H_5NH_2$ (Aniline): Phenyl group withdraws electrons via resonance, weakening the base.

$C_6H_5N(CH_3)_2$ (N,N-Dimethylaniline): Methyl groups donate electrons, but the phenyl group still withdraws, making it stronger than aniline.

CH_3NH_2 (Methylamine): Methyl group donates electrons inductively, making it a stronger base than aniline and dimethylaniline.

$(C_2H_5)_2NH$ (Diethylamine): Ethyl groups donate more electrons than methyl, making it the strongest base.

Increasing order of basic strength $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$

(iii) (a) p-Nitroaniline: The nitro group ($-NO_2$) is an electron-withdrawing group, which reduces the electron density on the nitrogen, making it less basic.

Aniline: The amino group ($-NH_2$) donates electron density to the aromatic ring, making the nitrogen more basic.

p-Toluidine: The methyl group ($-CH_3$) is an electron-donating group, which increases the electron density on the nitrogen, making it more basic than aniline.

p-Nitroaniline < Aniline < p-Toluidine

(b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$.

- $C_6H_5NH_2$ (Aniline): The amino group ($-NH_2$) is directly attached to the benzene ring, causing some electron withdrawal by the ring, reducing basicity.
- $C_6H_5NHCH_3$ (N-Methyl aniline): The methyl group ($-CH_3$) donates electron density to the nitrogen through inductive effect, increasing basicity compared to aniline.
- $C_6H_5CH_2NH_2$ (Phenylmethylamine): The $-CH_2$ group is an electron-donating group through induction, enhancing the electron density on nitrogen more than the other two, making it the most basic.

In increasing order of basic strength:

$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

(iv) In the gas phase, since there is no solvation effect, the basic strength of compounds is primarily determined by their +I (inductive) effect. The greater the +I effect, the stronger the base. Additionally, the more alkyl groups attached to the nitrogen, the higher the +I effect. Consequently, the compounds can be ordered in terms of their basic strengths in the gas phase as follows:

$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$.

(v) $(CH_3)_2NH$ (dimethylamine) has the lowest boiling point because it has weaker hydrogen bonding.

- $C_2H_5NH_2$ (ethylamine) has a higher boiling point due to stronger hydrogen bonding than dimethylamine.
- C_2H_5OH (ethanol) has the highest boiling point due to the strong hydrogen bonding between hydroxyl groups.

The increasing order of boiling points is:

$(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

(vii) $C_6H_5NH_2$ (aniline) has the least solubility because the aromatic ring makes it less polar.

- $(C_2H_5)_2NH$ (diethylamine) has higher solubility than aniline due to the presence of two ethyl groups, which are more polar than the aromatic ring.
- $C_2H_5NH_2$ (ethylamine) has the highest solubility because it is the smallest and most polar of the three.

The order of increasing solubility in water is:

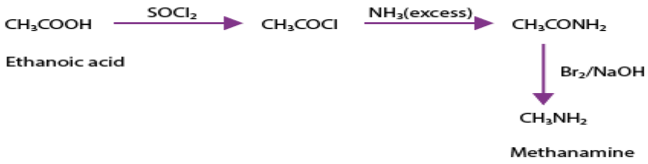
$C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

Q. 5. How will you convert?

(i) Ethanoic acid into methanamine
(ii) Hexanenitrile into 1-aminopentane
(iii) Methanol to ethanoic acid
(iv) Ethanamine into methanamine
(v) Ethanoic acid into propanoic acid
(vi) Methanamine into ethanamine
(vii) Nitromethane into dimethylamine
(viii) Propanoic acid into ethanoic acid

ANSWER:-

(i)



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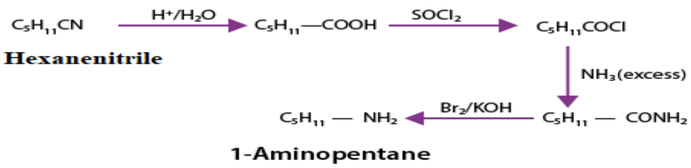

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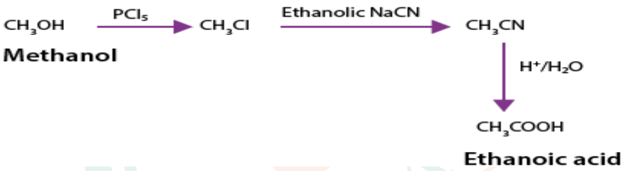

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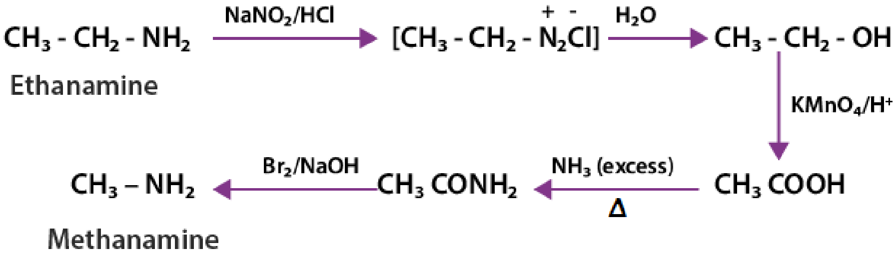

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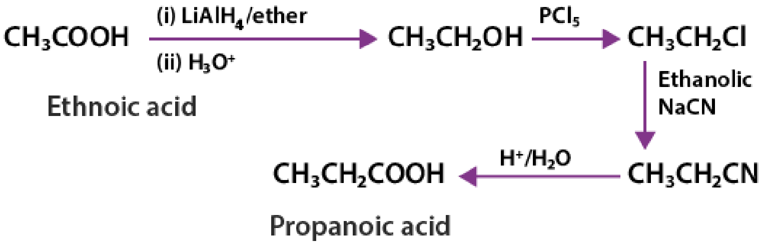

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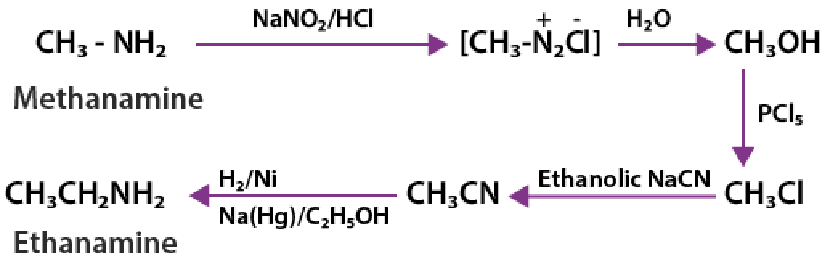

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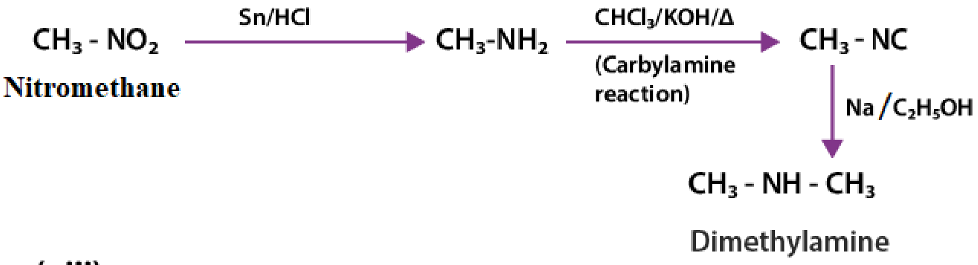

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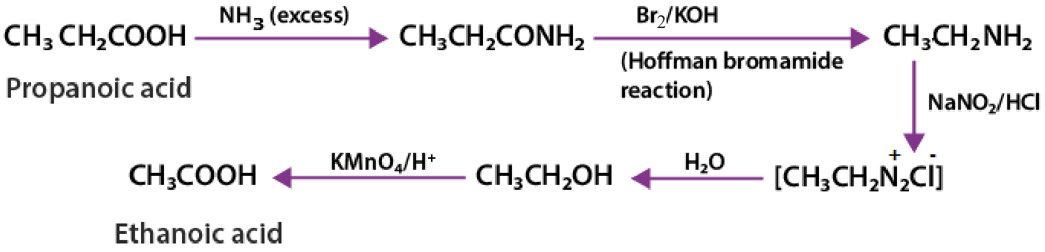
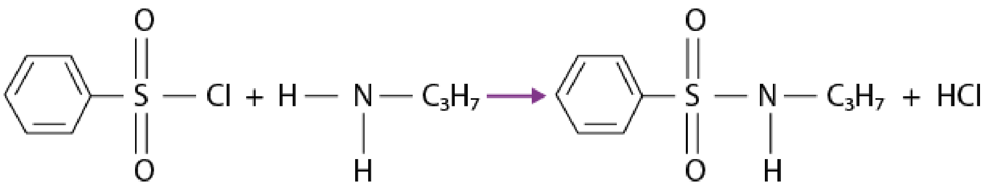


Q. 6. **Describe a method for the identification of primary, secondary and tertiary amines. Also, write chemical equations of the reactions involved.**

ANSWER:-

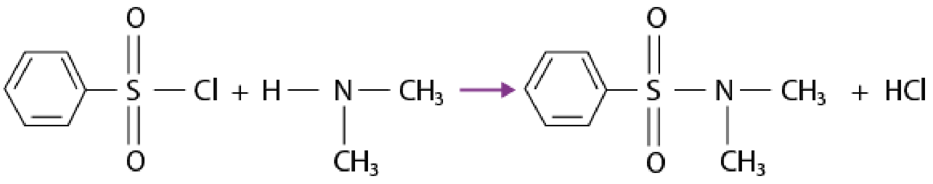
Hinsberg's test can be used to identify and differentiate primary, secondary, and tertiary amines. In this test, amines are treated with Hinsberg's reagent, benzene sulphonyl chloride ($C_6H_5SO_2Cl$). The three amine types react differently with the reagent, allowing for their distinction. Primary amines react with benzene sulphonyl chloride to form N-alkyl benzene sulphonyl amide, which is soluble in alkaline solutions.



Benzenesulphonyl Chloride Propanamine N - propylbenzenesulphonamide

The electron-withdrawing sulphonyl group in sulphonamides makes the nitrogen-hydrogen bond more acidic, allowing the H atom to easily dissociate as a proton, which causes it to dissolve in alkali.

Secondary amines react with Hinsberg's reagent to give a sulphonamide which is insoluble in alkali.



Benzenesulphonyl Chloride   Dimethylamine   N,N - Dimethylbenzenesulphonamide (insoluble in alkali)

Since there is no hydrogen atom attached to the nitrogen atom in the sulphonamide, it is not acidic and does not dissolve in alkali. In contrast, tertiary amines do not react with Hinsberg's reagent at all.

Q. 7. **Write short notes on the following.**

(i)	**Carbylamine reaction**	(ii)	**Diazotisation**
(iii)	**Hofmann's bromamide reaction**	(iv)	**Coupling reaction**
(v)	**Ammonolysis**	(vi)	**Acetylation**
(vii)	**Gabriel phthalimide synthesis.**		

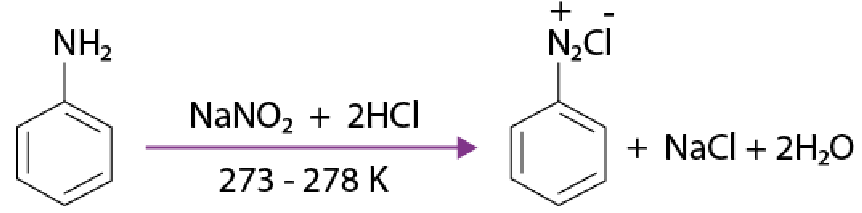
ANSWER:-

(i) **Carbylamine reaction:** The carbylamine reaction is employed to identify primary amines. When primary amines, both aliphatic and aromatic, are heated with chloroform and ethanolic potassium hydroxide, carbylamines (or isocyanides) are produced. These carbylamines emit a strong, unpleasant odor. Secondary and tertiary amines do not undergo this reaction.

$$\underset{\text{Primary amine}}{R-NH_2} + \underset{\text{Chloroform}}{CHCl_3} + \underset{\text{Potassium Hydroxide}}{3KOH(\text{ alc.})} \xrightarrow{\Delta} \underset{\text{Carbylamine}}{R-NC} + 3KCl + 3H_2O$$

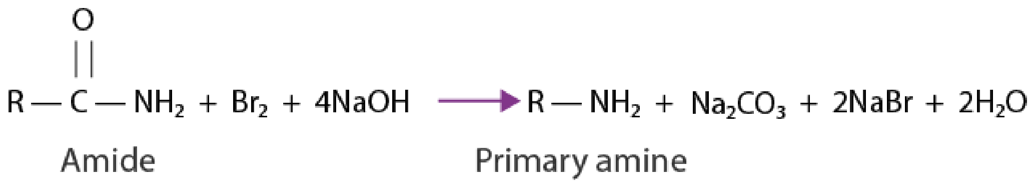
$$\underset{\text{Methanamine}}{CH_3-NH_2} + CHCl_3 + 3KOH(\text{ alc.}) \xrightarrow{\Delta} \underset{\text{Methyl carbylamine or methyl isocyanide}}{CH_3-NC} + 3KCl + 3H_2O$$

(ii) **Diazotisation:** Aromatic primary amines react with nitrous acid (which is generated in situ from $NaNO_2$ and a mineral acid like HCl) at low temperatures (273 – 278 K) to form diazonium salts. This process of converting aromatic primary amines into diazonium salts is called diazotization. For instance, when aniline is treated with $NaNO_2$ and HCl at 273 – 278 K, it produces benzene diazonium chloride, along with NaCl and H_2O as by-products.



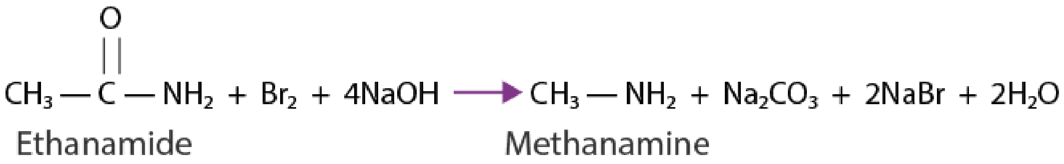
Aniline   Benzenediazonium Chloride

(iii) Hofmann's bromamide reaction: When an amide is treated with bromine in an aqueous or ethanolic solution of sodium hydroxide, a primary amine is formed, which has one fewer carbon atom than the original amide. This degradation reaction is referred to as the Hoffmann bromamide reaction. It involves the migration of an alkyl or aryl group from the carbonyl carbon of the amide to the nitrogen atom.

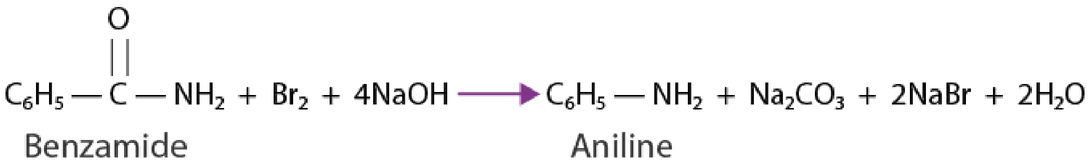


$$\underset{\text{Amide}}{R-\overset{\overset{\displaystyle O}{||}}{C}-NH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{Primary amine}}{R-NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

For example,

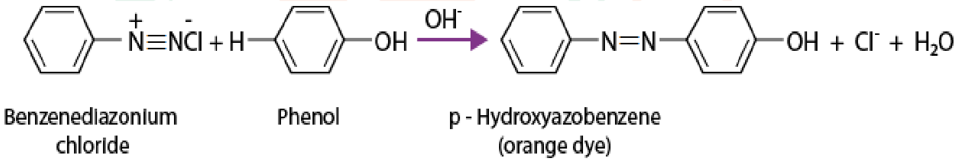


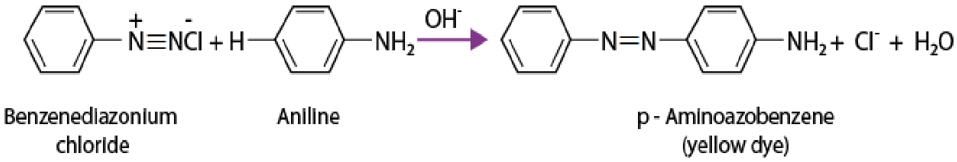
$$\underset{\text{Ethanamide}}{CH_3-\overset{\overset{\displaystyle O}{||}}{C}-NH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{Methanamine}}{CH_3-NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$



$$\underset{\text{Benzamide}}{C_6H_5-\overset{\overset{\displaystyle O}{||}}{C}-NH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{Aniline}}{C_6H_5-NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

(iv) Coupling reaction: The reaction that connects two aromatic rings via – N = N – bond is known as the coupling reaction. Arene diazonium salts, like benzene diazonium salt, react with phenol or aromatic amines to produce colored azo compounds. It is observed that the para-positions of phenol and aniline are coupled with the diazonium salt. This reaction occurs via electrophilic substitution.





(v) Ammonolysis: When an alkyl or benzyl halide reacts with an ethanolic solution of ammonia, it undergoes a nucleophilic substitution reaction in which the halogen atom is replaced by an amino (–NH_2) group. This process, involving the breaking of the carbon-halogen bond, is referred to as ammonolysis.

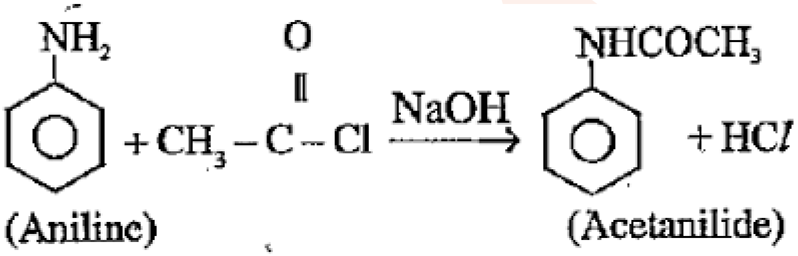
$$\underset{(1^0)}{RNH_2} \xrightarrow{RX} \underset{(2^0)}{R_2NH} \xrightarrow{RX} \underset{(3^0)}{R_3N} \xrightarrow{RX} \underset{\substack{\text{Quaternary}\\ \text{ammonium salt}}}{R_4\overset{+}{N}\overset{-}{X}}$$

When this substituted ammonium salt is treated with a strong base, such as sodium hydroxide, the amine is obtained.

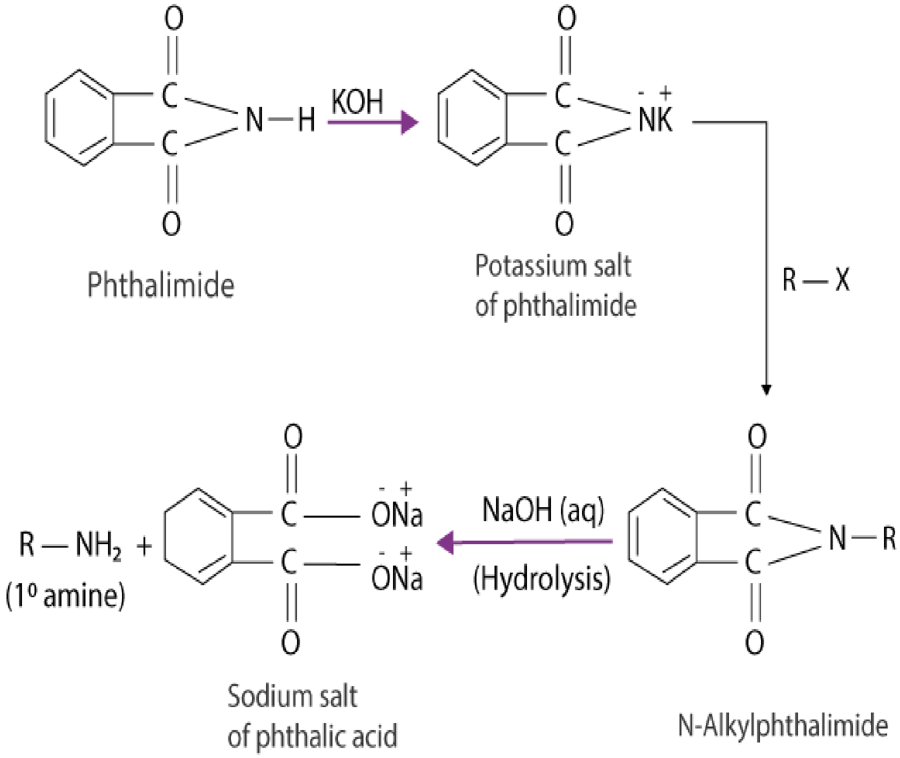
$$R-\overset{+}{N}H_3\overset{-}{X} + NaOH \longrightarrow \underset{\text{Amine}}{R-NH_2} + H_2O + NaX$$

(vi) Acetylation: Acetylation is the process of adding an acetyl group to a molecule.

Aliphatic and aromatic primary and secondary amines undergo acetylation through nucleophilic substitution when treated with acid chlorides, anhydrides, or esters. In this reaction, the hydrogen atom of the $-NH_2$ or $>NH$ group is replaced by the acetyl group, resulting in the formation of amides. To drive the equilibrium toward the formation of the product, the HCl produced during the reaction is promptly removed. This reaction is carried out in the presence of a base, such as pyridine, which is stronger than the amine.



(vii) Gabriel phthalimide synthesis: The Gabriel phthalimide synthesis is a method for preparing aliphatic primary amines. It involves the reaction of phthalimide with potassium hydroxide to form the potassium salt of phthalimide. This salt then reacts with an alkyl halide to produce an N-alkylphthalimide. Finally, alkaline hydrolysis cleaves the phthalimide ring, releasing the primary amine.

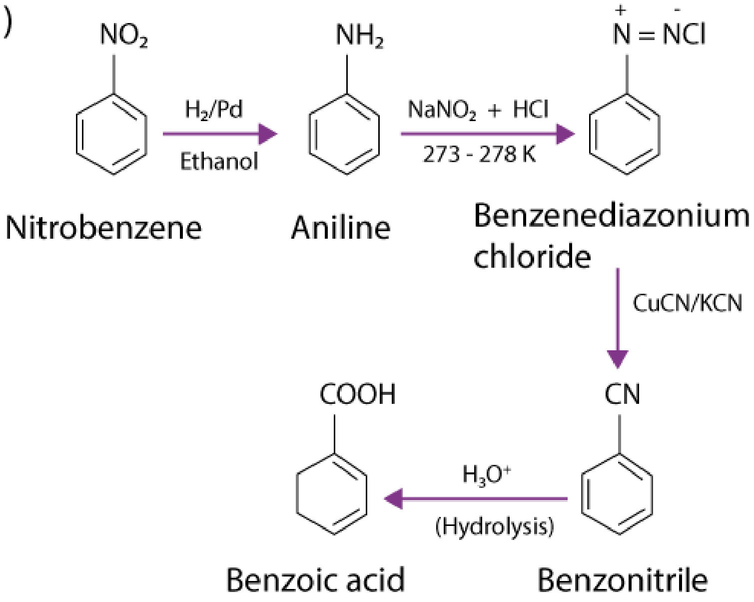


Q. 8. **Accomplish the following conversions.**

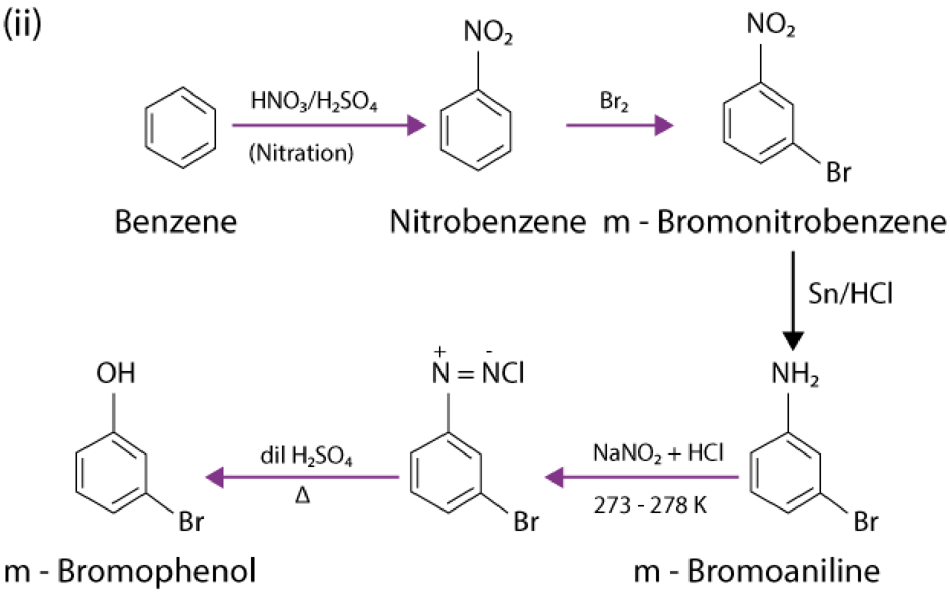
- **(i)** **Nitrobenzene to benzoic acid**
- **(ii)** **Benzene to m-bromophenol**
- **(iii)** **Benzoic acid to aniline**
- **(iv)** **Aniline to 2, 4 ,6-tribromofluorobenzene**
- **(v)** **Benzyl chloride to 2-phenylethanamine**
- **(vi)** **Chlorobenzene to p-chloroaniline**
- **(vii)** **Aniline to p-bromoaniline**
- **(viii)** **Benzamide to toluene**
- **(ix)** **Aniline to benzyl alchol**

ANSWER:-

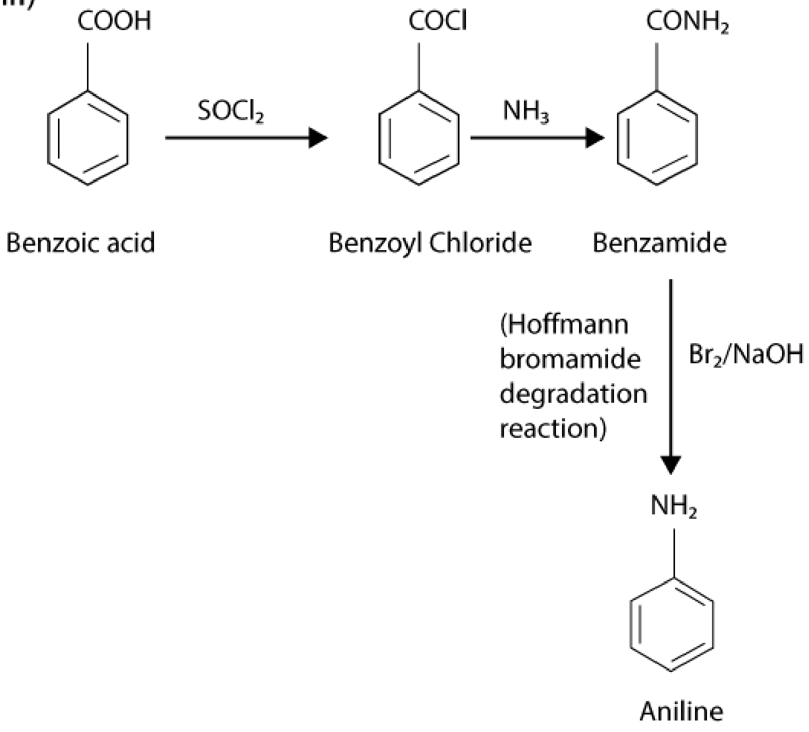
(i)



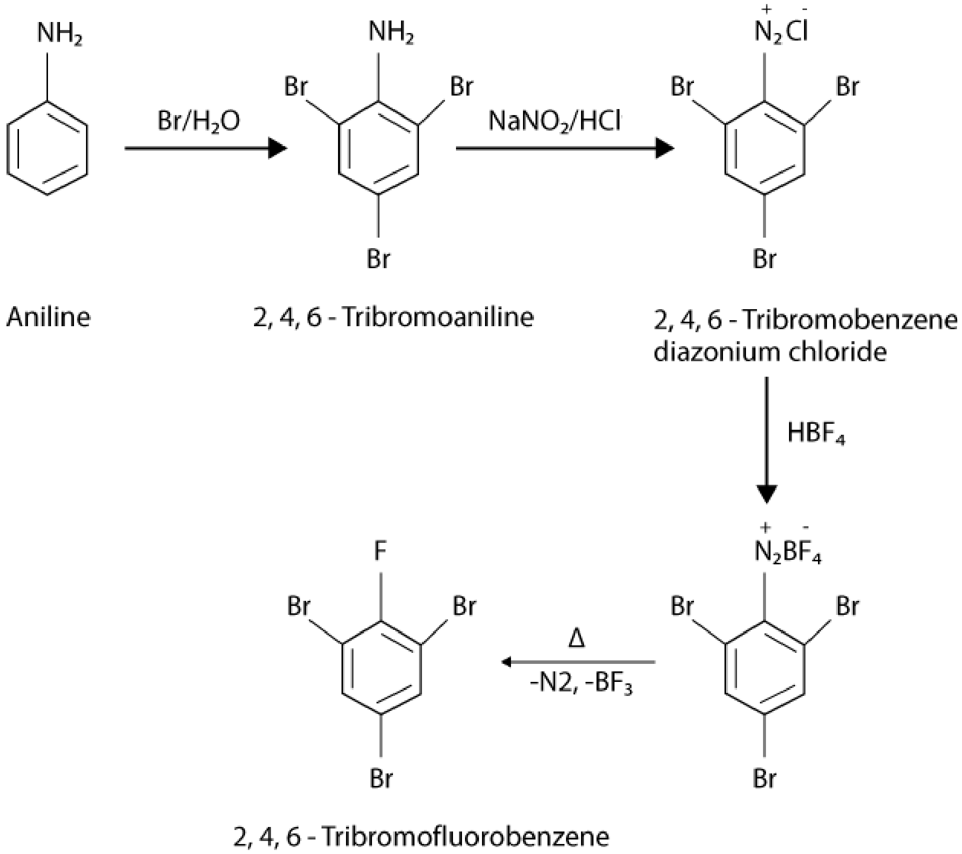
(ii)



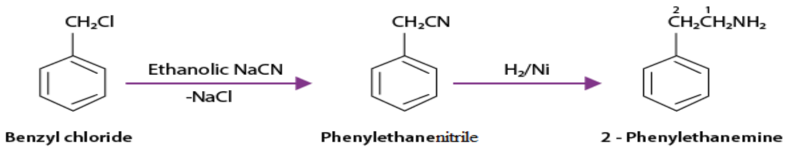
(iii)


COOH
SOCl2
COCl
NH3
CONH2
Benzoic acid
Benzoyl Chloride
Benzamide
(Hoffmann bromamide degradation reaction)
Br2/NaOH
NH2
Aniline

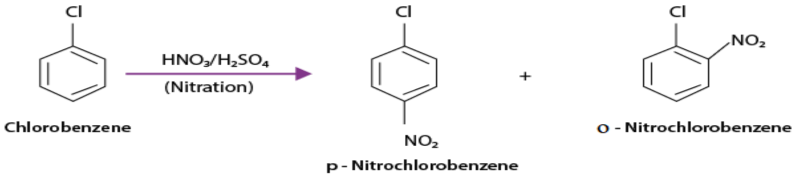
(iv)

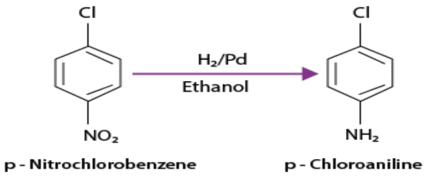

NH2
Br/H2O
NH2
Br
Br
Br
NaNO2/HCl
N2Cl
Br
Br
Br
Aniline
2, 4, 6 - Tribromoaniline
2, 4, 6 - Tribromobenzene diazonium chloride
HBF4
N2BF4
Br
Br
Br
Δ
-N2, -BF3
F
Br
Br
Br
2, 4, 6 - Tribromofluorobenzene

(v)

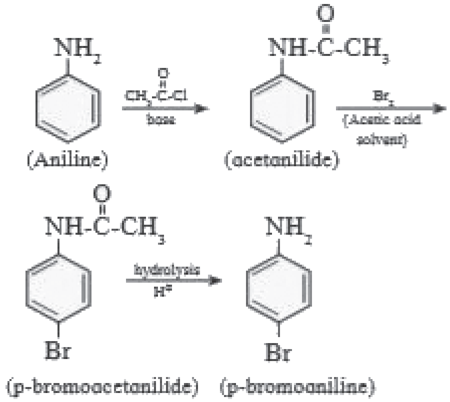


(vi)

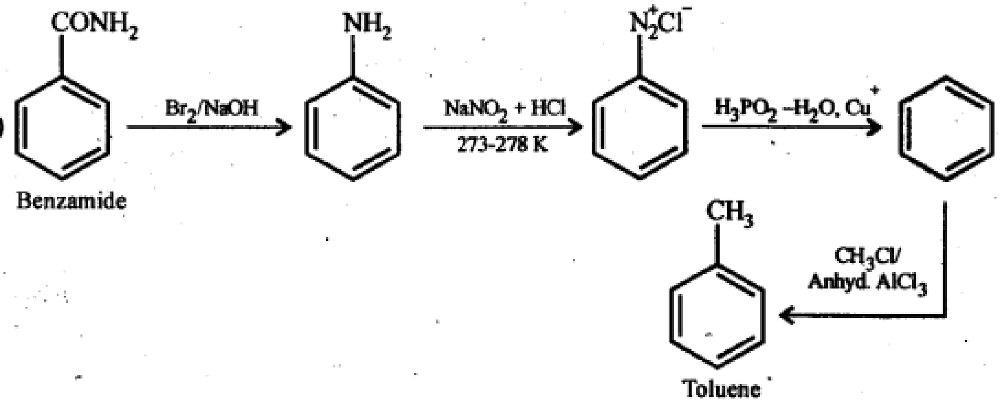




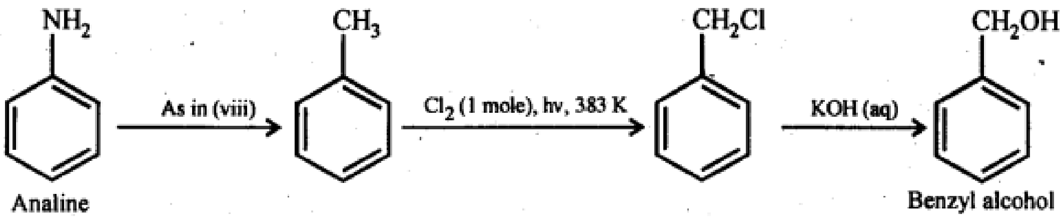
(vii)



(viii)



(ix)



Q. 9. **Give the structures of A, B, C in the following reactions:**

(i) $$CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH + Br_2} C$$

(ii) $$C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$$

(iii) $$CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0^0\,C]{HNO_2} C$$

(iv) $$C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{NaNO_2 + HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$$

(v) $$CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$$

(vi) $$C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{HNO_2} B \xrightarrow{C_6H_5OH} C$$

ANSWER:-

(i)

$$CH_3CH_2I \xrightarrow{NaCN} CH_3CH_2CN \xrightarrow[\text{Partial hydrolysis}]{OH^-} CH_3-CH_2-\overset{\overset{\large O}{||}}{C}-NH_2$$

Propanaitrile (A) — Propanamide (B)

$$CH_3-CH_2-\overset{\overset{O}{||}}{C}-NH_2 \xrightarrow{NaOH + Br_2} CH_3-CH_2-NH_2$$

Ethanamine (C)

(ii)

$$C_6H_5N_2Cl \xrightarrow{CuCN} C_6H_5CN \xrightarrow{H_2O\,/\,H^+} C_6H_5COOH$$

Cyanobenzane (A) — Benzoic acid (B)

$$C_6H_5COOH \xrightarrow[\Delta]{NH_3} C_6H_5CONH_2$$

Benzamide (C)

(iii)

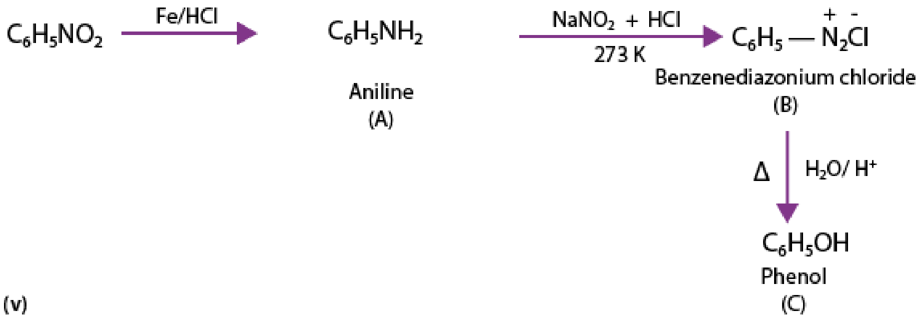
$$CH_3CH_2Br \xrightarrow{KCN} CH_3CH_2CN \xrightarrow{LiAlH_4} CH_3CH_2CH_2NH_2$$

Cyanoethane (A) — Propan - 1 - amine (B)

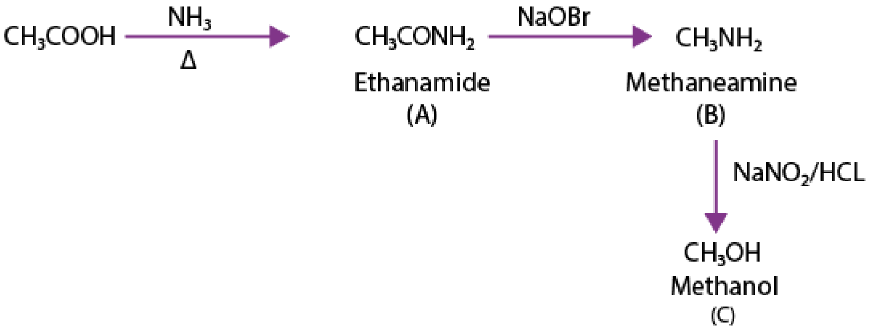
$$CH_3CH_2CH_2NH_2 \xrightarrow[0^oC]{HNO_2} CH_3CH_2CH_2OH$$

Propan - 1 - ol (C)

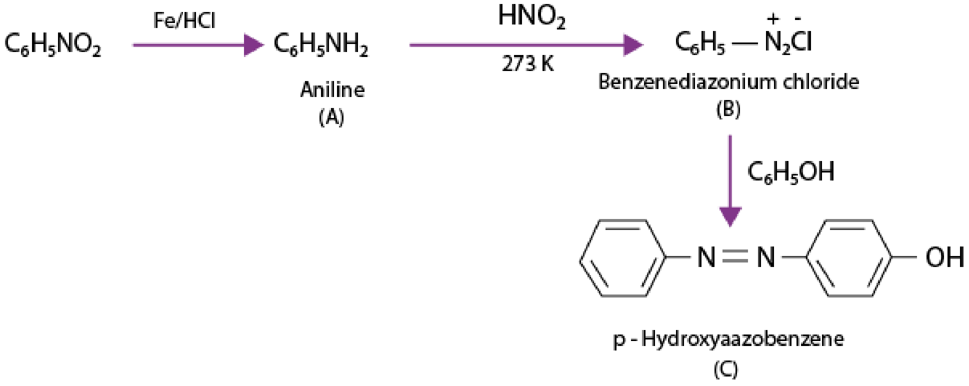
(iv)



(v)



(vi)



Q. 10. **An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B', which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.**

ANSWER:-

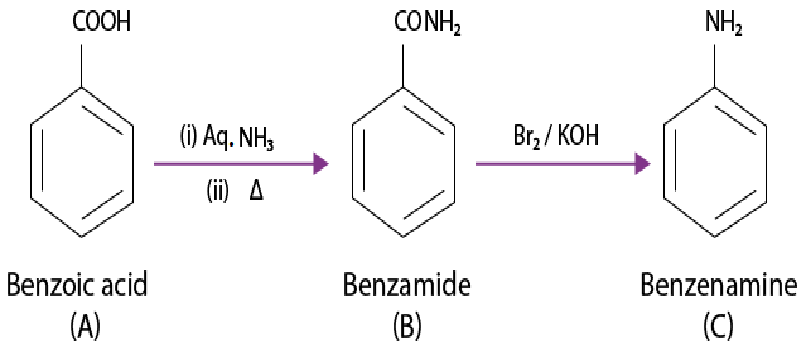
It is given that compound 'C' has the molecular formula C_6H_7N and is formed by heating compound 'B' with Br_2 and KOH, indicating a Hoffmann bromamide degradation reaction. As a result, compound 'B' must be an amide, and compound 'C' is an amine. The only amine with the molecular formula C_6H_7N is aniline ($C_6H_5NH_2$).

Therefore, compound 'B' (from which 'C' is formed) must be benzamide ($C_6H_5CONH_2$).

Further, benzamide is formed by heating compound 'A' with aqueous ammonia.

Therefore, compound 'A' must be benzoic acid.

The given reactions can be explained with the help of the following equations:



Q. 11. **Complete the following reactions:**

(i) $C_6H_5NH_2 + CHCl_3 + \text{alc. } KOH \rightarrow$

(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$

(iii) $C_6H_5NH_2 + H_2SO_4\ (\text{conc}) \rightarrow$

(iv) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$

(v) $C_6H_5NH_2 + Br_2\ (aq) \rightarrow$

(vi) $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow$

(vii) $C_6H_5N_2Cl \xrightarrow[\text{(ii) } NaNo_2/Cu]{\text{(i) } HBF_4}$

ANSWER:-

(i)

$$\underset{\text{Aniline}}{C_6H_5NH_2} + CHCl_3 + 3\text{alc } KOH \xrightarrow{\text{Carbylamine reaction}} 3H_2O + 3KCl + \underset{\text{Phenyl isocynide}}{C_6H_5-NC}$$

(ii)

$$\underset{\text{Benzenediazonium chloride}}{C_6H_5N_2Cl} + H_3PO_2 + H_2O \longrightarrow \underset{\text{Benzene}}{C_6H_6} + N_2 + H_3PO_3 + HCl$$

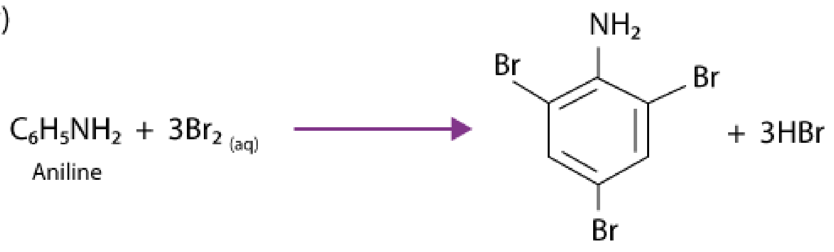
(iii)

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \text{conc. } H_2SO_4 \longrightarrow \underset{\text{Anilinium hydrogen sulphate}}{C_6H_5\overset{+}{N}H_2H\overset{-}{S}O_4}$$

(iv)

$$\underset{\text{Benzenediazonium chloride}}{C_6H_5N_2Cl} + \underset{\text{Ethanol}}{C_2H_5OH} \longrightarrow \underset{\text{Benzene}}{C_6H_6} + \underset{\text{Ethanal}}{CH_3CHO} + N_2 + HCl$$

(v)



2,4,6 - Tribromoaniline

(vi)

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \longrightarrow \underset{\text{N - Phenylethanamide}}{C_6H_5-\underset{\substack{|\\H}}{N}-\underset{\substack{||\\O}}{C}-CH_3} + \underset{\text{acetic acid}}{CH_3COOH}$$

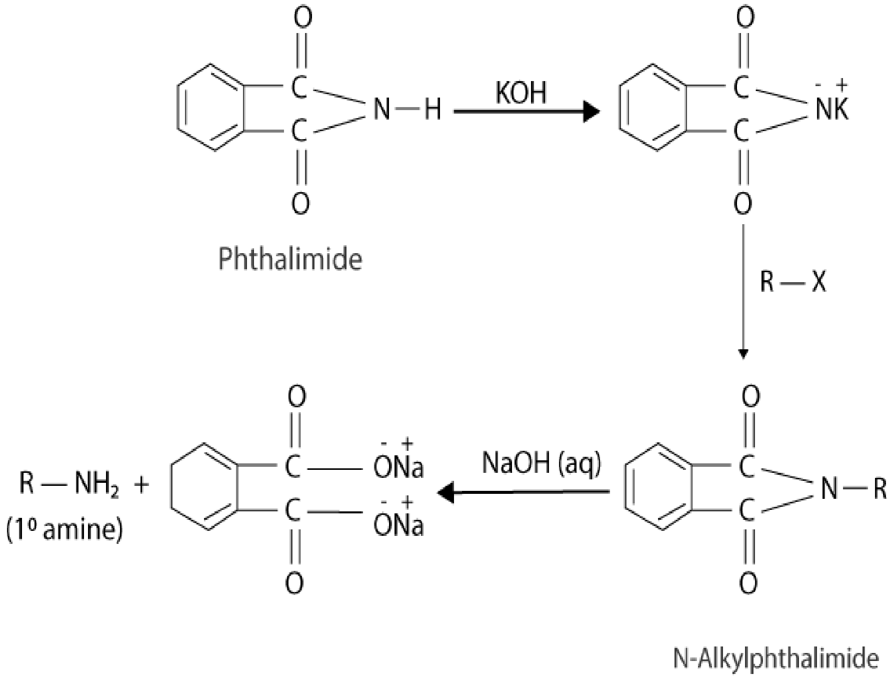
(vii)

$$\underset{\text{Benzenediazonium chloride}}{C_6H_5N_2Cl} + C_2H_5OH \xrightarrow[\text{(ii) } NaNO_2 / Cu\ \Delta]{\text{(i) } HBF_4} \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + N_2 + NaBF_4$$

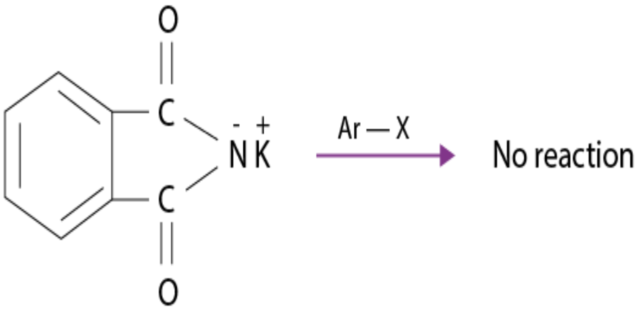
Q. 12. **Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?**

ANSWER:-

The Gabriel phthalimide synthesis is commonly used to form aliphatic primary amines. This process involves the nucleophilic substitution (SN2) of alkyl halides by the anion generated from phthalimide.



However, nucleophilic substitution with the anion formed from phthalimide does not occur with aryl halides.



Therefore, Gabriel phthalimide synthesis is not preferred for preparing aromatic primary amines.

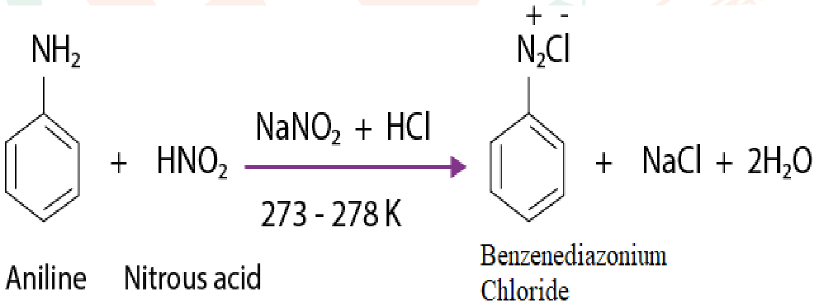
Q. 13. **Write the reactions of**

(i) **Aromatic with nitrous acid.**
(ii) **Aliphatic primary amines with nitrous acid.**

ANSWER:-

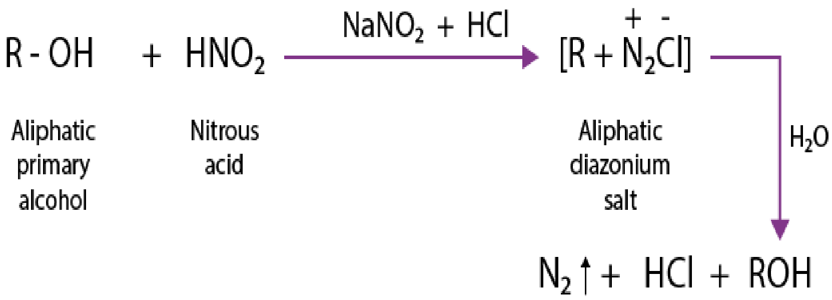
(i) Aromatic with nitrous acid.

When an aromatic amine reacts with nitrous acid (generated in situ from NaNO2 and a mineral acid like HCl) at temperatures between 273 and 278 K, stable aromatic diazonium salts are formed, along with NaCl and H2O.



(ii) Aliphatic primary amines with nitrous acid.

When aliphatic primary amines react with nitrous acid (prepared in situ from NaNO2 and a mineral acid like HCl), unstable aliphatic diazonium salts are formed. These salts subsequently decompose, producing alcohol and HCl, along with the release of N2 gas.



Q. 14. Give a plausible explanation for each of the following.

(i) Why are alcohols more acidic than amines of comparable molecular masses?

(ii) Why do tertiary amines have lower boiling points than primary amines?

(iii) Why are aromatic amines weaker bases than aliphatic amines?

ANSWER:-

(i) The loss of a proton from an amine results in the formation of an amide ion, while the loss of a proton from an alcohol produces an alkoxide ion. Since oxygen is more electronegative than nitrogen, the negative charge is better stabilized on the oxygen atom (RO) than on the nitrogen atom (RNH-). As a result, alcohols are more acidic than amines.

(ii) Tertiary amines have no hydrogen atoms bonded to the nitrogen atom and therefore are not hydrogen bond donors. Thus, tertiary amines cannot form intermolecular hydrogen bonds. As a result, they have lower boiling points than primary and secondary amines of comparable molecular weight.

(iii) In aliphatic amines, the $-NH_2$ group is attached to an alkyl group which is an electron donating group i.e, they have +I effect. So, the lone pair of electrons on nitrogen are readily available.

In aromatic amines, the $-NH_2$ group is attached to a $-C_6H_5$ group, which is an electron withdrawing group. So, the availability of a lone pair of electrons on N is decreased. Therefore aliphatic amines are more basic than aromatic amines.