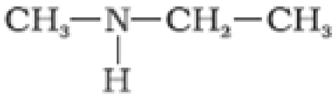
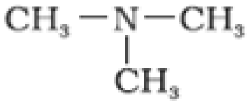
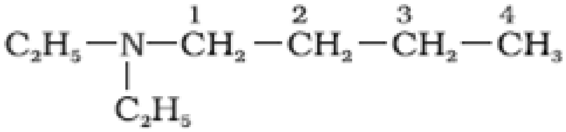
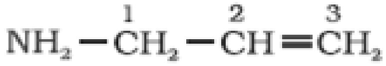
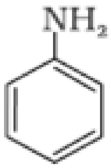
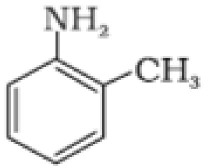
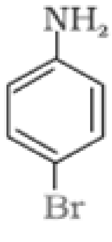
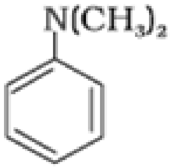
# UNIT 13:
# AMINES

| | | |
|---|---|---|
| 2. | Amines | 1. Ammonolysis of alkylholids, Gabriel Phthalimide synthesis, Hoffmann Bromamide Degradation.<br>2. Basic character of Amines($pK_b$) and comparisons in gaseous and aqueous phase.<br>3. Carbylomine Reaction ,Hinsberg's Test.<br>4. Electrophilic substitution.<br>5. Diazonium salts –reactions |

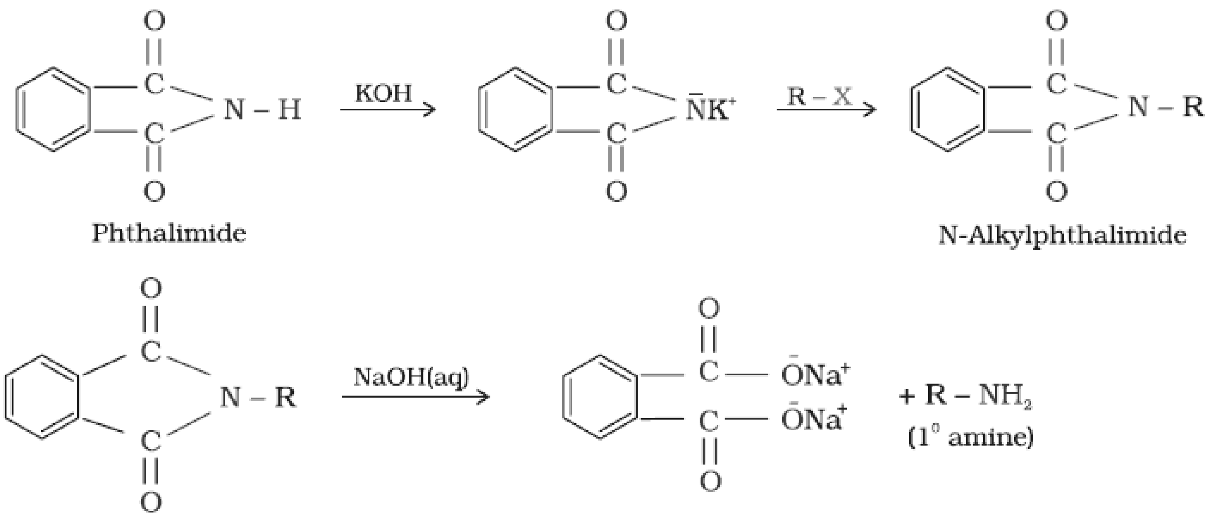
## IUPAC NOMENCLATURE

| Amine | IUPAC name |
|---|---|
| $CH_3-CH_2-NH_2$ | Ethanamine |
| $CH_3-CH_2-CH_2-NH_2$ | Propan-1-amine |
|  $CH_3-\underset{\displaystyle NH_2}{\underset{\vert}{CH}}-CH_3$ | Propan-2-amine |
|  $CH_3-\underset{\displaystyle H}{\underset{\vert}{N}}-CH_2-CH_3$ | N-Methylethanamine |
|  $CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{N}}-CH_3$ | N,N-Dimethylmethanamine |
|  $C_2H_5-\underset{\displaystyle C_2H_5}{\underset{\vert}{N}}-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_3$ | N,N-Diethylbutan-1-amine |
|  $NH_2-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H_2$ | Prop-2-en-1-amine |
| $NH_2-(CH_2)_6-NH_2$ | Hexane-1,6-diamine |
|  | Aniline or Benzenamine |
|  | 2-Aminotoluene |
|  | 4-Bromobenzenamine<br>or<br>4-Bromoaniline |
|  | N,N-Dimethylbenzenamine |

# NAME REACTIONS

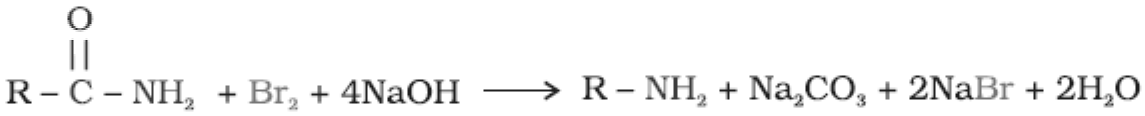
## 1. Gabriel phthalimide synthesis

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.



## 2. Hoffmann bromamide degradation reaction

Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. The amine so formed contains one carbon less than that present in the amide.



$$R-\overset{\overset{O}{||}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

## 3. Carbylamine reaction

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for primary amines.

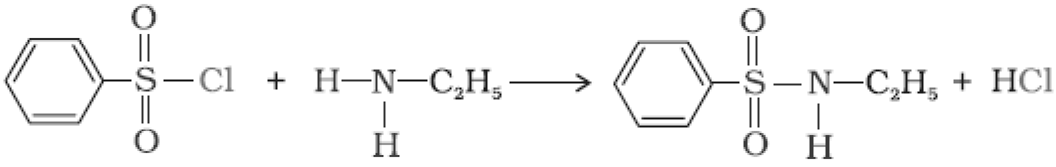
$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R-NC + 3KCl + 3H_2O$$

## 4. Hinsberg Test:

Benzenesulphonyl chloride ($C_6H_5SO_2Cl$), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.

(a) The reaction of benzenesulphonyl chloride with primary amine

yields N-ethylbenzenesulphonyl amide.

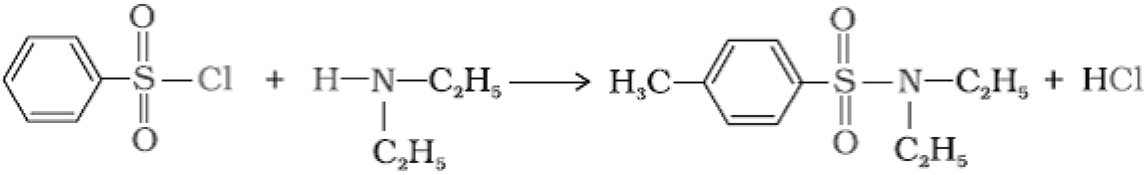


*N*-Ethylbenzenesulphonamide
(soluble in alkali)

The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

(b) In the reaction with secondary amine, N,N-diethylbenzenesulphonamide

is formed.



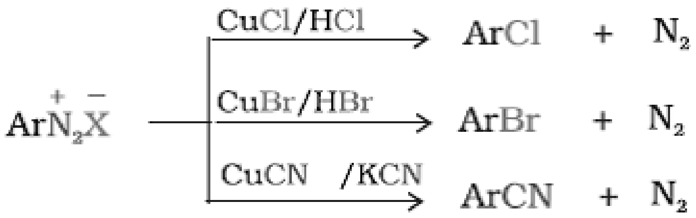
*N,N*-Diethylbenzenesulphonamide

Since N, N-diethylbenzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

(c) Tertiary amines do not react with benzenesulphonyl chloride. This property of amines reacting with benzenesulphonyl chloride in a different manner is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines.

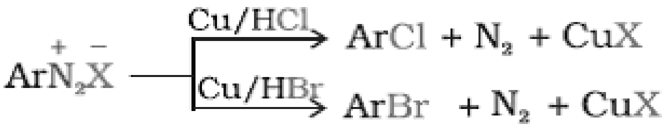
**5. Sandmeyer Reaction**

The Cl–, Br– and CN– nucleophiles can easily be introduced in the benzene ring of diazonium salts in the presence of Cu(I) ion.



## 6. Gatterman Reaction

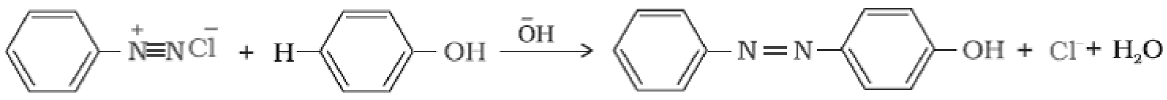
Chlorine or bromine can be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder.



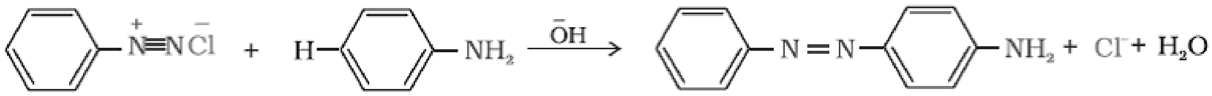
## 7. Coupling reactions

The azo products obtained have an extended conjugate system having both the aromatic rings joined through the –N=N– bond. These compounds are often coloured and are used as dyes. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form p-hydroxyazobenzene. This type of reaction is known as coupling reaction.

Similarly the reaction of diazonium salt with aniline yields p-aminoazobenzene.



*p*-Hydroxyazobenzene (orange dye)



*p*-Aminoazobenzene
(yellow dye)

## DISTINCTION BETWEEN PAIRS OF COMPOUNDS

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

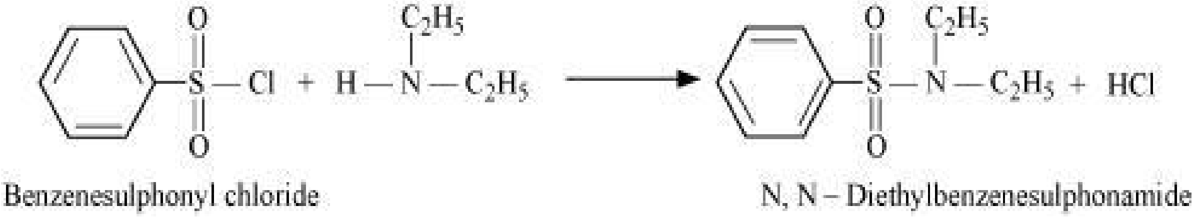
(v) Aniline and N-methylaniline.

ANS. (i) Methylamine and dimethylamine can be distinguished by the carbylamine test. Carbylamine test: Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form foul-smelling isocyanides or carbylamines. Methylamine (being an aliphatic primary amine) gives a positive carbylamine test, but dimethylamine does not.

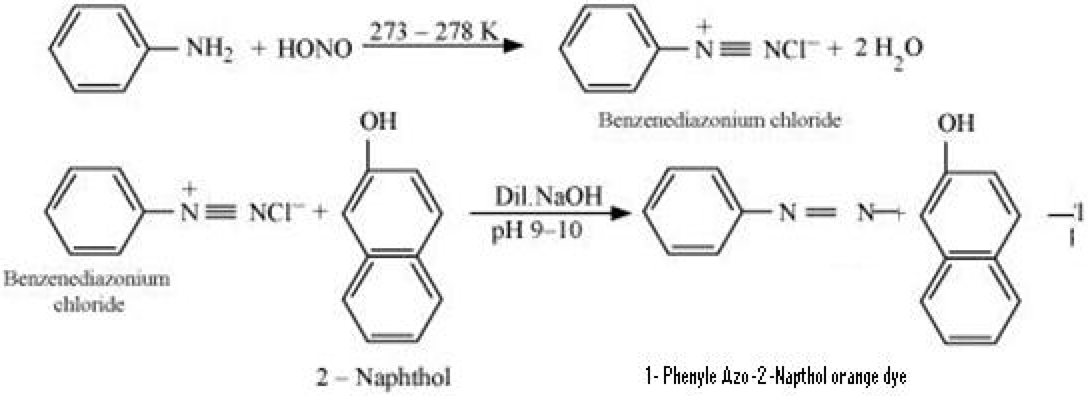
$$\underset{\text{Methylamine}(1^0)}{CH_3-NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\substack{\text{Methyl isocyanide}\\ \text{(foul smell)}}}{CH_3-NC} + 3KCl + 3H_2$$

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

(ii) Secondary and tertiary amines can be distinguished by allowing them to react with Hinsberg's reagent (benzenesulphonyl chloride, $C_6H_5SO_2Cl$).Secondary amines react with Hinsberg's reagent to form a product that is insoluble in an alkali. For example, N, N−diethylamine reacts with Hinsberg's reagent to form N, N−diethylbenzenesulphonamide, which is insoluble in an alkali. Tertiary amines, however, do not react with Hinsberg's reagent.



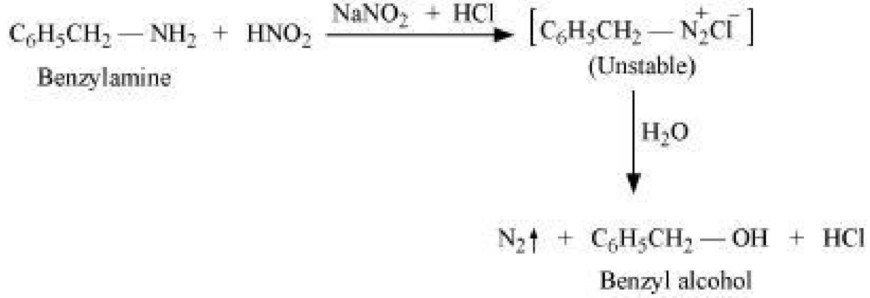
(iii) Ethylamine and aniline can be distinguished using the azo-dye test. A dye is obtained when aromatic amines react with $HNO_2$ ($NaNO_2$ + dil.HCl) at 0-5°C, followed by a reaction with the alkaline solution of 2-naphthol. The dye is usually yellow, red, or orange in colour. Aliphatic amines give a brisk effervescence due (to the evolution of $N_2$ gas) under similar conditions.



$$CH_3CH_2-NH_2 + HONO \xrightarrow{0\text{-}5^\circ C} C_2H_5OH + N_2\uparrow + H_2O$$

(iv) Aniline and benzylamine can be distinguished by their reactions with the help of nitrous acid, which is prepared in situ from a mineral acid and sodium nitrite.

Benzylamine reacts with nitrous acid to form unstable diazonium salt, which in turn gives alcohol with the evolution of nitrogen gas.



On the other hand, aniline reacts with $HNO_2$ at a low temperature to form stable diazonium salt. Thus, nitrogen gas is not evolved.

(v) Aniline and N-methylaniline can be distinguished using the Carbylamine test. Primary amines, on heating with chloroform and ethanolic potassium hydroxide, form foul-smelling isocyanides or carbylamines. Aniline, being an aromatic primary amine, gives positive carbylamine test. However, N-methylaniline, being a secondary amine does not.

$$\underset{\text{Benzylamine}(1^0)}{C_6H_5-NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\substack{\text{Benzyl isocyanide}\\(\text{foul smell})}}{C_6H_5-NC} + 3KCl + 3H_2O$$

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

## REASONING QUESTIONS

Q1. Account for the following:

(i) pKb of aniline is more than that of methylamine.

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

(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.

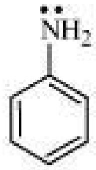
(iv) Although amino group is o– and p– directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.

(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.

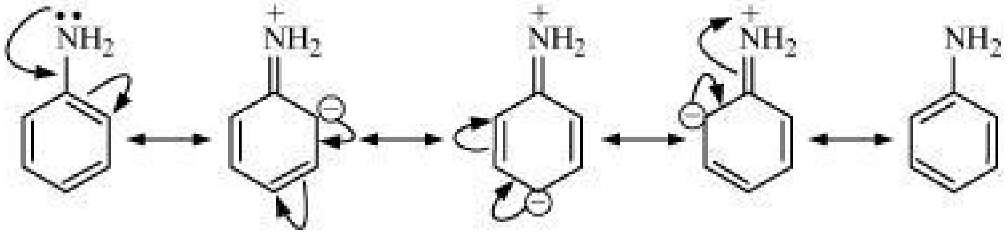
ANS. (i) $pK_b$ of aniline is more than that of methylamine:


Aniline


$CH_3-\ddot{N}H_2$

Methylamine

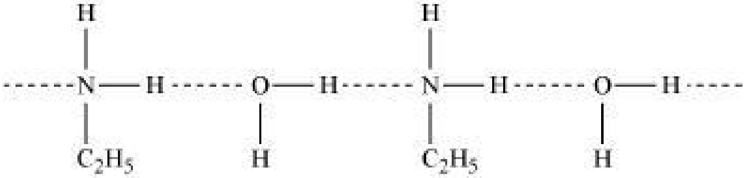
Aniline undergoes resonance and as a result, the electrons on the N-atom are delocalized over the benzene ring. Therefore, the electrons on the N-atom are less available to donate.



On the other hand, in case of methylamine (due to the +I effect of methyl group), the electron density on the N-atom is increased. As a result, aniline is less basic than methylamine. Thus, $pK_b$ of aniline is more than that of methylamine.

(ii) Ethylamine is soluble in water whereas aniline is not:

Ethylamine when added to water forms intermolecular H−bonds with water. Hence, it is soluble in water.



Ethylamine

But aniline does not undergo H−bonding with water to a very large extent due to the presence of a large hydrophobic $-C_6H_5$ group. Hence, aniline is insoluble in water.

(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide:

$$\underset{\text{Methylamine}}{CH_3 \longrightarrow NH_2} \qquad \underset{\text{Water}}{H - OH}$$

Due to the +I effect of $-CH_3$ group, methylamine is more basic than water. Therefore, in water, methylamine produces $OH^-$ ions by accepting $H^+$ ions from water.

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

Ferric chloride ($FeCl_3$) dissociates in water to form $Fe^{3+}$ and $Cl^-$ ions.

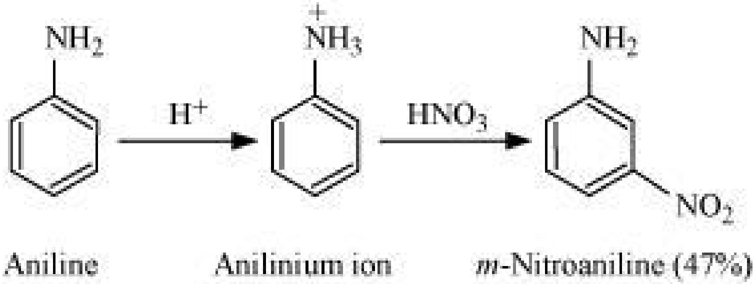
$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$$

Then, $OH^-$ ion reacts with $Fe^{3+}$ ion to form a precipitate of hydrated ferric oxide.

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

(iv) Although amino group is o,p− directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline:

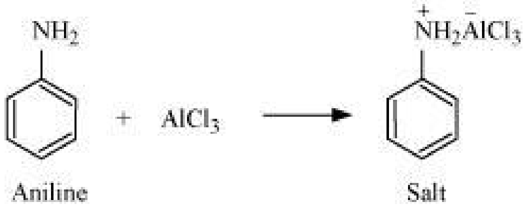
Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing).



For this reason, aniline on nitration gives a substantial amount of m-nitroaniline.

(v) Aniline does not undergo Friedel-Crafts reaction:

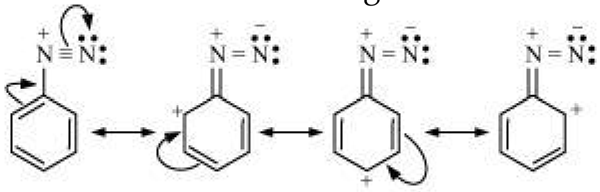
A Friedel-Crafts reaction is carried out in the presence of AlCl$_3$. But AlCl$_3$ is acidic in nature, while aniline is a strong base. Thus, aniline reacts with AlCl$_3$ to form a salt (as shown in the following equation).



Due to the positive charge on the N-atom, electrophilic substitution in the benzene ring is deactivated. Hence, aniline does not undergo the Friedel-Crafts reaction.

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

The diazonium ion undergoes resonance as shown below:



This resonance accounts for the stability of the diazonium ion. Hence, diazonium salts of aromatic amines are more stable than those of aliphatic amines.

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

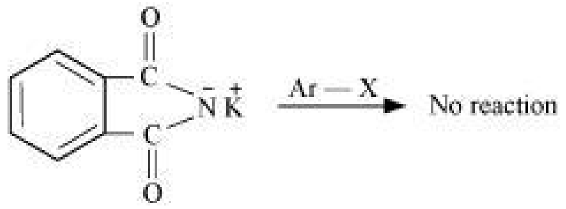
Gabriel phthalimide synthesis results in the formation of 1° amine only. 2° or 3° amines are not formed in this synthesis. Thus, a pure 1° amine can be obtained. Therefore, Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

Q2. Why cannot aromatic primary amines be prepared by Gabriel phthalimide

synthesis?

ANS. Gabriel phthalimide synthesis is used for the preparation of aliphatic primary amines. It involves nucleophilic substitution (S$_N$2) of alkyl halides by the anion formed by the phthalimide.

But aryl halides do not undergo nucleophilic substitution with the anion formed by the phthalimide.



Hence, aromatic primary amines cannot be prepared by this process.

Q3. Give plausible explanation for each of the following:

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

(ii) Why do primary amines have higher boiling point than tertiary amines?

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

<u>ANS.</u> (i) Amines undergo protonation to give amide ion.

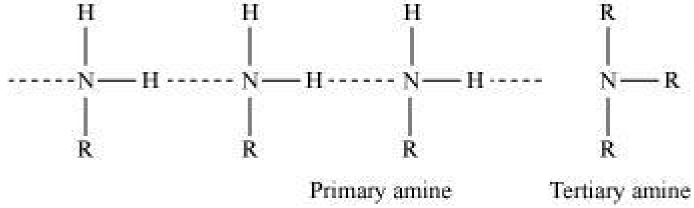
$$R-NH_2 \longrightarrow \underset{\text{Amide ion}}{R-\overset{-}{N}H} + H^+$$

Similarly, alcohol loses a proton to give alkoxide ion.

$$\underset{\text{Alcohol}}{R-OH} \longrightarrow \underset{\text{Alkoxide ion}}{R-\overset{-}{O}} + H^+$$

In an amide ion, the negative charge is on the N-atom whereas in alkoxide ion, the negative charge is on the O-atom. Since O is more electronegative than N, O can accommodate the negative charge more easily than N. As a result, the amide ion is less stable than the alkoxide ion. Hence, amines are less acidic than alcohols of comparable molecular masses.

(ii) In a molecule of tertiary amine, there are no H−atoms whereas in primary amines, two hydrogen atoms are present. Due to the presence of H−atoms, primary amines undergo extensive intermolecular H−bonding.



As a result, extra energy is required to separate the molecules of primary amines. Hence, primary amines have higher boiling points than tertiary amines.

(iii) Due to the −R effect of the benzene ring, the electrons on the N- atom are less available in case of aromatic amines. Therefore, the electrons on the N-atom in aromatic amines cannot be donated easily. This explains why aliphatic amines are stronger bases than aromatic amines.

## <u>SOLVED QUESTIONS</u>

### <u>1 MARK QUESTIONS</u>

Q1. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$(CH_3)_2CHNH_2$ 1-Methylethanamine ($1^0$ amine)

Q2. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$CH_3(CH_2)_2NH_2$ Propan-1-amine ($1^0$ amine)

Q3. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$CH_3NHCH(CH_3)_2$ N−Methyl-2-methylethanamine ($2^0$ amine)

Q4. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$(CH_3)_3CNH_2$ 2-Methylpropan-2-amine ($1^0$ amine)

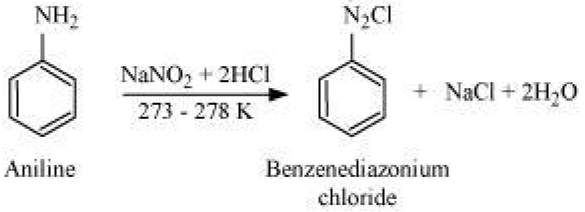
Q5. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$C_6H_5NHCH_3$ N−Methylbenzamine or N-methylaniline ($2^0$ amine)

Q6. Write short notes on diazotization

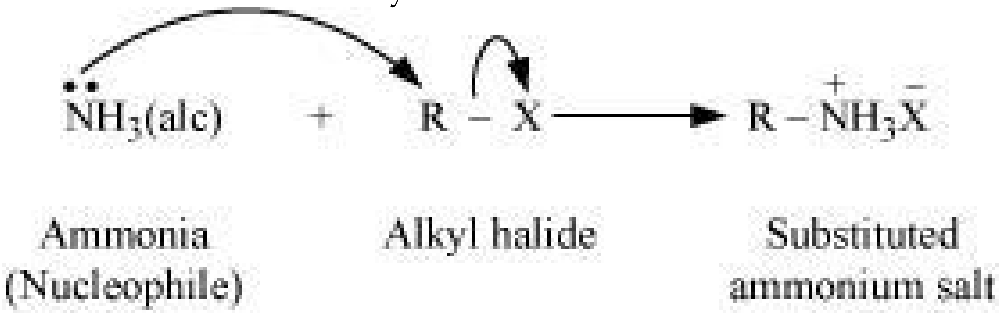
Aromatic primary amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) at low temperatures (273-278 K) to form diazonium salts. This conversion of aromatic primary amines into diazonium salts is known as diazotization.

For example, on treatment with $NaNO_2$ and HCl at 273−278 K, aniline produces benzenediazonium chloride, with NaCl and $H_2O$ as by-products.



Q7. Write short notes on ammonolysis

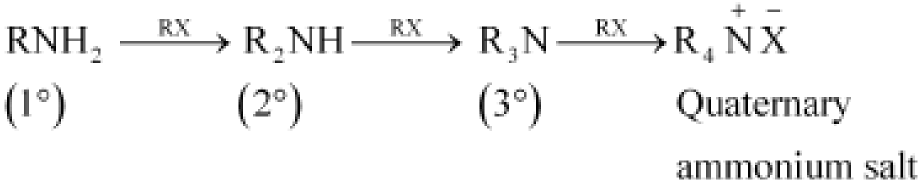
When an alkyl or benzyl halide is allowed to react with an ethanolic solution of ammonia, it undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino (−$NH_2$) group. This process of cleavage of the carbon-halogen bond is known as ammonolysis.



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

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

Though primary amine is produced as the major product, this process produces a mixture of primary, secondary and tertiary amines, and also a quaternary ammonium salt



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

Q8. Write short notes on acetylation.

Acetylation (or ethanoylation) is the process of introducing an acetyl group into a molecule. Aliphatic and aromatic primary and secondary amines undergo acetylation reaction by nucleophilic substitution when treated with acid chlorides, anhydrides or esters. This reaction involves the replacement of the hydrogen atom of $-NH_2$ or $> NH$ group by the acetyl group, which in turn leads to the production of amides. To shift the equilibrium to the right hand side, the HCl formed during the reaction is removed as soon as it is formed. This reaction is carried out in the presence of a base (such as pyridine) which is stronger than the amine.

$$C_2H_5NH_2 + CH_3COCl \xrightarrow{\text{pyridine}} C_2H_5NHCOCH_3 + HCl$$

Q9.Why are amines basic in character?

ANS. Like ammonia, the nitrogen atom in amines $RNH_2$ is trivalent and bears an unshared pair of electrons. Thus it acts like a Lewis base and donates the pair of electrons to electron-deficient species which further increases due to +I effect of alkyl radical.

Q10. Arrange the following in decreasing order of their basic strength:

$C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, $NH_3$

The decreasing order of basic strength of the above amines and ammonia

follows the following order:

$(C_2H_5)_2NH > C_2H_5NH_2 > NH_3 > C_6H_5NH_2$

## SOLVED EXAMPLES (2 Marks)

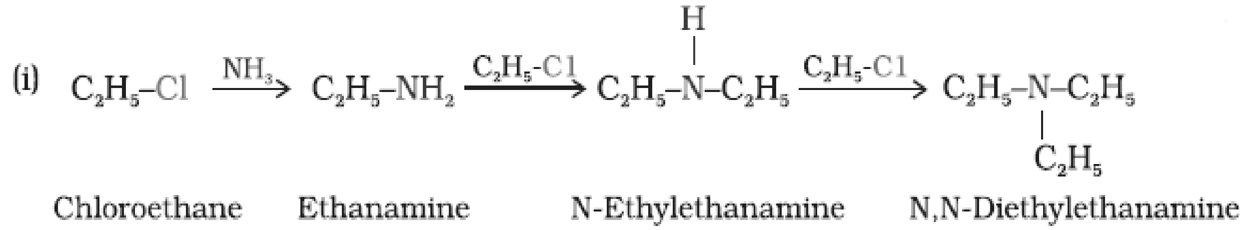
Q1. Write chemical equations for the following reactions:

(i) Reaction of ethanolic $NH_3$ with $C_2H_5Cl$.

(ii) Ammonolysis of benzyl chloride and reaction of amine so formed

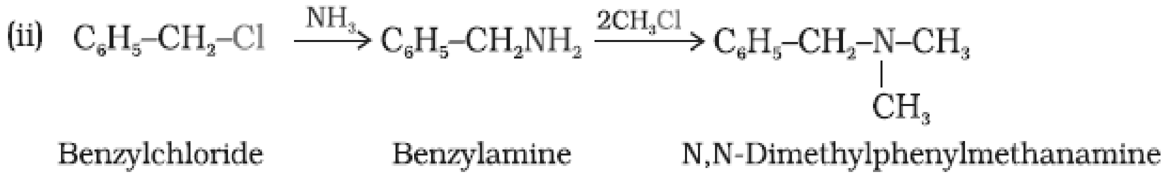
with two moles of $CH_3Cl$

ANS.



(i) $C_2H_5{-}Cl \xrightarrow{NH_3} C_2H_5{-}NH_2 \xrightarrow{C_2H_5\text{-}Cl} C_2H_5{-}\overset{H}{N}{-}C_2H_5 \xrightarrow{C_2H_5\text{-}Cl} C_2H_5{-}\underset{C_2H_5}{N}{-}C_2H_5$

Chloroethane  Ethanamine  N-Ethylethanamine  N,N-Diethylethanamine



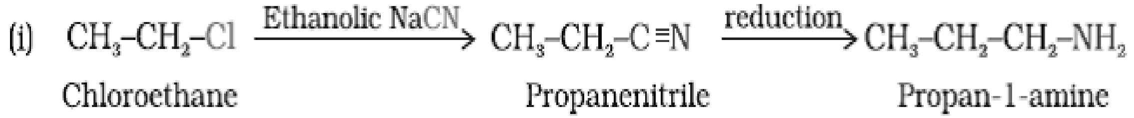
(ii) $C_6H_5{-}CH_2{-}Cl \xrightarrow{NH_3} C_6H_5{-}CH_2NH_2 \xrightarrow{2CH_3Cl} C_6H_5{-}CH_2{-}\underset{CH_3}{N}{-}CH_3$

Benzylchloride  Benzylamine  N,N-Dimethylphenylmethanamine

Q2. Write chemical equations for the following conversions:

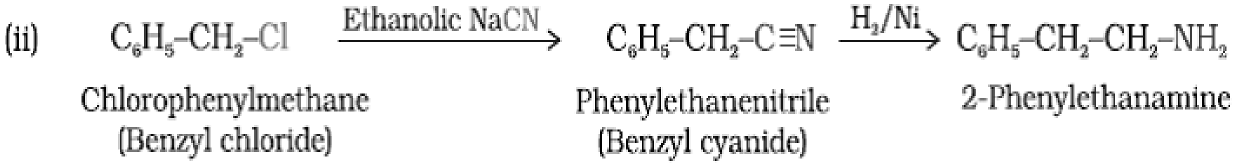
(i) $CH_3$ –$CH_2$ –Cl into $CH_3$ –$CH_2$ –$CH_2$ –$NH_2$

(ii) $C_6H_5$–$CH_5$ –Cl into $C_6H_5$ –$CH_2$ –$CH_2$ –$NH_2$



(i) $CH_3{-}CH_2{-}Cl \xrightarrow{\text{Ethanolic NaCN}} CH_3{-}CH_2{-}C{\equiv}N \xrightarrow{\text{reduction}} CH_3{-}CH_2{-}CH_2{-}NH_2$

Chloroethane  Propanenitrile  Propan-1-amine



(ii) $C_6H_5{-}CH_2{-}Cl \xrightarrow{\text{Ethanolic NaCN}} C_6H_5{-}CH_2{-}C{\equiv}N \xrightarrow{H_2/Ni} C_6H_5{-}CH_2{-}CH_2{-}NH_2$

Chlorophenylmethane (Benzyl chloride)  Phenylethanenitrile (Benzyl cyanide)  2-Phenylethanamine

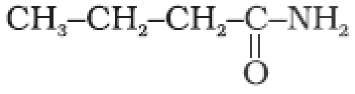
Q3.Write structures and IUPAC names of

(i) the amide which gives propanamine by Hoffmann bromamide

reaction.

(ii) the amine produced by the Hoffmann degradation of benzamide.

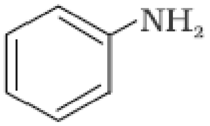
ANS. (i) Propanamine contains three carbons. Hence, the amide molecule must contain four carbon atoms. Structure and IUPAC name of the starting amide with four carbon atoms are given below:



$CH_3{-}CH_2{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}NH_2$

(Butanamide)

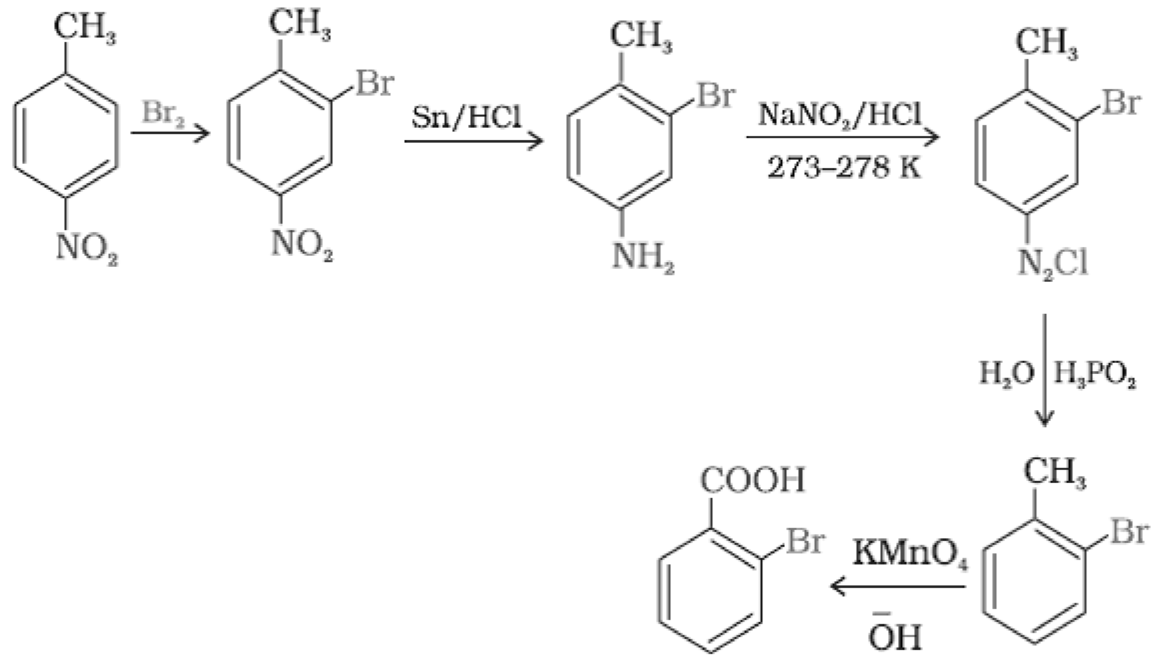
(ii) Benzamide is an aromatic amide containing seven carbon atoms. Hence, the amine formed from benzamide is aromatic primary amine containing six carbon atoms.



(Aniline or benzenamine)

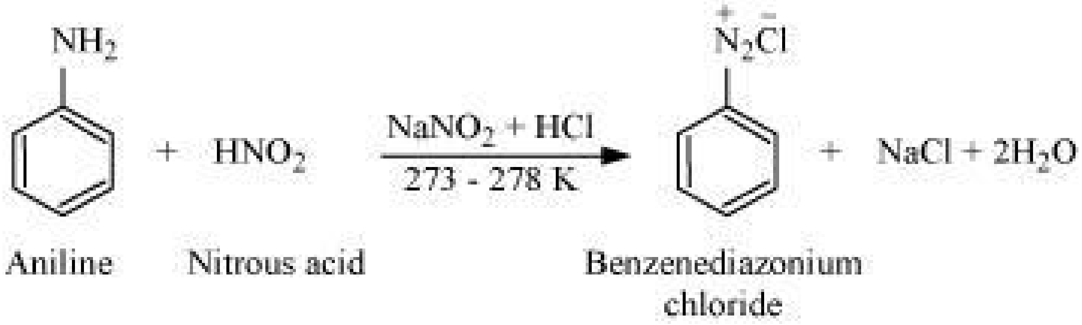
Q4. How will you convert 4-nitrotoluene to 2-bromobenzoic acid?

ANS.

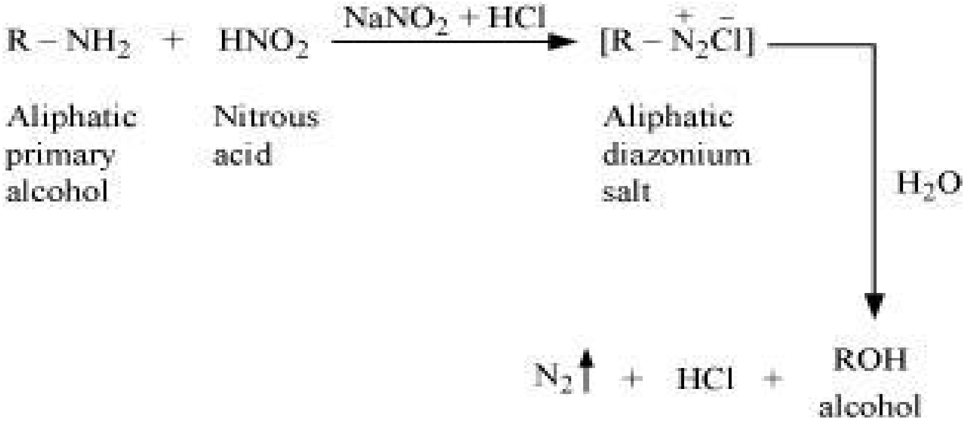


Q5. Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.

ANS. (i) Aromatic amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) at 273 − 278 K to form stable aromatic diazonium salts i.e., NaCl and $H_2O$.



(ii) Aliphatic primary amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) to form unstable aliphatic diazonium salts, which further produce alcohol and HCl with the evolution of $N_2$ gas.

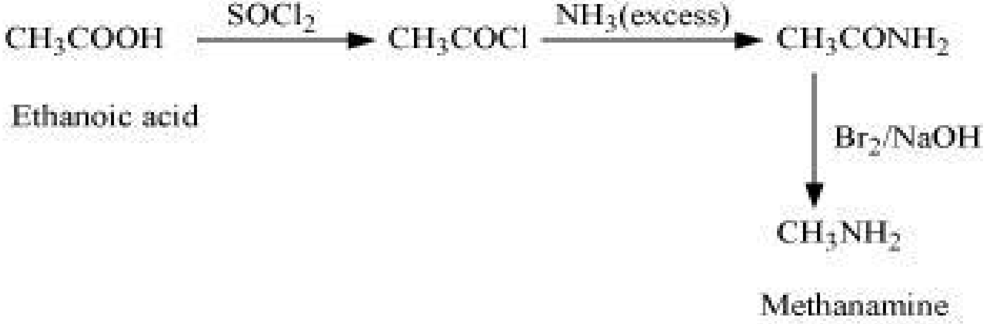


Q6. How will you convert:

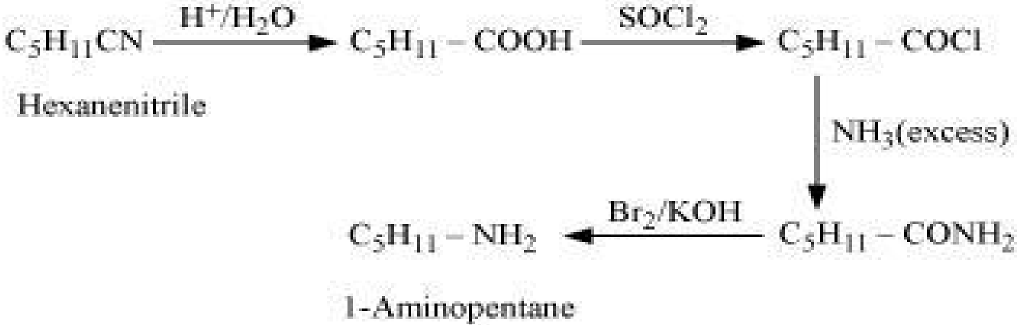
(i) Ethanoic acid into methanamine

(ii) Hexanenitrile into 1-aminopentane

ANS. (i)



(ii)

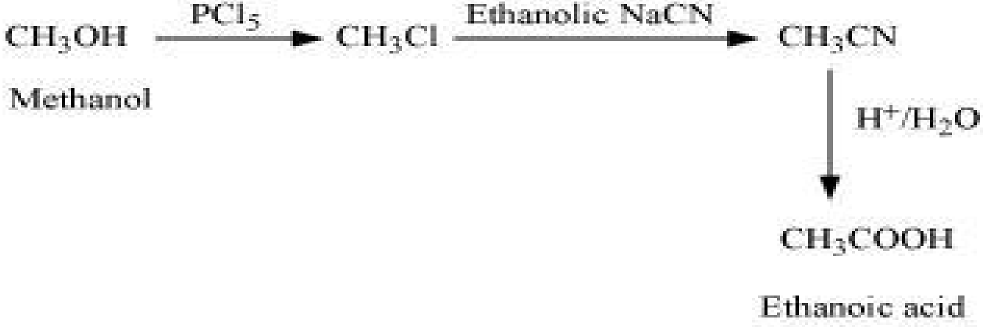


Q7. How will you convert:

(i) Methanol to ethanoic acid

(ii) Ethanamine into methanamine

ANS. (i)



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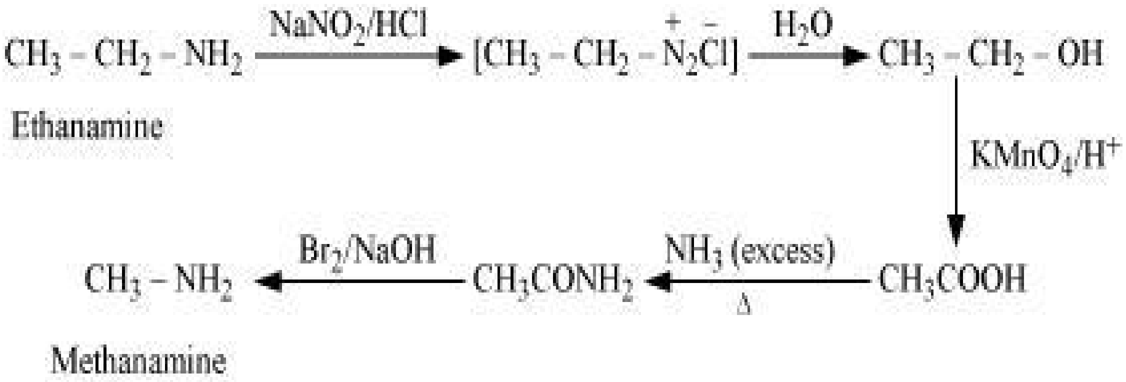
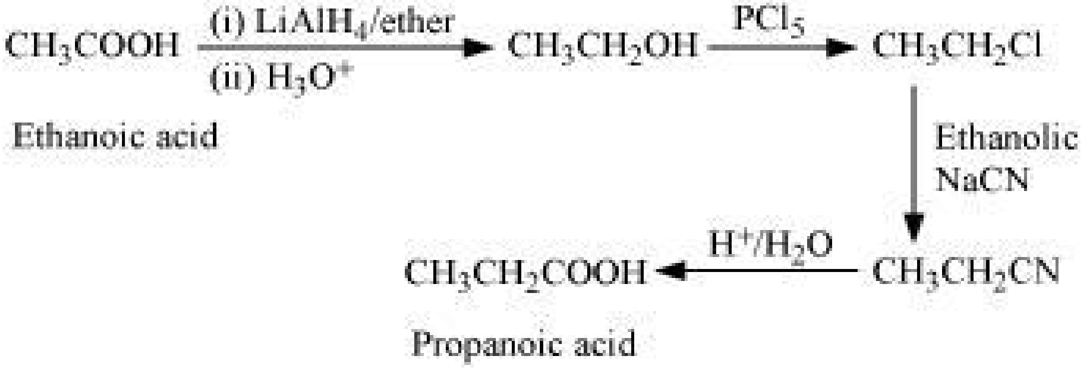


Q8. How will you convert

(i ) Ethanoic acid into propanoic acid

(ii) Methanamine into ethanamine

ANS. (i)



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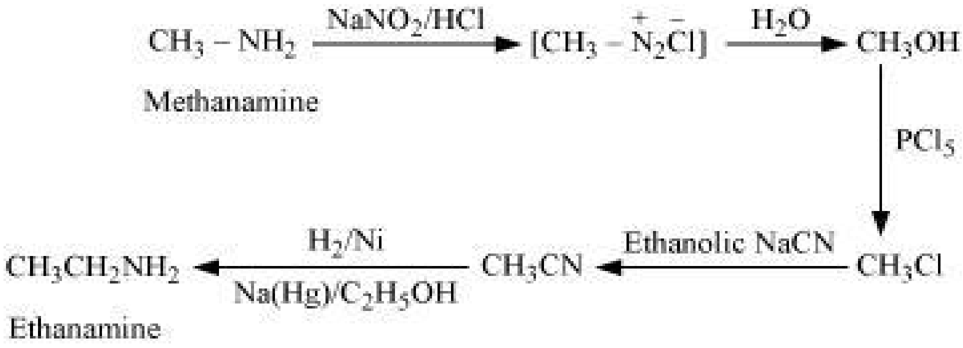
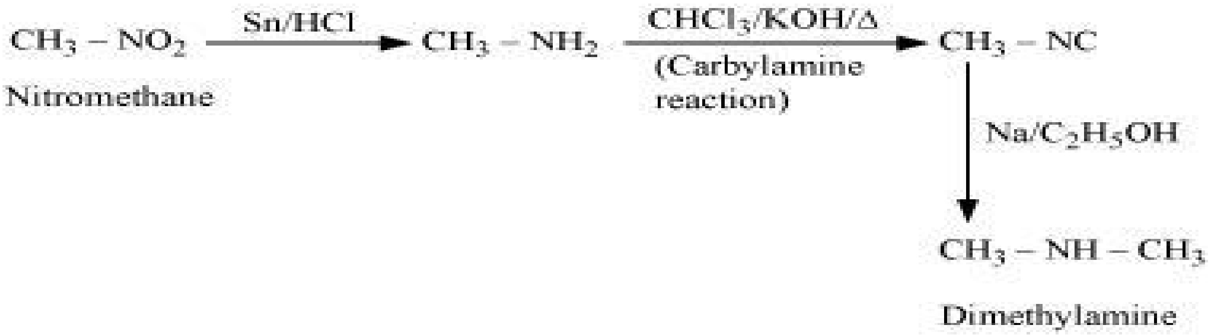


Q9. How will you convert

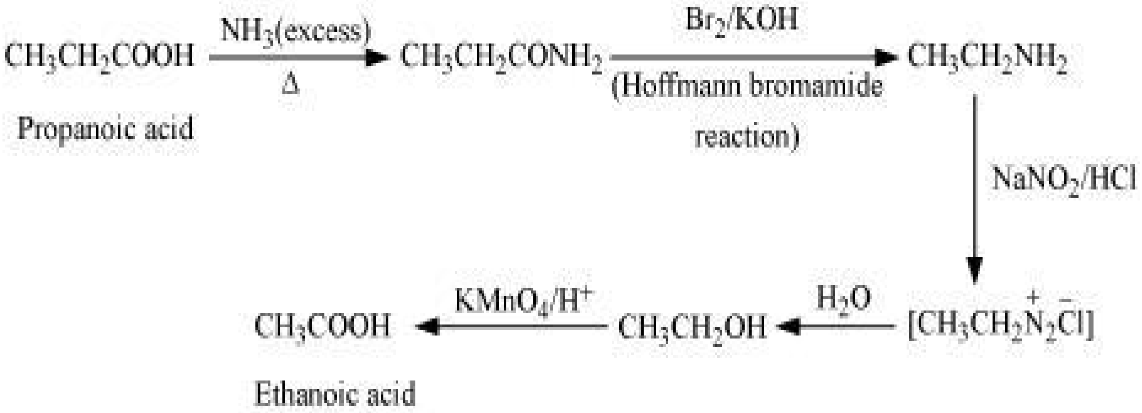
(i) Nitromethane into dimethylamine

(ii) Propanoic acid into ethanoic acid?

(i)

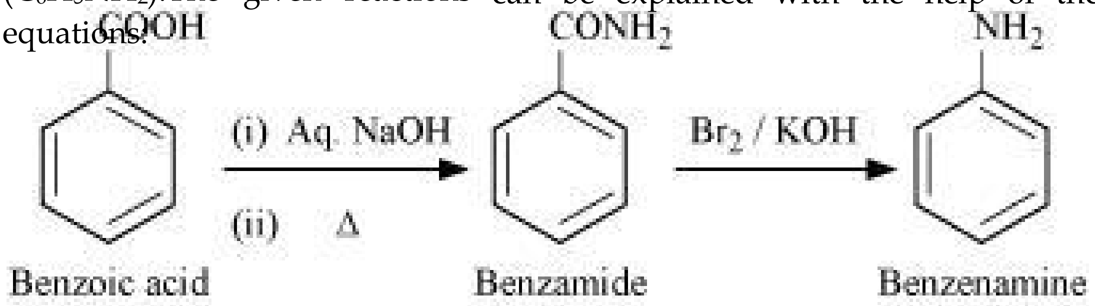


(ii)



Q10. 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.

ANS. It is given that compound ‗C′ having the molecular formula, $C_6H_7N$ is formed by heating compound ‗B′ with $Br_2$ and KOH. This is a Hoffmann bromamide degradation reaction. Therefore, compound ‗B′ is an amide and compound ‗C′ is an amine. The only amine having the molecular formula, $C_6H_7N$ is aniline, ($C_6H_5NH_2$).The given reactions can be explained with the help of the following equations:



Benzoic acid
(A)

Benzamide
(B)

Benzenamine
(C)

**3 MARKS QUESTIONS**

Q1. Arrange the following:

(i) In decreasing order of the pKb values:
$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

(ii) In increasing order of basic strength:

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$ , $(C_2H_5)_2$ NH and $CH_3NH_2$

(iii) In increasing order of basic strength:

Aniline, p-nitroaniline and p-toluidine

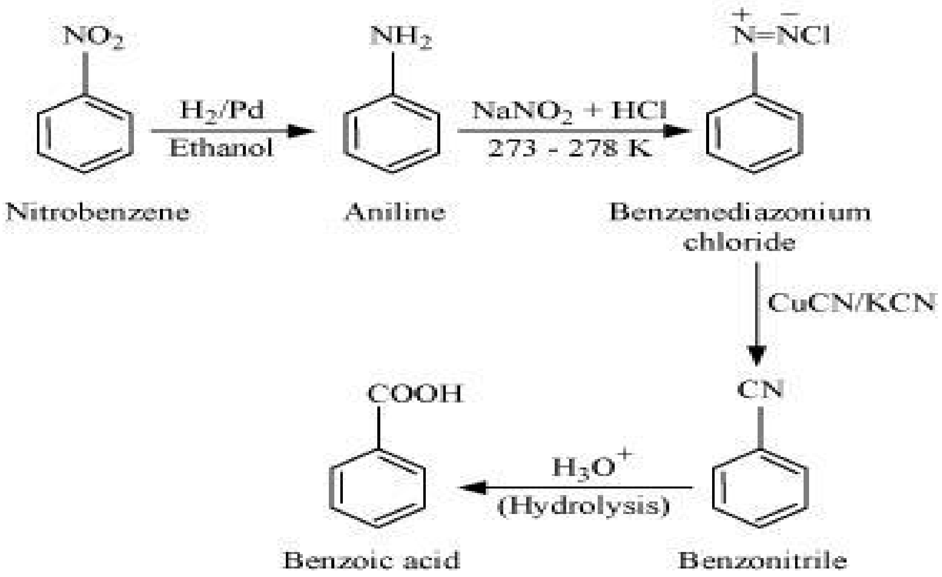
ANS. (i) The order of increasing basicity of the given compounds is as follows:
$C_6H_5NH_2 < C_6H_5NHCH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$
We know that the higher the basic strength, the lower is the $pK_b$ values.
$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$
(ii)The increasing order of the basic strengths of the given compounds is as follows:
$C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$
(iii) The increasing order of the basic strengths of the given compounds is :
p-Nitroaniline < Aniline < p-Toluidine

Q2. Arrange the following
(i) In decreasing order of basic strength in gas phase:
$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and $NH_3$
(ii) In increasing order of boiling point:
$C_2H_5OH$, $(CH_3)_2NH$, $C_2H_5NH_2$
(iii) In increasing order of solubility in water:
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$.

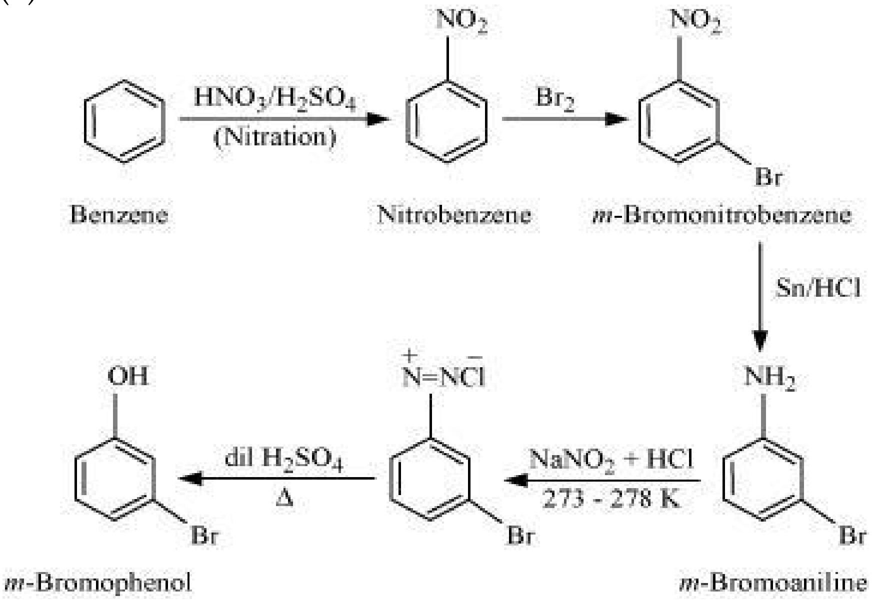
ANS. (i) The given compounds can be arranged in the decreasing order of their basic strengths in the gas phase as follows:
$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$
(ii) The given compounds can be arranged in the increasing order of their boiling points as follows:
$(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$
(iii) The more extensive the H−bonding, the higher is the solubility. $C_2H_5NH_2$ contains two H-atoms whereas $(C_2H_5)_2NH$ contains only one H-atom. Thus, $C_2H_5NH_2$ undergoes more extensive H−bonding than $(C_2H_5)_2NH$. Hence, the solubility in water of $C_2H_5NH_2$ is more than that of $(C_2H_5)_2NH$.

Q3. Accomplish the following conversions:
(i) Nitrobenzene to benzoic acid
(ii) Benzene to m-bromophenol
(iii) Benzoic acid to aniline

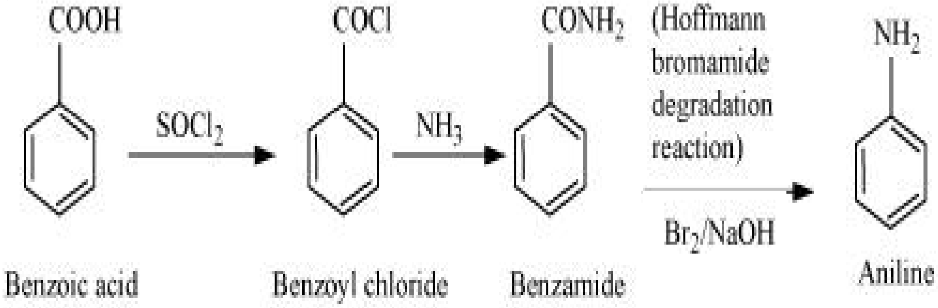
ANS. (i)



(ii)

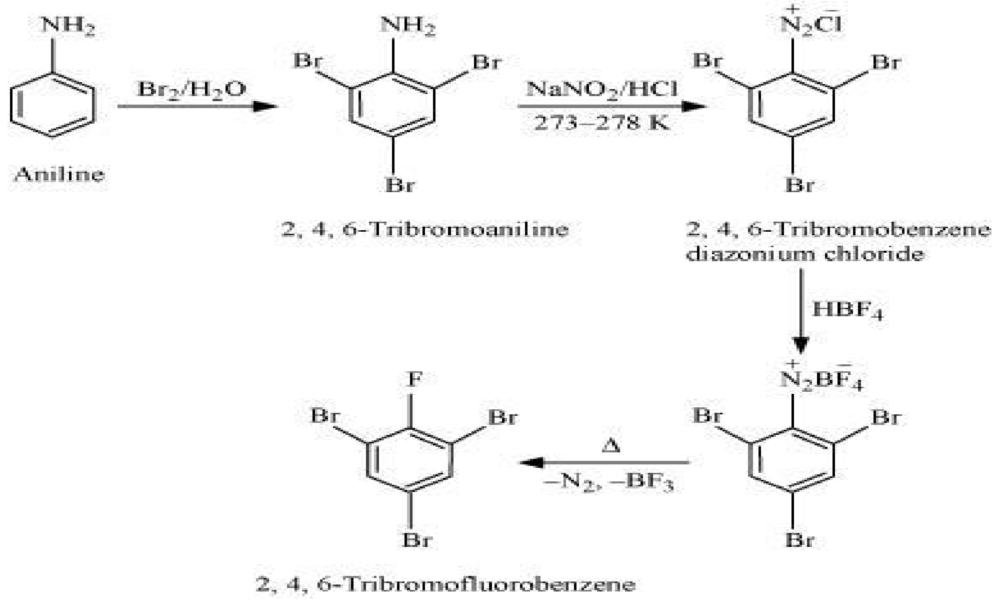


(iii)

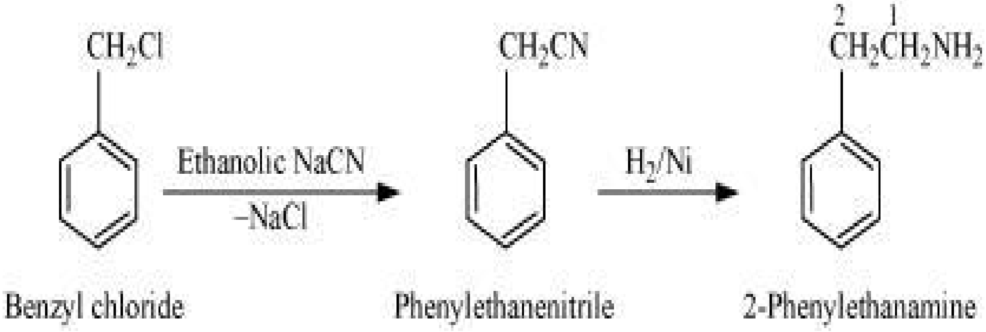


Q4. Accomplish the following conversions:
(i) Aniline to 2,4,6-tribromofluorobenzene
(ii) Benzyl chloride to 2-phenylethanamine
(iii) Chlorobenzene to p-chloroaniline

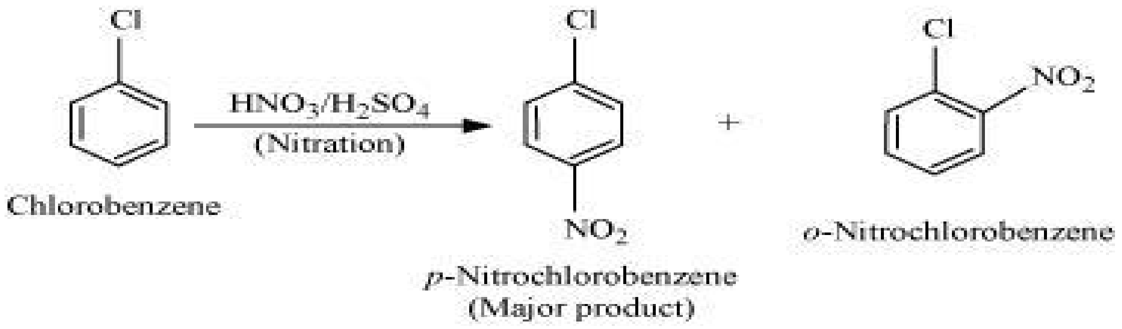
ANS. (i)

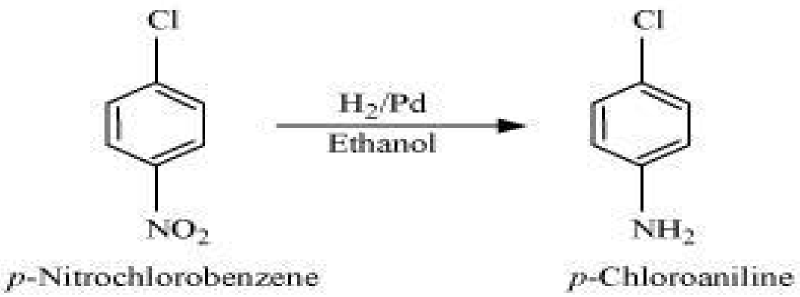

NH$_2$
Aniline
Br$_2$/H$_2$O
Br
2, 4, 6-Tribromoaniline
NaNO$_2$/HCl
273–278 K
$\overset{+}{N}_2\overset{-}{Cl}$
2, 4, 6-Tribromobenzene diazonium chloride
HBF$_4$
$\overset{+}{N}_2B\overset{-}{F}_4$
Δ
–N$_2$, –BF$_3$
F
2, 4, 6-Tribromofluorobenzene

(ii)


CH$_2$Cl
Benzyl chloride
Ethanolic NaCN
–NaCl
CH$_2$CN
Phenylethanenitrile
H$_2$/Ni
2 1
CH$_2$CH$_2$NH$_2$
2-Phenylethanamine

(iii)





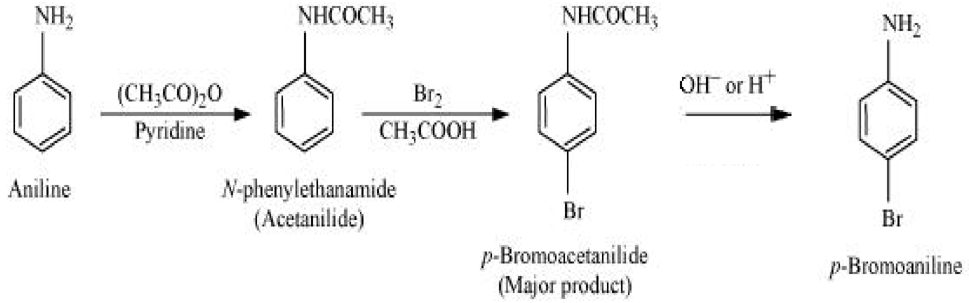
Q5. Accomplish the following conversions:

(i) Aniline to p-bromoaniline

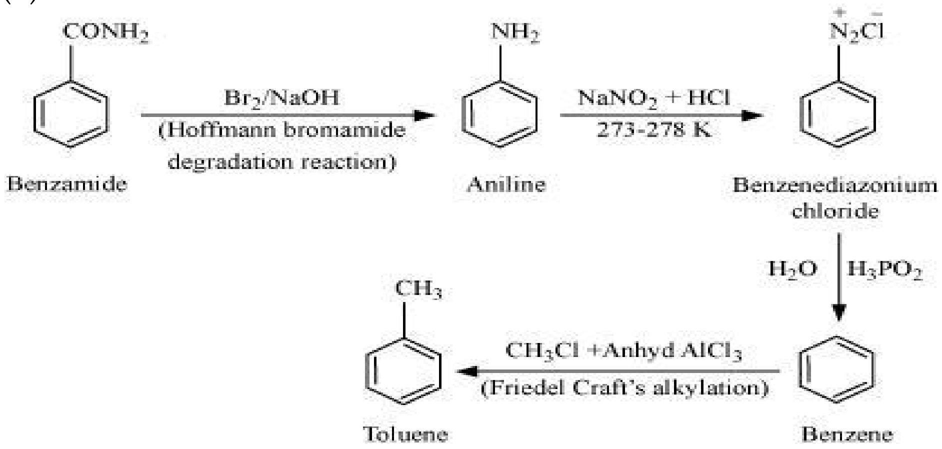
(ii) Benzamide to toluene

(iii) Aniline to benzyl alcohol.

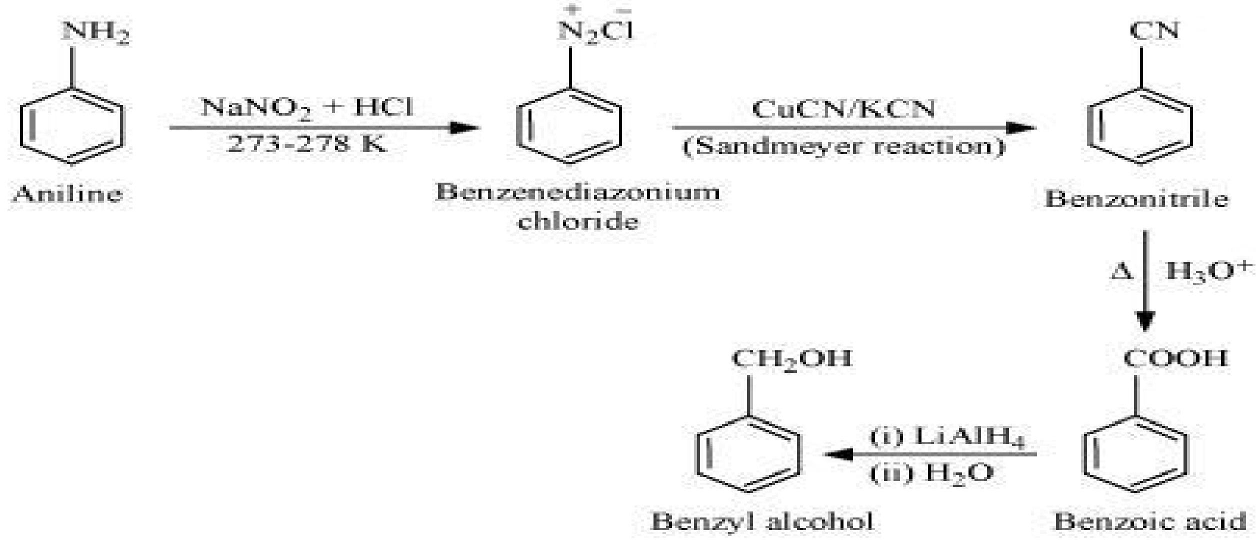
ANS. (i)



(ii)



(iii)



**5 MARKS QUESTIONS**

Q1. Give the structures of A, B and C in the following reactions:

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

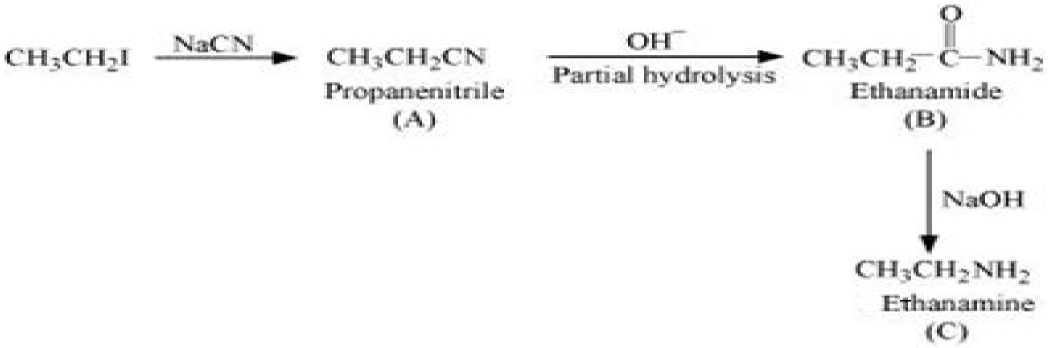
(ii) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

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

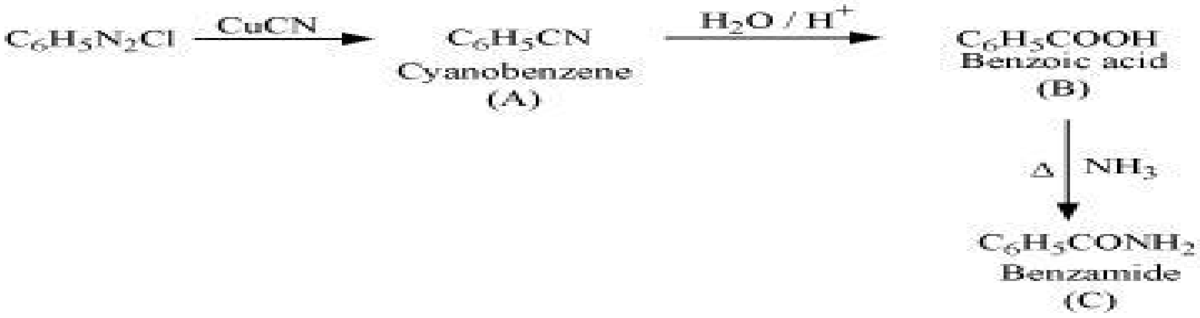
(iv) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{NaNO_2+HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$

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

ANS. (i)



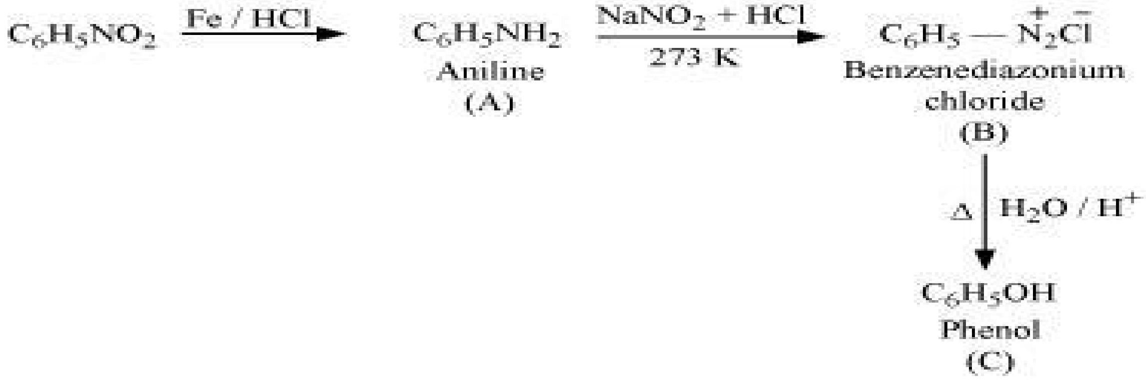
(ii)



(iii)

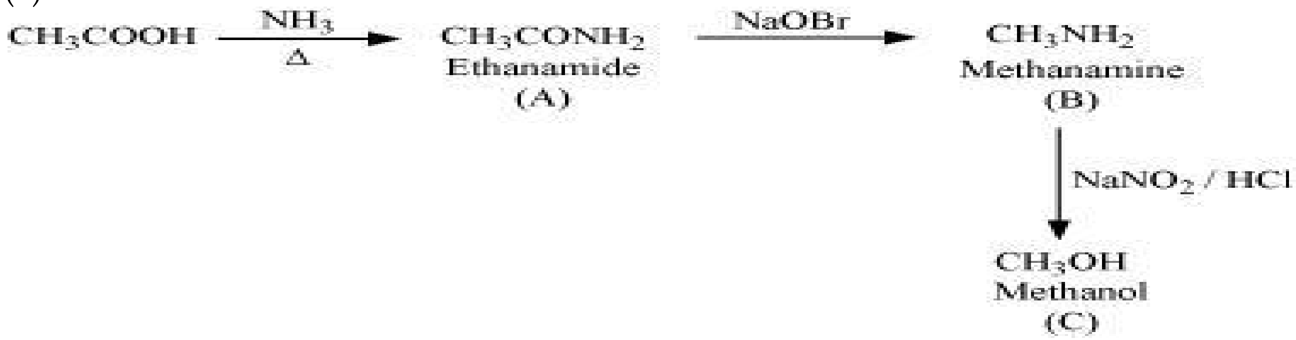
$$CH_3CH_2Br \xrightarrow{KCN} \underset{\substack{\text{Cyanoethane}\\(A)}}{CH_3CH_2CN} \xrightarrow{LiAlH_4} \underset{\substack{\text{Propan}-1-\text{amine}\\(B)}}{CH_3CH_2CH_2NH_2} \xrightarrow[0\,^\circ C]{HNO_2} \underset{\substack{\text{Propan}-1-\text{ol}\\(C)}}{CH_3CH_2CH_2OH}$$

(iv)



$$C_6H_5NO_2 \xrightarrow{Fe\,/\,HCl} \underset{\substack{\text{Aniline}\\(A)}}{C_6H_5NH_2} \xrightarrow[273\ K]{NaNO_2 + HCl} \underset{\substack{\text{Benzenediazonium}\\\text{chloride}\\(B)}}{C_6H_5-\overset{+}{N_2}\overset{-}{Cl}} \xrightarrow[\Delta]{H_2O\,/\,H^+} \underset{\substack{\text{Phenol}\\(C)}}{C_6H_5OH}$$

(v)



$$CH_3COOH \xrightarrow[\Delta]{NH_3} \underset{\substack{\text{Ethanamide}\\(A)}}{CH_3CONH_2} \xrightarrow{NaOBr} \underset{\substack{\text{Methanamine}\\(B)}}{CH_3NH_2} \xrightarrow{NaNO_2\,/\,HCl} \underset{\substack{\text{Methanol}\\(C)}}{CH_3OH}$$

Q2. Complete the following reactions:

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

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

(iii) $C_6H_5NH_2 + H_2SO_4(conc.) \rightarrow$

(iv) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$

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

ANS. (i)

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

(ii)

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

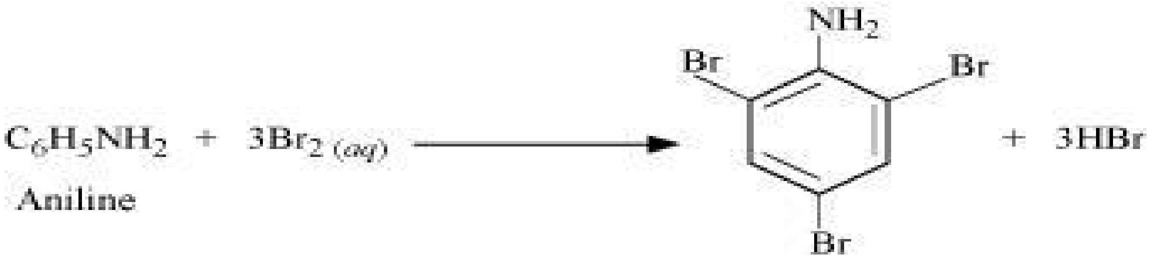
(iii)

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \text{conc.}H_2SO_4 \rightarrow \underset{\text{Anilinium hydrogen sulphate}}{C_6H_5\overset{+}{N}H_3HS\overset{-}{O}_4}$$

(iv)

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

(v)



2,4,6 – Tribromoaniline

# Assignments

## Level 1

1. Write IUPAC Name of $C_6H_5N(CH_3)_3Br$ ?
2. Which reaction is used for preparation of pure aliphatic & aralkyl primary amine ?
3. Name one reagent used for the separation of primary, secondary & tertiary amine ?
4. What amine salts are used for determing their molecular masses ?
5. What is the directive influence of amino group in arylamines?
6. Why are benzene diazonium salts soluble in water ?
7. Which is more basic: $CH_3NH_2$ & $(CH_3)_3N$ ?
8. Which is more acidic, aniline or ammonia ?
9. Write the IUPAC name of $C_6H_5NHCH_3$ ?
10. Mention two uses of sulphanilic acid?

## Level 2

1. What for are quaternary ammonium salts widely used ?
2. What product is formed when aniline is first diazotized and then treated with Phenol in alkaline medium ?

3. How is phenyl hydrazine prepared from aniline ?
4. What is the IUPAC name of a tertiary amine containing one methyl, one ethyl And one n-propyl group ?

5. Explain why silver chloride is soluble in aqueous solution of methylamine ?
6. Write the IUPAC name of $C_6H_5N(CH_3)_3$ Br ?
7. Primary amines have higher boiling points then tertiary amines why ?

8. Why is it necessary to maintain the temperature between 273 K & 278 K during diazotization?
9. Arrange the following in order of decreasing basic strength : Ethyl amine, Ammonia, Triethylamine ?
10. Why aniline is acetylated first to prepare mono bromo derivative?

## LEVEL 3

1. Arrange the following in decreasing order of their basic strength.

   $C_6H_5NH_2$, C2H5NH2,
   $(C_2H_5)_2NH$, $NH_3$

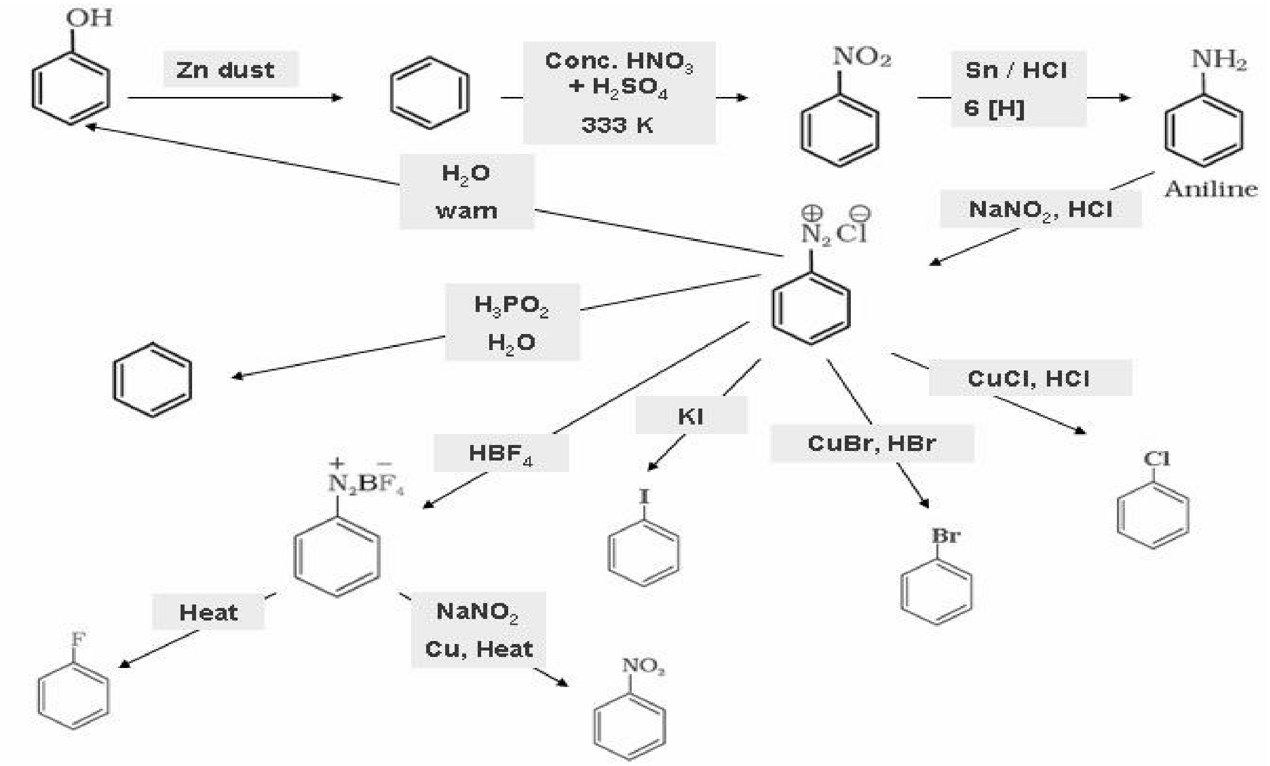
2. Write chemical equation for the conversion

   $CH_3$-$CH_2$-Cl into $CH_3$
   –$CH_2$-$CH_3$-$NH_2$

3. Write the equation involved in Carbylamines reactions?

4. How will you distinguish the following pairs? (i) Methanamine and N-methyl methane amine (ii) Aniline and ethyl amine

5. Write chemical sections involved in following name reactions. (i)
Hoffmann Bromoamide reaction. (ii)
Diazotisation reaction.



COMMON ERRORS

Basic character of amines in aqueous and in gaseous state, $p_{ka}$ and $p_{kb}$ values

## 1 MARK QUESTIONS

Q1. Arrange the following in decreasing order of their basic strength: $C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, $NH_3$

Q2. Arrange the following in decreasing order of the p*Kb* values: $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

Q3. p*Kb* of aniline is more than that of methylamine. Why?

Q4. Ethylamine is soluble in water whereas aniline is not. Give reason.

Q5. Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide. Why?

Q6. Although amino group is *o*– and *p*– directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of
*m*-nitroaniline. Give reason.

Q7. Aniline does not undergo Friedel-Crafts reaction. Why?

Q8. Diazonium salts of aromatic amines are more stable than those of aliphatic amines. Why?

Q9. Gabriel phthalimide synthesis is preferred for synthesising primary amines. Give reason

Q10. Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

Q11. Why do primary amines have higher boiling point than tertiary amines?

Q12. Why are aliphatic amines stronger bases than aromatic amines?

Q13. Direct nitration of aniline is not carried out. Give reason.

Q14. The presence of base is needed in the ammonolysis of alkyl halides. Why?

## 2 MARKS QUESTIONS

Q1. Write structures and IUPAC names of

(i) the amide which gives propanamine by Hoffmann bromamide reaction.

(ii) the amine produced by the Hoffmann degradation of benzamide.

Q2. Give one chemical test to distinguish between the following pairs of compounds.

(i) Methylamine and dimethylamine (ii) Ethylamine and aniline

Q3. Write short notes on the following:
(i) Carbylamine reaction (ii) Diazotisation
Q4. Explain the following with the help of an example.
(i) Hofmann's bromamide reaction (ii) Coupling reaction
Q5. Explain the following with the help of an example.
(i) Ammonolysis (ii) Gabriel phthalimide synthesis
Q6. How can you convert an amide into an amine having one carbon less than the starting compound? Name the reaction.
Q7. Give a chemical test to distinguish between:
(a) $C_6H_5NH_2$ & $CH_3NH_2$
(b) $CH_3NHCH_3$ & $(CH_3)_3N$
Q8. Give the IUPAC names of:
(a) $(CH_3)_2CHNH_2$
(b) $(CH_3CH_2)_2NCH_3$
Q9. Write the structures of:
(a) 3-Bromobenzenamine
(b) 3-Chlorobutanamide

## **3 MARKS QUESTIONS**

Q1. How will you convert
(i) Benzene into aniline (ii) Benzene into N, N-dimethylaniline
(iii) Aniline to Sulphanilic acid

Q2. An aromatic compound 'A' on treatment with aqueous ammonia and heatingforms 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.

Q3. How will you carry out the following conversions (Write Chemical equations and reaction conditions):
(a) Aniline to Phenol
(b)Acetamide to Ethylamine
(c) Aniline to *p*-nitroaniline