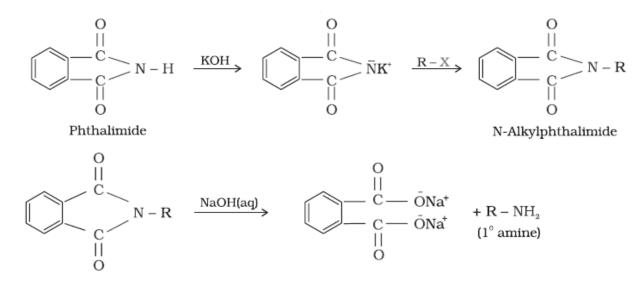
#### <u>UNIT -13</u>

#### ORGANIC COMPOUNDS CONTAINING NITROGEN AMINES

#### NAME REACTIONS

#### 1. Gabriel phthalimide synthesis

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolicpotassium hydroxide forms potassiumsalt 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. <u>Hoffmann bromamide (degradation)</u> reaction

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.

$$\begin{array}{c} O \\ || \\ R - C - NH_2 + Br_2 + 4NaOH \longrightarrow R - NH_2 + Na_2CO_3 + 2NaBr + 2H_2O \end{array}$$

#### 3. Carbylaminereaction

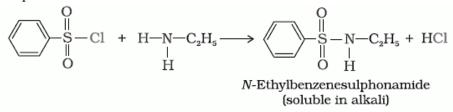
Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbyl aminereaction or iso cyanide test and is used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

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

### 4. Hinsberg Test:

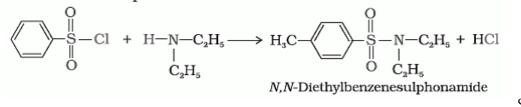
Benzene sulphonyl chloride ( $C_6H_5SO_2Cl$ ), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.

(a)The reaction of benzene sulphonyl chloride with primary amine yields N- ethyl benzene sulphonamide.



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 (NaOH Or KOH).

(b)In the reaction with secondaryamine, N,N-diethyl benzene sulphonamide is formed.



Since N,N-diethyl

benzene 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 Benzene sulphonyl chloride. This property of amines reacting with Benzene sulphonylchloride 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's Reaction

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

$$ArN_{2}^{+ -}X \xrightarrow{CuCl/HCl} ArCl + N_{2}$$

$$ArN_{2}^{+ -}X \xrightarrow{CuBr/HBr} ArBr + N_{2}$$

$$CuCN / KCN ArCN + N_{2}$$

# 6.Gatterman Reaction

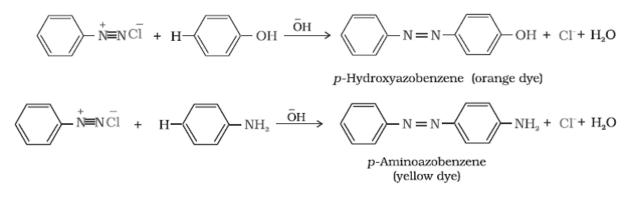
Chloride or bromide can be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder.

$$\begin{array}{c} & \stackrel{+}{\operatorname{ArN_2X}} \xrightarrow{\operatorname{Cu/HCl}} \operatorname{ArCl} + \operatorname{N_2} + \operatorname{CuX} \\ & \xrightarrow{\operatorname{Cu/HBr}} \operatorname{ArBr} + \operatorname{N_2} + \operatorname{CuX} \end{array}$$

## 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-hydroxy azobenzene (Orange dye). This type of reaction is known as coupling reaction.

Similarly the reaction of diazonium salt with aniline yields p-amino azobenzene(Yellow dye).



## **DISTINCTION BETWEEN PAIRS OF COMPOUNDS**

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

- (i) Methylamine and dimethyl amine
- (ii) Secondary and tertiary amines
- (iii) Ethyl amine and aniline
- (iv) Aniline and benzylamine
- (v) Aniline and N-methylaniline

<u>ANS.</u> (i) Methyl amine and dimethyl amine can be distinguished by the carbyl amine test. Carbyl amine test: Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form foul-smelling isocyanides or carbyl amines. Methyl amine (being an aliphatic primary amine) gives a positive carbyl amines test, but diethylamine does not.

 $\begin{array}{ll} CH_3 - NH_2 &+ CHCl_3 + 3 \text{KOH} \stackrel{\Delta}{\longrightarrow} CH_3 - NC + 3 \text{KCl} + 3H_2 \\ \text{Methylamine}(1^0) & \text{Methyl isocyanide} \\ & (\text{foul smell}) \\ (CH_3)_2 \text{NH} + CHCl_3 + 3 \text{KOH} \stackrel{\Delta}{\longrightarrow} \text{No reaction} \end{array}$ 

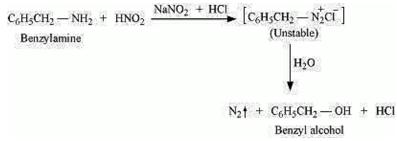
(ii) Secondary and tertiary amines can be distinguished by allowing them to react with Hinsberg's reagent (Benzene sulphonyl chloride,  $C_6H_5SO_2Cl$ ). Secondary amines react with Hinsberg's reagent to form a product that Is insoluble in an alkali. For example,

N, N-diethyl amide reacts with Hinsberg's reagent to form N, N-diethyl benzene sulphonamide, 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 action with the alkaline solution of 2-naphthol. The dye is usually yellow, red, ororange in colour. Aliphatic amines give a brisk effervescence (due to the evolution of N<sub>2</sub>gas) under similar conditions.

(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.

Benzyl amine 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-methyl aniline can be distinguished using the Carbylamine test.

Primary amines, on heating with chloroform and ethanolic potassium hydroxide, form foulsmelling isocyanides or carbylamines. Aniline, being an aromatic primary amine, gives positive carbylamines test. However, N-methyl aniline, being a secondary amine does not.

# **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 synthesizingprimary amines.

<u>ANS.(i)</u> pK<sub>b</sub>of aniline is more than that of methylamine:

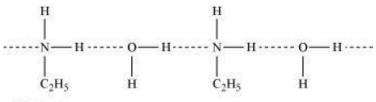
CH2 - NH2 Methylamine Aniline

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 methyl amine (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.



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Ethylamine
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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 withferric chloride to precipitate hydrated ferric oxide:

CH<sub>3</sub> → NH<sub>2</sub> H — OH Methylamine Water

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.

Ferric chloride (FeCl3) dissociates in water to form  $Fe^{3+}$  and  $Cl^{-}$  ions.

Then, OH<sup>-</sup> ion reacts with Fe<sup>3+</sup>ion to form a precipitate of hydrated ferric oxide.

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

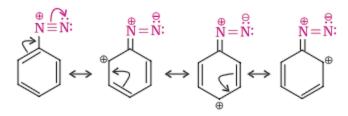
(iv) Although amino group is o,p- directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline:

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:

Friedel-Crafts reaction is carried out in the presence of an. AlCl<sub>3</sub>. But an. AlCl<sub>3</sub> is acidic in nature, while aniline is a strong base. Thus, aniline reacts with an. AlCl<sub>3</sub>to form a salt 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:

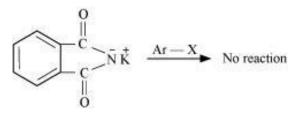


This resonance accounts for the stability of the diazonium ion. Hence, diazonium salts of aromatic amines are more stable than those of aliphatic amines.

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

Gabriel phthalimide synthesis results in the formation of 1° amine only. 2° or 3° aminesare 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? Gabriel phthalimide synthesis is used for the preparation of aliphatic primary amines. It involves nucleophilic substitution ( $SN_2$ ) of alkyl halides by the anion formed by the phthalimide. But aryl halides do not undergo nucleophilic substitution with the anion formed by the Phthalimde.



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

Q3.Give possible 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 aliphatic amines stronger are bases than aromatic amines?

<u>ANS.(i)</u> Amines undergo deprotonation to give RN<sup>-</sup>H and H<sup>+</sup>ion.

 $R - NH_2 \longrightarrow R - NH + H^+$ 

Similarly, alcohol loses a proton to give alkoxide ion.

In an RN<sup>-</sup>H 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 where as 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.

## SOLVED QUESTIONS

## **1 MARK QUESTIONS**

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

- a) (CH<sub>3</sub>)<sub>2</sub>CHNH<sub>2</sub>
- b) CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>
- c) CH<sub>3</sub>NHCH(CH<sub>3</sub>)<sub>2</sub>
- d) (CH<sub>3</sub>)<sub>3</sub>CNH<sub>2</sub>
- e) C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub>

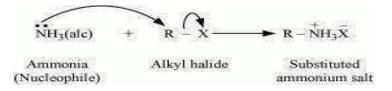
Ans.

- a) 1-Methylethanamine(1<sup>0</sup> amine)
- b) Propan-l-amine (1<sup>0</sup> amine)
- c) N–Methyl-2-methylethanamine (2<sup>0</sup> amine)
- d) 2-Methylpropan-2-amine(1<sup>0</sup> amine)
- e) N–Methylbenzamine or N-methyl aniline(2<sup>0</sup> amine)
- Q2.Write short notes on diazotization

Aromatic primary amines react with nitrous acid (prepared in situfrom NaNO<sub>2</sub> and a mineral acid such as HCl) at low temperatures (273-278K) to form diazonium salts. This conversion of aromatic primary amines intodiazonium salts is known as diazotization. For example, on treatment with NaNO<sub>2</sub> and HCl at 273–278 K, aniline produces benzene diazonium chloride, with NaCl and  $H_2O$  as by-products.

Q3.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<sub>2</sub>)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.

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

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

$$RNH_{2} \xrightarrow{RX} R_{2}NH \xrightarrow{RX} R_{3}N \xrightarrow{RX} R_{4} \stackrel{+}{N} \stackrel{-}{X} (1^{\circ}) \qquad (2^{\circ}) \qquad (3^{\circ}) \qquad Quaternary ammonium salt$$

Q4.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 there placement of the hydrogen atom of–NH2 or>NHGroup 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.

C2 H5NH2+ CH3CO Cl <sup>Pyridine</sup>C2H5NHCOCH3 + HCl

Q5. Why are amines basic in character?

<u>ANS</u>. 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.

Q6. Arrange the following in decreasing order of the basic strength:

C6H5NH2,C2H5 NH2,(C2H5)2NH,NH3

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 (2Marks)**

Q1. Write chemical equations for the following reactions:

(i) Reaction of ethanolic NH3 with  $C_2H_5Cl$ .

(ii) Ammonolysis of benzyl chloride and reaction of amine so formed with two moles of  $CH_3Cl$ 

#### ANS.

(i)  $C_{2}H_{5}-Cl \xrightarrow{NH_{3}} C_{2}H_{5}-NH_{2} \xrightarrow{C_{2}H_{5}-Cl} C_{2}H_{5}-N-C_{2}H_{5} \xrightarrow{C_{2}H_{5}-Cl} C_{2}H_{5}-N-C_{2}H_{5}$ Chloroethane Ethanamine N-Ethylethanamine N,N-Diethylethanamine (ii)  $C_{6}H_{5}-CH_{2}-Cl \xrightarrow{NH_{3}} C_{6}H_{5}-CH_{2}NH_{2} \xrightarrow{2CH_{3}Cl} C_{6}H_{5}-CH_{2}-N-CH_{3}$ Benzylchloride Benzylamine N,N-Dimethylphenylmethanamine

Q2.Write chemical equations for the following conversions:

(i)CH3 -CH2 -Cl into CH3-CH2 -CH2 -NH2 (ii)C6H5-CH5 -Cl into C6H5 -CH2 -CH2 -NH2

(i)	CH <sub>3</sub> -CH <sub>2</sub> -Cl Ethan	$\xrightarrow{\text{nolic NaCN}}$ CH <sub>3</sub> -C	$CH_2 - C = N = \frac{reduce}{1 + 1}$	$\xrightarrow{\text{uction}} CH_3 - CH_2 - CH_2 - NH_2$
	Chloroethane	Proj	panenitrile	Propan-1-amine
(ii)	C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> -Cl Chlorophenylmetha (Benzyl chloride)	ane	C <sub>6</sub> H <sub>5</sub> –CH <sub>2</sub> –C Phenylethanen (Benzyl cyanic	•

### 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.

(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:

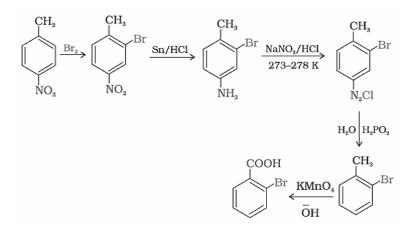
 $CH_3-CH_2-CH_2-C-NH_2$ O (Butanamide)

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



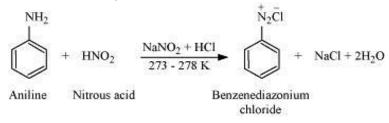
Q4. How will you convert 4-nitrotoluene to 2-bromobenzoicacid?

ANS.

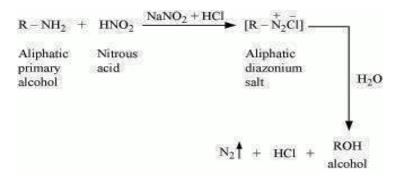


Q5.Write the reactions of (i)aromatic and(ii) aliphatic primary amines with nitrous acid.

<u>ANS.(i)</u>Aromatic amines react with nitrous acid(prepared in situ from NaNO<sub>2</sub>and a mineral acid such as HCl) at 273-278K to form stable aromatic diazonium salts i.e., NaCl and H<sub>2</sub>O.



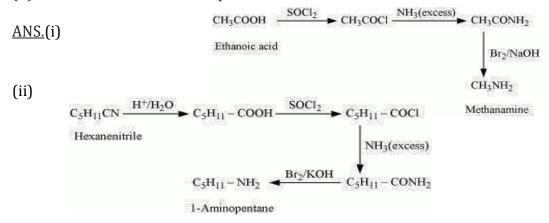
(ii)Aliphatic primary amines react with nitrous acid (prepared in situ from  $NaNO_2$  and a mineral acid such as HCl ) to form unstable aliphatic diazonium salts, which further produce alcohol and HCl with the evolution of  $N_2$  gas.



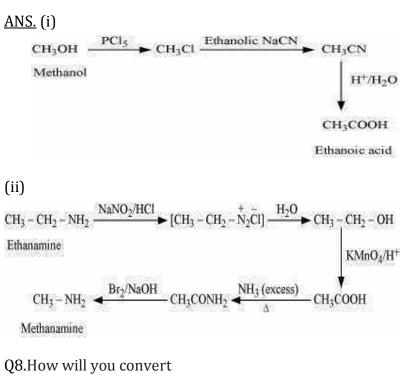
Q6.How will you convert

(i) Ethanoic acid into methanamine

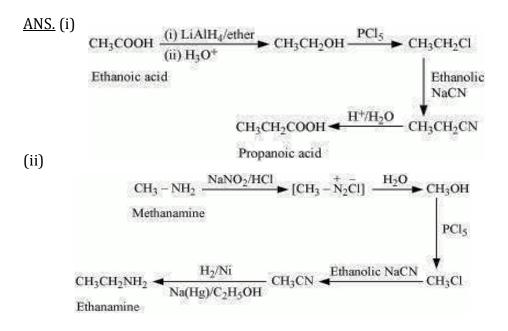
(ii)Hexanenitrile into 1-aminopentane



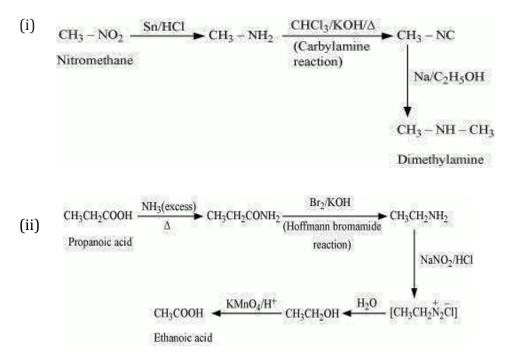
- Q7.How will you convert:
- (i) Methanol to ethanoic acid
- (ii) Ethanamine into methanamine



- (i ) Ethanoic acid into propanoic acid
- (ii) Methanamine into ethanamine



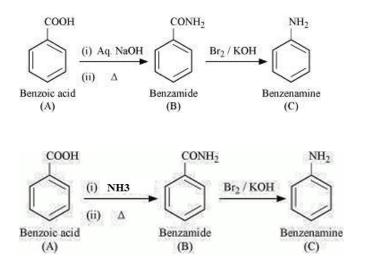
- Q9.How will you convert
- (i)Nitromethane into dimethylamine
- (ii) Propanoicacid into ethanoicacid?



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**.

<u>ANS.</u> It is given that compound **C** having the molecular formula,  $C_6H_7N$  is formed by heating compound **B**with Br2 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:



#### **<u>3 MARKS QUESTIONS</u>**

Q1. Arrange the following:

(i)In decreasing order of the p<sup>Kb</sup>values:

 $C_2H_5NH_2$ ,  $C_6H5NHCH_3$ ,  $(C_2H_5)_2NH$  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: Aniline, p-nitroaniline and p-toluidine

<u>ANS.(i)</u> The order of increasing basicity of the given compounds is as follows:

C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub><C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub><C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub><(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH

We know that the higher the basic strength, the lower is the pKb values.

 $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$ 

(ii) The increasing order of the basic strength 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:

 $C_2H_5OH$ , ( $CH_3$ )<sub>2</sub>NH,  $C_2H_5NH_2$ 

(iii) In increasing order of solubility in water: C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>,(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH,C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>.

<u>ANS.(i)</u>The given compounds can be arranged in the decreasing order of their basic strengths in the gas phase as follows:

(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH>C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>>NH<sub>3</sub>

(ii)The given compounds can be arranged in the increasing order of their boiling points as follows:

(CH<sub>3</sub>)<sub>2</sub>NH<C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub><C<sub>2</sub>H<sub>5</sub>OH

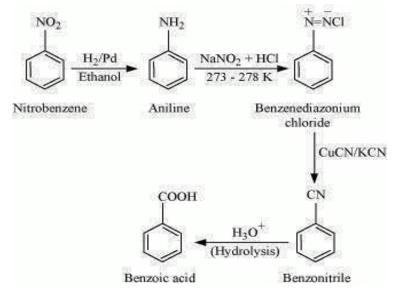
(iii)The more extensive the H–bonding, the higher is the solubility.  $C_2H_5NH_2$  contains two Hatoms whereas  $(C_2H_5)_2NH$  contains only one H-atom. Thus,  $C_2H_5NH_2$  undergoes more extensive H–bonding than  $(C_2H_5)_2NH$ . Hence, the solubility in water of  $C_2H_5NH_2$  is more than that of  $(C_2H_5)_2NH$ .

Q3.Accomplishthefollowingconversions:

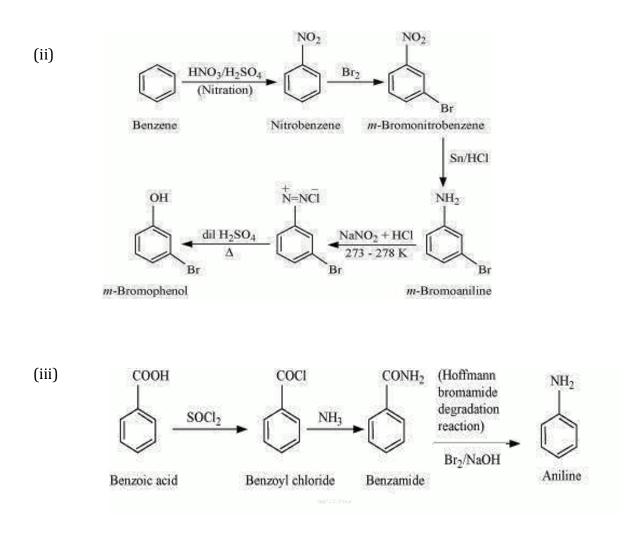
(i) Nitrobenzene to benzoic acid

(ii)Benzene to m-bromophenol

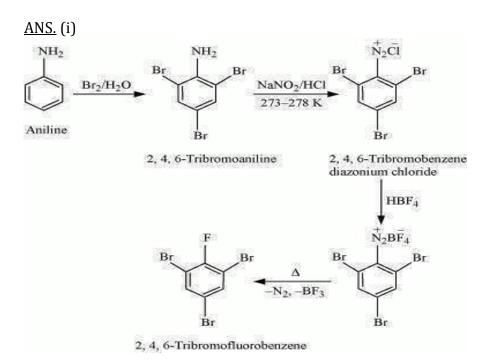
(iii)Benzoic acid to aniline

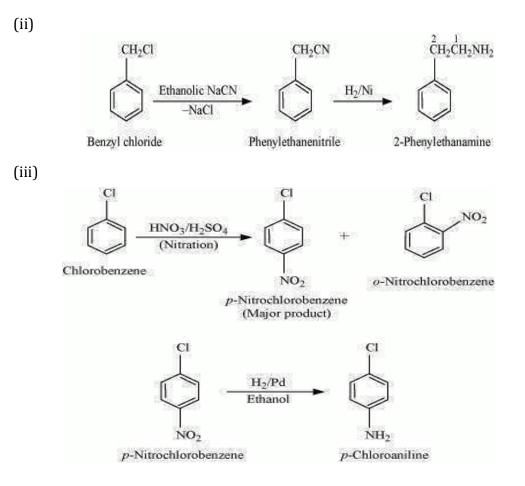


(i)



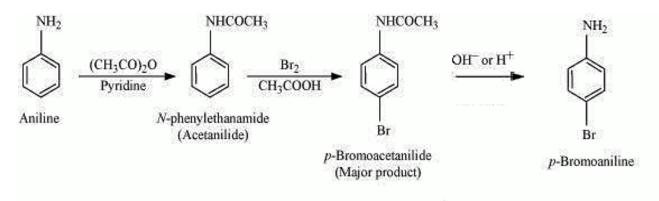
Q4. Accomplish the following conversions: (i)Aniline to 2,4,6-tribromo fluoro benzene (ii)Benzyl chloride to2-phenyl ethanamine (iii)Chloro benzene to p-chloro aniline

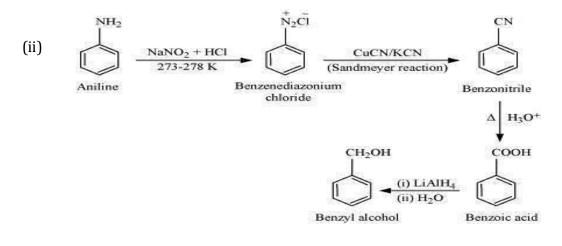




- Q5.Accomplish the following conversions:
- (i) Aniline to p-bromoaniline
- (ii)Aniline to benzyl alcohol.

<u>ANS.</u> (i)





#### **5 MARKS QUESTIONS**

Q1..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) 
$$C_6H_5NH_2 + CHCl_3 + 3alc KOH \xrightarrow{reaction} 3H_2O + 3KCl + C_6H_5 - NC$$
  
Aniline  $Phenyl$   
isocyanide  
(ii)  $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow C_6H_6 + N_2 + H_3PO_3 + HCl$   
Benzenediazonium Benzene  
chloride  
(iii)  $C_6H_5NH_2 + conc.H_2SO_4 \rightarrow C_6H_5 \overset{+}{N}H_3HSO_4$   
Aniline Anilinium hydrogen sulphate  
(iv)  $C_6H_5N_2Cl + C_2H_5OH \rightarrow C_6H_6 + CH_3CHO + N_2 + HCl$   
Benzenediazonium Ethanol Benzene Ethanal  
chloride  
(v)  $C_6H_5NH_2 + 3Br_{2(aq)} \xrightarrow{H_2} H_2 \overset{+}{H_2} H_2 \overset{+}{H_3} H_3 \overset{+}{H_3} \overset{+}{H_3} H_3 \overset{+}{H_3} \overset{$ 

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

(i) 
$$CH_{3}CH_{2}I \xrightarrow{NaCN} A \xrightarrow{OH^{-}} B \xrightarrow{NaOH_{3}B_{2}} C$$
  
(ii)  $C_{6}H_{5}N_{2}CI \xrightarrow{CuCN} A \xrightarrow{H_{2}O/H^{+}} B \xrightarrow{NH_{3}} C$   
(iii)  $CH_{3}CH_{2}Br \xrightarrow{KCN} A \xrightarrow{LiAIH_{4}} B \xrightarrow{HNO_{2}} C$   
(iv)  $C_{6}H_{5}NO_{2} \xrightarrow{Fe/HCI} A \xrightarrow{NaNO_{2}+HCI} B \xrightarrow{H_{2}O/H^{+}} C$   
(v)  $CH_{3}COOH \xrightarrow{NH_{3}} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_{2}/HCI} C$ 

<u>ANS.</u>

## Additional Questions

### **1 MARK QUESTIONS**

Q1. Arrange the following in decreasing order of their basic strength:

 $\mathsf{C}_6\mathsf{H}_5\mathsf{NH}_2$  ,  $\mathsf{C}_2\mathsf{H}_5\mathsf{NH}_2$  ,  $(\mathsf{C}_2\mathsf{H}_5)_2\mathsf{NH}$  ,  $\mathsf{NH}_3$ 

- 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 where as 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 synthesizing primary amines. Give reason

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

Q11.Whydo primary amines have higher boiling point than tertiary amines?

Q12. Why are aliphatic amine 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)  $C_6H_5NH_2$  C  $H_3NH_2$ (b) C  $H_3NHCH_3$  (C  $H_3$ )  $_3N$  Q8.Give the IUPAC names of:

 $(a)(CH_3)_2CHNH_2$ 

(b)(CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>3</sub> Q9.Write the structures of:

(a)3-Bromobenzenamine

(b)3-Chloro butanamide

## **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 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.

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

# VALUE BASED QUESTIONS

1. Sushi's friend wants to play Holi with synthetic colours, eggs, muddy water etc. Sunil persuades his friends to play Holi with natural colours. He reminds them that last time one of their friends had developed skin allergy after playing Holi with synthetic colours. It took him a long time to recover.

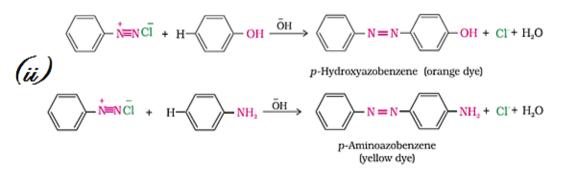
Sushi's friends agreed and prepared natural colours using leaves and flowers.

(i) Mention the values shown by Sushi.

(ii) Write the names and reaction of preparation of two azo dyes (synthetic)

(iii) Write the name of two pigments present in natural colours.

ANS: (i) Social responsibility



## (iii) Indigo & Saffron

Q2. Raghu and Raghav took organic compound synthesis as their chemistry project. They prepare benzene diazonium chloride. Raghu wanted to store it and synthesis dye from it next day but Raghav said we can't store it and need to use immediately after preparation. Whom do you think is right and why? Write the value associated with it.

ANS: Raghu is right as aryl diazonium salts are stable .

Critical thinking and decision making

Q3. Creatinine is a break-down product of creatine phosphate in muscle, and is usually produced at a fairly constant rate by the body. It belong to amines. Its presence can be tested in our blood and urine. Does this test help us to be aware of our health? Explain. Write the value associated with it.

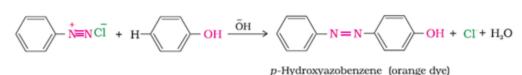
Ans: Yes a raise in the level of creatinine indicates kidney damage.

Sense of wellbeing

- Q4. Aromatic amines react with nitrous acid at 273-278K to produce diazonium salts which are widely used for preparation of a variety of aromatic compounds. They also couple with phenols/amines to form azo dyes which are used either as indicators or as dyes for fabrics. Now answer the following questions:
  - (i) What is the colour of the dye formed by the reaction between benzene diazonium chloride and phenol/amine?
  - (ii) Write the chemical reaction between benzene diazonium chloride and phenol?
  - (iii) Write the value associated with it

ANS: (i) Orange and Yellow

(ii)



(iii) Applying the knowledge of chemistry in daily life situations.

In organic chemistry stress must be laid on the following name reactions. Carbylamine Reaction (Isocyanide Test), Cannizzaro Reaction, Clemmensen Reduction, Coupling Reaction, Rosenmund's Reaction, Riemer-Tiemann Reaction, Fries Rearrangement, Friedel-Crafts Acylation Reaction, Gabriel Phthalimide Reaction, Hinsberg's Test, Hoffmann Bromamide Reaction, Sandmeyer's Reaction, Diazotization. These not only help in organic conversions but also in solving word problems.