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## Chapter – 13 (Amines)

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### Exercise Questions:

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

- I.  $(\text{CH}_3)_2\text{CHNH}_2$
- II.  $\text{CH}_3(\text{CH}_2)\text{NH}_2$
- III.  $\text{CH}_3\text{NHCH}(\text{CH}_3)_2$
- IV.  $(\text{CH}_3)_3\text{CNH}_2$
- V.  $\text{C}_6\text{H}_5\text{NHCH}_3$
- VI.  $(\text{CH}_3\text{CH}_2)_2\text{NCH}_3$
- VII. **m-BrC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>**

Answer:

- i.) 1 – Methylethanamine ( $1^\circ$ amine)
- ii.) Propan – 1 – amine ( $1^\circ$ amine)
- iii.) N – Methyl – 2 – methyl ethanamine ( $2^\circ$ amine)
- iv.) 2 – Methylpropan – 2- amine ( $1^\circ$ amine)
- v.) N – Methyl benzamine or N – methylaniline ( $2^\circ$ amine)
- vi.) N – Ethyl – N – methyl ethanamine ( $3^\circ$ amine)
- vii.) 3 – Bromobenzenamine or 3 – bromoaniline ( $1^\circ$ amine)

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

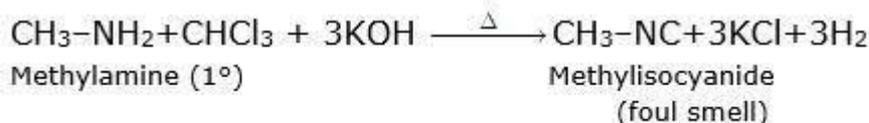
- I. **Methylamine and dimethylamine**
- II. **Secondary and tertiary amines**
- III. **Ethylamine and aniline**
- IV. **Aniline and benzylamine**
- V. **Aniline and N-methylaniline.**

Answer:

(i) Methylamine and dimethylamine :

Carbylamine test.

Methyl amine, on heating with alc. KOH solution and chloroform forms foul smelling methyl isocyanide. This test is not given by dimethylamine.

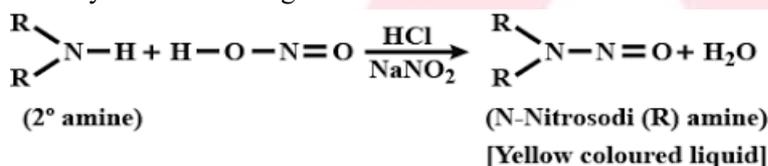


(ii) Secondary and tertiary amines :

Secondary amines give Libermann nitrosoamine test.

On heating with nitrous acid (prepared in situ), they give yellow coloured oily N-nitrosoamine.

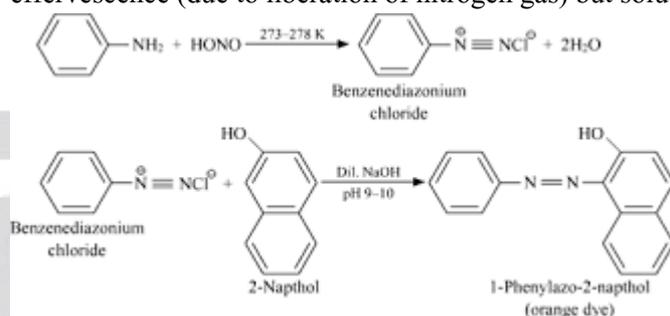
Tertiary amines do not give such test.



(iii) Ethylamine and aniline :

Azo dye test.

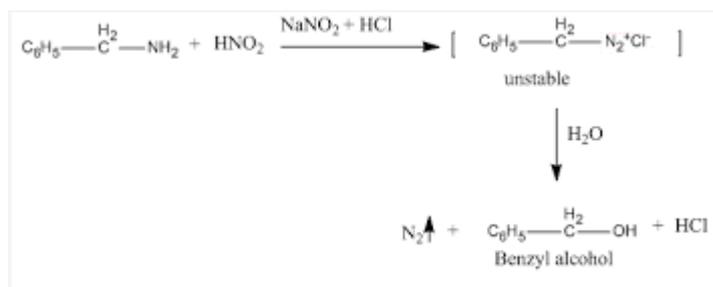
Aniline on diazotization (ice cold nitrous acid solution) followed by coupling with 2-naphthol (in alkaline solution) forms brilliant orange or red dye. Ethylamine will not form dye. It will give brisk effervescence (due to liberation of nitrogen gas) but solution remains clear.



(iv) Aniline and benzylamine :

Azo dye test.

Aniline on diazotization (ice cold nitrous acid solution) followed by coupling with 2-naphthol (in alkaline solution) forms brilliant orange or red dye. Benzylamine will not give such test.

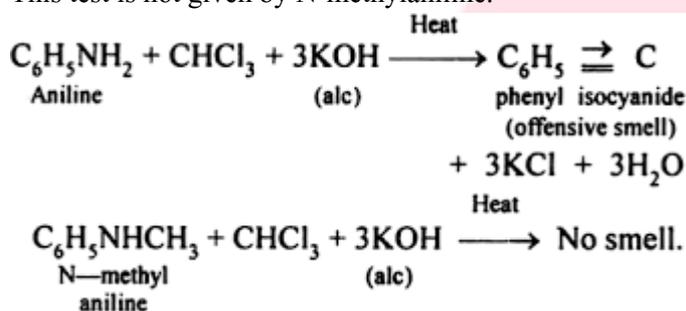


(v) Aniline and N-methylaniline :

Carbylamine test.

Aniline, on heating with alc. KOH solution and chloroform forms foul smelling methyl isocyanide.

This test is not given by N-methylaniline.

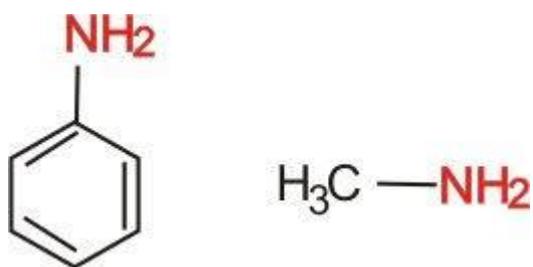


**Question :3 Account for the following :**

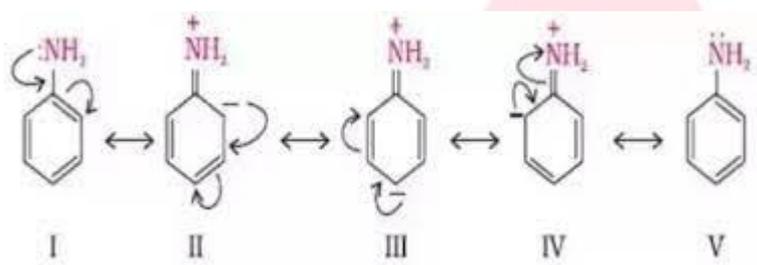
- I. **pK<sub>b</sub> of aniline is more than that of methylamine.**
- II. **Ethylamine is soluble in water whereas aniline is not.**
- III. **Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.**
- IV. **Although amino group is o- and p- directing in aromatic electrophilic 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.**

Answer: i.)

P K<sub>b</sub> of methylamine is lesser than that of aniline:



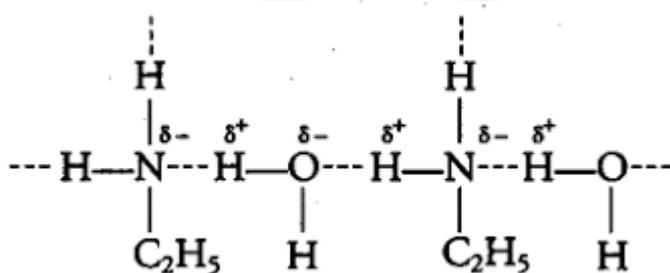
Aniline undergoes resonance and as a result, the electrons on the N-atom are delocalized over the benzene ring. Therefore, the electrons on the N-atom are less available to donate.



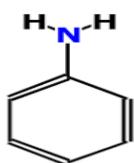
On the other hand, in case of methylamine (due to the +I effect of methyl group), the electron density on the N-atom is increased. As a result, aniline is less basic than methylamine. Thus,  $pK_b$  of aniline is more than that of methylamine.

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

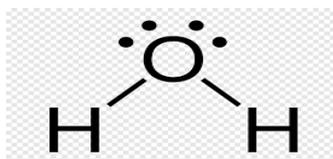
Ethylamine when added to water forms intermolecular H - bonds with water. Hence, it is soluble in water.



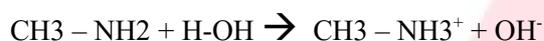
But aniline does not undergo H - bonding with water to a very large extent due to the presence of a large hydrophobic - C<sub>6</sub>H<sub>5</sub> group. Hence, aniline is insoluble in water.



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



Due to the +I effect of -CH<sub>3</sub> group, methylamine is more basic than water. Therefore, in water, methylamine produces OH<sup>-</sup> ions by accepting H<sup>+</sup> ions from water.



Ferric chloride (FeCl<sub>3</sub>) dissociates in water to form Fe<sup>3+</sup> and Cl<sup>-</sup> ions.

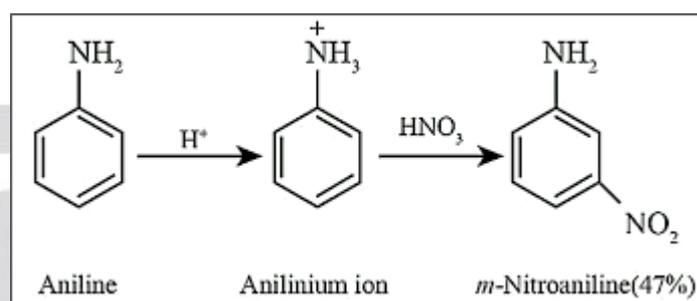


Then, OH<sup>-</sup> ion reacts with Fe<sup>3+</sup> ion to form a precipitate of hydrated ferric oxide.



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

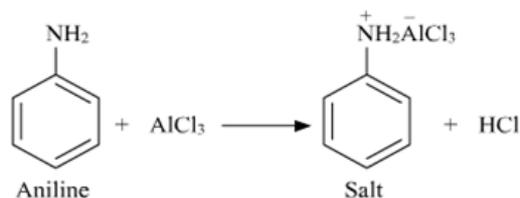
Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing).



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

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

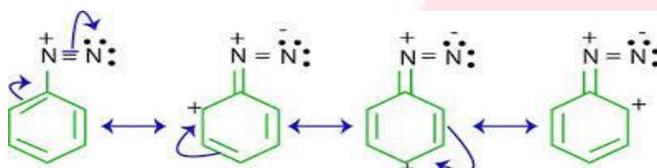
A Friedel-Crafts reaction is carried out in the presence of AlCl<sub>3</sub>. But AlCl<sub>3</sub> is acidic in nature, while aniline is a strong base. Thus, aniline reacts with AlCl<sub>3</sub> to form a salt (as shown in the following equation).



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.

**Question :4 Arrange the following :**

- I. In decreasing order of the pK<sub>b</sub> values:  
CH<sub>2</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>)<sub>2</sub>NH, and C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>
- II. In increasing order of basic strength :  
C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>2</sub>, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH and CH<sub>3</sub>NH<sub>2</sub>
- III. In increasing order of basic strength :
  - a. Aniline, p-nitroaniline and p-toluidine.
  - b. 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>6</sub>H<sub>5</sub>CH<sub>2</sub>NH<sub>2</sub>.
- IV. In decreasing order of basic strength in gas phase:  
C<sub>2</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>)<sub>3</sub>N and NH<sub>3</sub>

V. In increasing order of boiling point:

$C_2H_5OH$ ,  $(CH_3)_2NH$ ,  $C_2H_5NH_2$

VI. In increasing order of solubility in water:

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

Answer:

(i) In  $C_2H_5NH_2$ , only one  $-C_2H_5$  group is present while in  $(C_2H_5)_2NH$ , two  $-C_2H_5$  groups are present. Thus, the +I effect is more in  $(C_2H_5)_2NH$  than in  $C_2H_5NH_2$ . Therefore, the electron density over the N-atom is more in  $(C_2H_5)_2NH$  than in  $C_2H_5NH_2$ . Hence,  $(C_2H_5)_2NH$  is more basic than  $C_2H_5NH_2$ .

Also, both  $C_6H_5NHCH_3$  and  $C_6H_5NH_2$  are less basic than  $(C_2H_5)_2NH$  and  $C_2H_5NH_2$  due to the delocalization of the lone pair in the former two. Further, among  $C_6H_5NHCH_3$  and  $C_6H_5NH_2$ , the former will be more basic due to the +T effect of  $-CH_3$  group. Hence, 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.

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

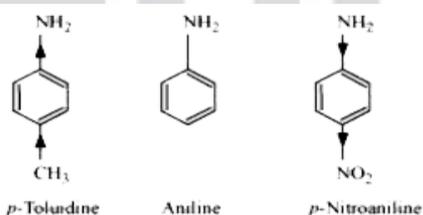
(ii)  $C_6H_5N(CH_3)_2$  is more basic than  $C_6H_5NH_2$  due to the presence of the +I effect of two  $-CH_3$  groups in  $C_6H_5N(CH_3)_2$ . Further,  $CH_3NH_2$  contains one  $-CH_3$  group while  $(C_2H_5)_2NH$  contains two  $-C_2H_5$  groups. Thus,  $(C_2H_5)_2NH$  is more basic than  $C_2H_5NH_2$ .

Now,  $C_6H_5N(CH_3)_2$  is less basic than  $CH_3NH_2$  because of the -R effect of  $-C_6H_5$  group.

Hence, 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) (a)



In *p*-toluidine, the presence of electron-donating  $-CH_3$  group increases the electron density on the N-atom. Thus, *p*-toluidine is more basic than aniline.

On the other hand, the presence of electron-withdrawing  $-NO_2$  group decreases the electron density over the N-atom in *p*-nitroaniline. Thus, *p*-nitroaniline is less basic than aniline.

Hence, the increasing order of the basic strengths of the given compounds is as follows:

p-Nitroaniline < Aniline < p-Toluidine

(b)  $C_6H_5NHCH_3$  is more basic than  $C_6H_5NH_2$  due to the presence of electron-donating  $-CH_3$  group in  $C_6H_5NHCH_3$ . Again, in  $C_6H_5NHCH_3$ ,  $-C_6H_5$  group is directly attached to the N-atom. However, it is not so in  $C_6H_5CH_2NH_2$ . Thus, in  $C_6H_5NHCH_3$ , the -R effect of  $-C_6H_5$  group decreases the electron density over the N-atom. Therefore,  $C_6H_5CH_2NH_2$  is more basic than  $C_6H_5NHCH_3$ .

Hence, the increasing order of the basic strengths of the given compounds is as follows:

$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$ .

(iv) In the gas phase, there is no solvation effect. As a result, the basic strength mainly depends upon the +I effect. The higher the +I effect, the stronger is the base. Also, the greater the number of alkyl groups, the higher is the +I effect. Therefore, the given compounds can be arranged in the decreasing order of their basic strengths in the gas phase as follows:

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

(v) The boiling points of compounds depend on the extent of H-bonding present in that compound. The more extensive the H-bonding in the compound, the higher is the boiling point.  $(CH_3)_2NH$  contains only one H-atom whereas  $C_2H_5NH_2$  contains two H-atoms. Then,  $C_2H_5NH_2$  undergoes more extensive H-bonding than  $(CH_3)_2NH$ . Hence, the boiling point of  $C_2H_5NH_2$  is higher than that of  $(CH_3)_2NH$ .

Further, O is more electronegative than N. Thus,  $C_2H_5OH$  forms stronger H-bonds than  $C_2H_5NH_2$ . As a result, the boiling point of  $C_2H_5OH$  is higher than that of  $C_2H_5NH_2$  and  $(CH_3)_2NH$ .

Now, the given compounds can be arranged in the increasing order of their boiling points as follows:

$(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

(vi) 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  $(C_2H_5)_2NH$ .

Further, the solubility of amines decreases with increase in the molecular mass. This is because the molecular mass of amines increases with an increase in the size of the hydrophobic part. The molecular mass of  $C_6H_5NH_2$  is greater than that of  $C_2H_5NH_2$  and  $(C_2H_5)_2NH$ .

Hence, the increasing order of their solubility in water is as follows:

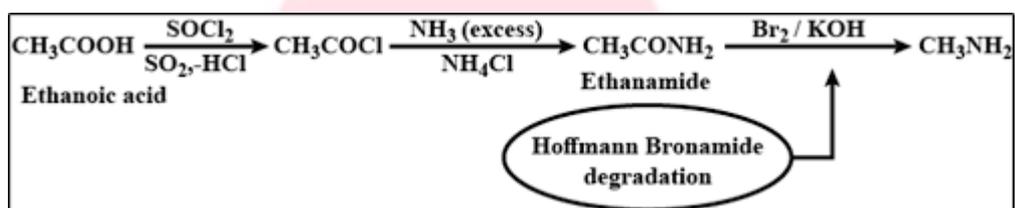
$C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

Question :5 How will you convert:

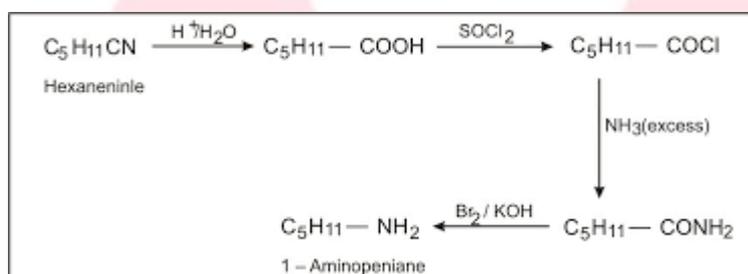
- I. Ethanoic acid into methanamine.
- II. Hexanenitrile into 1-aminopentane
- III. Methanol to ethanoic acid
- IV. Ethanamine into methanamine
- V. Ethanoic acid into propanoic acid
- VI. Methanamine into ethanamine
- VII. Nitromethane into dimethylamine
- VIII. Propanoic acid into ethanoic acid?

Answer:

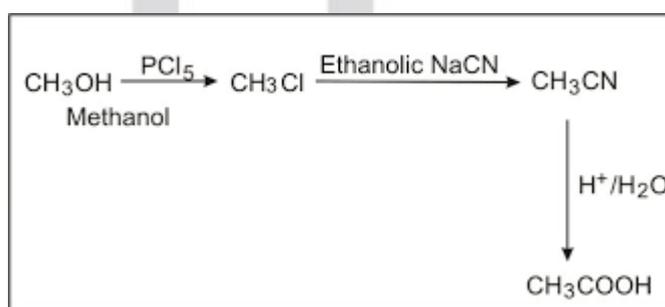
i.)

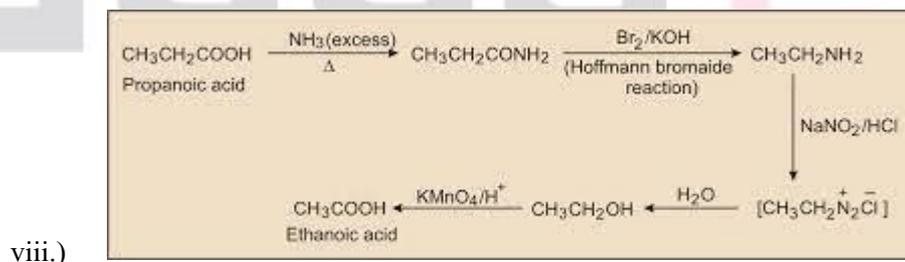
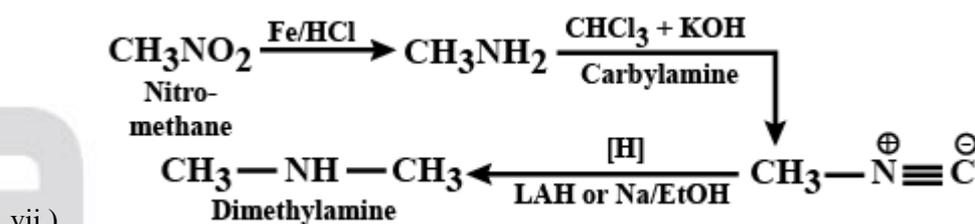
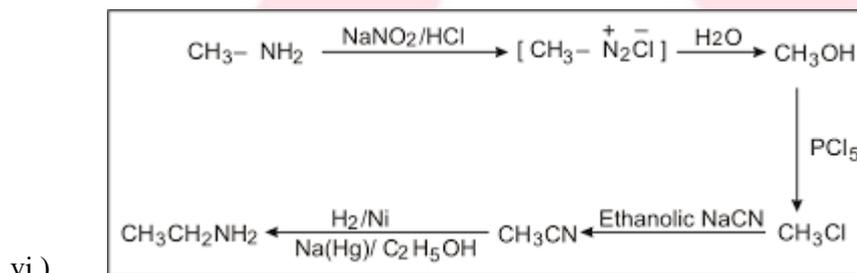
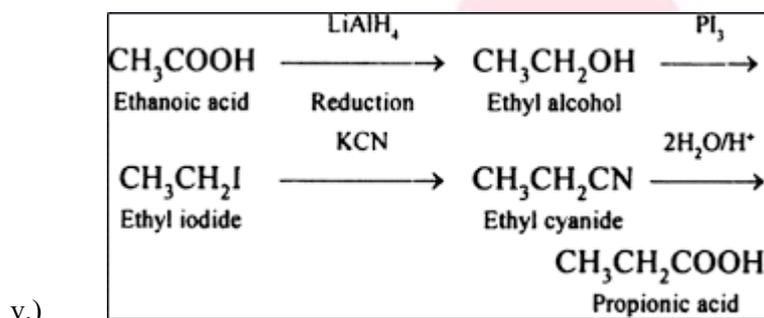
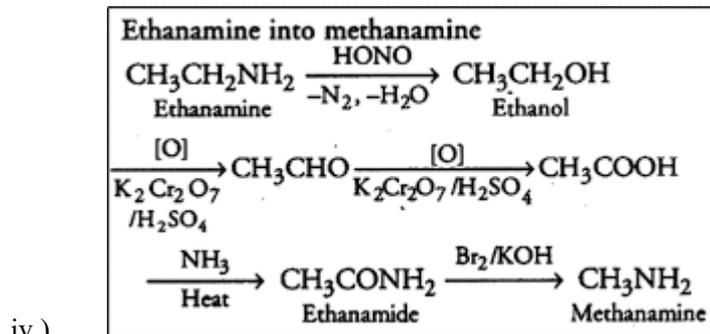


ii.)



iii.)



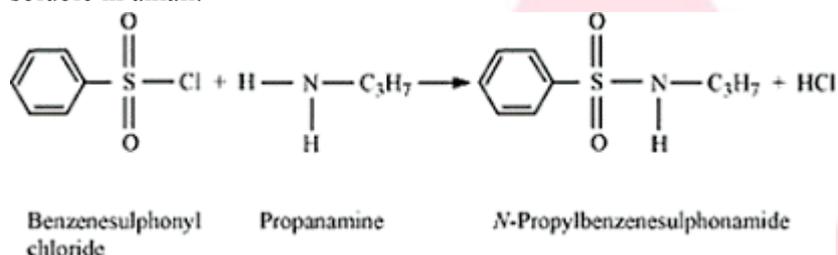


**Question :6 Describe a method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved.**

Answer:

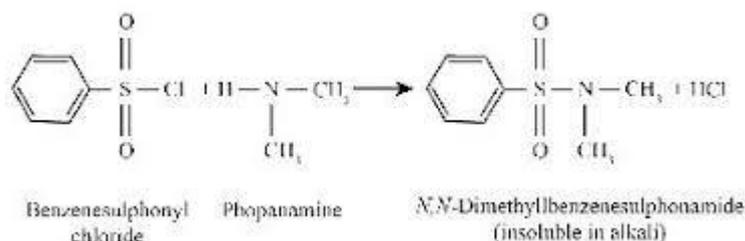
Primary, secondary and tertiary amines can be identified and distinguished by Hinsberg's test. In this test, the amines are allowed to react with Hinsberg's reagent, benzenesulphonyl chloride ( $C_6H_5SO_2Cl$ ). The three types of amines react differently with Hinsberg's reagent. Therefore, they can be easily identified using Hinsberg's reagent.

Primary amines react with benzenesulphonyl chloride to form N-alkylbenzenesulphonyl amide which is soluble in alkali.



Due to the presence of a strong electron-withdrawing sulphonyl group in the sulphonamide, the H-atom attached to nitrogen can be easily released as proton. So, it is acidic and dissolves in alkali.

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



There is no H-atom attached to the N-atom in the sulphonamide. Therefore, it is not acidic and insoluble in alkali.

On the other hand, tertiary amines do not react with Hinsberg's reagent at all.

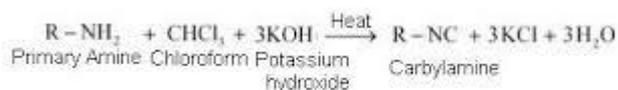
**Question :7 Write short notes on the following :**

- I. Carbylamine reaction
- II. Diazotisation
- III. Hofmann's bromamide reaction
- IV. Coupling reaction
- V. Ammonolysis
- VI. Acetylation
- VII. Gabriel phthalimide synthesis

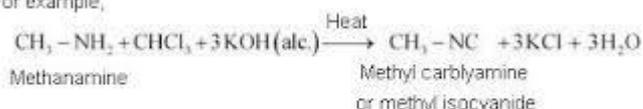
Answer:

(i) Carbylamine reaction

Carbylamine reaction is used as a test for the identification of primary amines. When aliphatic and aromatic primary amines are heated with chloroform and ethanolic potassium hydroxide, carbylamines (or isocyanides) are formed. These carbylamines have very unpleasant odours. Secondary and tertiary amines do not respond to this test.



For example,



(ii) Diazotisation

Aromatic primary amines react with nitrous acid (prepared in situ from  $\text{NaNO}_2$  and a mineral acid such as  $\text{HCl}$ ) at low temperatures (273-278 K) to form diazonium salts. This conversion of aromatic primary amines into diazonium salts is known as diazotization.

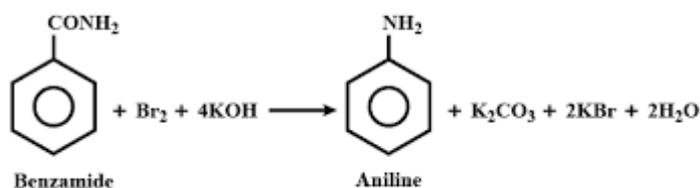
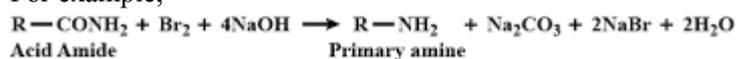
For example, on treatment with  $\text{NaNO}_2$  and  $\text{HCl}$  at 273 - 278 K, aniline produces benzenediazonium chloride, with  $\text{NaCl}$  and  $\text{H}_2\text{O}$  as by-products.



(iii) Hoffmann bromamide reaction

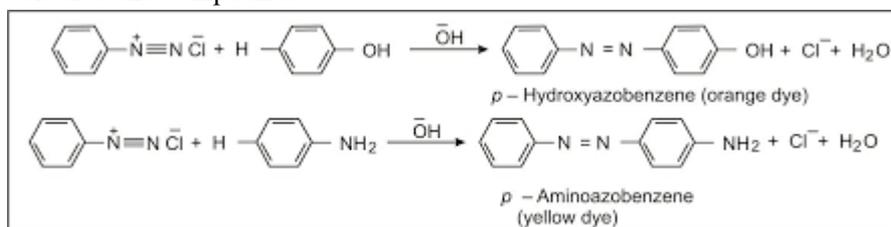
When an amide is treated with bromine in an aqueous or ethanolic solution of sodium hydroxide, a primary amine with one carbon atom less than the original amide is produced. This degradation reaction is known as Hoffmann bromamide reaction. This reaction involves the migration of an alkyl or aryl group from the carbonyl carbon atom of the amide to the nitrogen atom.

For example,



#### (iv) Coupling reaction

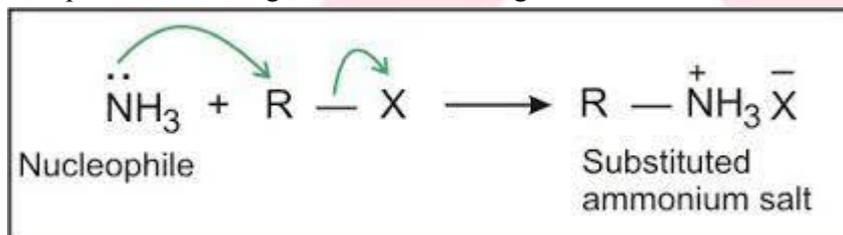
The reaction of joining two aromatic rings through the -N=N- bond is known as coupling reaction. Arenediazonium salts such as benzene diazonium salts react with phenol or aromatic amines to form coloured azo compounds.



It can be observed that, the para-positions of phenol and aniline are coupled with the diazonium salt. This reaction proceeds through electrophilic substitution.

#### (v) 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.

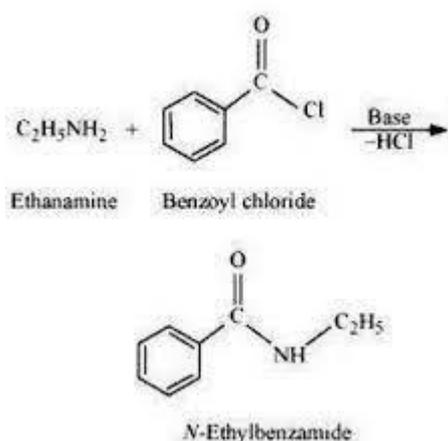
Though primary amine is produced as the major product, this process produces a mixture of primary, secondary and tertiary amines, and also a quaternary ammonium salt as shown.

#### (vi) 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<sub>2</sub> 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.

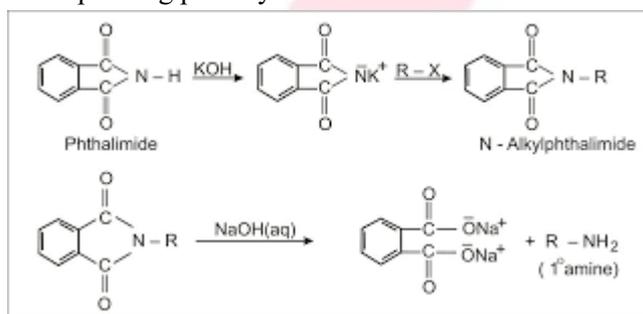
When amines react with benzoyl chloride, the reaction is also known as benzoylation.

For example,



(vii) Gabriel phthalimide synthesis

Gabriel phthalimide synthesis is a very useful method for the preparation of aliphatic primary amines. It involves the treatment of phthalimide with ethanolic potassium hydroxide to form potassium salt of phthalimide. This salt is further heated with alkyl halide, followed by alkaline hydrolysis to yield the corresponding primary amine.



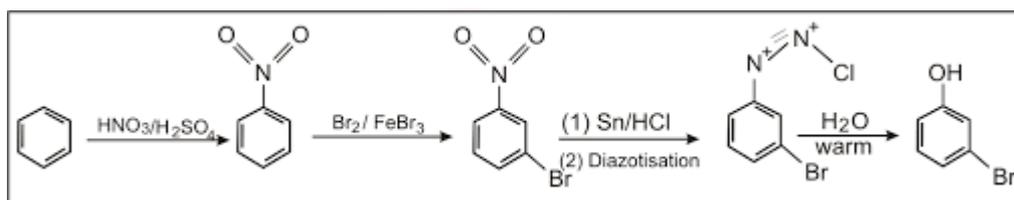
**Question :8 Accomplish the following conversions:**

- 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 alcohol.

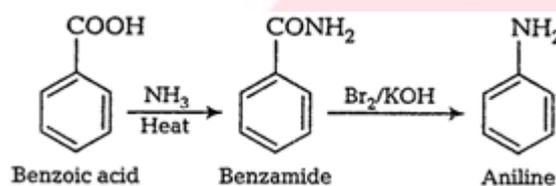
Answer:



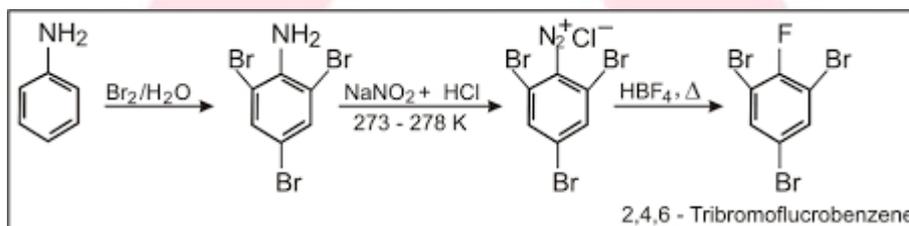
i.)



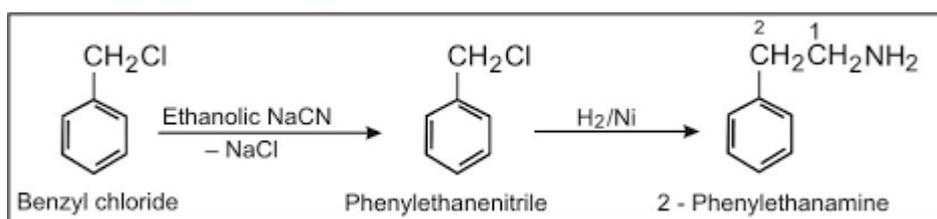
ii.)



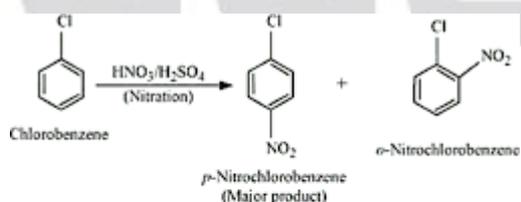
iii.)



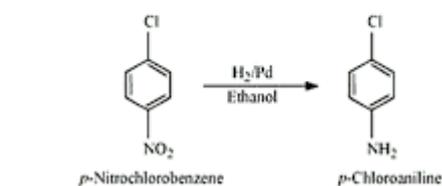
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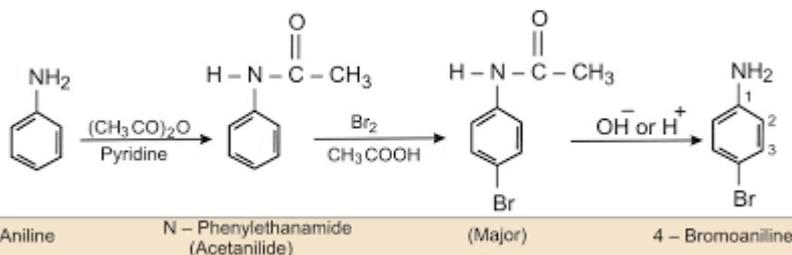


v.)

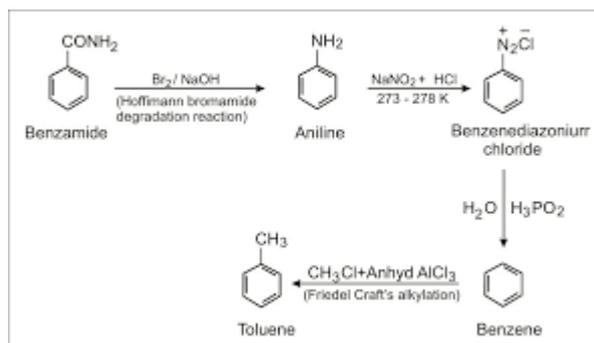


vi.)

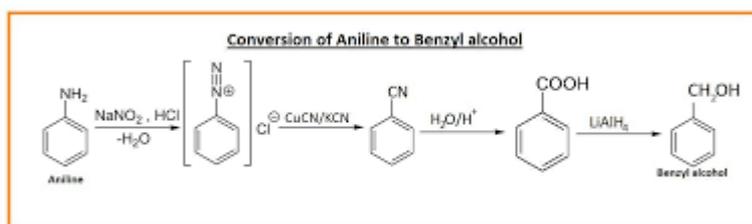




vii.)



viii.)

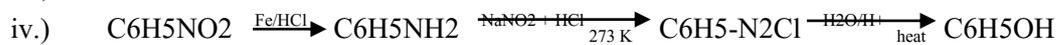
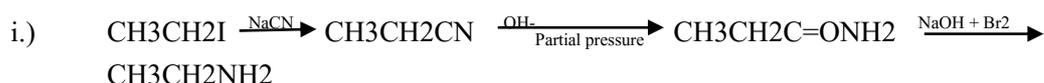


ix.)

**Question :9 Give the structures of A, B and C in the following reactions :**



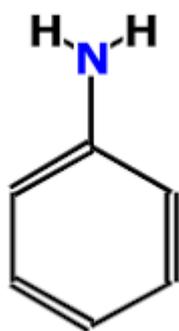
Answer:



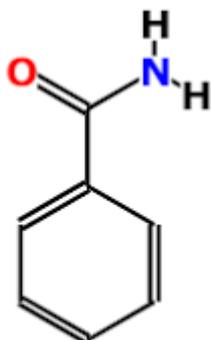
**Question :10** An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br<sub>2</sub> and KOH forms a compound 'C' of molecular formula C<sub>6</sub>H<sub>7</sub>N. Write the structures and IUPAC names of compounds A, B and C.

Answer:

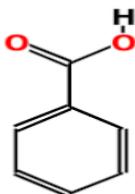
It is given that compound 'C' having the molecular formula, C<sub>6</sub>H<sub>7</sub>N is formed by heating compound 'B' with Br<sub>2</sub> and KOH. This is a Hoffmann bromamide degradation reaction. Therefore, compound 'B' is an amide and compound 'C' is an amine. The only amine having the molecular formula, C<sub>6</sub>H<sub>7</sub>N is aniline, (C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>).



Therefore, compound 'B' (from which 'C' is formed) must be benzamide, (C<sub>6</sub>H<sub>5</sub>CONH<sub>2</sub>).



Further, benzamide is formed by heating compound 'A' with aqueous ammonia. Therefore, compound 'A' must be benzoic acid.



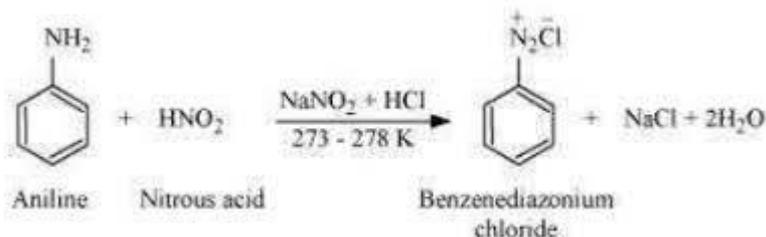


**Question :13 Write the reactions of**

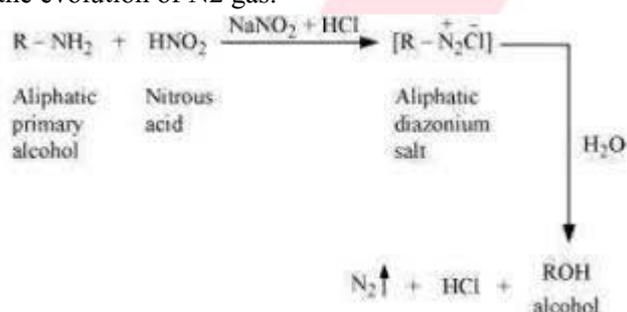
- I. **Aromatic and**
- II. **Aliphatic primary amines with nitrous acid.**

Answer:

(i) Aromatic amines react with nitrous acid (prepared in situ from  $\text{NaNO}_2$  and a mineral acid such as  $\text{HCl}$ ) at 273 - 278 K to form stable aromatic diazonium salts i.e.,  $\text{NaCl}$  and  $\text{H}_2\text{O}$ .



(ii) Aliphatic primary amines react with nitrous acid (prepared in situ from  $\text{NaNO}_2$  and a mineral acid such as  $\text{HCl}$ ) to form unstable aliphatic diazonium salts, which further produce alcohol and  $\text{HCl}$  with the evolution of  $\text{N}_2$  gas.



**Question :14 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.?**

Answer:

(i) Amines lose a proton to form amide ion. Alcohols lose a proton to form alkoxide ion.



O is more electronegative than N, the negative charge is more easily accommodated in  $\text{RO}^-$  than in  $\text{R-NH}^-$ . Hence, amines are less acidic than alcohols of comparable molecular masses.

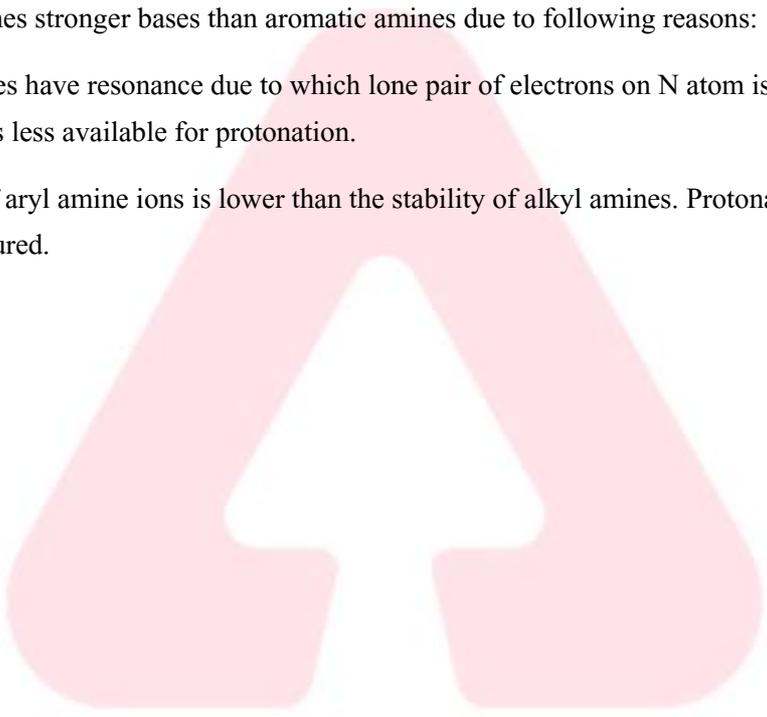
(ii) In primary amines, N atoms have two H atoms which results in extensive intermolecular H bonding. In tertiary amines, N atoms do not have H atoms and hydrogen bonding is not possible.

Hence, primary amines have higher boiling point than tertiary amines.

(iii) Aliphatic amines stronger bases than aromatic amines due to following reasons:

(a) Aromatic amines have resonance due to which lone pair of electrons on N atom is delocalized over benzene ring and is less available for protonation.

(b) The stability of aryl amine ions is lower than the stability of alkyl amines. Protonation of aromatic amines is not favoured.

  
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