NCERT Solutions for Class 12 Chemistry Chapter 13 Amines

Q . 13.1 :

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

(i) $(CH_3)_2 CH NH_2$

(ii) $CH_3 (CH_2)_2 NH_2$

(iii) $CH_3 NH CH (CH_3)_2$

(iv) $(CH_3)_3 CNH_2$

(v) $C_6 H_5 NH CH_3$

(vi) $(CH_3 CH_2)_2 N CH_3$

(vii) $m - Br C_6 H_4 NH_2$

Solution :

(i) 1 – Methylethanamine (10 amine)

(ii) Propan – 1 – amine (10 amine)

(iii) N – Methyl – 2 – methyl ethanamine (20 amine)

(iv) 2 – Methylpropan – 2 – amine (10 amine)

(v) N – Methyl benzamine or N – methylaniline (20 amine)

(vi) N – Ethyl – N – methyl ethanamine (30 amine)

(vii) 3 – Bromobenzenamine or 3 – bromoaniline (10 amine)

Q . 13.2 :

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

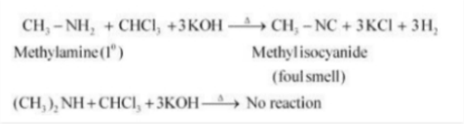
(i) Methylamine and dimethylamine (ii) Secondary and tertiary amines
(iii) Ethylamine and aniline (iv) Aniline and benzylamine
(v) Aniline and N-methylaniline.

Solution :

(i) ***dimethylamine & Methylamine*** can be made notable by the carbylamine test.

Carbylamine test: foul-smelling isocyanides or carbylamines are formed when Aliphatic & aromatic primary amines are heated with chloroform & ethanol potassium hydroxide .

Methylamine (being an aliphatic primary amine) gives a positive carbylamine test, but dimethylamine does not.

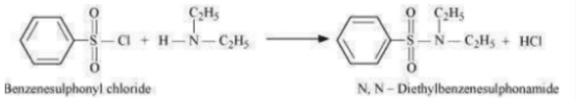


$$\underset{\text{Methylamine}(1^\circ)}{CH_3-NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\substack{\text{Methylisocyanide}\\(\text{foul smell})}}{CH_3-NC} + 3KCl + 3H_2$$

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

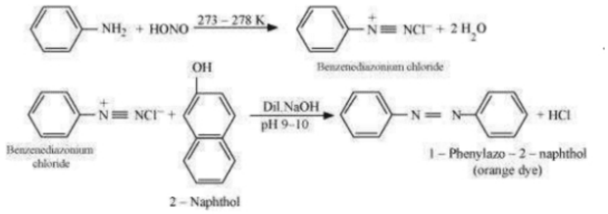
(ii) Tertiary amines & Secondary can be made notable by allowing them to react with Hinsberg's reagent (benzene sulphonyl chloride, $C_6 H_5 SO_2 Cl$).

A product which is insoluble in alkali is formed when Secondary amines react with Hinsberg's reagent to form a product that is insoluble in an alkali. For example, N, N – diethyl amine 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.



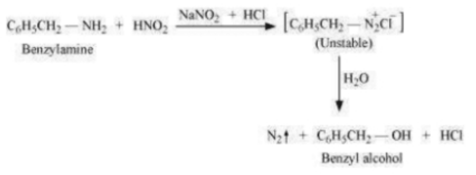
(iii) azo – dye test can distinguish aniline & Ethylamine.

When aromatic amines are made to react with HNO_2 ($NaNO_2$ + dil. HCl) at 0 – 5 ° C, A dye is obtained which is followed by making it react with the alkaline solution of 2 – naphthol. The dye is observed to be in the following colours: yellow, red, or orange in color. A brisk effervescence is given out by Aliphatic amines due to the evolution of N_2 gas under analogous conditions.



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

(iv) benzylamine & Aniline can be made notable by reacting them with nitrous acid, which is made ready in situ from a sodium nitrite & mineral acid. Unstable diazonium salt is formed when nitrous acid reacts with Benzylamine, which gives a by – product as alcohol along with the evolution of N_2 gas



$$\underset{\text{Benzylamine}}{C_6H_5CH_2-NH_2} + HNO_2 \xrightarrow{NaNO_2 + HCl} \underset{\text{(Unstable)}}{[C_6H_5CH_2-\overset{+}{N_2}Cl^-]} \xrightarrow{H_2O} N_2\uparrow + \underset{\text{Benzyl alcohol}}{C_6H_5CH_2-OH} + HCl$$

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

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

(v) N – methylaniline & Aniline can be made notable by using the Carbylamine test.

On heating Primary amines with ethanolic , chloroform & potassium hydroxide, foul-smelling isocyanides or carbylamines are formed. As Aniline is a primary aromatic primary, it gives a positive carbylamines test. On the other h&, as, N – methyl aniline is a secondary amine it does not give a positive carbylamines test.

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

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

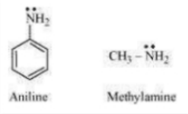
Q . 13.3 :

Account for the following:

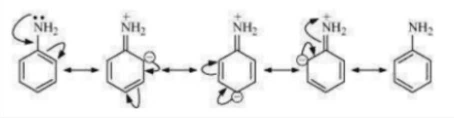
(i) pKb of aniline is more than that of methylamine.
(ii) Ethylamine is soluble in water whereas aniline is not.
(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.
(iv) Although amino group is o– and p– directing in aromatic electrophilic substitution reactions, 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

Solution :

(i) p K_b of methylamine is lesser than that of aniline :



When, in the above process, Aniline is under resonance, the electrons available on the N – atom are delocalized over the benzene ring. Hence, the electrons on the N – atom is available in less quantity to donate.



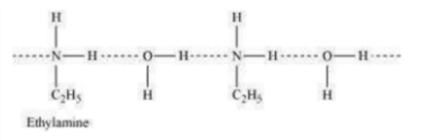
While considering the case of methylamine (due to the + I effect of methyl group), the electron density on the N – atom is improved. As an outcome we see that methylamine is more basic than aniline.

Hence, ***p K_b of methylamine is lesser than that of aniline***.

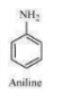
(ii) Aniline is not soluble in water while Ethylamine is.

When Ethylamine is reacted with water, it tends to forms intermolecular H – bonds with water.

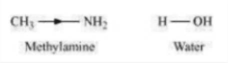
Thus, it becomes soluble in water.



However, aniline does form H – bonding with water to a very great extent reason being the presence of a large hydrophobic – C_6H_5 group. Therefore, aniline is not soluble in water.



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



Due to the presence of – CH_3 group & + I effect of, water is less basic than methylamine.

In water, thus, methylamine gives out OH^- ions by gaining H^+ ions from water.

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

In the above process, Ferric chloride ($FeCl_3$) splits forming Fe^{3+} & Cl^- ions in water.

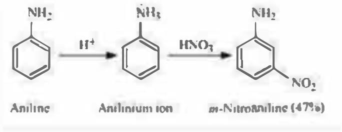
$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$$

OH^- ion then combines with Fe^{3+} ion and forms an impulsive of hydrated ferric oxide.

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

(iv) Aniline when nitrated gives a substantial amount of m – nitroaniline, while the amino group is o, p – directing in aromatic electrophilic substitution reactions.

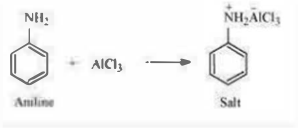
Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta – directing).



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

(v) Aniline does not take Friedel – Crafts reaction.

Friedel – Crafts reaction is performed in the presence of Al Cl $_3$. But, as we know that, Al Cl $_3$ has a acidic nature, whereas aniline does not. Aniline is basic in nature. Therefore, aniline is then reacted with Al Cl $_3$ forming a salt (this has been shown in the equation given below).

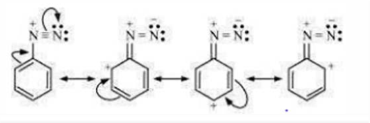


The electrophilic substitution in the benzene ring is deactivated because of the positive charge on the

N – atom, Hence, aniline does not undergo the Friedel – Crafts reaction.

(vi) On comparing the stabilities, we observe that the stability of Diazonium salts of aromatic amines is more than that of aliphatic amines.

Resonance is undergone by the diazonium ion, which is depicted in the figure given below.



The stability of the diazonium ion is accounted for by this resonance. Thus, the stability of diazonium salts of aromatic amines is higher than that of aliphatic amines.

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

Gabriel phthalimide synthesis is chosen because only 1 ° amine are formed.

This synthesis does not form 2° or 3° amines. Therefore, a pure 1° amine could be formed. Hence, Gabriel phthalimide synthesis is chosen for the synthesis of primary amines.

Q . 13.4 :

Arrange the following:
(i) In decreasing order of the pKb values:
C2H5NH2, C6H5NHCH3, (C2H5)2NH and C6H5NH2
(ii) In increasing order of basic strength:
C6H5NH2, C6H5N(CH3)2, (C2H5)2NH and CH3NH2
(iii) In increasing order of basic strength:
(a) Aniline, p-nitroaniline and p-toluidine
(b) C6H5NH2, C6H5NHCH3, C6H5CH2NH2.
(iv) In decreasing order of basic strength in gas phase:
C2H5NH2, (C2H5)2NH, (C2H5)3N and NH3
(v) In increasing order of boiling point:
C2H5OH, (CH3)2NH, C2H5NH2
(vi) In increasing order of solubility in water:
C6H5NH2, (C2H5)2NH, C2H5NH2.

Solution :

(i) $C_2H_5NH_2$ à presence of one – C_2H_5 group

(C_2H_5)$_2$ NH à presence of two – C_2H_5 groups.

Therefore, the + I effect is additional in (C_2H_5) $_2$ NH than in $C_2H_5NH_2$. Therefore, the electron density over the N-atom is more in (C_2H_5) $_2$ NH than in $C_2H_5NH_2$. Hence, (C_2H_5)$_2$ NH is more basic than C_2

H_5NH_2.

Also, both $C_6H_5NHCH_3$ & $C_6H_5NH_2$ are less basic than $(C_2H_5)_2NH$ & $C_2H_5NH_2$ due to the delocalization of the lone pair in the former two. Further, among $C_6H_5NHCH_3$ & $C_6H_5NH_2$, 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

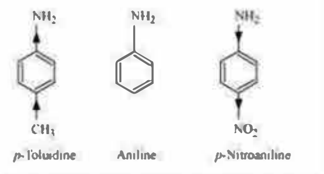
$(C_2H_5)_2NH$ contains two $-C_2H_5$ groups. Thus, $(C_2H_5)_2NH$ is more basic than $C_2H_5NH_2$.

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. In the other case, 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 extent of H-bonding existing in any compound decides the boiling point of compounds. The higher extensive the H − bonding in the compound, the higher will be the boiling point. $(CH_3)_2NH$ has only one H − atom while $C_2H_5NH_2$ has two H − atoms. Subsequently, $C_2H_5NH_2$ undergoes more extensive H-bonding than $(CH_3)_2NH$. Therefore, the boiling point of $C_2H_5NH_2$ is more than that of $(CH_3)_2NH$.

Also, 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 $C_2H_5NH_2$ & $(CH_3)_2NH$.

Based on the above explanation, the compounds given in the question can be arranged in the ascending order of their boiling points, which is given below :

$(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

(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 $(C_2H_5)_2$

NH. 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 an 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 $C_2H_5NH_2$ & $(C_2H_5)_2NH$.

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

$C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

Q . 13.5 :

How will you convert:

(i) Ethanoic acid into methanamine

(ii) Hexanenitrile into 1 – aminopentane

(iii) Methanol to ethanoic acid

(iv) Ethanamine into methanamine

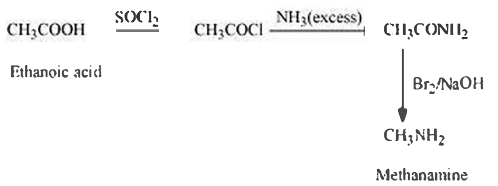
(v) Ethanoic acid into propanoic acid

(vi) Methanamine into ethanamine

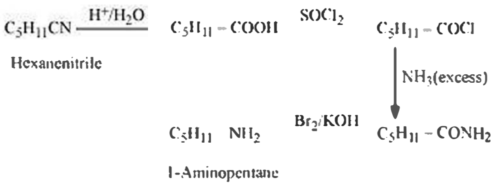
(vii) Nitromethane into dimethylamine

(viii) Propanoic acid into ethanoic acid

Solution :



(ii)



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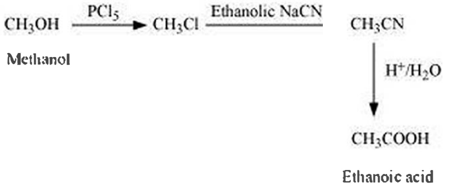

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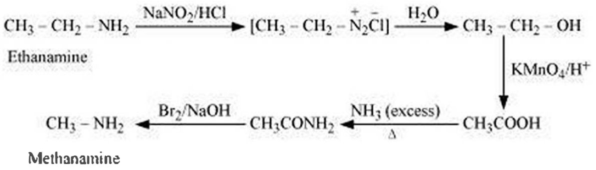

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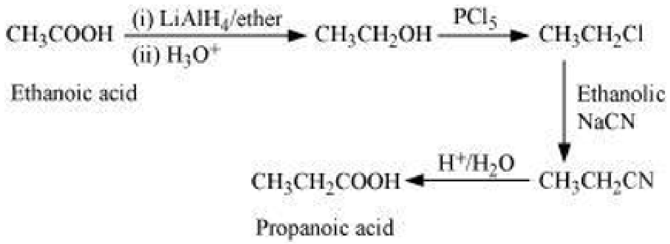

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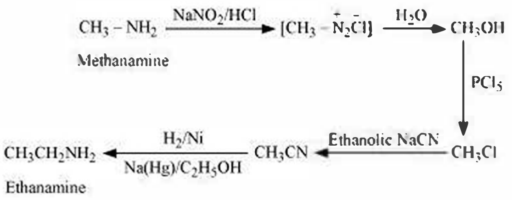

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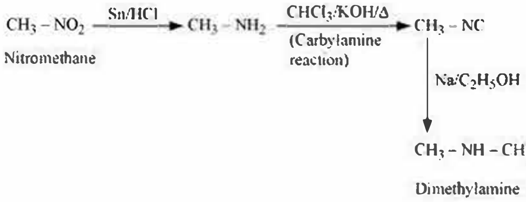

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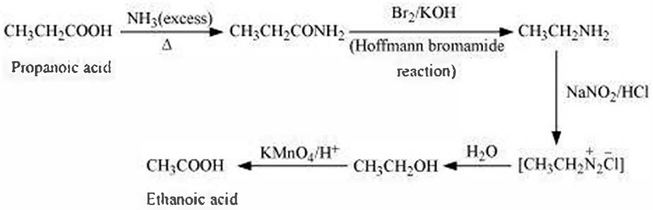
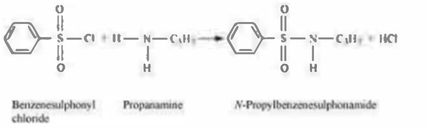


Question 13.6 :

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

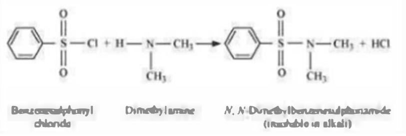
Solution :

Primary, secondary & tertiary amines can be identified & distinguished by Hinsberg's test. In this test, the amines are allowed to react with Hinsberg's reagent, benzene sulphonyl chloride ($C_6 H_5 SO_2 Cl$). The three types of amines react differently to Hinsberg's reagent. Therefore, they can be easily identified using Hinsberg's reagent. Primary amines react with benzene sulphonyl chloride to form N-alkyl benzene sulphonyl 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 a proton. So, it is acidic & 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 & insoluble in alkali. On the other tertiary amines do not react with Hinsberg's reagent at all.

Question 13.7:

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.

Solution :

(i) Carbylamine reaction

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

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

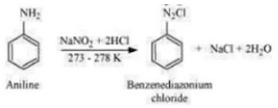
For example,

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

(ii) Diazotization

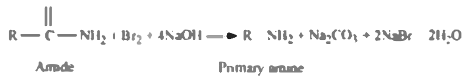
Aromatic primary amines react with nitrous acid (prepared in situ from $NaNO_2$ & a mineral acid such as HCl) at low temperatures (273 – 278 K) to form diazonium salts. This conversion of aromatic primary amines into diazonium salts is known as diazotization.

For example, on treatment with $NaNO_2$ & HCl at 273 – 278 K, aniline produces benzene diazonium chloride, with NaCl & H_2O as by-products.



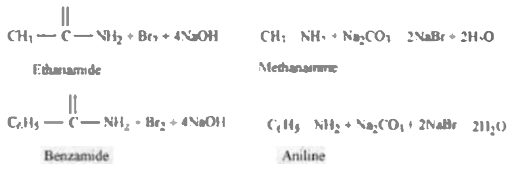
(iii) Hoffmann bromamide reaction

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 the 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.



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

For example,

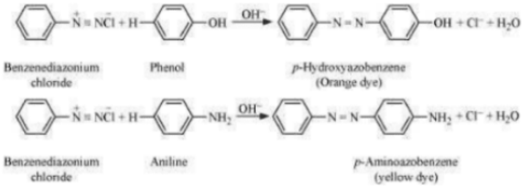


$$\underset{\text{Ethanamide}}{CH_3-\overset{\overset{O}{\parallel}}{C}-NH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{Methanamine}}{CH_3-NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

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

(iv) Coupling reaction

The reaction of joining two aromatic rings through the – N = N – bond is known as coupling reaction. Arene diazonium 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 & aniline are coupled with the diazonium salt. This reaction proceeds through electrophilic substitution.

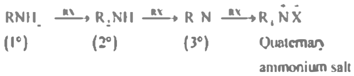
(v) Ammonolysis

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 $_2$) group. This process of cleavage of the carbon-halogen bond is known as ammonolysis.

$$R-NH_3X + NaOH \longrightarrow \underset{\text{Amine}}{R-NH_2} + H_2O + NaX$$

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



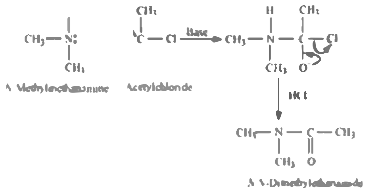
$$\underset{(1^\circ)}{RNH_2} \xrightarrow{RX} \underset{(2^\circ)}{R_2NH} \xrightarrow{RX} \underset{(3^\circ)}{R_3N} \xrightarrow{RX} \underset{\substack{\text{Quaternary}\\\text{ammonium salt}}}{R_4\overset{+}{N}\bar{X}}$$

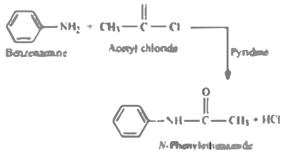
Though primary amine is produced as the major product, this process produces a mixture of primary, secondary & tertiary amines, & also a quaternary ammonium salt as shown.

(vi) Acetylation

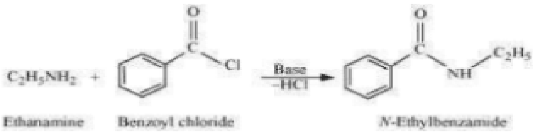
Acetylation (or ethanoylation) is the process of introducing an acetyl group into a molecule.

Aliphatic & aromatic primary & 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 results in the formation of amides. In order to transfer the equilibrium to the right-hand side, the HCl that is produced while the reaction is on, is removed almost immediately as it is produced. This reaction is performed in the existence of a base (such as pyridine) which is comparatively stronger than the amine.



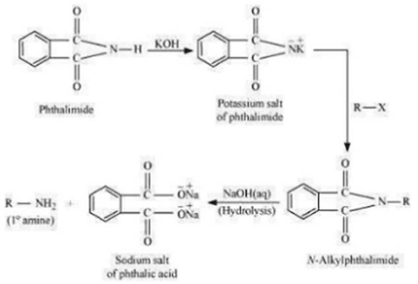


the reaction is also known as benzoylation is the reaction that occurs when amines react with benzoyl chloride. One of the examples is illustrated below :



(vii) Gabriel phthalimide synthesis

Gabriel phthalimide synthesis is a convenient and important method for the synthesis of aliphatic primary amines. It includes the reaction between phthalimide with ethanolic potassium hydroxide forming potassium salt of phthalimide. This salt is then heated with an alkyl halide, which is succeeded by alkaline hydrolysis to give in the resultant primary amine.



Question 13.8:

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**

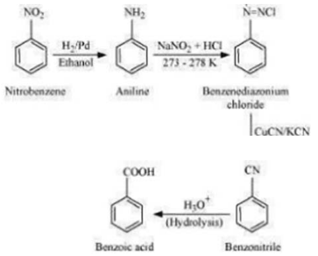
(vii) **Aniline to p – bromoaniline**

(viii) **Benzamide to toluene**

(ix) **Aniline to benzyl alcohol.**

Solution :

(i)



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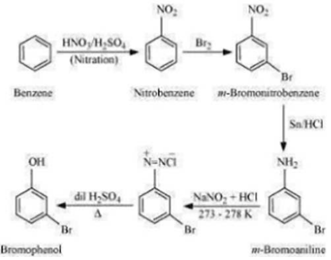

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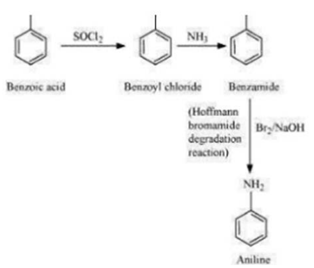

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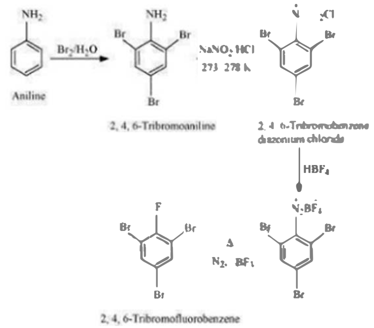

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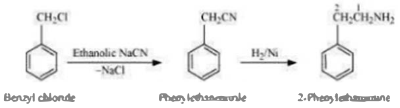
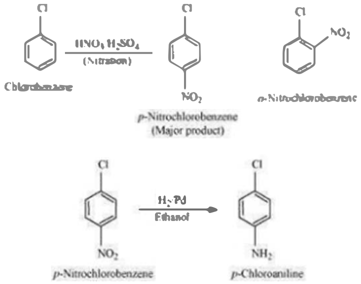


(vi)



Question 13.9 :

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) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow{NH_3} C$

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

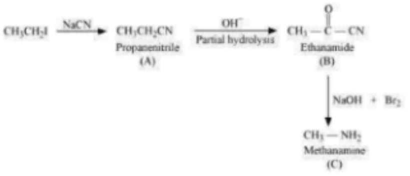
(iv) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{NaNO_2 + HCl} B \xrightarrow{H_2O/H^+} C$

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

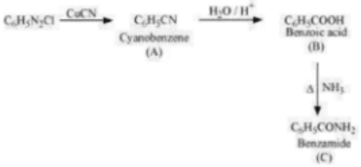
(vi) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{HNO_2} B \xrightarrow{C_6H_5OH} C$

Solution :

(i)



(ii)



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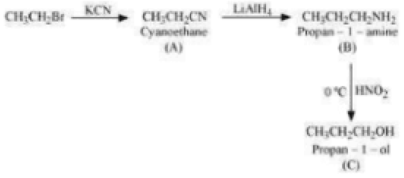

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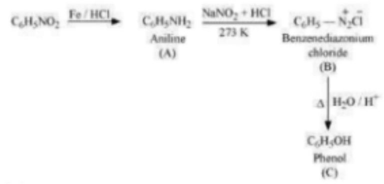
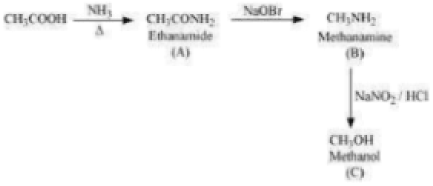
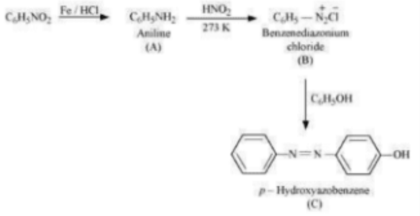


(v)



(vi)

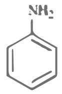


Question 13.10:

An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br2 and KOH forms a compound 'C' of molecular formula C6H7N. Write the structures and IUPAC names of compounds A, B and C.

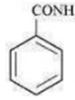
Solution :

It is given that compound 'C' having the molecular formula, C_6H_7N is formed by heating compound 'B' with Br_2 & KOH. This is a Hoffmann bromamide degradation reaction. Therefore, compound 'B' is an amide & compound 'C' is an amine. The only amine having the molecular formula, C_6H_7N is aniline, ($C_6H_5NH_2$).



Aniline

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



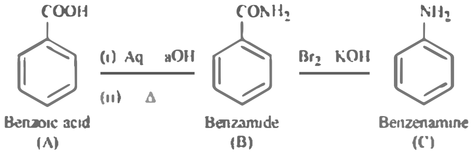
Benzamide

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

Therefore, compound 'A' must be benzoic acid.

Benzoic acid

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



Question 13.11:

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) $C_6H_5NH_2 + Br_2(aq) \rightarrow$

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

(vii) $C_6H_5N_2Cl \xrightarrow[\text{(ii)}NaNO_2/Cu,\Delta]{\text{(i)}HBF_4}$

Solution :

(i)

$C_6H_5NH_2 + CHCl_3 + 3alc\ KOH \quad 3H_2O + 3KCl + C_6H_5NC$

Aniline — Phenyl isocyanide

(ii)

$C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow C_6H_6 + N_2 + H_3PO_3 + HCl$

Benzenediazonium chloride — Benzene

(iii)

$C_6H_5NH_2 + conc\ H_2SO_4 \rightarrow C_6H_5NH_3HSO_4$

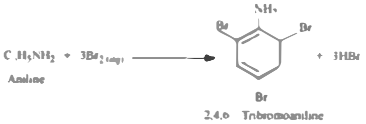
Aniline — Anilinium hydrogen sulphate

(iv)

$C_6H_5N_2Cl + C_2H_5OH \rightarrow C_6H_6 + CH_3CHO + N_2 + HCl$

Benzenediazonium chloride — Ethanol — Benzene — Ethanal

(v)



(vi)

$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5-\underset{H}{N}-\underset{O}{C}-CH_3 + CH_3COOH$

(vii)

$C_6H_5N_2Cl \xrightarrow[\text{(ii)}NaNO_2/Cu,\Delta]{\text{(i)}HBF_4} C_6H_5NO_2 + N_2 + NaBF_4$

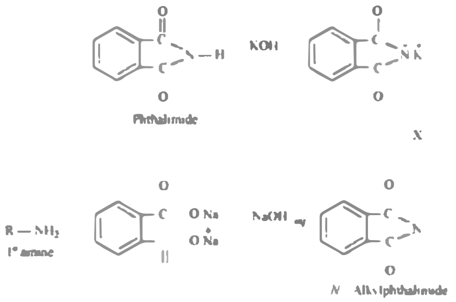
Benzenediazonium chloride — Nitrobenzene

Question 13.12:

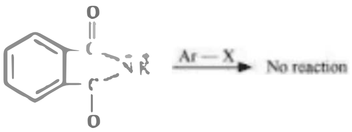
Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

solution :

Gabriel phthalimide synthesis is usually used for the formation of aliphatic primary amines. This includes nucleophilic substitution (SN_2) of alkyl halides by the anion produced by the phthalimide.



however, nucleophilic substitution with the anion formed by the phthalimide is not undergone by aryl halides .



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

Question 13.13 :

Write the reactions of

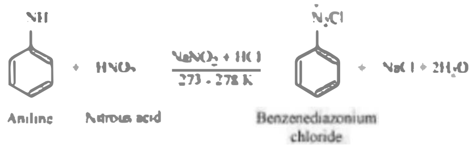
(i) Aromatic with nitrous acid.

(ii) Aliphatic primary amines with nitrous acid.

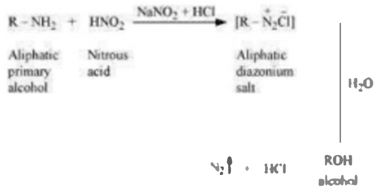
Solution :

(i) Aromatic amine when reacts with nitrous acid (which is made in situ from $NaNO_2$ & a mineral acid such as

(HCl) at 273 – 278 K forming stable aromatic diazonium salts i.e., NaCl & H_2O.



(ii) Aliphatic primary amines when are reacted with nitrous acid (made in situ from $NaNO_2$ & a mineral acid such as HCl forming unstable aliphatic diazonium salts, which later produces alcohol & HCl along with the evolution of N_2 gas.



Question 13.14 :

Give plausible explanation for each of the following:

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

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

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

Solution :

(i) protonation of amines gives amide ion.

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

Amide ion

in the same way, alcohol gives away a proton which results in alkoxide ion.

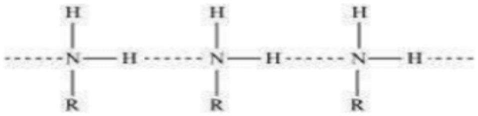
$$R-OH \dashrightarrow R-O + H$$

Alcohol

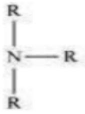
Alkoxide ion

In an amide ion, N-atom has the negative charge is on it , while in alkoxide ion, O – atom has the negative charge is on it. In view of the fact that O is more electronegative than N, O has the ability to hold the negative charge more effortlessly than N. consequently, the alkoxide ion is more stable than the amide ion. Therefore, **alcohols more acidic than amines of comparable molecular masses**

(ii), there are no H – atoms present in a molecule of tertiary amine while two hydrogen atoms are present in primary amines. Primary amines undergo extensive intermolecular H – bonding because of the presence of H – atoms.



Primary amine



Tertiary amine

Consequently, additional energy would be required to detach the molecules of primary amines. Therefore, tertiary amines have a lower boiling points than primary amines.

(iii) The availability of N – atom is fewer in aromatic amines, this is because of the – R effect of the benzene ring. Thus, the electrons on the N – atom in aromatic amines cannot be donated easily. This explains why aliphatic amines are stronger bases than aromatic amines.