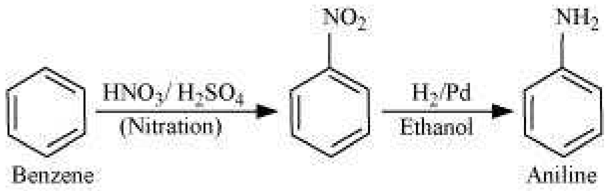
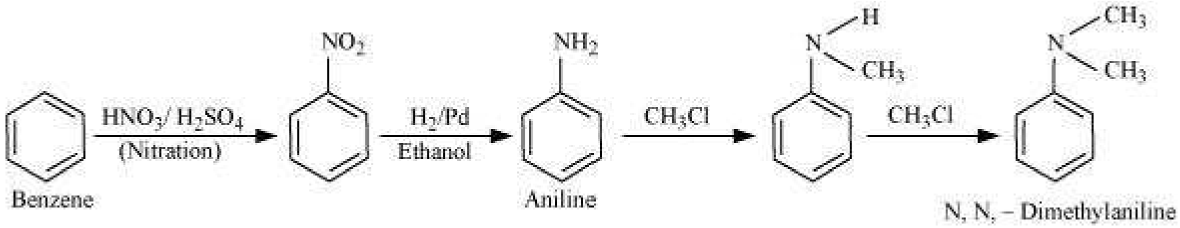
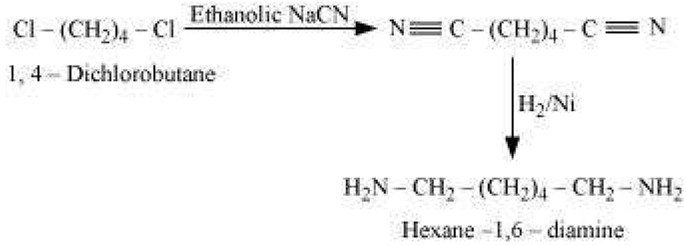
(i)



(ii)



(iii)



Question 13.4:

Arrange the following in increasing order of their basic strength:

(i) $C_2H_5NH_2$, $C_6H_5NH_2$, NH_3, $C_6H_5CH_2NH_2$ and $(C_2H_5)_2NH$

(ii) $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, $C_6H_5NH_2$

(iii) CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$.

Answer

(i) Considering the inductive effect of alkyl groups, NH_3, $C_2H_5NH_2$, and $(C_2H_5)_2NH$ can be arranged in the increasing order of their basic strengths as:

$$NH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$$

Again, $C_6H_5NH_2$ has proton acceptability less than NH_3. Thus, we have:

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

Due to the −I effect of C_6H_5 group, the electron density on the N-atom in $C_6H_5CH_2NH_2$ is lower than that on the N-atom in $C_2H_5NH_2$, but more than that in NH_3. Therefore, the given compounds can be arranged in the order of their basic strengths as:

$$C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$$

(ii) Considering the inductive effect and the steric hindrance of the alkyl groups, $C_2H_5NH_2$, $(C_2H_5)_2NH_2$, and their basic strengths as follows:

$$C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$$

Again, due to the −R effect of C_6H_5 group, the electron density on the N atom in $C_6H_5NH_2$ is lower than that on the N atom in $C_2H_5NH_2$. Therefore, the basicity of $C_6H_5NH_2$ is lower than that of $C_2H_5NH_2$. Hence, the given compounds can be arranged in the increasing order of their basic strengths as follows:

$$C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$$

(iii) Considering the inductive effect and the steric hindrance of alkyl groups, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$ can be arranged in the increasing order of their basic strengths as:

$$(CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$$

In $C_6H_5NH_2$, N is directly attached to the benzene ring. Thus, the lone pair of electrons on the N−atom is delocalized over the benzene ring. In $C_6H_5CH_2NH_2$, N is not directly attached to the benzene ring. Thus, its lone pair is not delocalized over the benzene ring. Therefore, the electrons on the N atom are more easily available for protonation in $C_6H_5CH_2NH_2$ than in $C_6H_5NH_2$ i.e., $C_6H_5CH_2NH_2$ is more basic than $C_6H_5NH_2$.

Again, due to the −I effect of C_6H_5 group, the electron density on the N−atom in $C_6H_5CH_2NH_2$ is lower than that on the N−atom in $(CH_3)_3N$. Therefore, $(CH_3)_3N$ is more basic than $C_6H_5CH_2NH_2$. Thus, the given compounds can be arranged in the increasing order of their basic strengths as follows.

$$C_6H_5NH_2 < C_6H_5CH_2NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$$

Question 13.5:

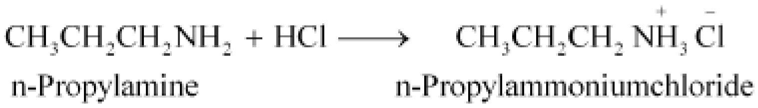
Complete the following acid-base reactions and name the products:

(i) $CH_3CH_2CH_2NH_2 + HCl \rightarrow$

(ii) $(C_2H_5)_3N + HCl \rightarrow$

Answer

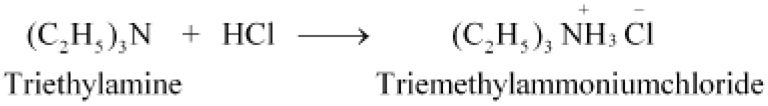
(i)



$CH_3CH_2CH_2NH_2 + HCl \longrightarrow CH_3CH_2CH_2\overset{+}{N}H_3\overset{-}{Cl}$

n-Propylamine n-Propylammoniumchloride

(ii)



$(C_2H_5)_3N + HCl \longrightarrow (C_2H_5)_3\overset{+}{N}H_3\overset{-}{Cl}$

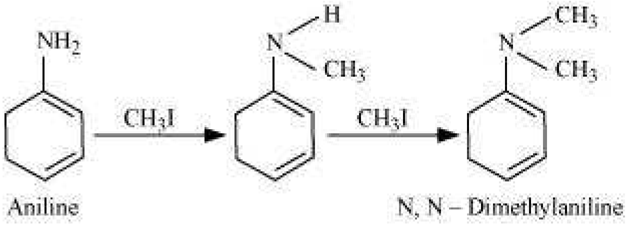
Triethylamine Triemethylammoniumchloride

Question 13.6:

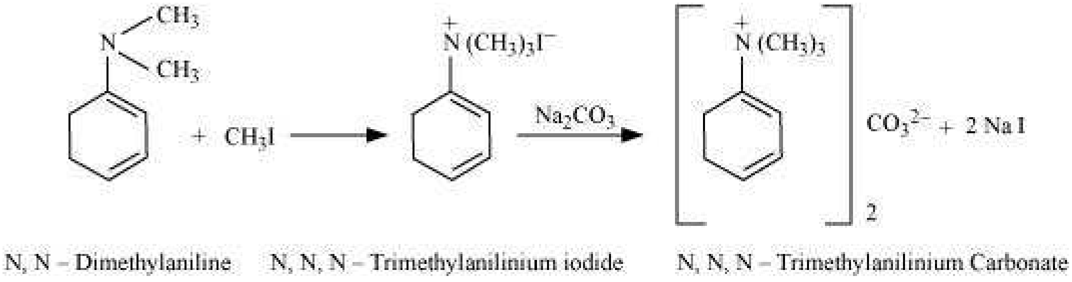
Write reactions of the final alkylation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.

Answer

Aniline reacts with methyl iodide to produce N, N-dimethylaniline.



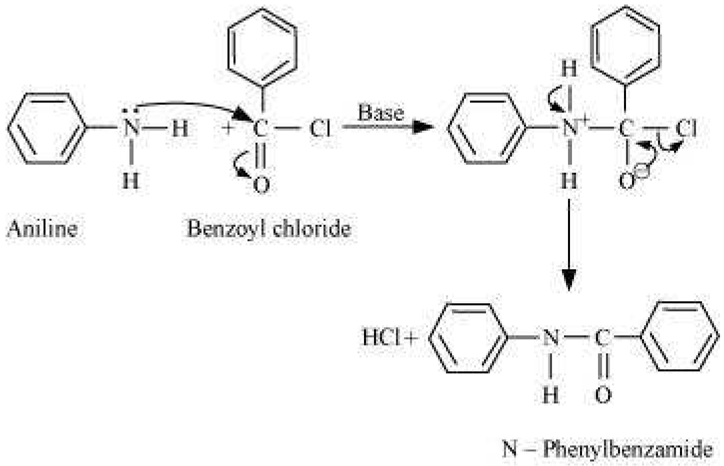
With excess methyl iodide, in the presence of Na2CO3 solution, N, N-dimethylaniline produces N, N, N−trimethylanilinium carbonate.



Question 13.7:

Write chemical reaction of aniline with benzoyl chloride and write the name of the product obtained.

Answer



Question 13.8:

Write structures of different isomers corresponding to the molecular formula, C_3H_9N. Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.

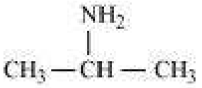
Answer

The structures of different isomers corresponding to the molecular formula, C_3H_9N are given below:

(a) $CH_3-CH_2-CH_2-NH_2$

Propan-1-amine (1^0)

(b)



$$CH_3-\overset{NH_2}{\overset{|}{C}H}-CH_3$$

Propan-2-amine (1^0)

(c)

$CH_3\text{-}NH\text{-}C_2H_5$

N-Methylethanamine (2^0)

(d)

$$CH_3-\overset{CH_3}{\overset{|}{N}}-CH_3$$

N,N-Dimethylmethanamine (3^0)

1^0amines, (a) propan-1-amine, and (b) Propan-2-amine will liberate nitrogen gas on treatment with nitrous acid.

$$CH_3CH_2CH_2NH_2 + HNO_2 \longrightarrow CH_3CH_2CH_2OH + N_2 + HCl$$

Propan-1-amine Propan-1-ol

$$\underset{\displaystyle NH_2}{CH_3-\underset{|}{CH}-CH_3} + HNO_2 \longrightarrow \underset{\displaystyle OH}{CH_3-\underset{|}{CH}-CH_3} + N_2 + HCl$$

Propan – 2 – amine Propan – 2 – ol

Question 13.9:

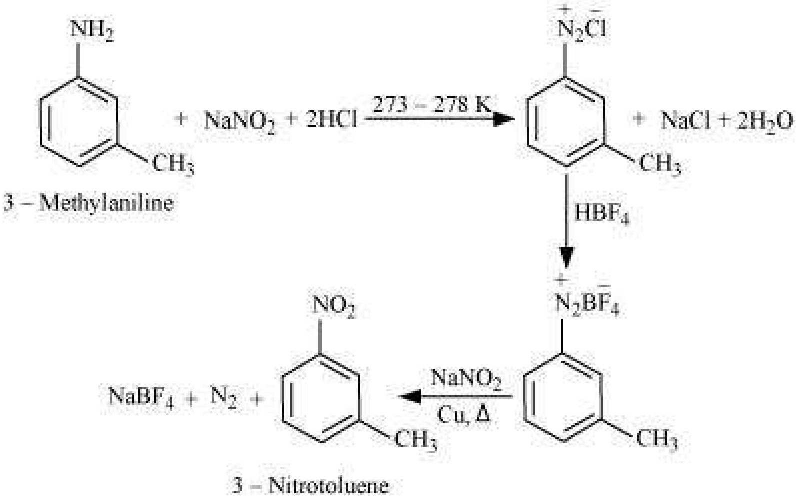
Convert

(i) 3-Methylaniline into 3-nitrotoluene.

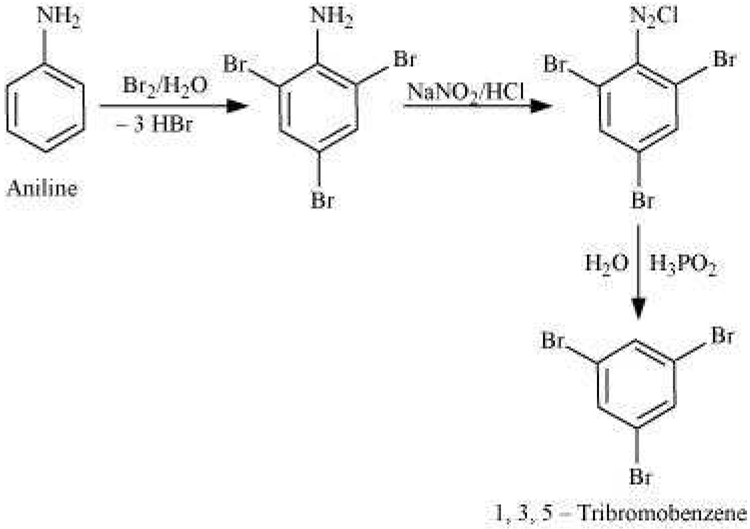
(ii) Aniline into 1,3,5-tribromobenzene.

Answer

(i)



(ii)



Question 13.1:

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

(i) $(CH_3)_2\,CHNH_2$ **(ii)** $CH_3(CH_2)_2NH_2$

(iii) $CH_3NHCH(CH_3)_2$ **(iv)** $(CH_3)_3CNH_2$

(v) $C_6H_5NHCH_3$ **(vi)** $(CH_3CH_2)_2NCH_3$

(vii) *m*−$BrC_6H_4NH_2$

Answer

(i) 1-Methylethanamine (1^0 amine)

(ii) Propan-1-amine (1^0 amine)

(iii) N−Methyl-2-methylethanamine (2^0 amine)

(iv) 2-Methylpropan-2-amine (1^0 amine)

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

(vi) N-Ethyl-N-methylethanamine (3^0 amine)

(vii) 3-Bromobenzenamine or 3-bromoaniline (1^0 amine)

Question 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.

Answer

(i) Methylamine and dimethylamine can be distinguished by the carbylamine test.

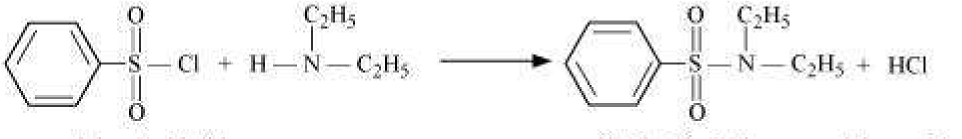
Carbylamine test: Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form foul-smelling isocyanides or carbylamines. Methylamine (being an aliphatic primary amine) gives a positive carbylamine test, but dimethylamine does not.

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

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

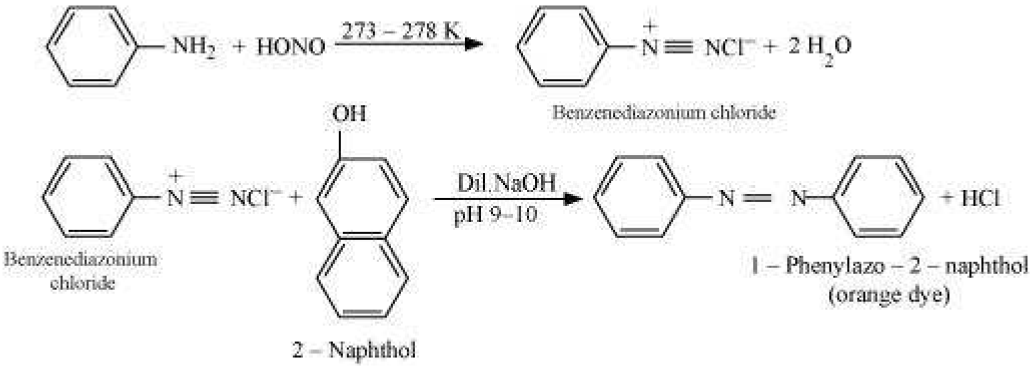
(ii) Secondary and tertiary amines can be distinguished by allowing them to react with Hinsberg's reagent (benzenesulphonyl chloride, $C_6H_5SO_2Cl$).

Secondary amines react with Hinsberg's reagent to form a product that is insoluble in an alkali. For example, N, N−diethylamine reacts with Hinsberg's reagent to form N, N−diethylbenzenesulphonamide, which is insoluble in an alkali. Tertiary amines, however, do not react with Hinsberg's reagent.



Benzenesulphonyl chloride N, N – Diethylbenzenesulphonamide

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



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

(iv) Aniline and benzylamine can be distinguished by their reactions with the help of nitrous acid, which is prepared in situ from a mineral acid and sodium nitrite. Benzylamine reacts with nitrous acid to form unstable diazonium salt, which in turn gives alcohol with the evolution of nitrogen gas.

$$\begin{tikzcd} \underset{\text{Benzylamine}}{C_6H_5CH_2-NH_2} + HNO_2 \arrow[r, "NaNO_2 + HCl"] & \underset{\text{(Unstable)}}{[C_6H_5CH_2-\overset{+}{N}_2\overset{-}{Cl}]} \arrow[d, "H_2O"] \\ & N_2\uparrow + \underset{\text{Benzyl alcohol}}{C_6H_5CH_2-OH} + HCl \end{tikzcd}$$

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

$$C_6H_5NH_2 \xrightarrow[273-278K]{NaNO_2+HCl} C_6H_5-\overset{+}{N}_2\overset{-}{Cl} + NaCl + 2H_2O$$

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

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

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

Question 13.3:

Account for the following:

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

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

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

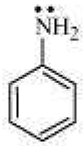
(v) Aniline does not undergo Friedel-Crafts reaction.

(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) pK_b of aniline is more than that of methylamine:

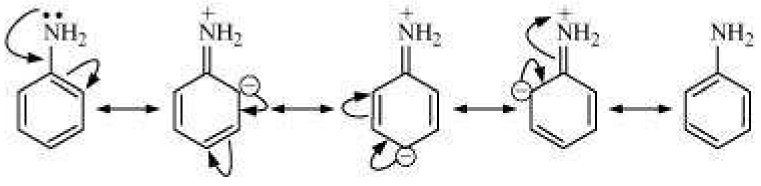


Aniline

$CH_3-\ddot{N}H_2$

Methylamine

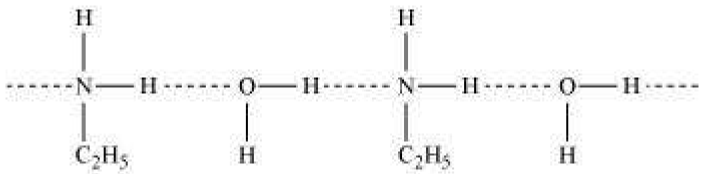
Aniline undergoes resonance and as a result, the electrons on the N-atom are delocalized over the benzene ring. Therefore, the electrons on the N-atom are less available to donate.



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

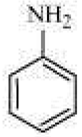
(ii) Ethylamine is soluble in water whereas aniline is not:

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



Ethylamine

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



Aniline

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

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.

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

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

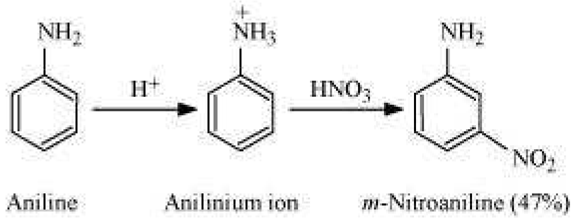
$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$$

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

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

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

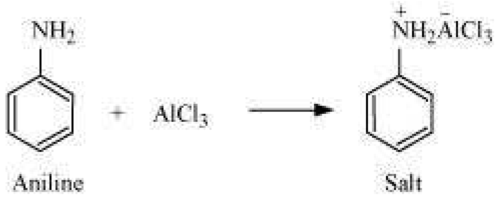
Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing).



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

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

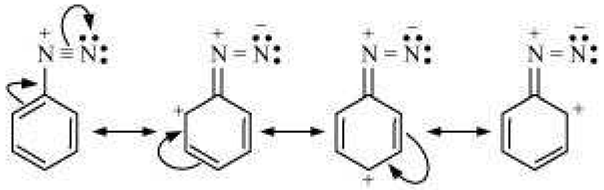
A Friedel-Crafts reaction is carried out in the presence of $AlCl_3$. But $AlCl_3$ is acidic in nature, while aniline is a strong base. Thus, aniline reacts with $AlCl_3$ to form a salt (as shown in the following equation).



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

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

The diazonium ion undergoes resonance as shown below:



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

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

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

Question 13.4:

Arrange the following:

(i) In decreasing order of the p$K_b$values:

$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

(ii) In increasing order of basic strength:

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2

(iii) In increasing order of basic strength:

(a) Aniline, *p*-nitroaniline and *p*-toluidine

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

(iv) In decreasing order of basic strength in gas phase:

$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3

(v) In increasing order of boiling point:

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

(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.

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

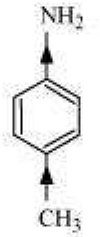
(ii) $C_6H_5N(CH_3)_2$ is more basic than $C_6H_5NH_2$ due to the presence of the +I effect of two $-CH_3$ groups in $C_6H_5N(CH_3)_2$. Further, CH_3NH_2 contains one $-CH_3$ group while $(C_2H_5)_2NH$ contains two $-C_2H_5$ groups. Thus, $(C_2H_5)_2$ NH is more basic than $C_2H_5NH_2$.

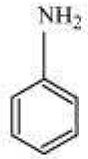
Now, $C_6H_5N(CH_3)_2$ is less basic than CH_3NH_2 because of the−R effect of $-C_6H_5$ group.

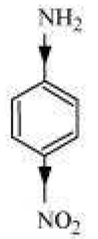
Hence, the increasing order of the basic strengths of the given compounds is as follows:

$C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$

(iii) (a)


p-Toluidine


Aniline


p-Nitroaniline

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 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

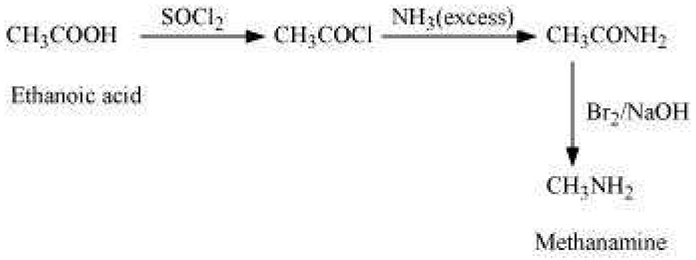
(vi) Methanamine into ethanamine

(vii) Nitromethane into dimethylamine

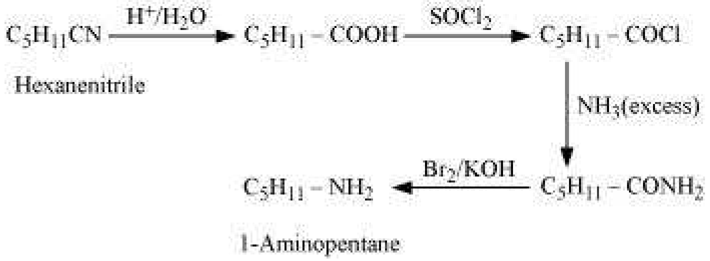
(viii) Propanoic acid into ethanoic acid

Answer

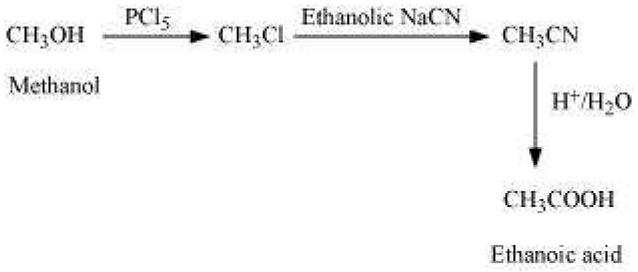
(i)


CH_3COOH
$SOCl_2$
CH_3COCl
NH_3(excess)
CH_3CONH_2
Ethanoic acid
Br_2/NaOH
CH_3NH_2
Methanamine

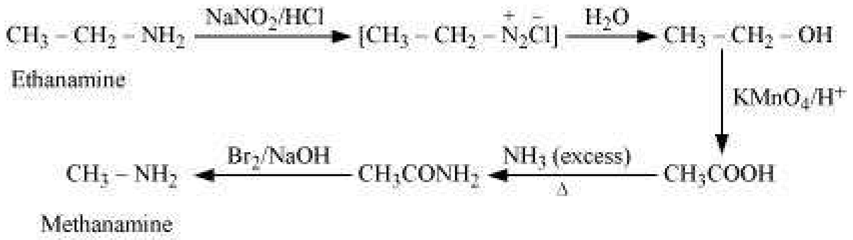
(ii)


$C_5H_{11}CN$
H^+/H_2O
$C_5H_{11}-COOH$
$SOCl_2$
$C_5H_{11}-COCl$
Hexanenitrile
NH_3(excess)
Br_2/KOH
$C_5H_{11}-NH_2$
$C_5H_{11}-CONH_2$
1-Aminopentane

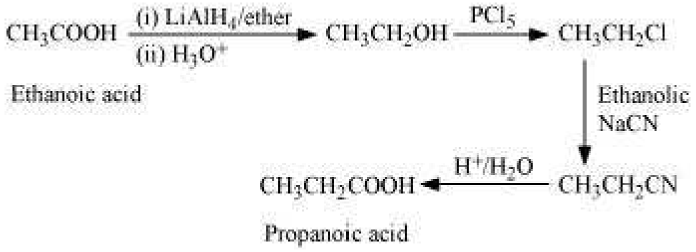
(iii)


CH_3OH
PCl_5
CH_3Cl
Ethanolic NaCN
CH_3CN
Methanol
H^+/H_2O
CH_3COOH
Ethanoic acid

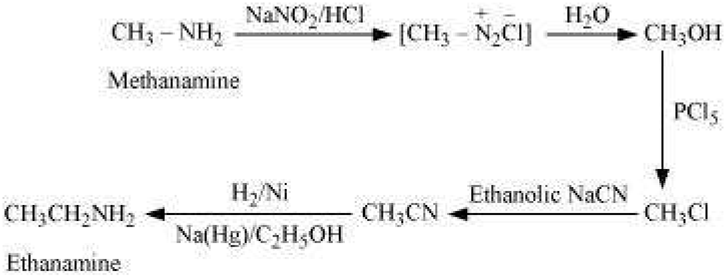
(iv)


$CH_3-CH_2-NH_2$
$NaNO_2/HCl$
$[CH_3-CH_2-\overset{+}{N_2}\overset{-}{Cl}]$
H_2O
CH_3-CH_2-OH
Ethanamine
$KMnO_4/H^+$
CH_3-NH_2
Br_2/NaOH
CH_3CONH_2
NH_3 (excess)
Δ
CH_3COOH
Methanamine

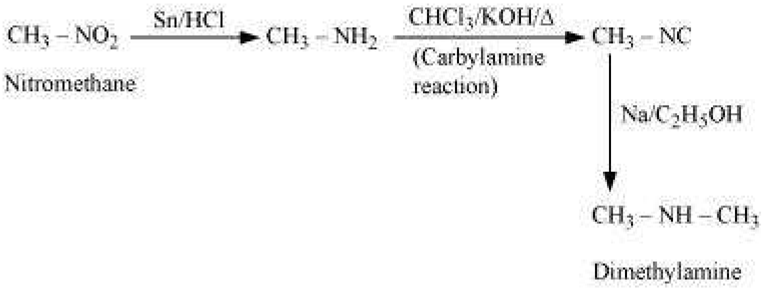
(v)


CH_3COOH
(i) $LiAlH_4$/ether
(ii) H_3O^+
CH_3CH_2OH
PCl_5
CH_3CH_2Cl
Ethanoic acid
Ethanolic NaCN
H^+/H_2O
CH_3CH_2COOH
CH_3CH_2CN
Propanoic acid

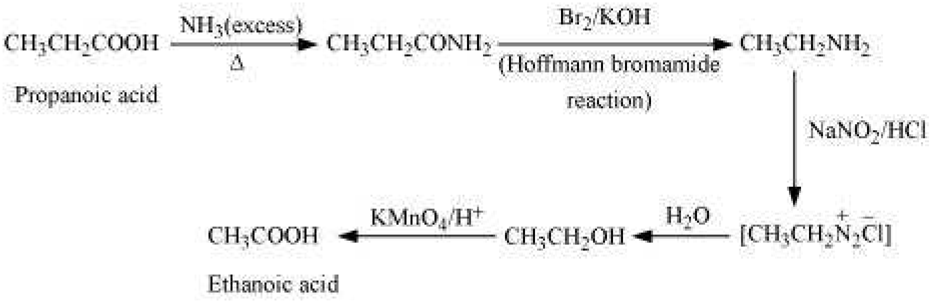
(vi)



(vii)



(viii)



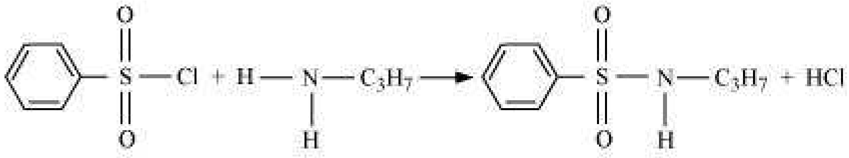
Question 13.6:

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.

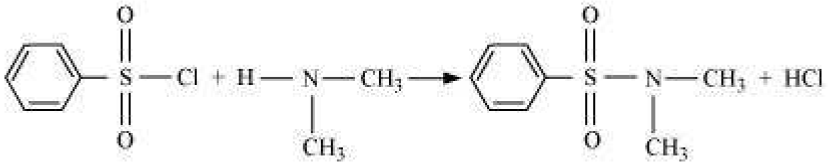
Primary amines react with benzenesulphonyl chloride to form N-alkylbenzenesulphonyl amide which is soluble in alkali.



Benzenesulphonyl chloride
Propanamine
N-Propylbenzenesulphonamide

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.



Benzenesulphonyl chloride
Dimethylamine
N, *N*-Dimethylbenzenesulphonamide (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 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.

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.

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

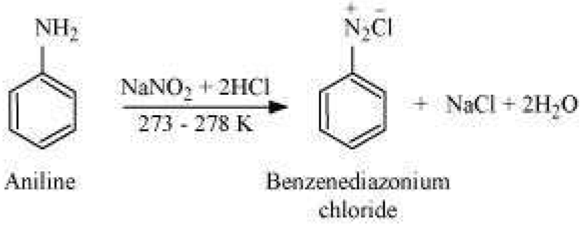
For example,

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

(ii) Diazotisation

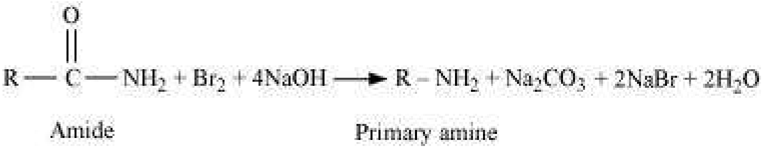
Aromatic primary amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) at low temperatures (273-278 K) to form diazonium salts. This conversion of aromatic primary amines into diazonium salts is known as diazotization.

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



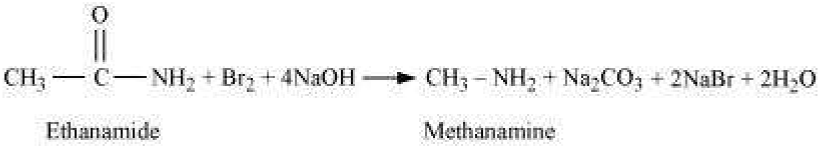
(iii) Hoffmann bromamide reaction

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.

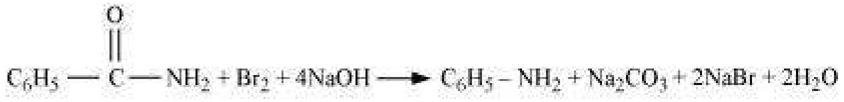


$$\underset{\text{Amide}}{R-\overset{\overset{\displaystyle O}{||}}{C}-NH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{Primary amine}}{R-NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

For example,



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

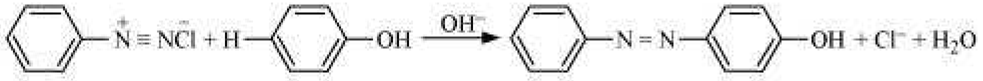


$$C_6H_5-\overset{\overset{\large O}{||}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow C_6H_5-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

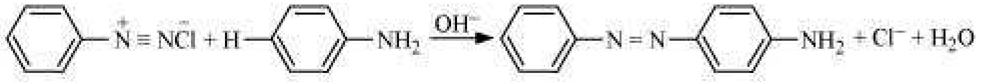
Benzamide Aniline

(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.



Benzenediazonium chloride Phenol *p*-Hydroxyazobenzene (Orange dye)



Benzenediazonium chloride Aniline *p*-Aminoazobenzene (yellow dye)

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 ($-NH_2$) group. This process of cleavage of the carbon-halogen bond is known as ammonolysis.

Ammonia (Nucleophile) Alkyl halide Substituted ammonium salt

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

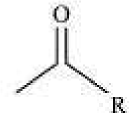
$$R-\overset{+}{N}H_3\overset{-}{X} + NaOH \longrightarrow \underset{\text{Amine}}{R-NH_2} + H_2O + NaX$$

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

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

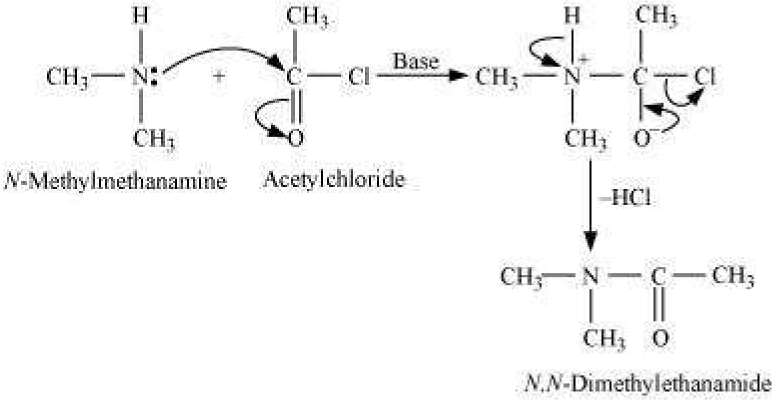
(vi) Acetylation

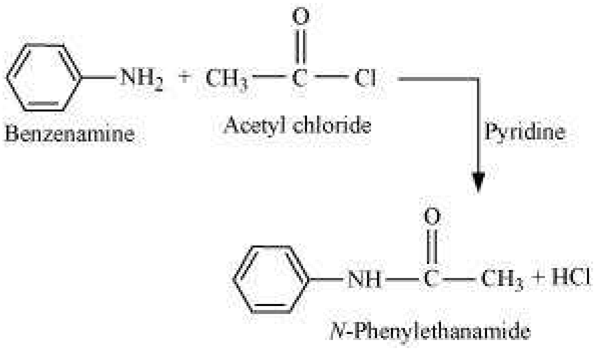
Acetylation (or ethanoylation) is the process of introducing an acetyl group into a molecule.



Acetyl group

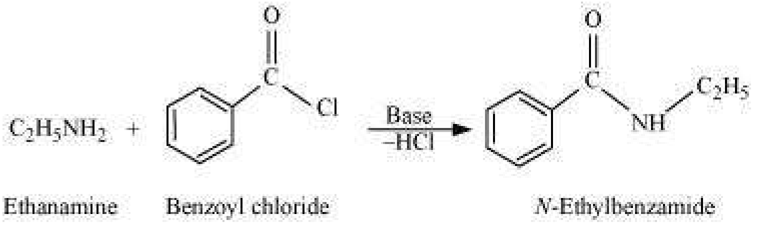
Aliphatic and aromatic primary and secondary amines undergo acetylation reaction by nucleophilic substitution when treated with acid chlorides, anhydrides or esters. This reaction involves the replacement of the hydrogen atom of $-NH_2$ or > NH group by the acetyl group, which in turn leads to the production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





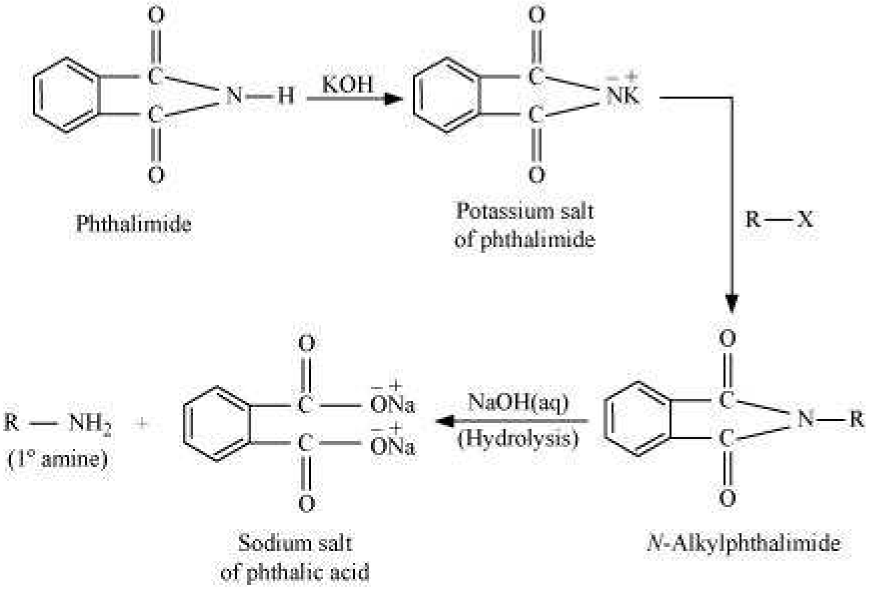
When amines react with benzoyl chloride, the reaction is also known as benzoylation.

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 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

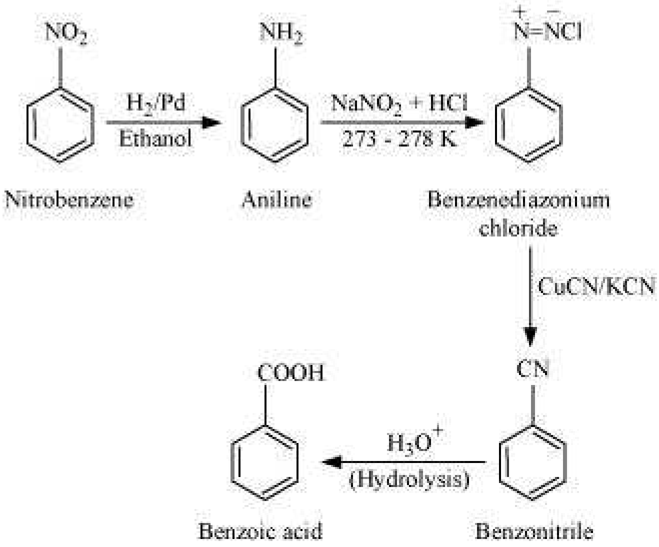
(vii) Aniline to *p*-bromoaniline

(viii) Benzamide to toluene

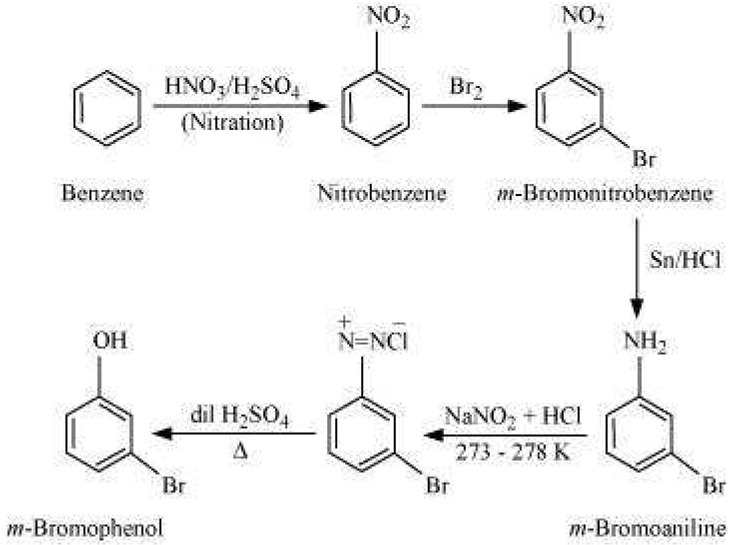
(ix) Aniline to benzyl alcohol.

Answer

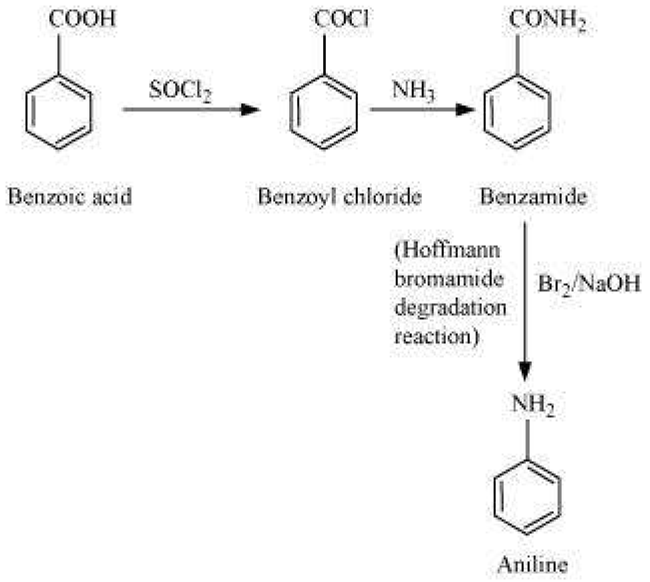
(i)



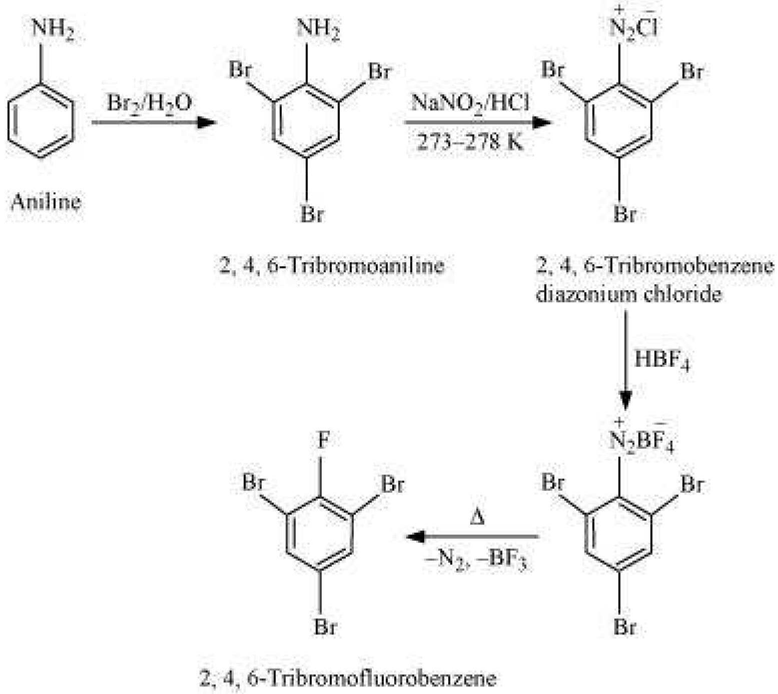
(ii)



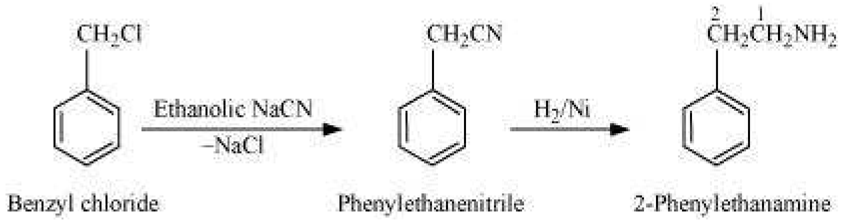
(iii)


COOH
SOCl$_2$
COCl
NH$_3$
CONH$_2$
Benzoic acid
Benzoyl chloride
Benzamide
(Hoffmann bromamide degradation reaction)
Br$_2$/NaOH
NH$_2$
Aniline

(iv)

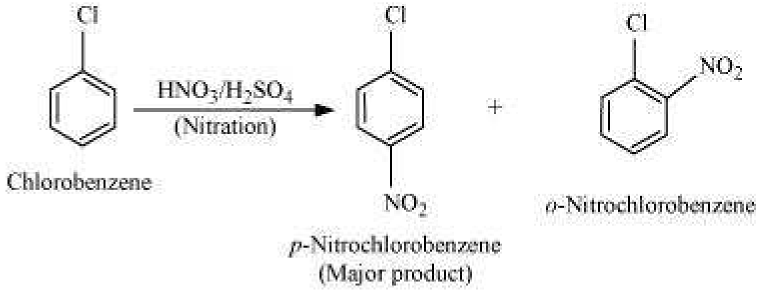

NH$_2$
Aniline
Br$_2$/H$_2$O
NH$_2$
Br
Br
Br
2, 4, 6-Tribromoaniline
NaNO$_2$/HCl
273–278 K
$\overset{+}{N}_2\overset{-}{Cl}$
Br
Br
Br
2, 4, 6-Tribromobenzene diazonium chloride
HBF$_4$
$\overset{+}{N}_2\overset{-}{BF_4}$
Br
Br
Br
Δ
–N$_2$, –BF$_3$
F
Br
Br
Br
2, 4, 6-Tribromofluorobenzene

(v)

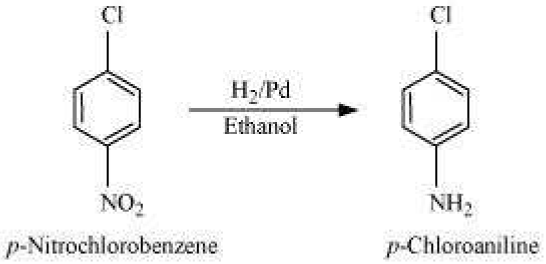


CH2Cl
Ethanolic NaCN
–NaCl
CH2CN
H2/Ni
2 1
CH2CH2NH2
Benzyl chloride
Phenylethanenitrile
2-Phenylethanamine

(vi)

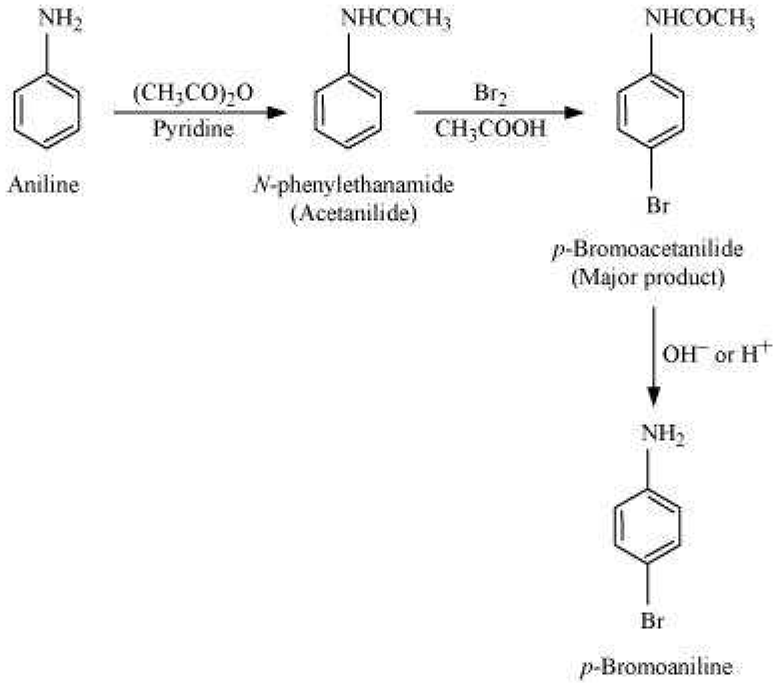


Cl
HNO3/H2SO4
(Nitration)
Chlorobenzene
Cl
NO2
p-Nitrochlorobenzene
(Major product)
+
Cl
NO2
o-Nitrochlorobenzene

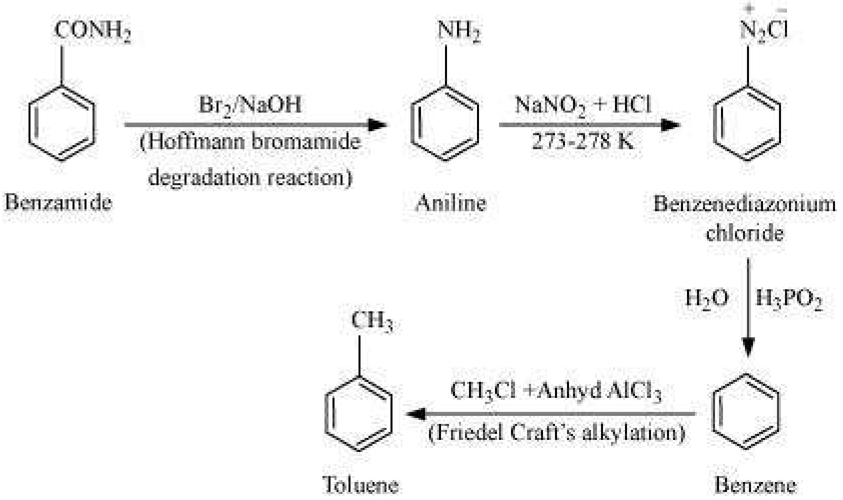


Cl
NO2
p-Nitrochlorobenzene
H2/Pd
Ethanol
Cl
NH2
p-Chloroaniline

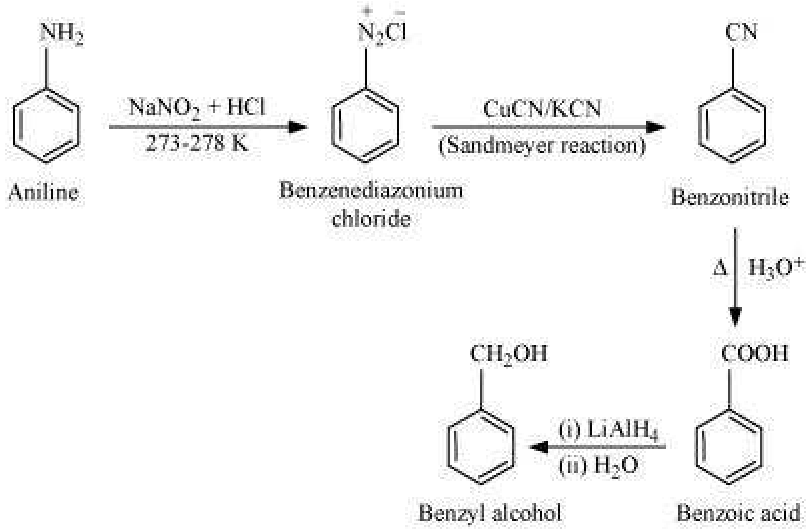
(vii)


NH₂
Aniline
(CH₃CO)₂O
Pyridine
NHCOCH₃
N-phenylethanamide
(Acetanilide)
Br₂
CH₃COOH
NHCOCH₃
Br
p-Bromoacetanilide
(Major product)
OH⁻ or H⁺
NH₂
Br
p-Bromoaniline

(viii)


CONH₂
Benzamide
Br₂/NaOH
(Hoffmann bromamide
degradation reaction)
NH₂
Aniline
NaNO₂ + HCl
273-278 K
N₂⁺Cl⁻
Benzenediazonium
chloride
H₂O
H₃PO₂
Benzene
CH₃Cl +Anhyd AlCl₃
(Friedel Craft's alkylation)
CH₃
Toluene

(ix)



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

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

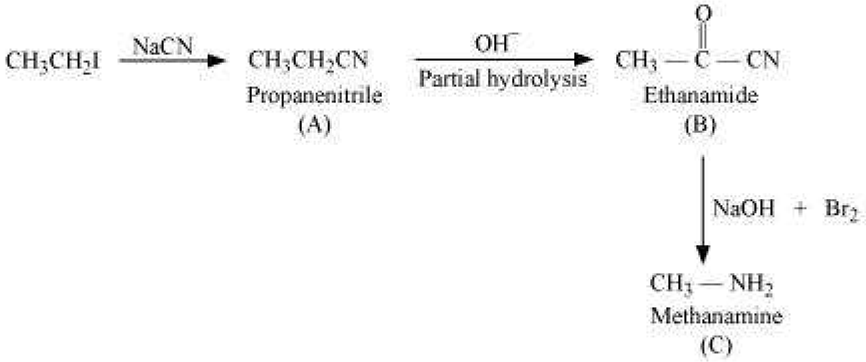
(iv) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{NaNO_2+HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$

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

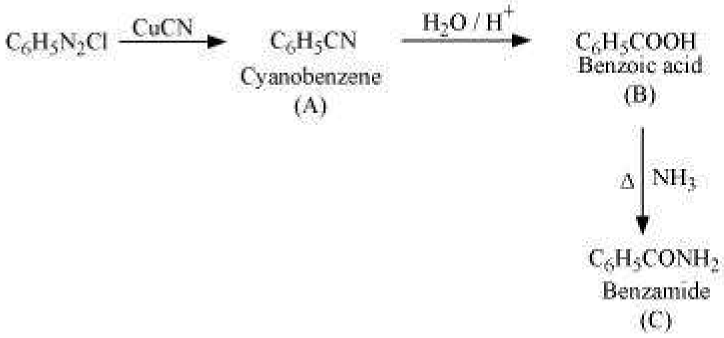
(vi) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{HNO_2} B \xrightarrow{C_6H_5OH} C$

Answer

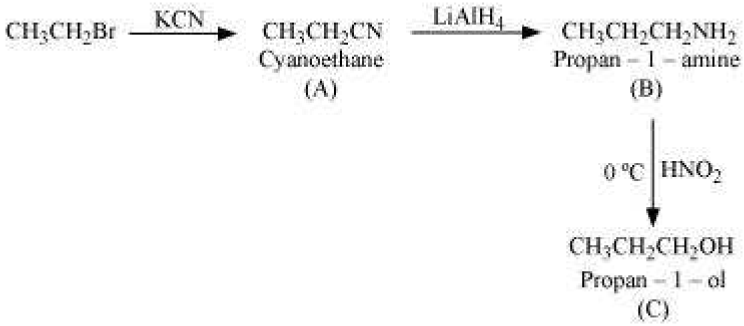
(i)


CH₃CH₂I
NaCN
CH₃CH₂CN
Propanenitrile
(A)
OH⁻
Partial hydrolysis
O
CH₃ — C — CN
Ethanamide
(B)
NaOH + Br₂
CH₃ — NH₂
Methanamine
(C)

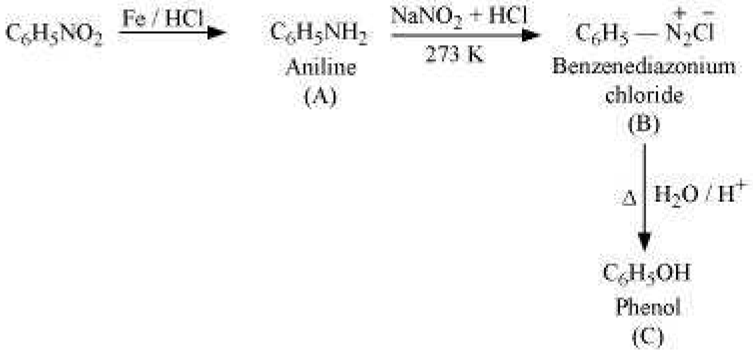
(ii)


C₆H₅N₂Cl
CuCN
C₆H₅CN
Cyanobenzene
(A)
H₂O / H⁺
C₆H₅COOH
Benzoic acid
(B)
Δ
NH₃
C₆H₅CONH₂
Benzamide
(C)

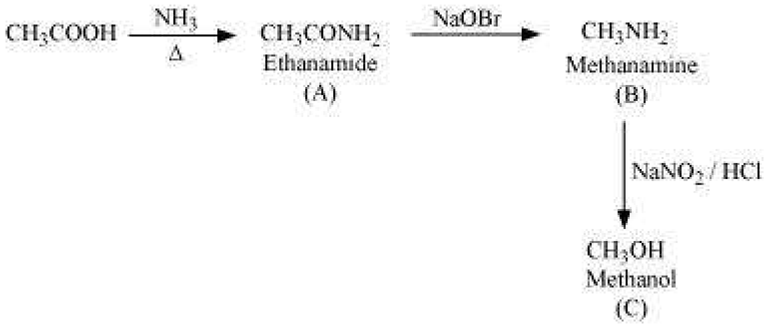
(iii)


CH₃CH₂Br
KCN
CH₃CH₂CN
Cyanoethane
(A)
LiAlH₄
CH₃CH₂CH₂NH₂
Propan – 1 – amine
(B)
0 °C
HNO₂
CH₃CH₂CH₂OH
Propan – 1 – ol
(C)

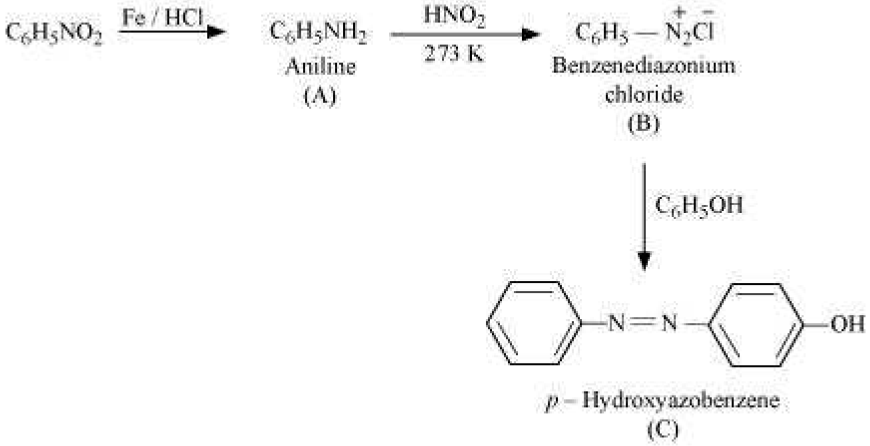
(iv)


C₆H₅NO₂
Fe / HCl
C₆H₅NH₂
Aniline
(A)
NaNO₂ + HCl
273 K
C₆H₅ — N₂⁺Cl⁻
Benzenediazonium
chloride
(B)
Δ
H₂O / H⁺
C₆H₅OH
Phenol
(C)

(v)



(vi)

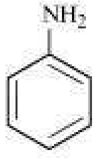


Question 13.10:

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

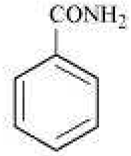
Answer

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



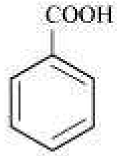
Aniline

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



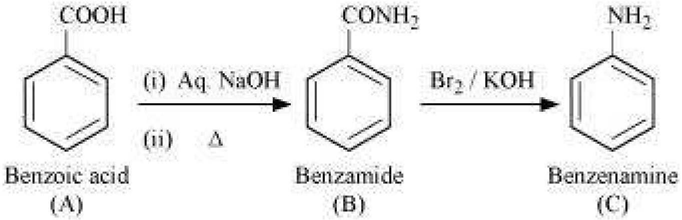
Benzamide

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

Answer

(i)

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

(ii)

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

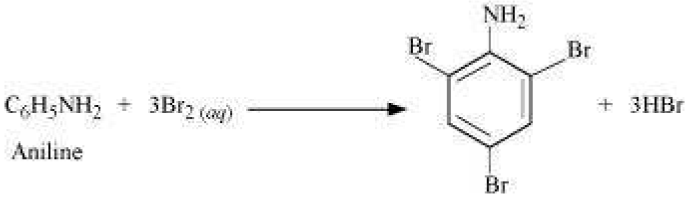
(iii)

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

(iv)

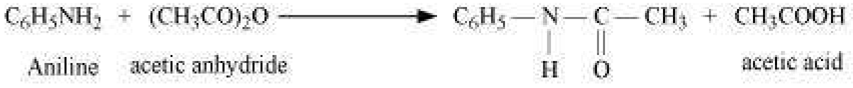
$$\underset{\text{Benzenediazonium chloride}}{C_6H_5N_2Cl} + \underset{\text{Ethanol}}{C_2H_5OH} \rightarrow \underset{\text{Benzene}}{C_6H_6} + \underset{\text{Ethanal}}{CH_3CHO} + N_2 + HCl$$

(v)



2,4,6 – Tribromoaniline

(vi)



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

N – Phenylethanamide

(vii)

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

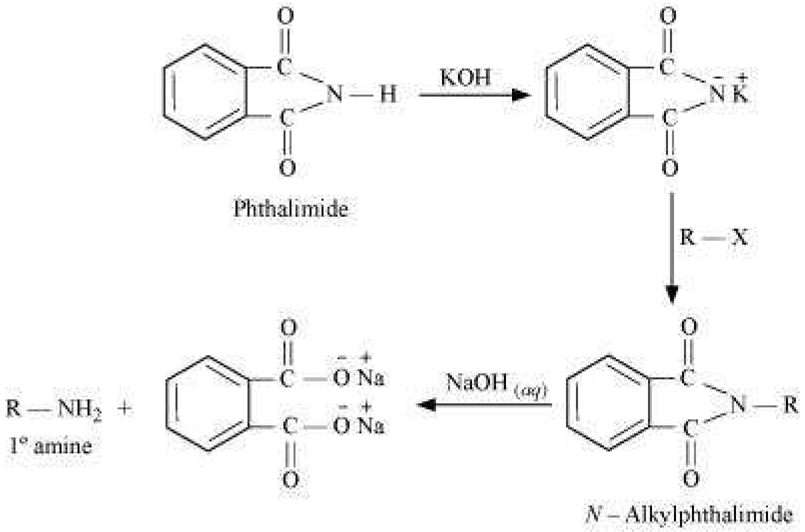
Benzenediazonium chloride — Nitrobenzene

Question 13.12:

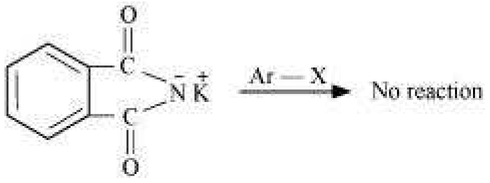
Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

Answer

Gabriel phthalimide synthesis is used for the preparation of aliphatic primary amines. It involves nucleophilic substitution (S_N2) of alkyl halides by the anion formed by the phthalimide.



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



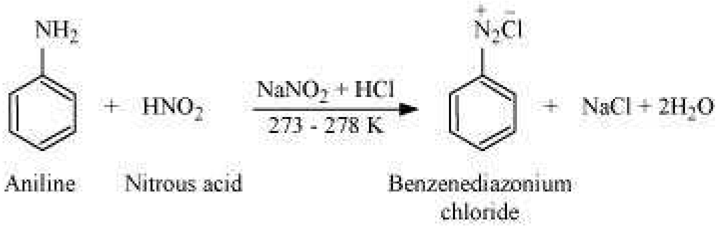
Hence, aromatic primary amines cannot be prepared by this process.

Question 13.13:

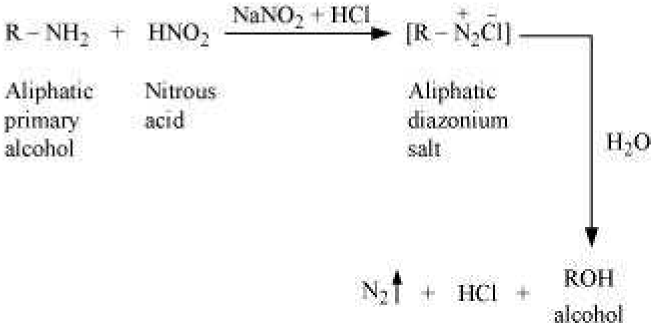
Write the reactions of **(i)** aromatic and **(ii)** aliphatic primary amines with nitrous acid.

Answer

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



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



Question 13.14:

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 undergo protonation to give amide ion.

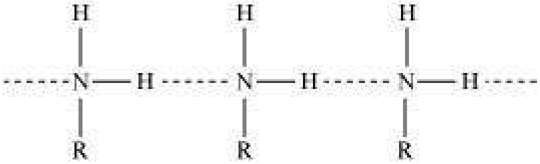
$$R-NH_2 \longrightarrow \underset{\text{Amide ion}}{R-\overset{-}{N}H} + H^+$$

Similarly, alcohol loses a proton to give alkoxide ion.

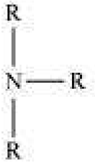
$$\underset{\text{Alcohol}}{R-OH} \longrightarrow \underset{\text{Alkoxide ion}}{R-\overset{-}{O}} + H^+$$

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

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



Primary amine



Tertiary amine

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.

Question 14.1:

Glucose or sucrose are soluble in water but cyclohexane or benzene (simple six membered ring compounds) are insoluble in water. Explain.

Answer

A glucose molecule contains five −OH groups while a sucrose molecule contains eight −OH groups. Thus, glucose and sucrose undergo extensive H-bonding with water.

Hence, these are soluble in water.

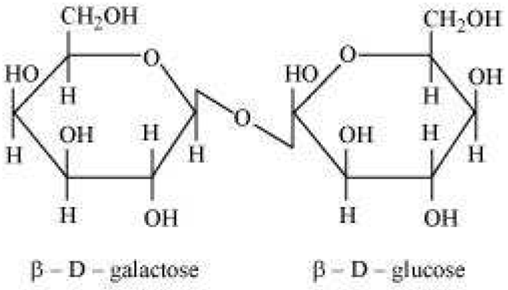
But cyclohexane and benzene do not contain −OH groups. Hence, they cannot undergo H-bonding with water and as a result, are insoluble in water.

Question 14.2:

What are the expected products of hydrolysis of lactose?

Answer

Lactose is composed of β-D galactose and β-D glucose. Thus, on hydrolysis, it gives β-D galactose and β-D glucose.



Lactose

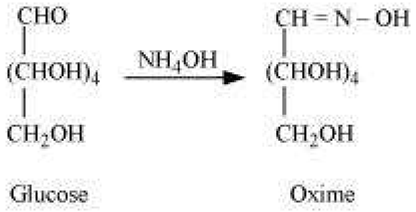
$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{D-(+)-Glucose}}{C_6H_{12}O_6} + \underset{\text{D-(+)-Galactose}}{C_6H_{12}O_6}$$

Question 14.3:

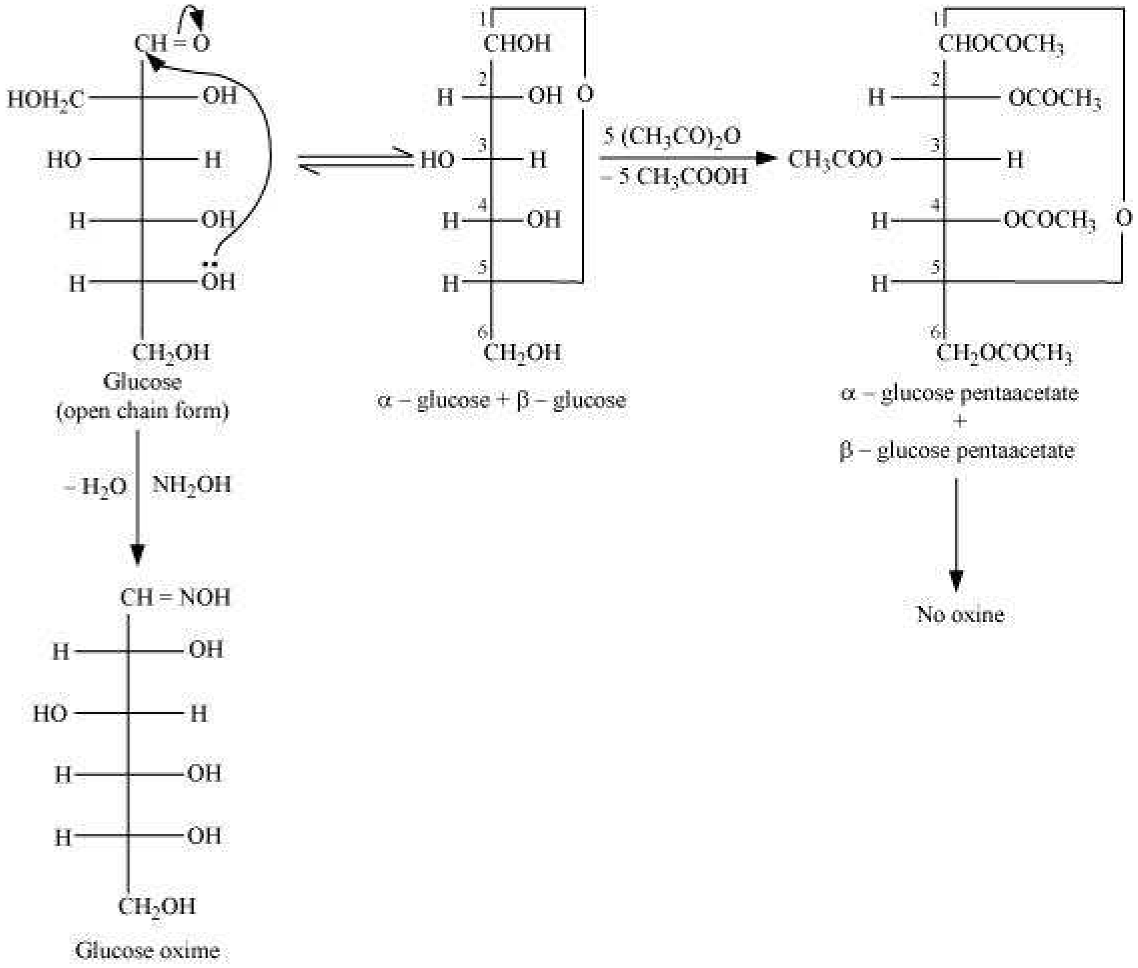
How do you explain the absence of aldehyde group in the pentaacetate of D-glucose?

Answer

D-glucose reacts with hydroxylamine (NH_2OH) to form an oxime because of the presence of aldehydic (−CHO) group or carbonyl carbon. This happens as the cyclic structure of glucose forms an open chain structure in an aqueous medium, which then reacts with NH_2OH to give an oxime.



But pentaacetate of D-glucose does not react with NH_2OH. This is because pentaacetate does not form an open chain structure.



Question 14.4:

The melting points and solubility in water of amino acids are generally higher than that of the corresponding halo acids. Explain.

Answer