Chapter 13
Amines

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1 Mark Questions

1.For an amine RNH_2, write an expression to indicate its basic strength.

Ans.

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$$

$$K_b = \frac{[RNH_3^+]\ [OH^-]}{[RNH_2]}$$

2. Give one use of quaternary ammonium salts.

Ans. Quaternary ammonium salts are widely used for manufacture of synthetic detergents.

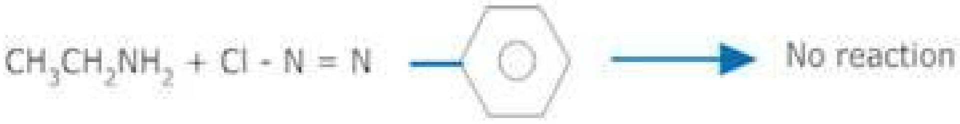
3. Give one example of Hoffmann – Bromamide reaction

Ans. In Hoffmann – Bromamide reaction an acid amide is reacted with Bromine in presence of a base to give a primary amine having one carbon less than the starting amide.

$$RCONH_2 + Br_2 + 4\ NaOH \rightarrow RNH_2 + Na_2\ CO_3 + 2\ NaBr + 2\ H_2O$$

4. Distinguish between ethylamine and aniline.

Ans. Ethylamine and aniline can be distinguished by azodye test. On treating aniline with benzene diazonium salt, orange or red coloured azodye is formed which is not formed with ethyl amine.



5.The IUPAC name of secondary amine having lowest molecular mass is ________.

Ans. N- Methylmethanamine.

6.Give an example of diazotization

Ans. During diazotization benzene diazonium chloride is prepared by the reaction of aniline with nitrous acid at 273 – 278 K

7. Write one use of diazonium salt

Ans. Diazonium salts are used in preparation of substituted aromatic compounds.

8.How can the reactivity of aromatic amines be controlled?

Ans. The reactivity of aromatic amines can be controlled by acylation.

9.Give one use of tertiary amines.

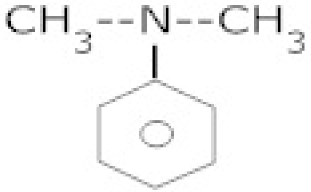
Ans. Tertiary amines like trimethylamine are used as insect attractants.

10. Name a reagent which can distinguish between primary, secondary and tertiary amine

Ans. P- Toluenesulphonyl chloride Hinsberg reagent can be used as a distinguishing reagent for primary, secondary and tertiary amines.

11.Give IUPAC name of

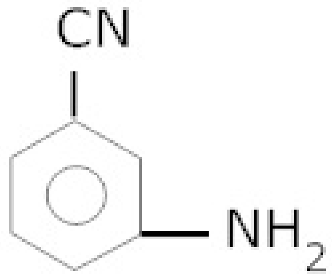
(i)



Ans.N, N–dimethylaniline

(ii) $m - NC\ C_6H_4NH_2$

Ans.



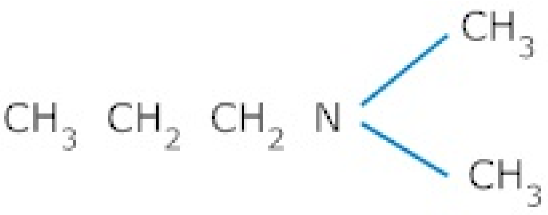
3-aminobenzonitrile

(iii)

$CH_3\ \underset{\underset{NO_2}{|}}{CH} - CH_2\ CH_2\ NH - CH_3$

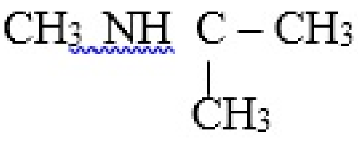
Ans.N- methyl -3 – nitro -1- butanamine

(iv)



Ans.N, N – dimethylpropanamine

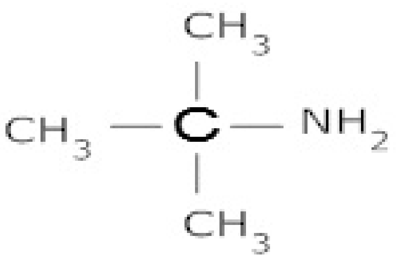
(v)



$CH_3\ NH\ \underset{\underset{CH_3}{|}}{C} - CH_3$

Ans.N- methyl -2- aminopropanamine

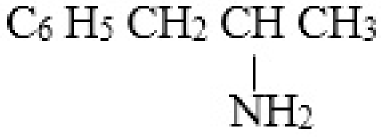
(vi)



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

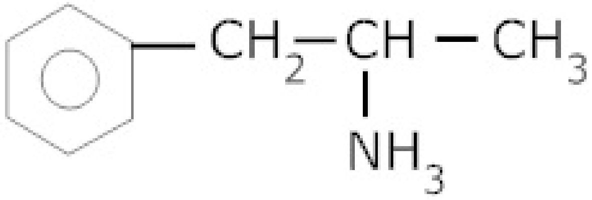
Ans.2- Methyl propane

(vii)



$C_6H_5CH_2\underset{\substack{|\\ NH_2}}{CH}CH_3$

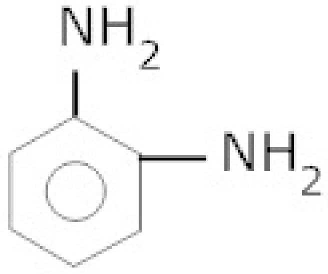
Ans.



1-phenyl-2-propanamine

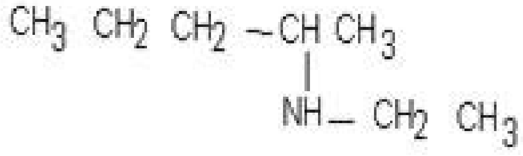
(viii) $O-(NH_2)_2C_6H_4$

Ans.



1, 2-benzenediamine

(ix)



$CH_3\ CH_2\ CH_2-\underset{\substack{|\\ NH-\ CH_2\ CH_3}}{CH}\ CH_3$

Ans.N, N – Dimethyl-4-nitro aniline

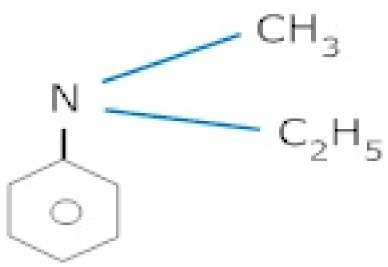
12.Write structure of following

(i) Aminobut -2- ene

Ans. $NH_2CH_2CH\ =\ CH\ CH_3$

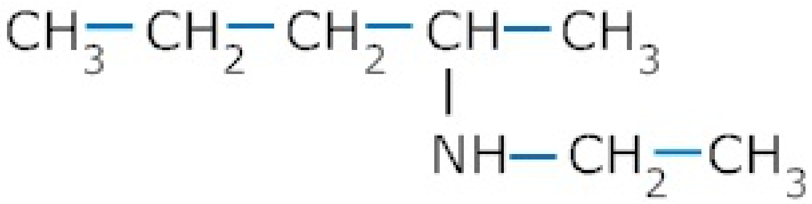
(ii) N- Methyl –N- ethylaniline

Ans.



(iii) N- Ethyl -2- pentanamine

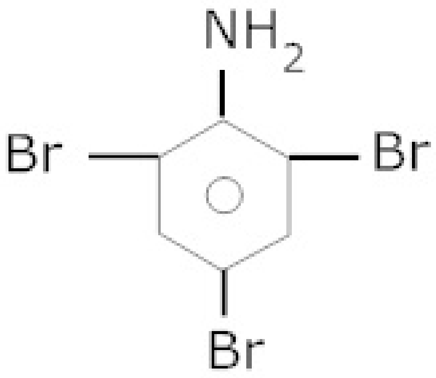
Ans.



$$CH_3-CH_2-CH_2-\underset{\substack{|\\ NH-CH_2-CH_3}}{CH}-CH_3$$

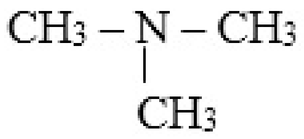
(iv) 2,4,6 – Tribromoaniline

Ans.



(v) N, N- Dimethyl methanamine

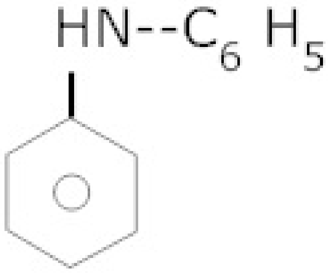
Ans.



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{N}-CH_3$$

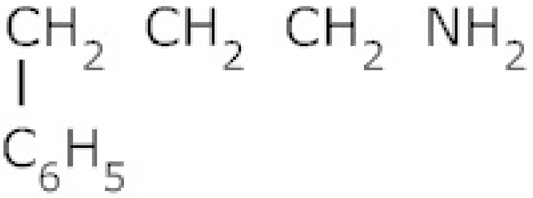
(vi) N- Phemylaniline

Ans.



(vii) 3-Phenyl propanamine

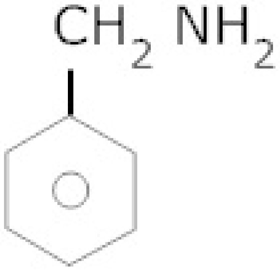
Ans.



$$\underset{\underset{\displaystyle C_6H_5}{|}}{CH_2}\ CH_2\ CH_2\ NH_2$$

(viii) Benzylamine

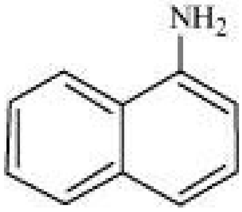
Ans.

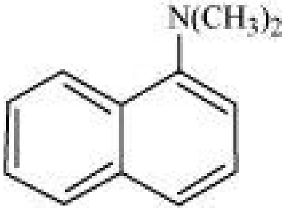


IUPAC name - 1- Phemylmethamine

13.Classify the following amines as primary, secondary or tertiary:

(i)



(ii) 

(iii) $\left(C_2H_5\right)_2 CHNH_2$

(iv) $\left(C_2H_5\right)_2 NH$

Ans. Primary: **(i)** and **(iii)**
Secondary: **(iv)**
Tertiary: **(ii)**

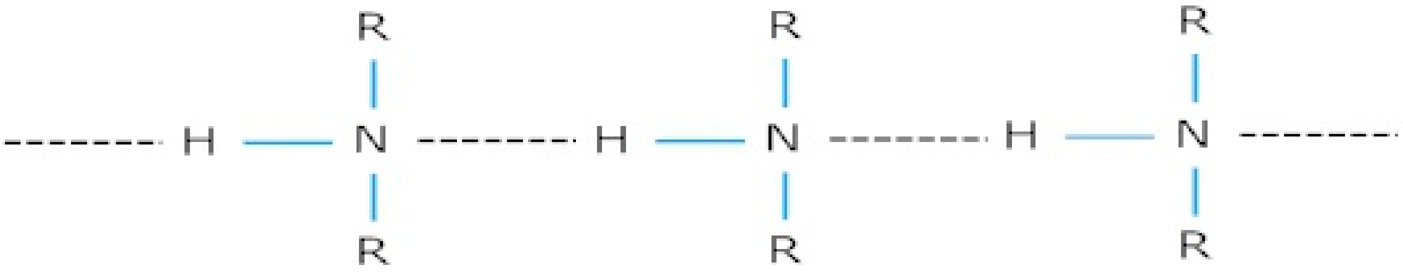
2 Mark Questions

1. It is difficult to prepare pure amines by ammonolysis of alkylhalides.

Ans. The process of ammonolysis yields a mixture of primary, secondary, tertiary amines and quaternary salts. The separation of this amines is a very complicated process and difficult. Therefore it is difficult to prepare pure amines by ammonolysis of alkyl halides.

2. Amines have higher boiling points than hydrocarbons of similar molecular mass.

Ans. Amines have higher boiling points than hydrocarbons of comparable molecular mass due to the presence of intermolecular hydrogen bond in amines which is absent in hydrocarbons. Therefore, amines exist as associated molecules and have higher boiling points.

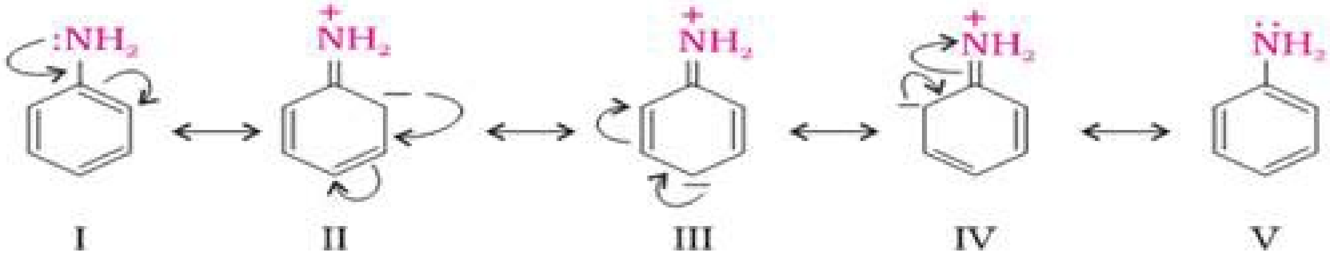


In alcohols and carboxylic acids, the electro- negativity of oxygen is more than nitrogen of amines. Therefore the hydrogen bonds of alcohols and acids are stronger than in amines and alcohols & carboxylic acids have higher boiling points.

3. Aniline is weaker base than cyclohexylamine.

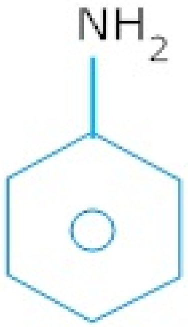
Ans. As a result of resonance in aniline; the lone pair on nitrogen delocalized over the benzene ring and is less available for protonation than in cyclohexyl amine which does not undergo resonance.

Resonating structure of aniline –

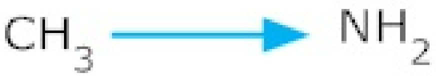


4. Methylamine is a stronger base than aniline.

Ans. Due to electron donating nature of CH_3, group, electron pair. Availability at N- atom in methyl amine is much higher than that in aniline; in aniline the benzene ring decreases the electron density at N- atom in aniline. Thus CH_3NH_2 is a stronger base than aniline.



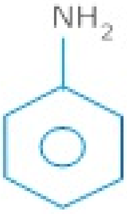
Aniline



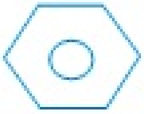
Methylamine

5. Before nitration, aniline is converted to acetanilide.

Ans. Aniline is very much susceptible to nitration and nitric acid is a strong oxidizing agent. Therefore to avoid oxidation of aniline, $-NH_2$ group is protected by its acetylation to acetanilide which undergo nitration smoothly without any oxidation.



Aniline



Benzene

6. It is easier to brominate aniline as compared to benzene.

Ans. In aniline, due to +R effect of $-NH_2$ group the benzene ring gets activated to a large extent and it becomes easier to brominates aniline as compared to benzene.

7. Reduction of nitro compound to aniline using iron scrap and HCl is preferred.

Ans. For reduction of nitro compounds to aniline, iron scrap and HCl is preferred because $FeCl_2$ formed gets hydrolysed to release HCl during the reaction & therefore only a small amount of HCl is required to initiate the reaction.

8. Aromatic amines cannot be prepared by Gabriel Phthalimide synthesis.

Ans. Aromatic amines cannot be prepared by Gabriel pythalimide synthesis as aryl halides do not undergo nucleophilic substitution with the anion formed by pythalimide.

9. During acylation of amines, pyridine is added.

Ans. Acylation of amines is carried out in presence of pyridine or another base stronger than amines as it removes HCl so formed and shifts the equilibrium in forward direction.

$$C_2H_5\,NH_2 + CH_3\,COCl \xrightleftharpoons{\text{Base}} C_2H_5\,NHCO\,CH_3 + HCl$$

10. Aniline does not undergo Friedel – Craft's reaction.

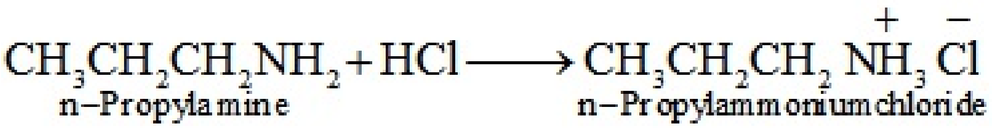
Ans. During Fridel Craft's reaction, aniline forms salt with aluminum chloride, the catalyst of reaction due to which nitrogen acquires a positive charge and acts as a strong deactivating group for further reaction.

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

(i) $CH_3CH_2CH_2NH_2 + HCl \rightarrow$

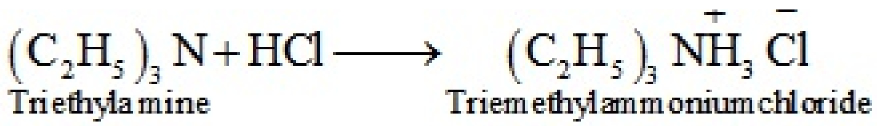
(ii) $(C_2H_5)_3\,N + HCl \rightarrow$

Ans. (i)



$$\underset{\text{n−Propylamine}}{CH_3CH_2CH_2NH_2} + HCl \longrightarrow \underset{\text{n−Propylammoniumchloride}}{CH_3CH_2CH_2\,\overset{+}{N}H_3\,\overset{-}{Cl}}$$

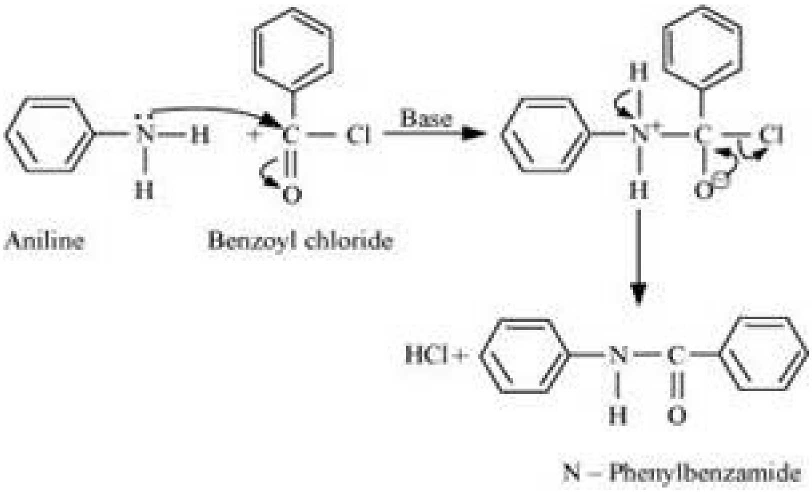
(ii)



$$\underset{\text{Triethylamine}}{(C_2H_5)_3\,N} + HCl \longrightarrow \underset{\text{Triemethylammoniumchloride}}{(C_2H_5)_3\,\overset{+}{N}H_3\,\overset{-}{Cl}}$$

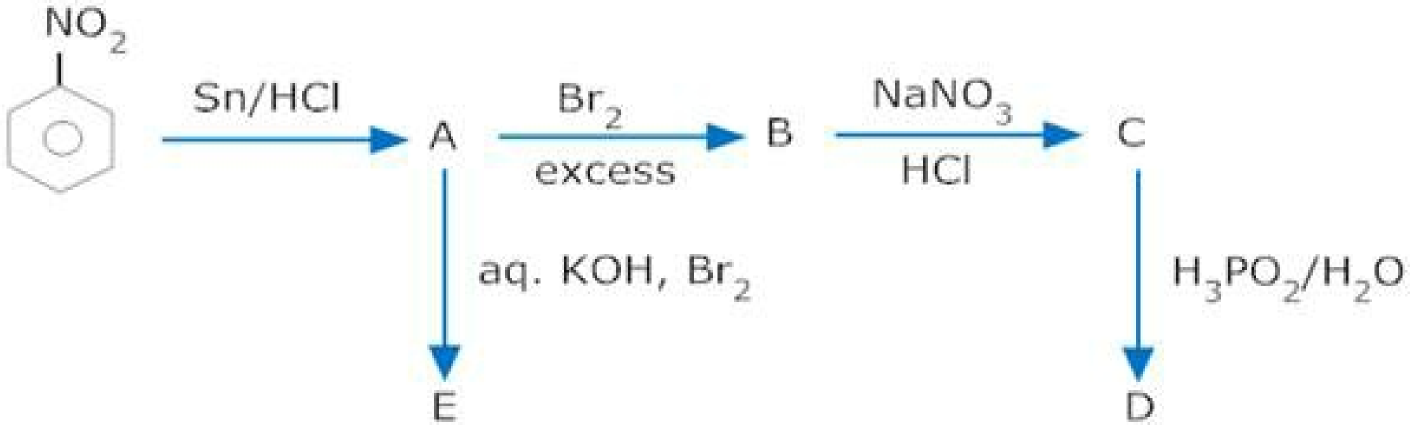
12. Write chemical reaction of aniline with benzoyl chloride and write the name of the product obtained.

Ans.

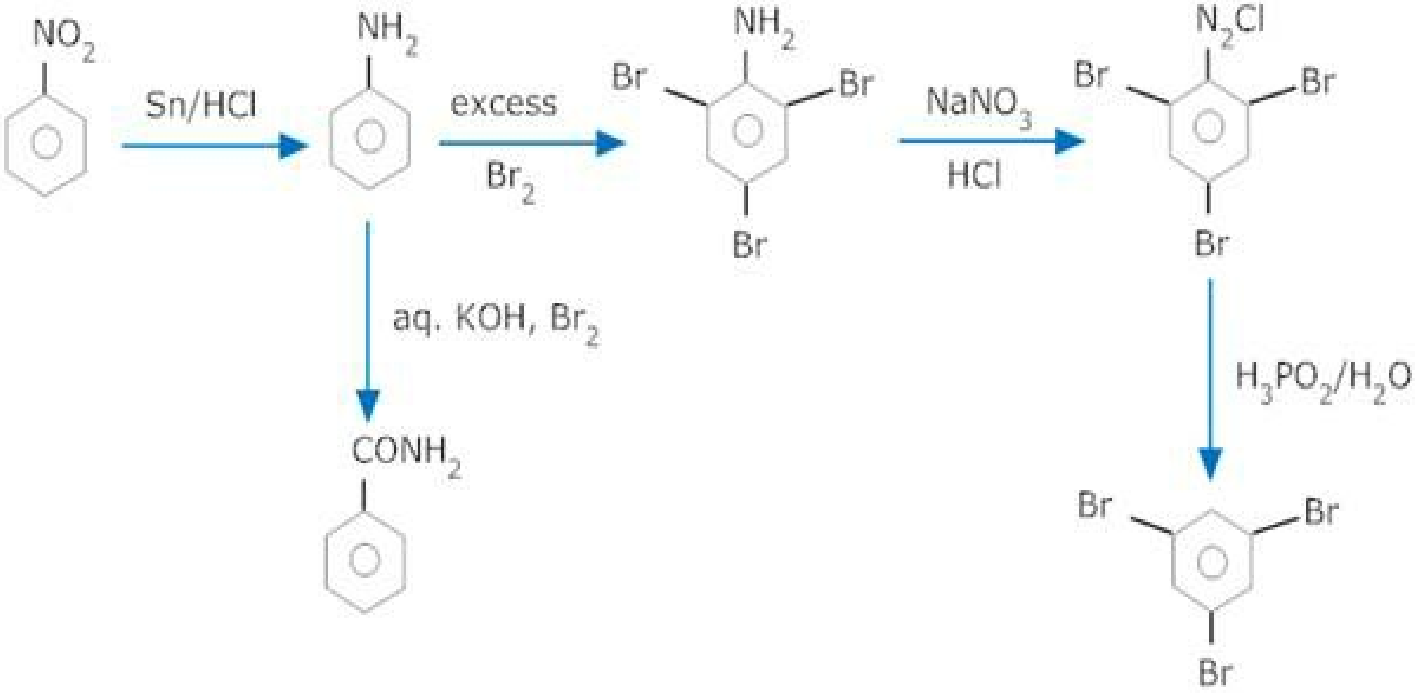


3 Mark Questions

1.



Ans.



2.A compound (X) having formula C_3H_7 NO reacts with Br_2 in the presence of NaOH to give

another compound (Y). Compound (Y) reacts with HNO_2 to form ethanol and N_2 gas . Identify (X) and (Y) . Write the reaction involved.

Ans.

$$X\ (C_3H_7NO) + Br_2 \xrightarrow{NaOH} Y \xrightarrow{HNO_2} CH_3\,CH_2\,OH + N_2$$

Since Y gives ethanol and N_2 gas with HNO_2 , therefore it is $CH_3CH_2NH_2$.

Ethan amine (Y) is formed on reacting (X) with Br_2 and NaOH;

Therefore X is $CH_3CH_2CO\ NH_2$.

Therefore

X= $CH_3CH_2CONH_2$

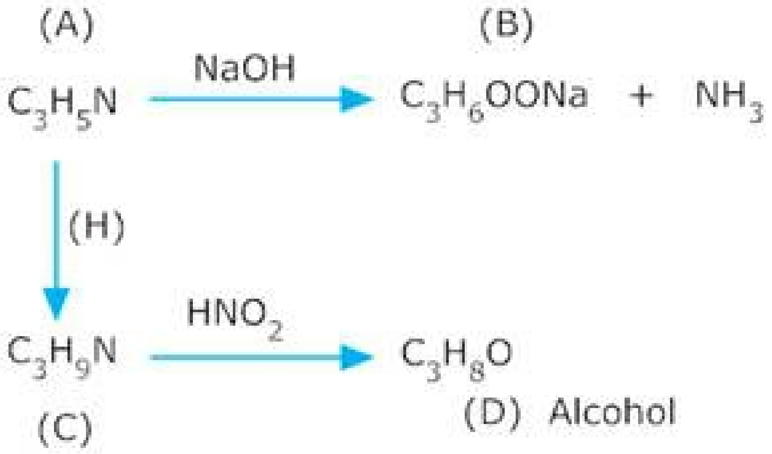
Y = $CH_3CH_2NH_2$

The reactions are –

$$CH_3CH_2CONH_2 + Br_2 \xrightarrow{NaOH} CH_3CH_2NH_2\ (Y) \xrightarrow{HNO_2} CH_3CH_2OH + N_2$$

3.An organic compound A (C_3H_5N) on boiling with alkali gives NH_3 and sodium salt of an acid B $(C_3H_6O_2)$. The compound A on reduction gives $C(C_3H_9N)$ which on treatment with nitrous acid gives an alcohol $D(C_3H_8O)$. Identify A to D

Ans.

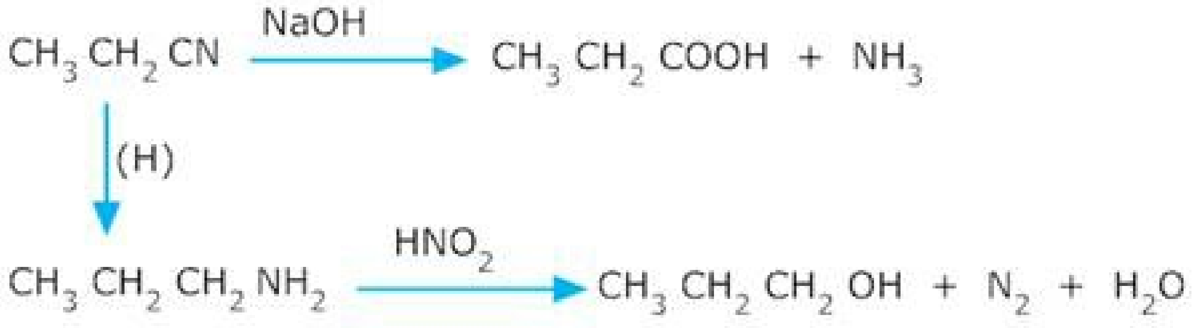


Since the compound (A) gives sodium salt and ammonia, (A) is cyanide. The compound (C) is a primary amine as it reacts with HNO_2 and forms an alcohol (D) Therefore

A= CH_3CH_2CN ,B= CH_3CH_2COOH,

C= $CH_3CH_2CH_2NH_2$,D= $CH_3CH_2CH_2OH$

Equations are-

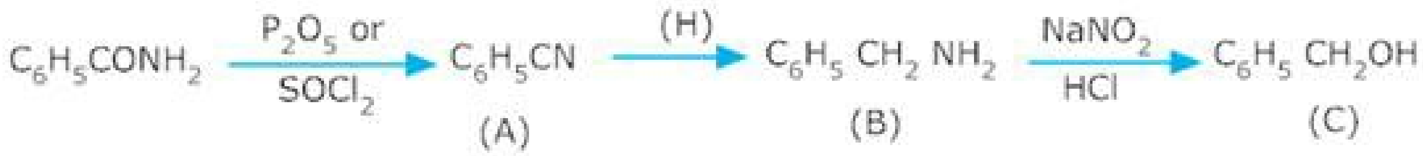


$$\begin{tikzcd}
CH_3CH_2CN \arrow[r, "NaOH"] \arrow[d, "(H)"] & CH_3CH_2COOH + NH_3 \\
CH_3CH_2CH_2NH_2 \arrow[r, "HNO_2"] & CH_3CH_2CH_2OH + N_2 + H_2O
\end{tikzcd}$$

4.

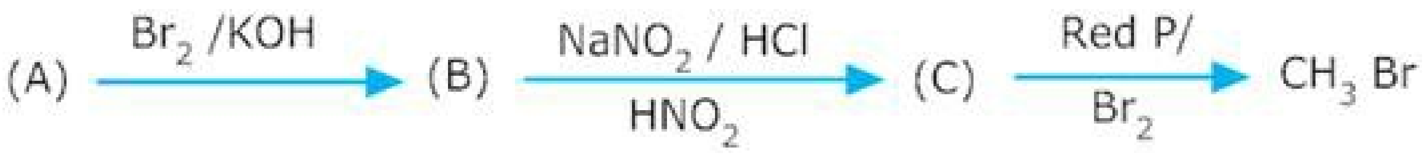
$$C_6H_5CONH_2 \xrightarrow[SOCl_2]{P_2O_5 \text{ or}} (A) \xrightarrow{\text{catalytic reduction}} (B) \xrightarrow[NaNO_2 / HCl]{HONO \text{ or}} (C)$$

Ans.



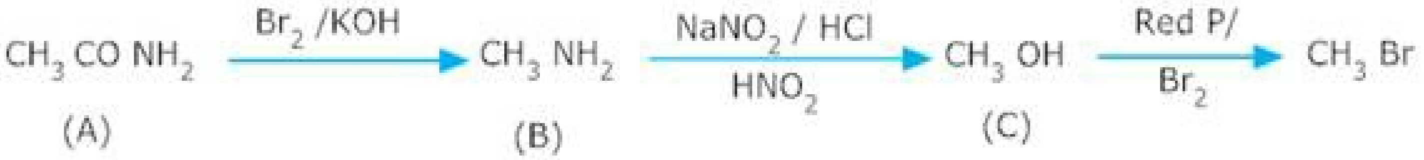
$$C_6H_5CONH_2 \xrightarrow[SOCl_2]{P_2O_5 \text{ or}} \underset{(A)}{C_6H_5CN} \xrightarrow{(H)} \underset{(B)}{C_6H_5CH_2NH_2} \xrightarrow[HCl]{NaNO_2} \underset{(C)}{C_6H_5CH_2OH}$$

5.



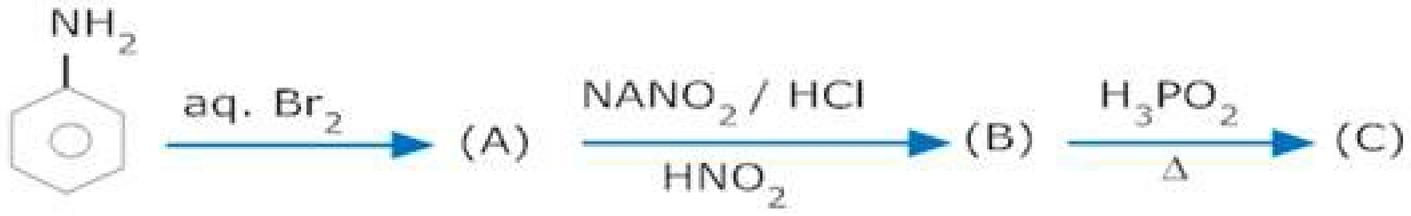
$$(A) \xrightarrow{Br_2 /KOH} (B) \xrightarrow[HNO_2]{NaNO_2 / HCl} (C) \xrightarrow[Br_2]{\text{Red } P/} CH_3Br$$

Ans.

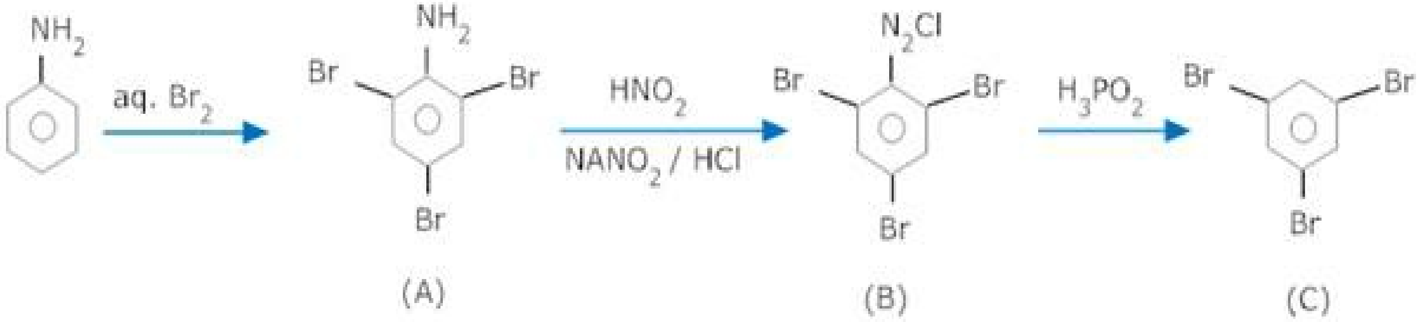


$$\underset{(A)}{CH_3\,CO\,NH_2} \xrightarrow{Br_2\,/KOH} \underset{(B)}{CH_3\,NH_2} \xrightarrow[HNO_2]{NaNO_2\,/\,HCl} \underset{(C)}{CH_3\,OH} \xrightarrow[Br_2]{Red\ P/} CH_3\,Br$$

6.



Ans.



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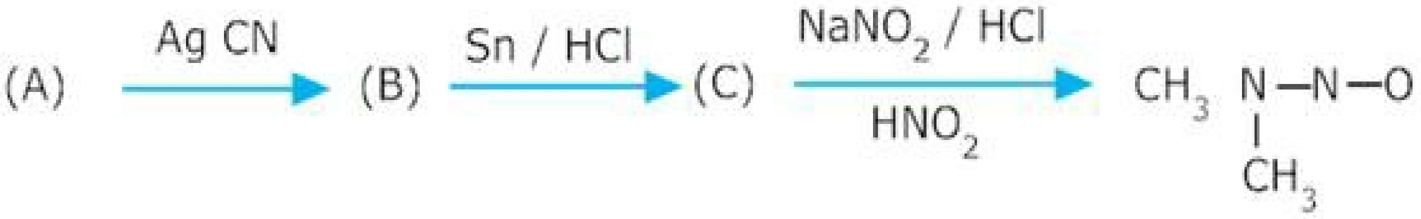


$$(A) \xrightarrow{Ag\ CN} (B) \xrightarrow{Sn\,/\,HCl} (C) \xrightarrow[HNO_2]{NaNO_2\,/\,HCl} CH_3\ \underset{\underset{CH_3}{|}}{N}-N-O$$

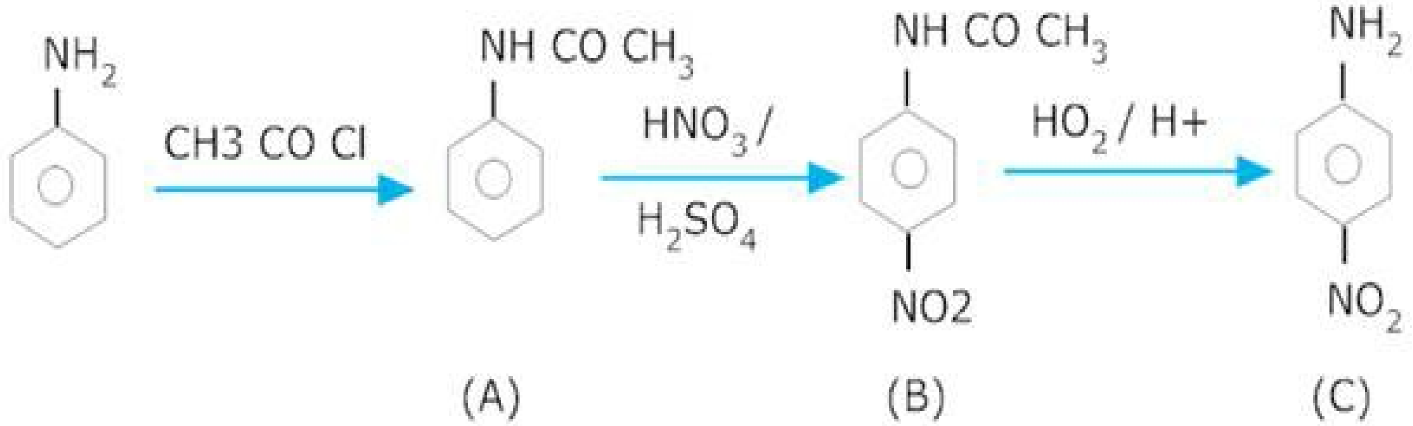
Ans.

$$\underset{(A)}{CH_3\,Br} \xrightarrow{Ag\ CN} \underset{(B)}{CH_3\,NC} \xrightarrow{Sn\,/\,HCl} \underset{(C)}{CH_3\,N\,H\,CH_3} \xrightarrow[HNO_2]{NaNO_2\,/\,HCl} CH_3-\underset{\underset{CH_3}{|}}{N}-N=O$$

8.

$$C_6H_5NH_2 \xrightarrow{CH3\ CO\ Cl} (A) \xrightarrow[H_2SO_4]{HNO_3/} (B) \xrightarrow{HO_2/H+} (C)$$

Ans.



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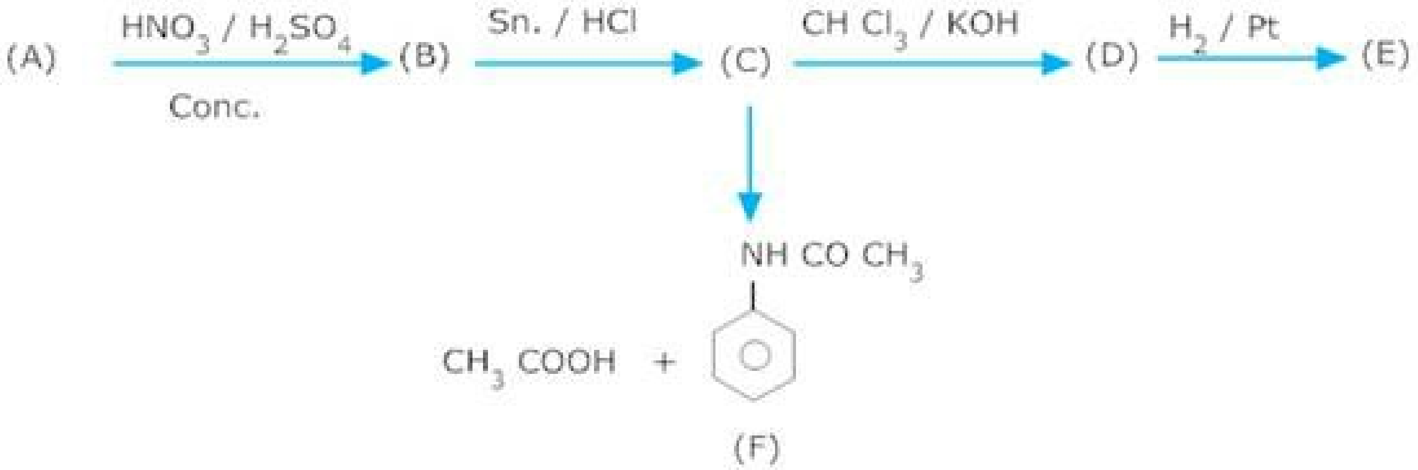
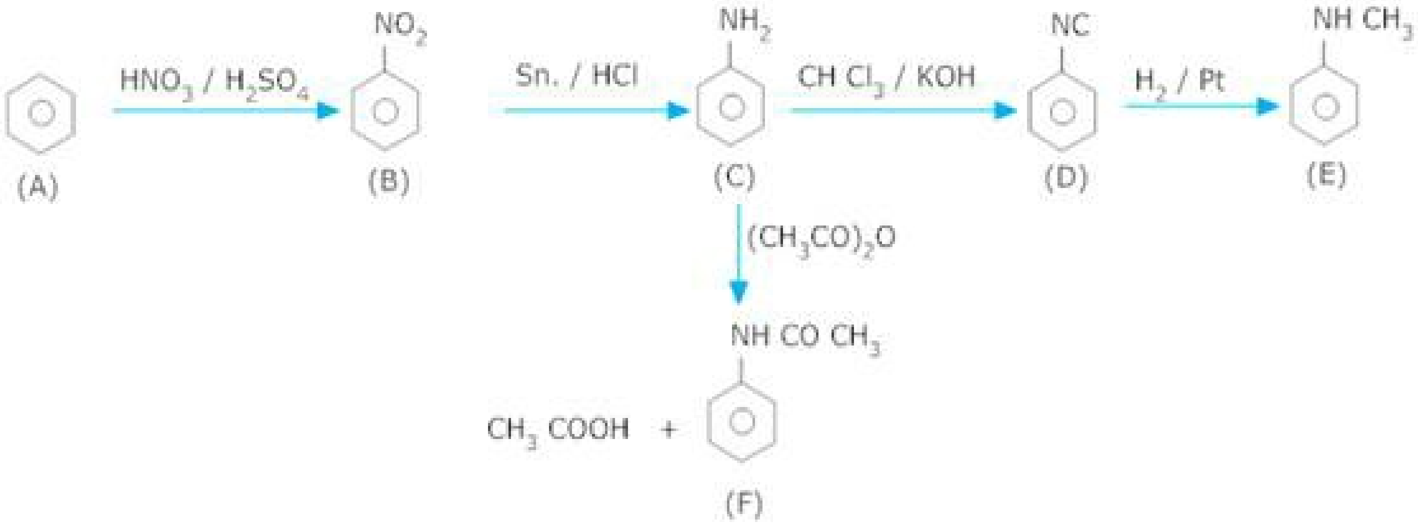
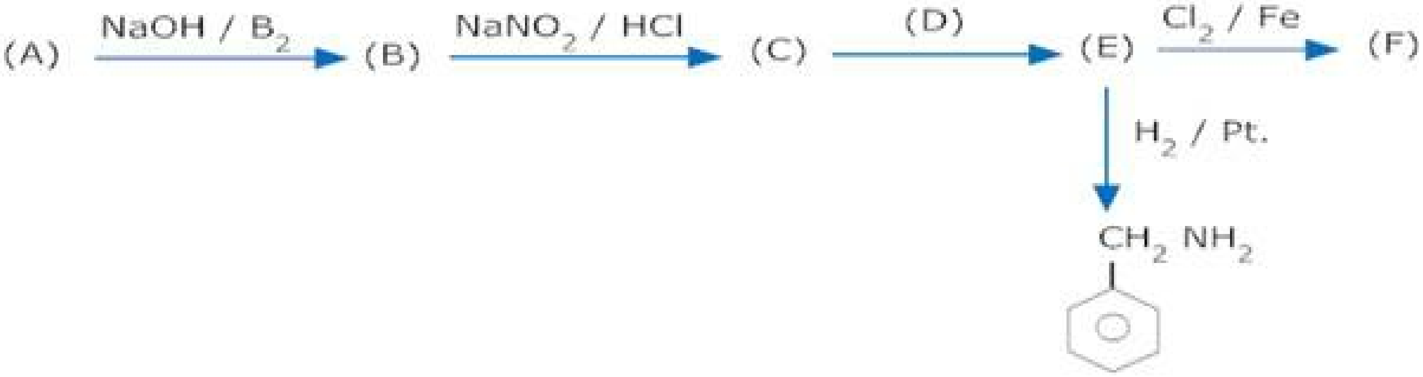


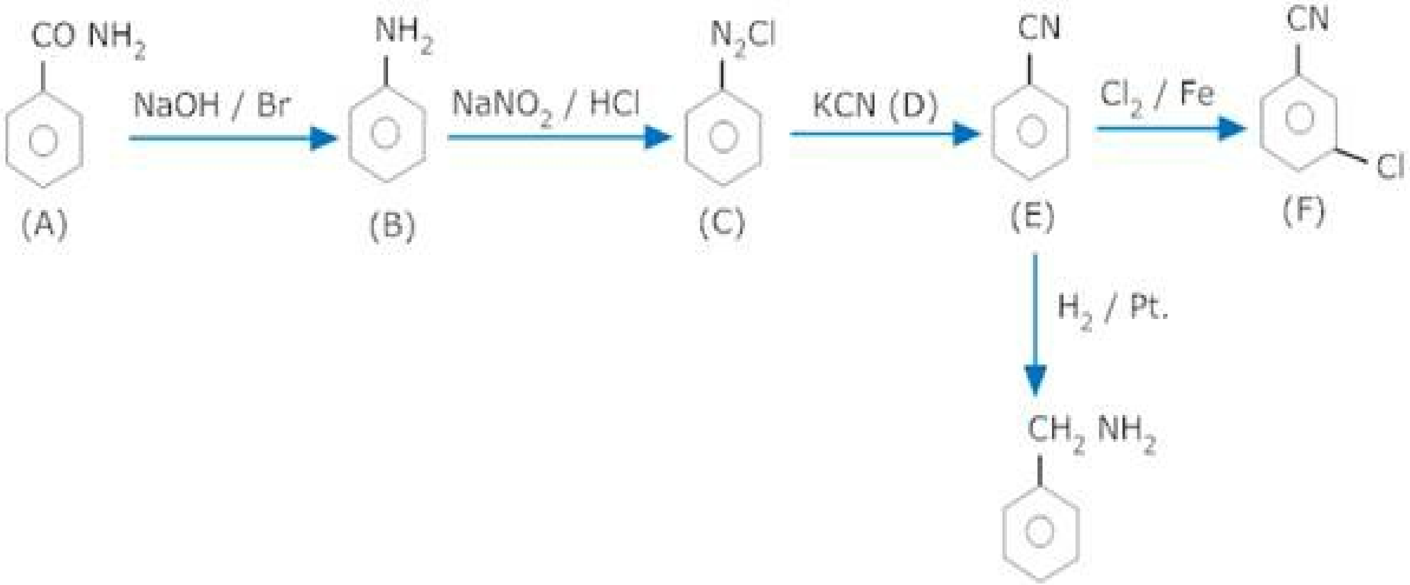
Ans.


HNO3 / H2SO4
NO2
Sn. / HCl
NH2
CH Cl3 / KOH
NC
H2 / Pt
NH CH3
(A)
(B)
(C)
(D)
(E)
(CH3CO)2O
NH CO CH3
CH3 COOH +
(F)

10.


(A)
NaOH / B2
(B)
NaNO2 / HCl
(C)
(D)
(E)
Cl2 / Fe
(F)
H2 / Pt.
CH2 NH2

Ans.


CO NH2
NaOH / Br
NH2
NaNO2 / HCl
N2Cl
KCN (D)
CN
Cl2 / Fe
CN
Cl
(A)
(B)
(C)
(E)
(F)
H2 / Pt.
CH2 NH2

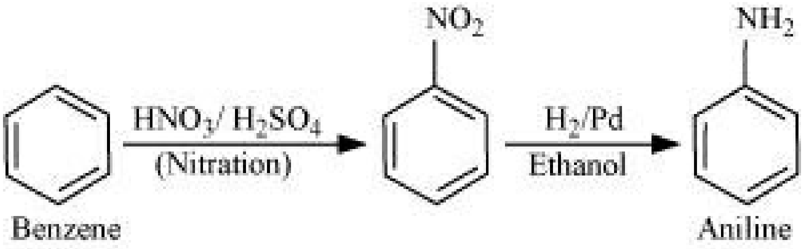
11.How will you convert?

(i) Benzene into aniline

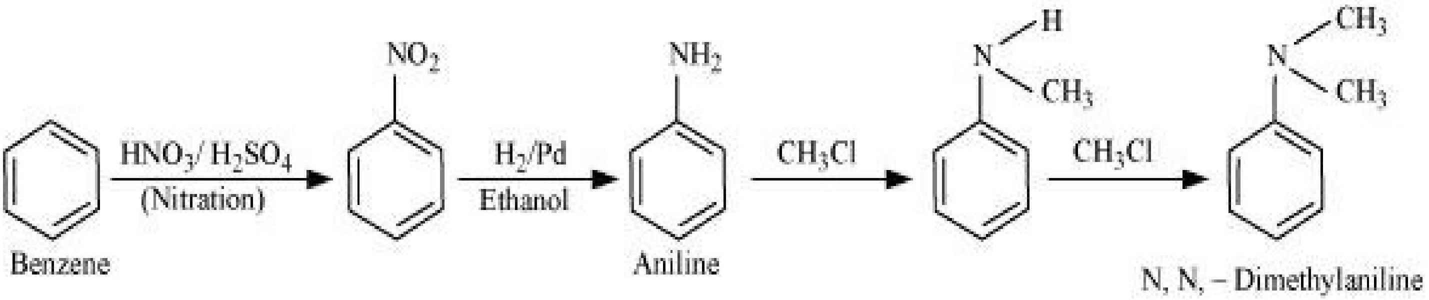
(ii) Benzene into N, N-dimethylaniline

(iii) $Cl\text{-}(CH_2)_4\text{-}Cl$ **into hexan-1, 6-diamine?**

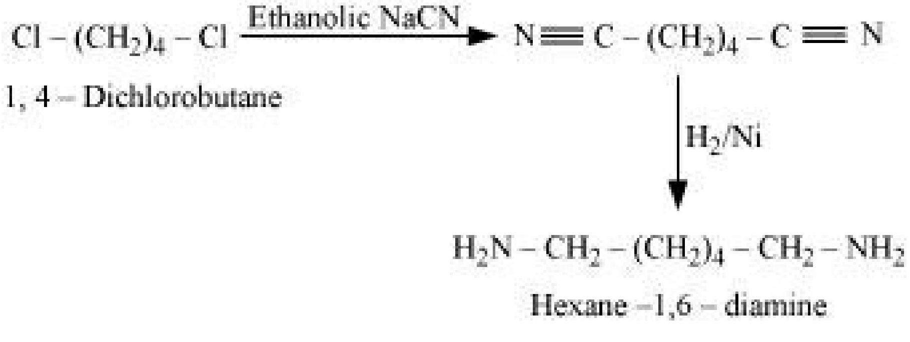
Ans.(i)



(ii)

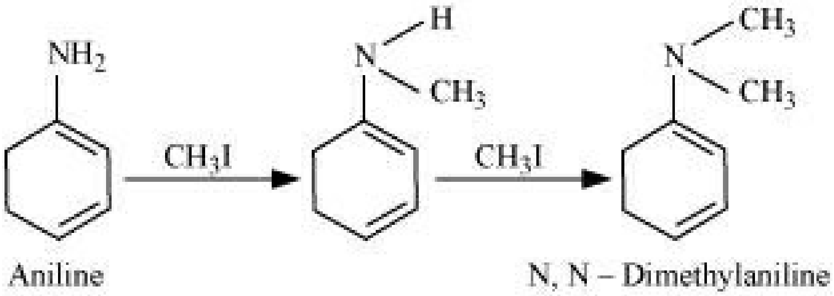


(iii)

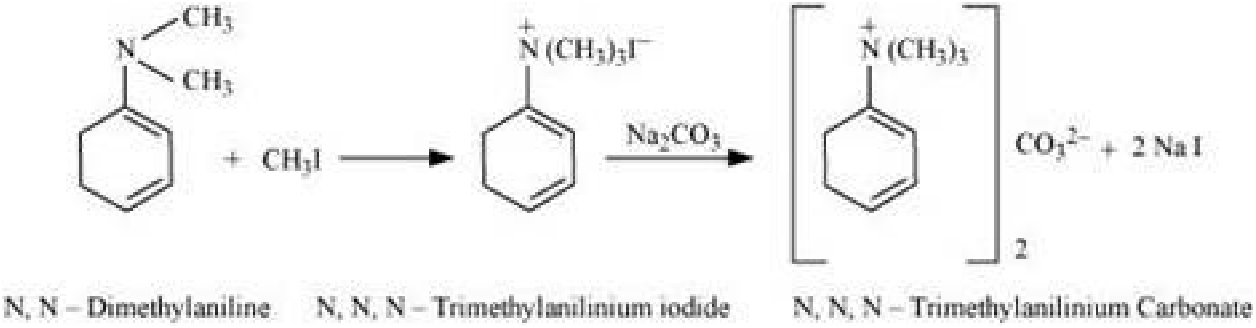


12. Write reactions of the final alkylation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.

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



With excess methyl iodide, in the presence of Na_2CO_3 solution, N, N-dimethylaniline produces N, N, N-trimethylanilinium carbonate.

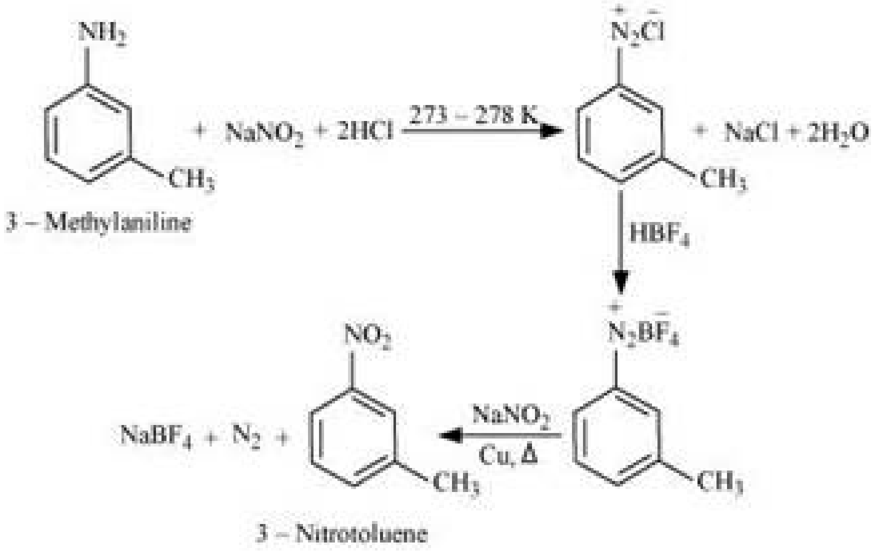


13.Convert

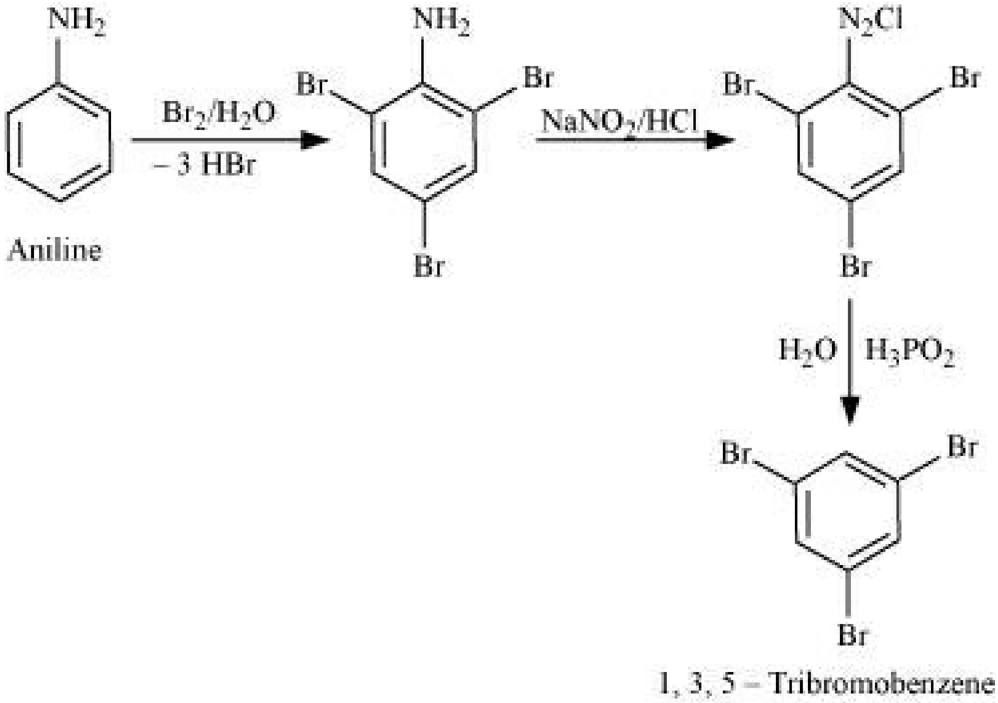
(i) 3-Methylaniline into 3-nitrotoluene.

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

Ans.(i)



(ii)


NH2
Aniline
Br2/H2O
– 3 HBr
NH2
Br
Br
Br
NaNO2/HCl
N2Cl
Br
Br
Br
H2O
H3PO2
Br
Br
Br
1, 3, 5 – Tribromobenzene

5 Mark Questions

1. (i) Write structures of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$

(ii) Write IUPAC names of all the isomers.

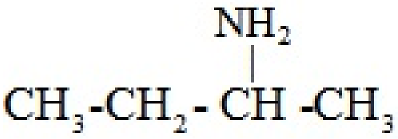
(iii) What type of isomerism is exhibited by different pairs of amines?

Ans. (i), (ii) The structures and their IUPAC names of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$ are given below:

(a) $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$

Butanamine $(1°)$

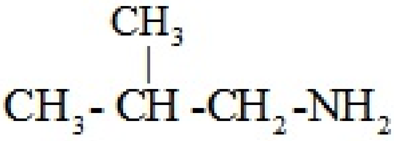
(b)



$$CH_3\text{-}CH_2\text{-}\overset{NH_2}{\overset{|}{CH}}\text{-}CH_3$$

Butan-2-amine $(1°)$

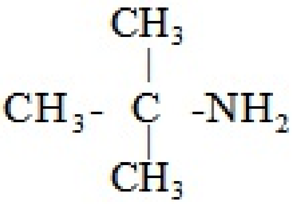
(c)



$$CH_3\text{-}\overset{CH_3}{\overset{|}{CH}}\text{-}CH_2\text{-}NH_2$$

2-Methylpropanamine $(1°)$

(d)



$$CH_3\text{-}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}\text{-}NH_2$$

2-Methylpropan-2-amine $(1°)$

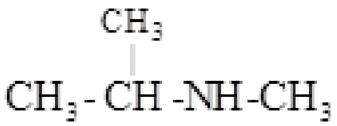
(e) $CH_3\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_3$

N-Methylpropanamine $(2°)$

(f) $CH_3-CH_2-NH-CH_2-CH_3$

N-Ethylethanamine (2°)

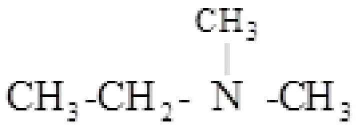
(g)



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

N-Methylpropan-2-amine (2°)

(h)



$CH_3-CH_2-\overset{\overset{CH_3}{|}}{N}-CH_3$

N, N-Dimethylethanamine (3°)

(iii) The pairs (a) and (b) and (e) and (g) exhibit position isomerism.

The pairs (a) and (c); (a) and (d); (b) and (c); (b) and (d) exhibit chain isomerism.

The pairs (e) and (f) and (f) and (g) exhibit metamerism.

All primary amines exhibit functional isomerism with secondary and tertiary amines and vice-versa.

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

Ans. (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:

$$NH_3 < C_2H_5NH_2 < (C_2H_5)_5\ NH$$

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

$$C_6H_5NH_2 < NH_3 < C_2H_5NH_2 < (C_2H_5)_2\ NH$$

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:

$$C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2\ NH$$

(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:

$$C_2H_5NH_2 < (C_2H_5)_2\ N < (C_2H_5)_2\ NH$$

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:

$$C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3\ N < (C_2H_5)_2\ NH$$

(iii) Considering the inductive effect and the steric hindrance of alkyl groups,

$CH_3NH_2, (CH_3)_2\ NH$, and .$(CH_3)_3\ N$ .can be arranged in the increasing order of their basic strengths as:

$$(CH_3)_3\ N < CH_3NH_2 < (CH_3)_2\ NH$$

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.

$$C_6H_5 < C_6H_5CH_2NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$$

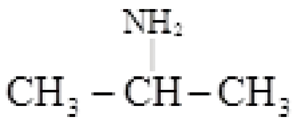
3. Write structures of different isomers corresponding to the molecular formula, C_3H_9N. Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.

Ans. 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 $(1°)$

(b)



$$CH_3-\overset{NH_2}{\overset{|}{CH}}-CH_3$$

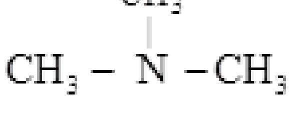
Propan-2-amine $(1°)$

(c)

$CH_3-NH-C_2H_5$

N–Methylethanamine(2°)

(d)

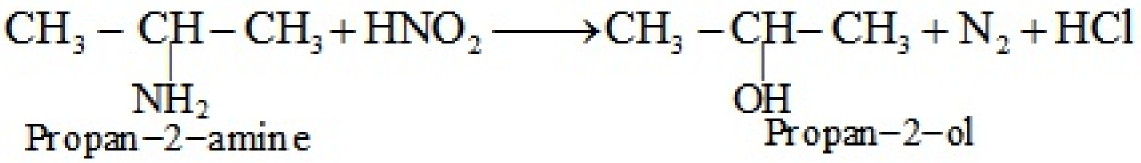


$$CH_3-\overset{CH_3}{\overset{|}{N}}-CH_3$$

N, N-Dimethylmethanamine (3°)

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

$$\underset{\text{Propan-1-amine}}{CH_3CH_2CH_2NH_2} + HNO_2 \longrightarrow \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} + N_2 + HCL$$



$$\underset{\text{Propan-2-amine}}{CH_3-\underset{NH_2}{\underset{|}{CH}}-CH_3} + HNO_2 \longrightarrow \underset{\text{Propan-2-ol}}{CH_3-\underset{OH}{\underset{|}{CH}}-CH_3} + N_2 + HCl$$

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

(i) $(CH_3)_2CHNH_2$ **(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)** $m-BrC_6H_4NH_2$

Ans. (i) 1-Methylethanamine (1° amine)

(ii) Propan-1-amine (1° amine)

(iii) N-Methyl-2-methylethanamine (2° amine)

(iv) 2-Methylpropan-2-amine (1° amine)

(v) N-Methylbenzamine or N-methylaniline (2° amine)

(vi) N-Ethyl-N-methylethanamine (3° amine)

(vii) 3-Bromobenzenamine or 3-bromoaniline (1° amine)

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

(i) Methylamine and dimethylamine

(ii) Secondary and tertiary amines

(iii) Ethylamine and aniline

(iv) Aniline and benzylamine

(v) Aniline and N-methylaniline.

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

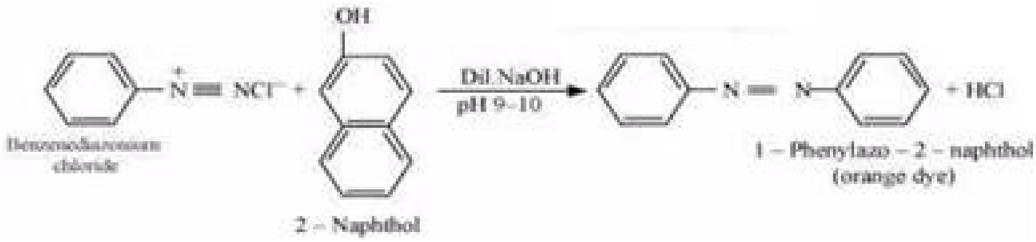
Carbylamine test: Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form foul-smelling isocyanides or carbylamines. Methylamine (being an aliphatic primary amine) gives a positive carbylamine test, but dimethylamine does not.

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

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

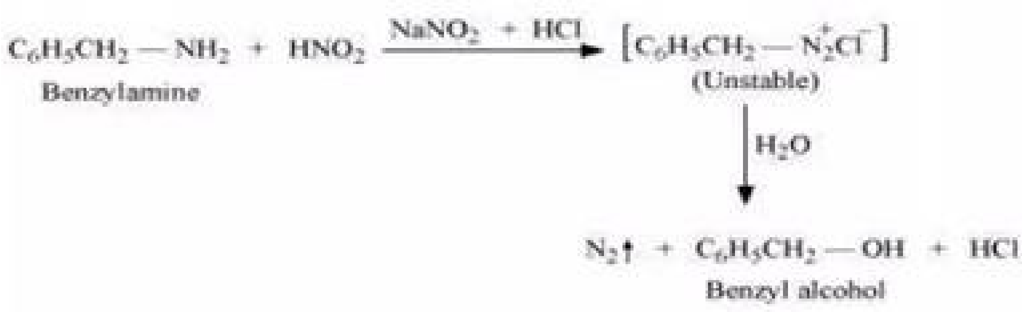
(iii) Ethylamine and aniline can be distinguished using the azo-dye test. A dye is obtained when aromatic amines react with $HNO_2(NaNO_2 + \text{dil. } HCl)$ at $0-5\,°C$, followed by a reaction with the alkaline solution of 2-naphthol. The dye is usually yellow, red, or orange in colour. Aliphatic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

effervescence due (to the evolution of N_2 gas) under similar conditions.



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

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



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

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

(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.

6. Account for the following:

(i) p*Kb* 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.

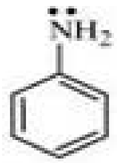
(iv) Although amino group is *o*, *p*- directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline.

(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.

Ans. (i) p*Kb*of aniline is more than that of methylamine:

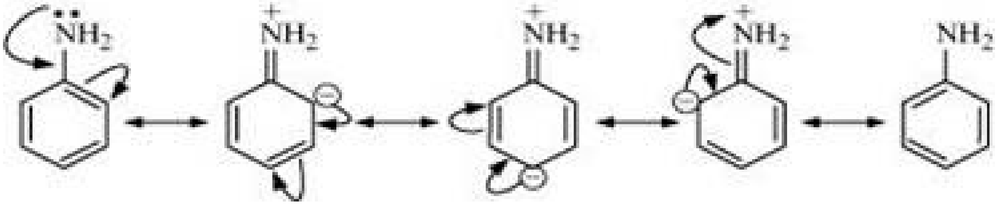


Aniline

$CH_3 - \ddot{N}H_2$

Methylamine

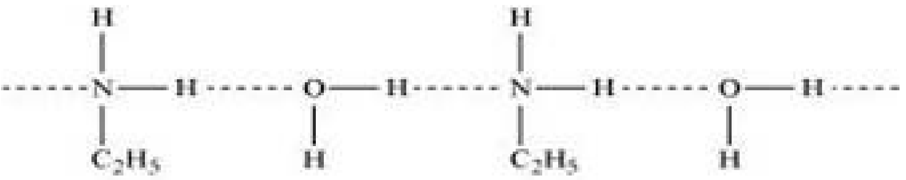
Aniline undergoes resonance and as a result, the electrons on the N-atom are delocalized over the benzene ring. Therefore, the electrons on the N-atom are less available to donate.



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, *pKb* 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 - C6H5 group. Hence, aniline is insoluble in water.

Aniline

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

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

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

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

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

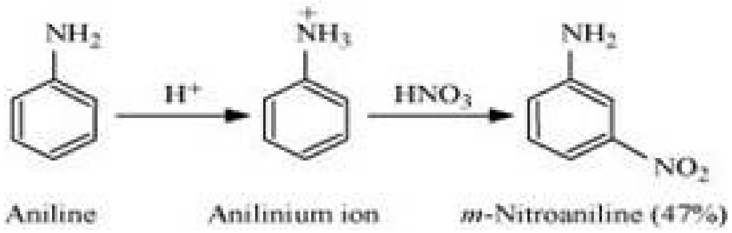
$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$$

Then, OH - ion reacts with Fe3+ 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:

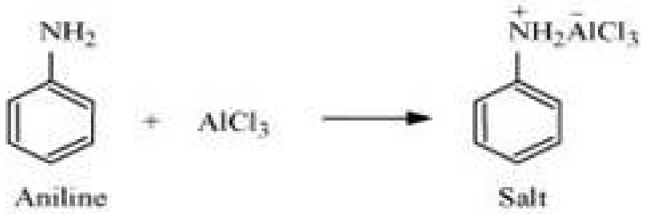
Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing).



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

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

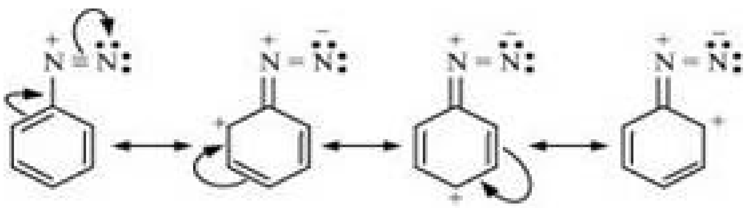
A Friedel-Crafts reaction is carried out in the presence of $AlCl_3$. But $AlCl_3$ is acidic in nature, while aniline is a strong base. Thus, aniline reacts with $AlCl_3$ to form a salt (as shown in the following equation).



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 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.

7. **Arrange the following:**

(i) In decreasing order of the p*Kb*values:

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

(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:

$C_2H_5NH_2$, **(C2H5)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:

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

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

Also, both $C_6H_5NHCH_3$ and $C_6H_5NH_2$ are less basic than $\left(C_2H_5\right)_2NH$ 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:

$$C_6H_5NH_2 < C_6H_5NHCH_3 < C_2H_5NH_2 < \left(C_2H_5\right)_2NH$$

We know that the higher the basic strength, the lower is the p*Kb* values.

$$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > \left(C_2H_5\right)_2NH$$

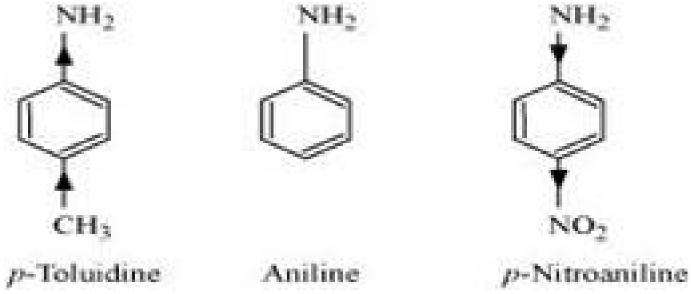
(ii) $C_6H_5N\left(CH_3\right)_2$ is more basic than $C_6H_5NH_2$ due to the presence of the +I effect of two -CH3 groups in $C_6H_5N\left(CH_3\right)_2$. Further, CH_3NH_2 contains one - CH_3 group while $\left(C_2H_5\right)_2NH$ contains two - C_2H_5 groups. Thus, $\left(C_2H_5\right)_2NH$ is more basic than $C_2H_5NH_2$.

Now, $C_6H_5N\left(CH_3\right)_2$ is less basic than CH3NH2 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:

$$C_6H_5NH_2 < C_6H_5N\left(CH_3\right)_2 < CH_3NH_2 < \left(C_2H_5\right)_2NH$$

(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 $C_6H_5NH_2NH_2$. Thus, in $C_6H_5NHCH_3$, the -R effect of -C_6H_5 group decreases the electron density over the N-atom. Therefore, $C_6H_5NHCH_3$ is more basic than $C_6H_5NHCH_3$.

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

$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5NH_2NH_2$.

(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:

$$(C_2H_5)_3N > (C_2H_5)_3NH > C_2H_5NH_2 > NH_3$$

(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:

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

8. How will you convert:

(i) Ethanoic acid into methanamine

(ii) Hexanenitrile into 1-aminopentane

(iii) Methanol to ethanoic acid

(iv) Ethanamine into methanamine

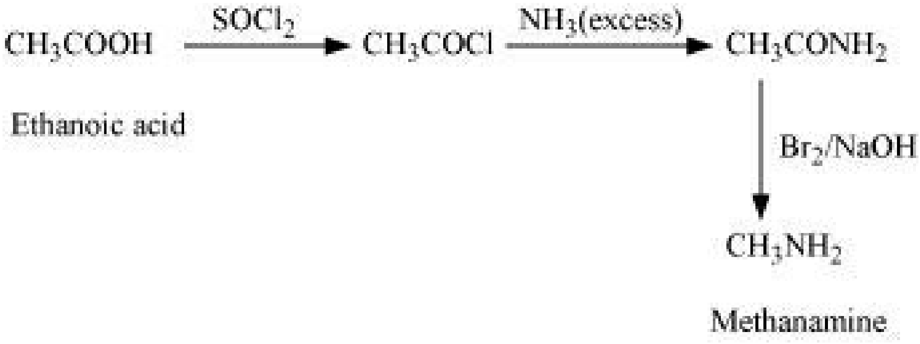
(v) Ethanoic acid into propanoic acid

(vi) Methanamine into ethanamine

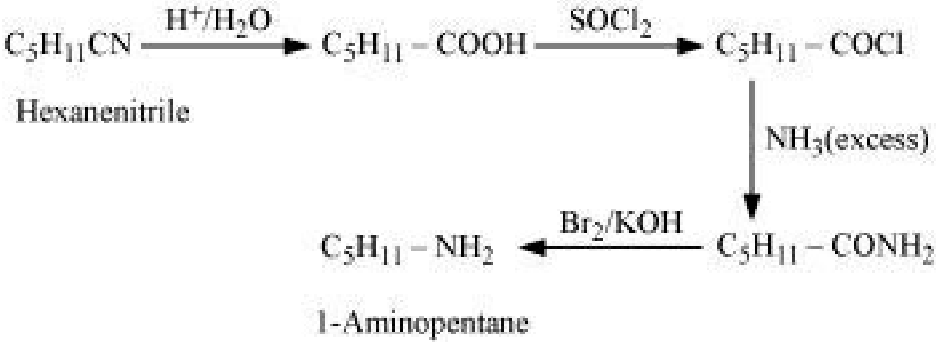
(vii) Nitromethane into dimethylamine

(viii) Propanoic acid into ethanoic acid

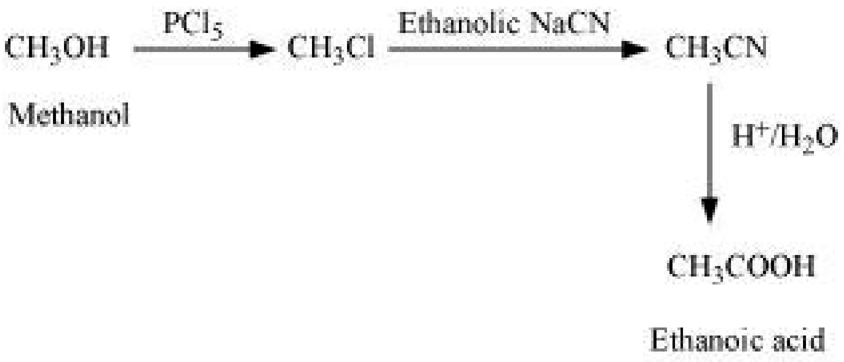
Ans. (i)



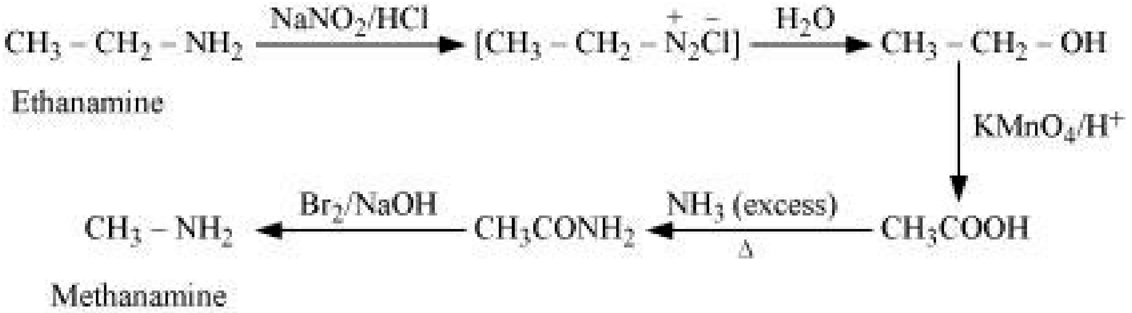
(ii)



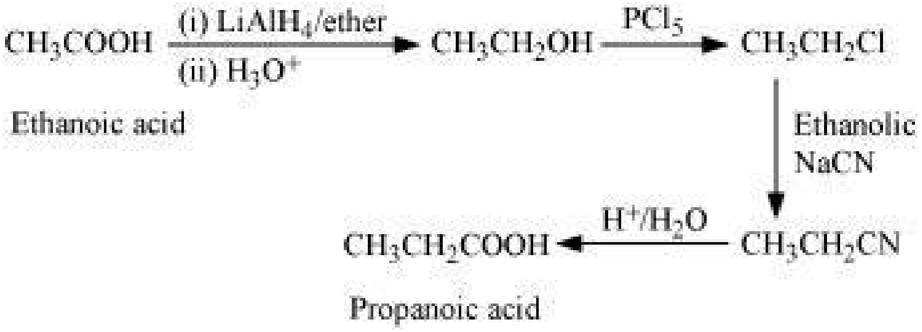
(iii)


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

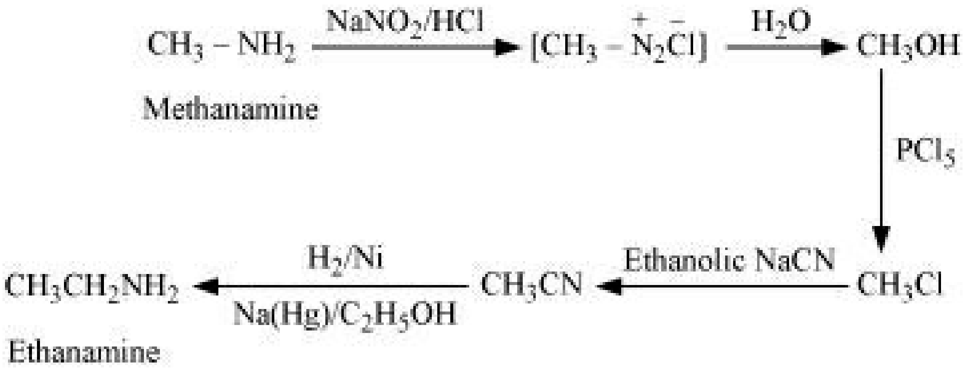
(iv)


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

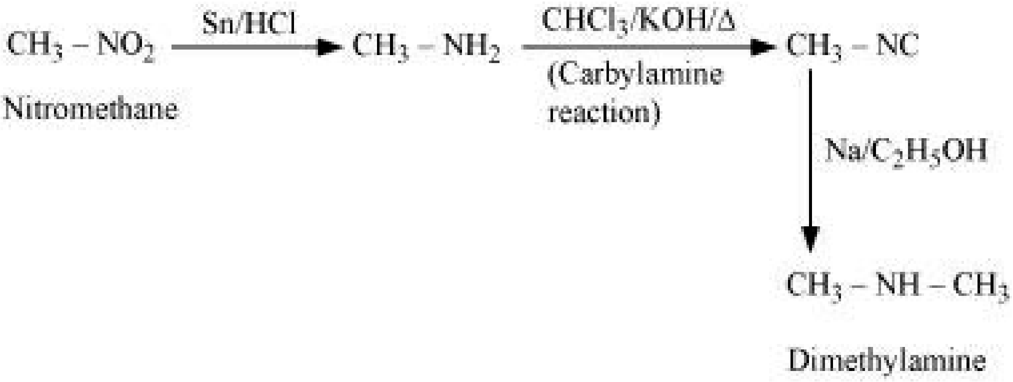
(v)


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

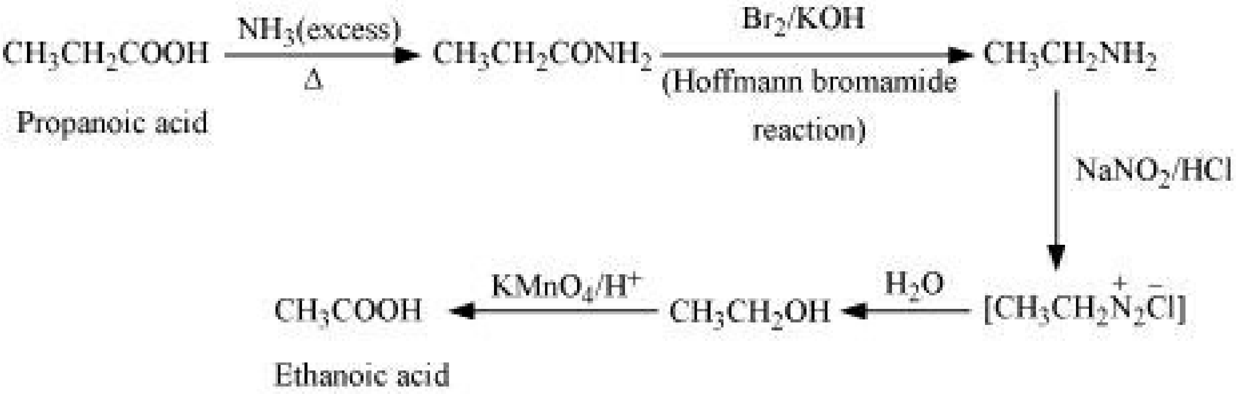
(vi)


CH_3-NH_2
Methanamine
$NaNO_2/HCl$
$[CH_3-\overset{+}{N_2}\overset{-}{Cl}]$
H_2O
CH_3OH
PCl_5
CH_3Cl
Ethanolic NaCN
CH_3CN
H_2/Ni
$Na(Hg)/C_2H_5OH$
$CH_3CH_2NH_2$
Ethanamine

(vii)



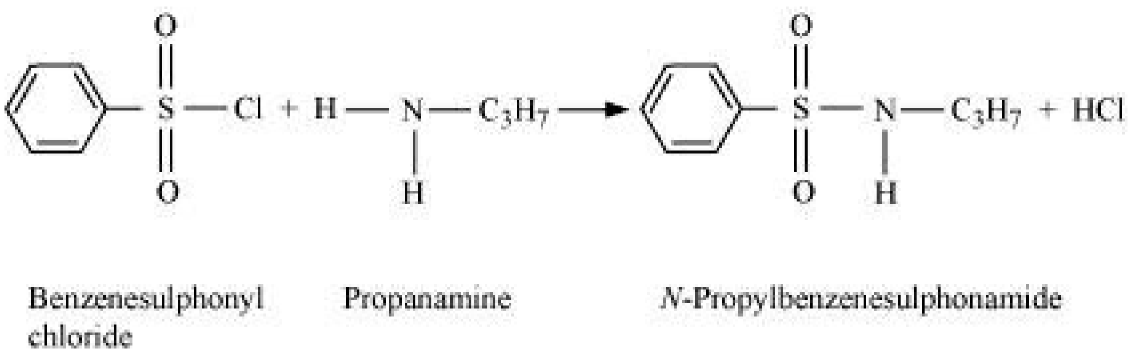
(viii)



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

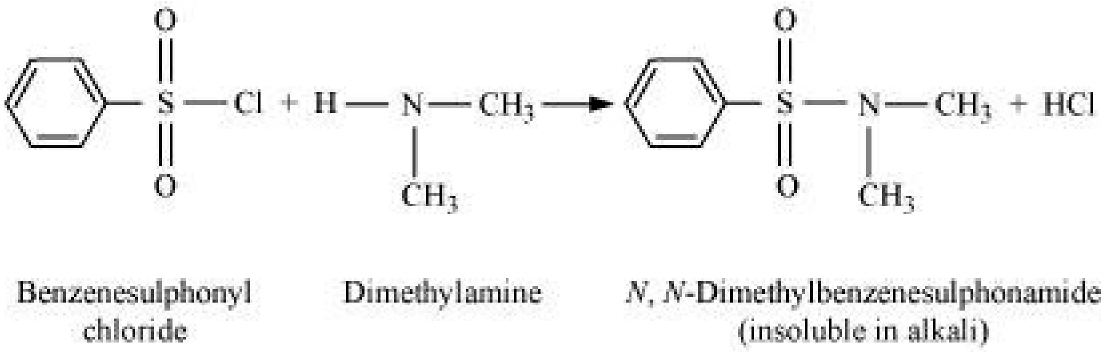
Ans. Primary, secondary and tertiary amines can be identified and distinguished by Hinsberg's test.In this test, the amines are allowed to react with Hinsberg's reagent, benzenesulphonyl chloride $\left(C_6H_5SO_2Cl\right)$. The three types of amines react differently with Hinsberg's reagent. Therefore,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

10. 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.

Ans. (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.

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

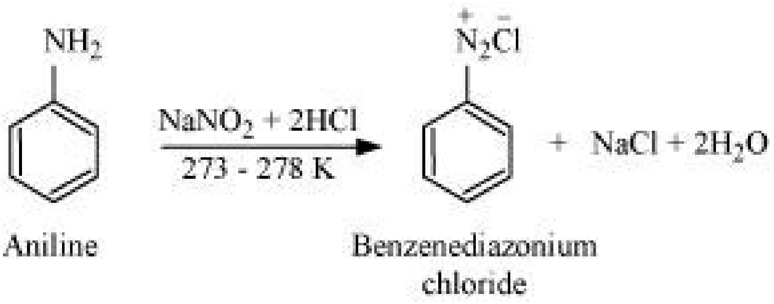
For example,

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

(ii)Diazotisation

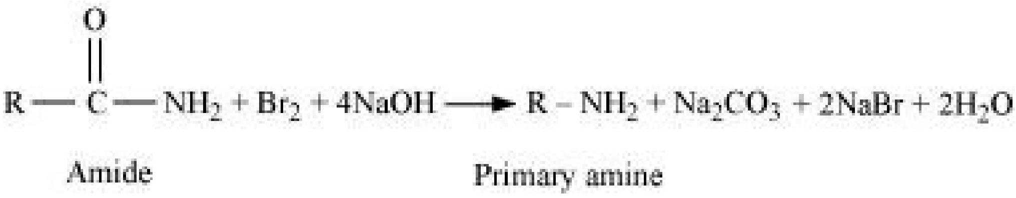
Aromatic primary amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) at low temperatures (273-278 K) to form diazonium salts. This conversion of aromatic primary amines into diazonium salts is known as diazotization.

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.



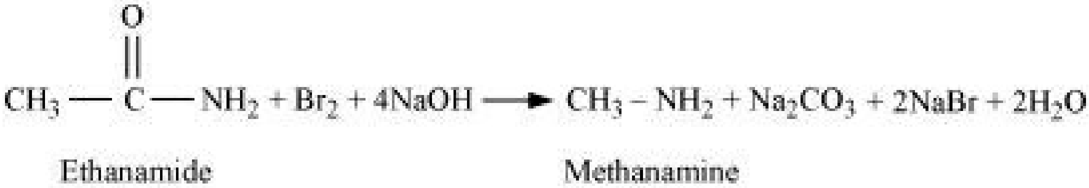
(iii)Hoffmann bromamide reaction

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.

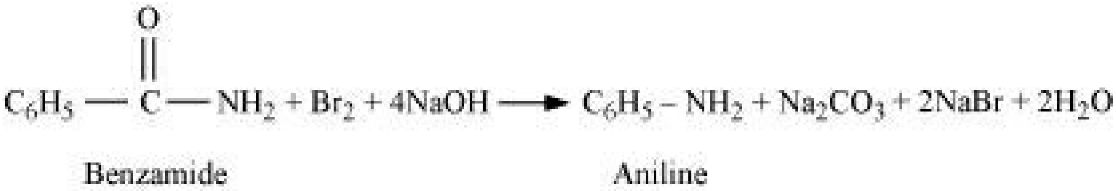


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

For example,



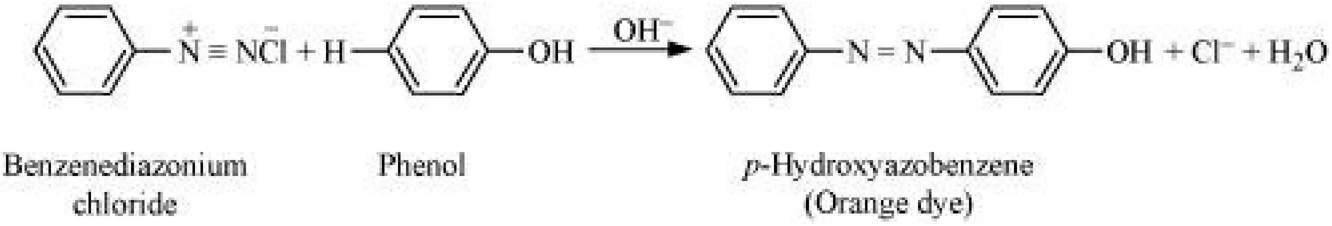
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow CH_3-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

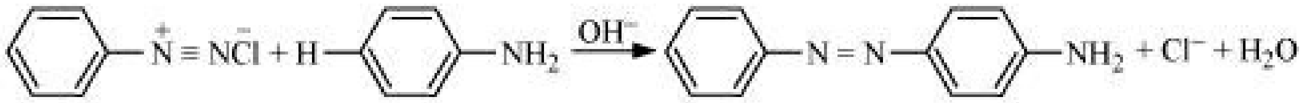


$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow C_6H_5-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

(iv)Coupling reaction

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



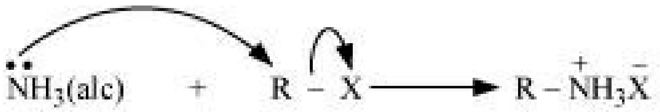


Benzenediazonium chloride Aniline *p*-Aminoazobenzene (yellow dye)

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.

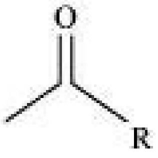
$$R-\overset{+}{N}H_3\overset{-}{X} + NaOH \longrightarrow \underset{\text{Amine}}{R-NH_2} + H_2O + NaX$$

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.

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

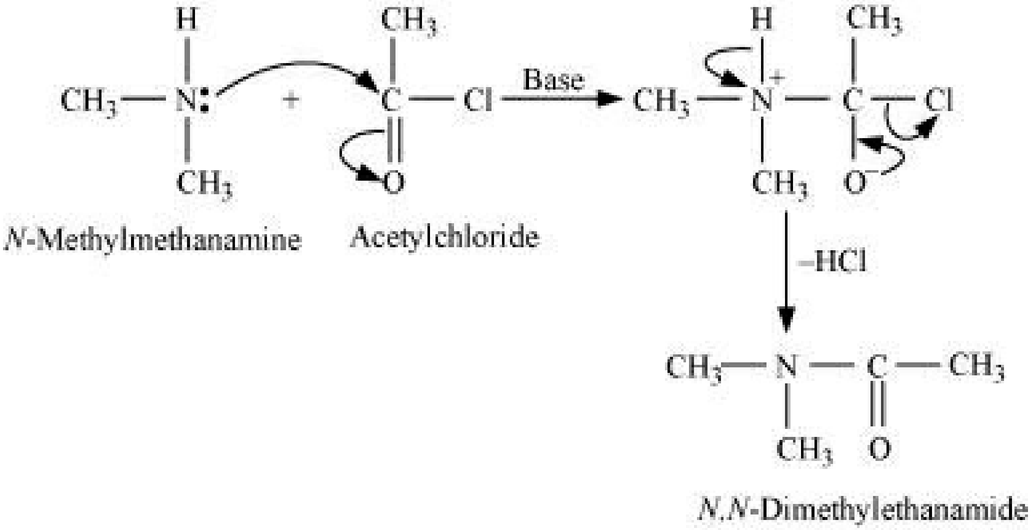
(vi)Acetylation

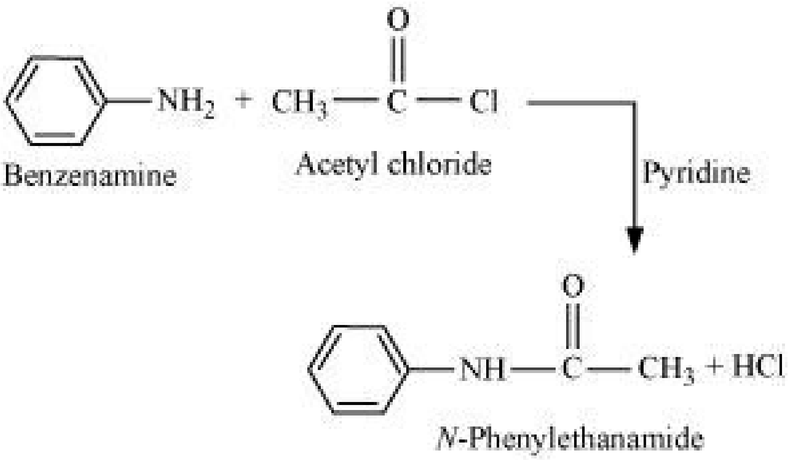
Acetylation (or ethanoylation) is the process of introducing an acetyl group into a molecule.



Acetyl group

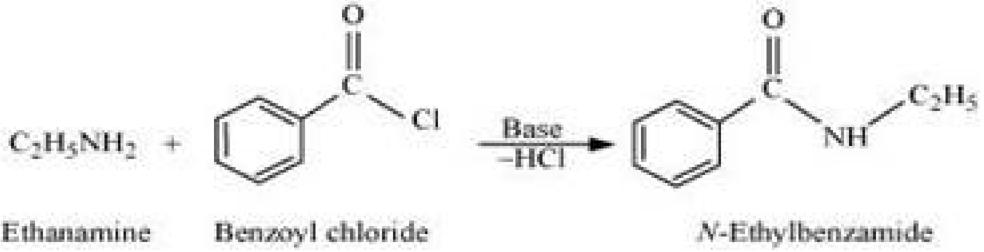
Aliphatic and aromatic primary and secondary amines undergo acetylation reaction by nucleophilic substitution when treated with acid chlorides, anhydrides or esters. This reaction involves the replacement of the hydrogen atom of - NH_2 or > NH group by the acetyl group, which in turn leads to the production 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.





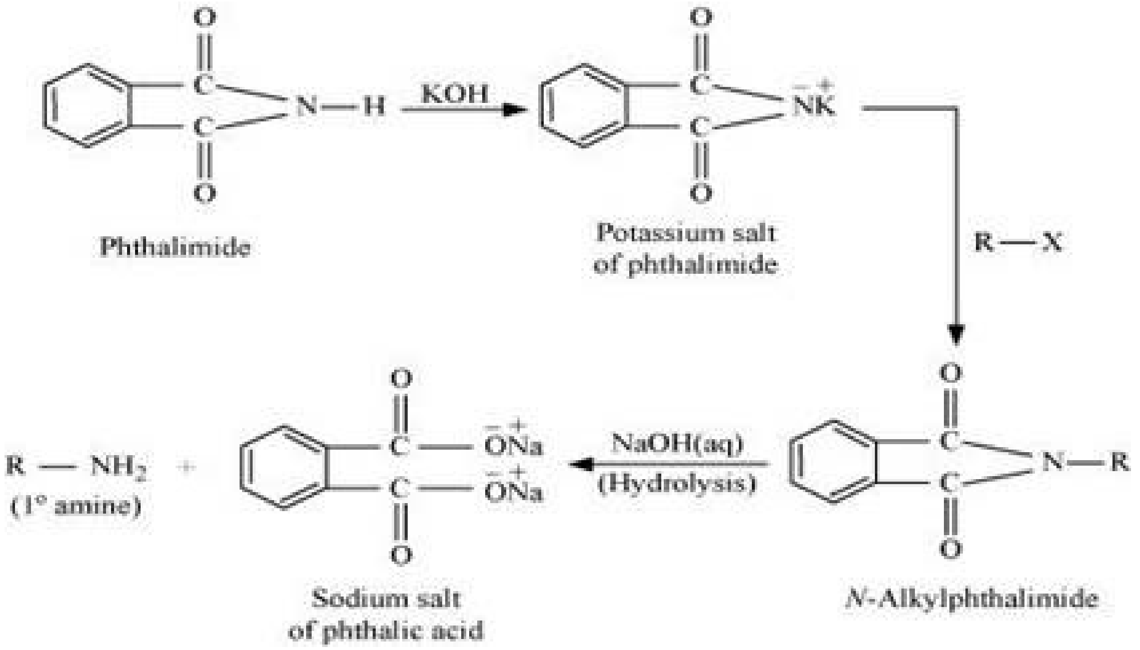
When amines react with benzoyl chloride, the reaction is also known as benzoylation.

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.



11. 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

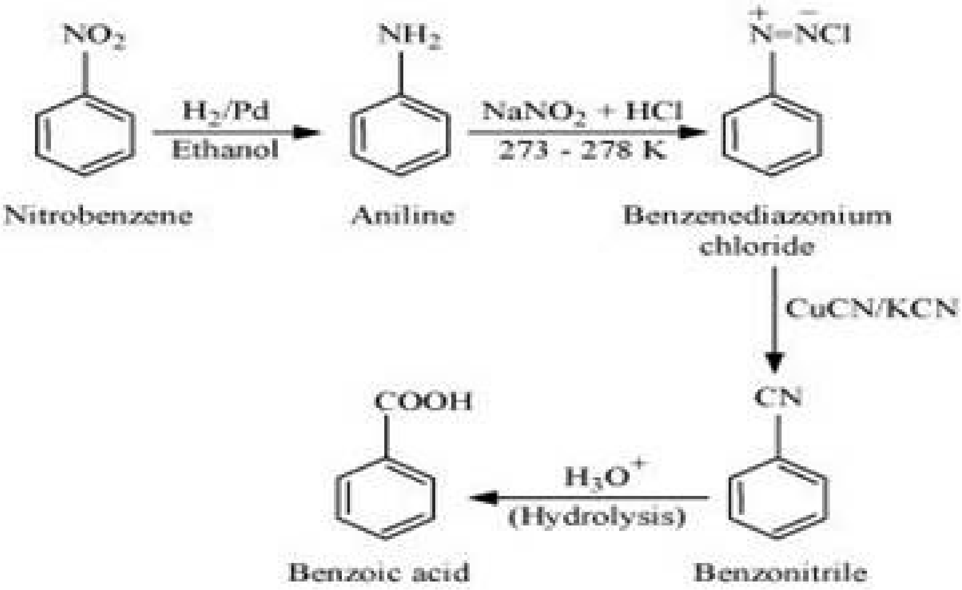
(vi) Chlorobenzene to *p*-chloroaniline

(vii) Aniline to *p*-bromoaniline

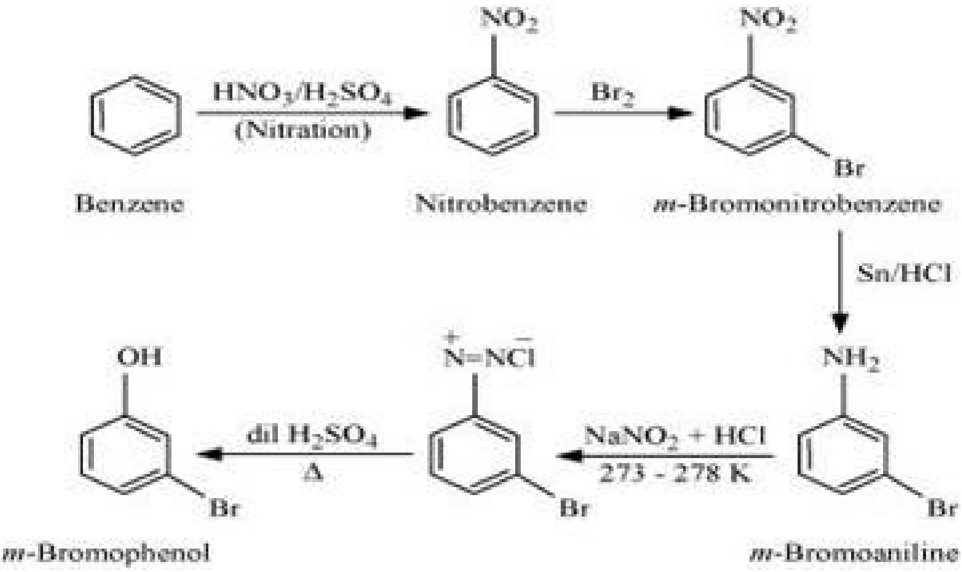
(viii) Benzamide to toluene

(ix) Aniline to benzyl alcohol.

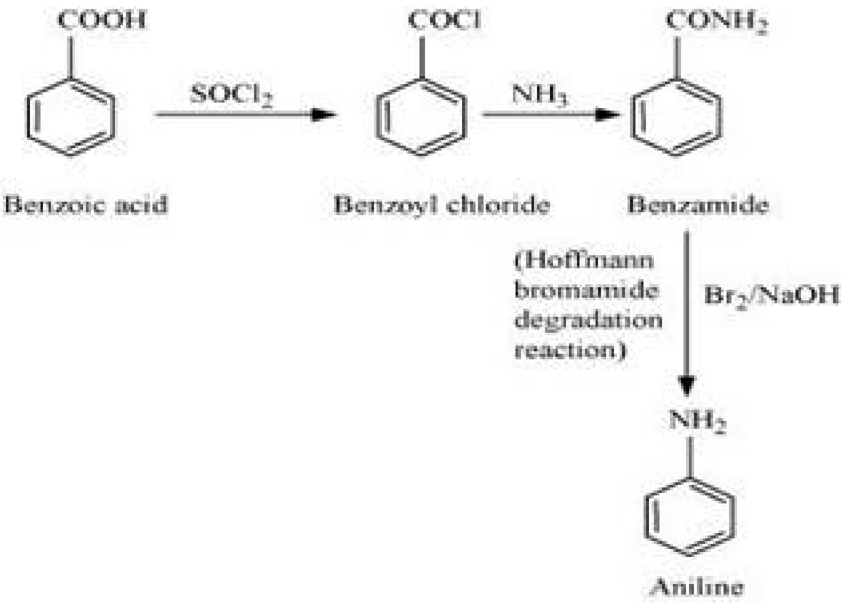
Ans. (i)


NO_2
H_2/Pd
Ethanol
NH_2
$NaNO_2 + HCl$
273 - 278 K
$\overset{+}{N}{\equiv}N\overset{-}{Cl}$
Nitrobenzene
Aniline
Benzenediazonium chloride
CuCN/KCN
COOH
CN
H_3O^+
(Hydrolysis)
Benzoic acid
Benzonitrile

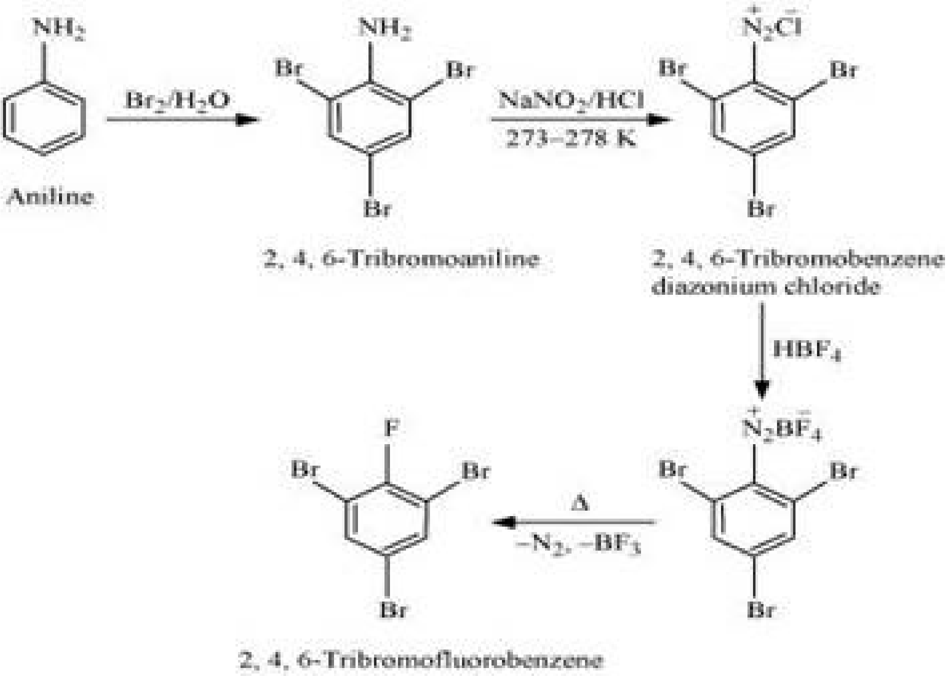
(ii)


NO_2
NO_2
HNO_3/H_2SO_4
(Nitration)
Br_2
Br
Benzene
Nitrobenzene
m-Bromonitrobenzene
Sn/HCl
OH
$\overset{+}{N}{\equiv}N\overset{-}{Cl}$
NH_2
dil H_2SO_4
Δ
$NaNO_2 + HCl$
273 - 278 K
Br
Br
Br
m-Bromophenol
m-Bromoaniline

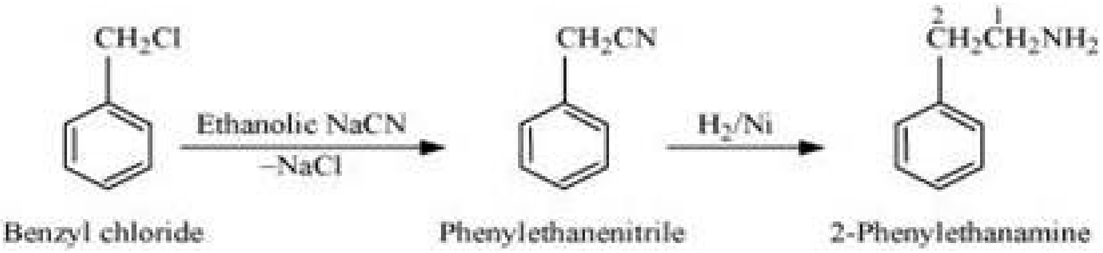
(iii)


COOH
$SOCl_2$
COCl
NH_3
$CONH_2$
Benzoic acid
Benzoyl chloride
Benzamide
(Hoffmann bromamide degradation reaction)
$Br_2/NaOH$
NH_2
Aniline

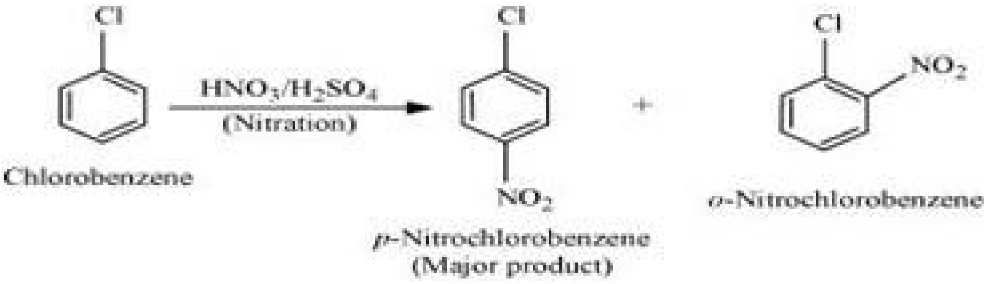
(iv)

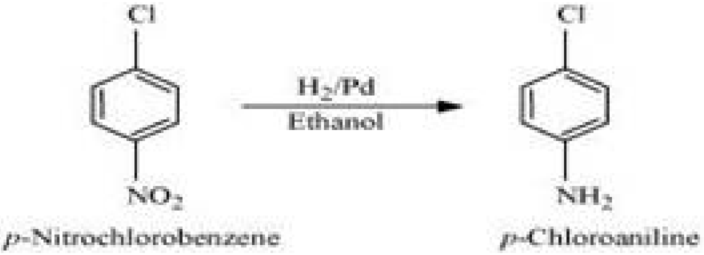

NH_2
Br_2/H_2O
Aniline
NH_2
Br
Br
Br
2, 4, 6-Tribromoaniline
$NaNO_2/HCl$
273–278 K
$\overset{+}{N}_2\overset{-}{Cl}$
Br
Br
Br
2, 4, 6-Tribromobenzene diazonium chloride
HBF_4
$\overset{+}{N}_2\overset{-}{BF_4}$
Br
Br
Br
Δ
$-N_2, -BF_3$
F
Br
Br
Br
2, 4, 6-Tribromofluorobenzene

(v)

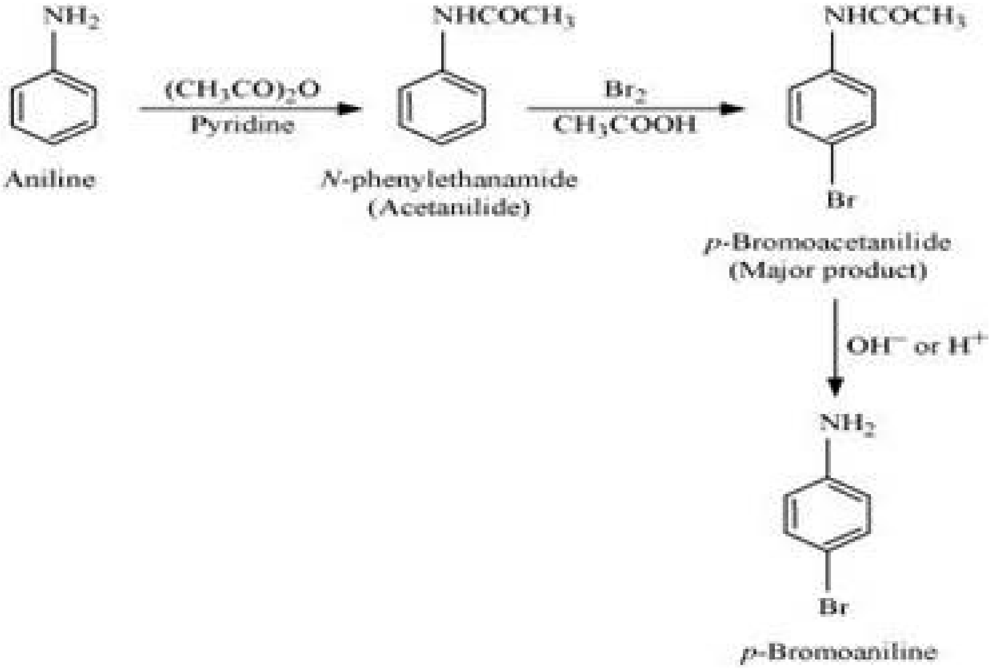

CH_2Cl
Ethanolic NaCN
−NaCl
CH_2CN
H_2/Ni
$\overset{2}{C}H_2\overset{1}{C}H_2NH_2$
Benzyl chloride
Phenylethanenitrile
2-Phenylethanamine

(vi)

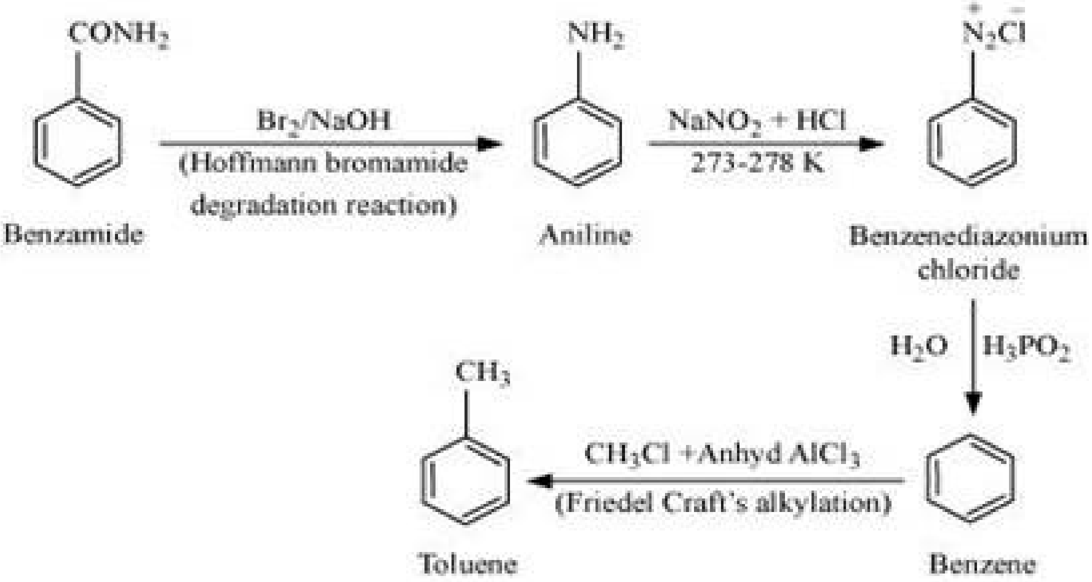

Cl
Chlorobenzene
HNO3/H2SO4
(Nitration)
Cl
NO2
p-Nitrochlorobenzene
(Major product)
+
Cl
NO2
o-Nitrochlorobenzene


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

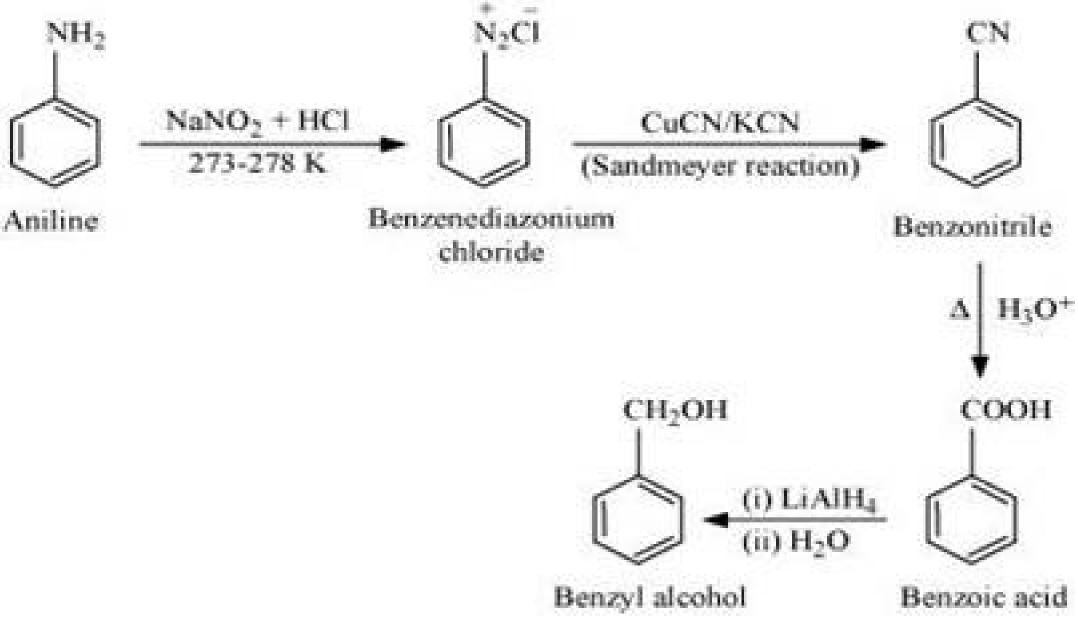
(vii)


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)



(ix)



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

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

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

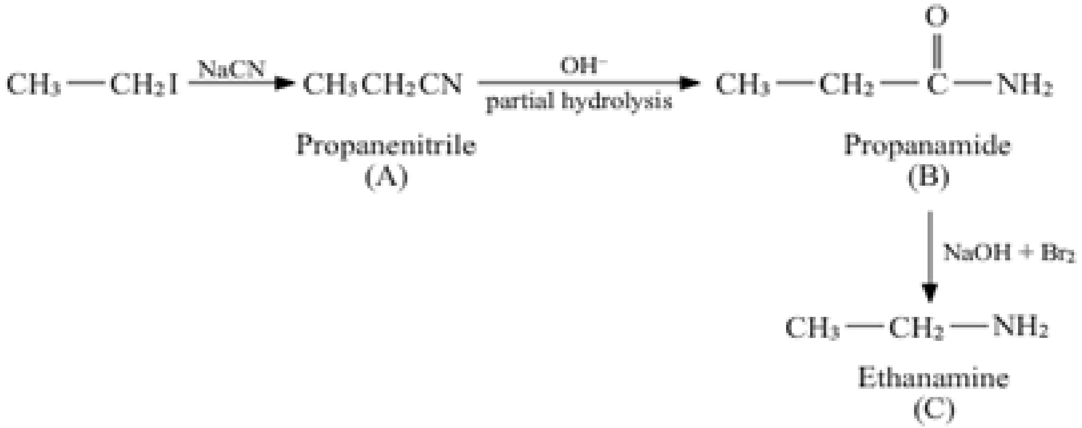
(iii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0^0 C]{HNO_2} C$

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

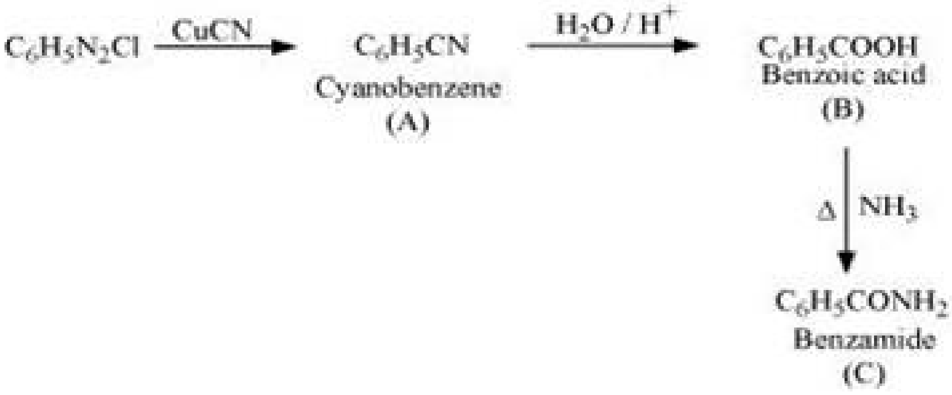
(v) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

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

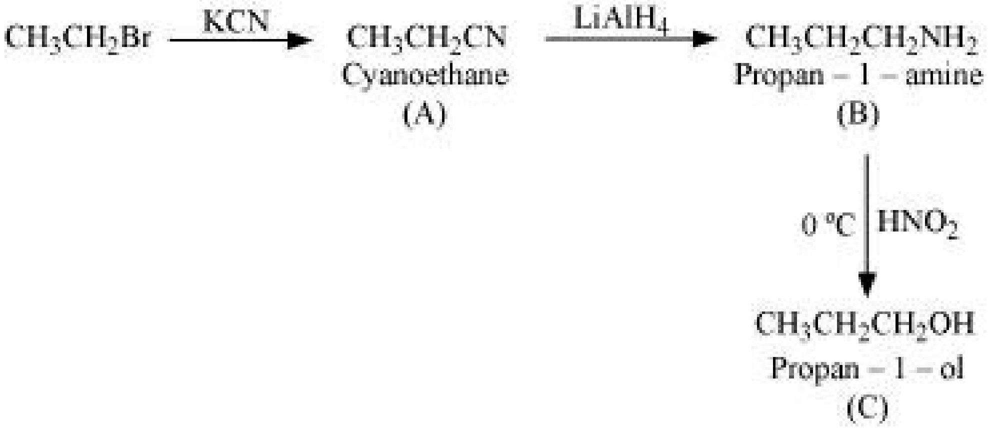
Ans. (i)



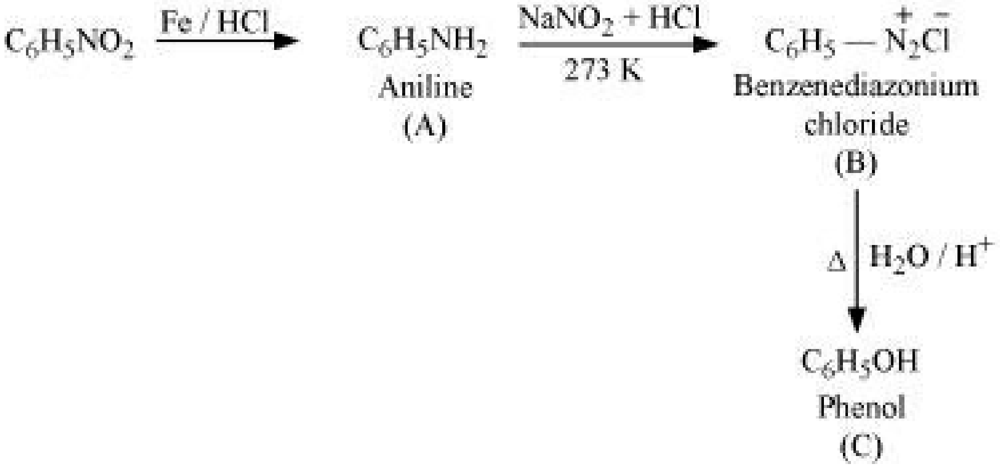
(ii)



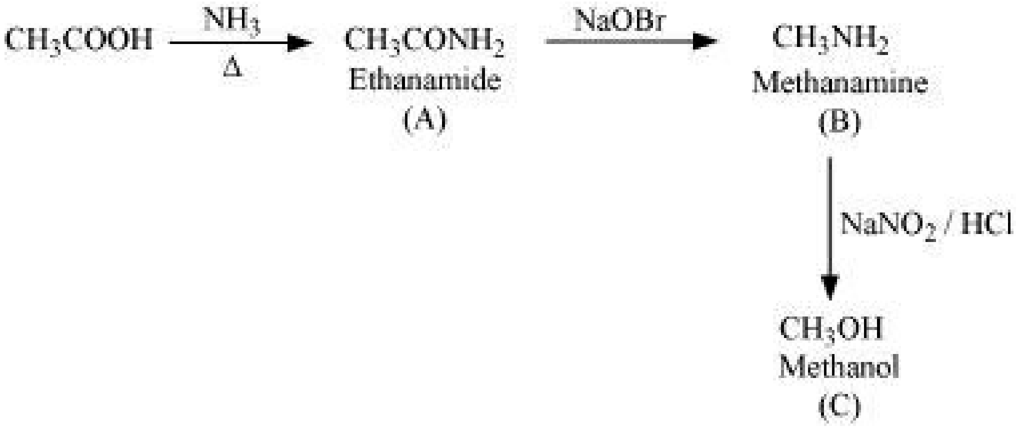
(iii)



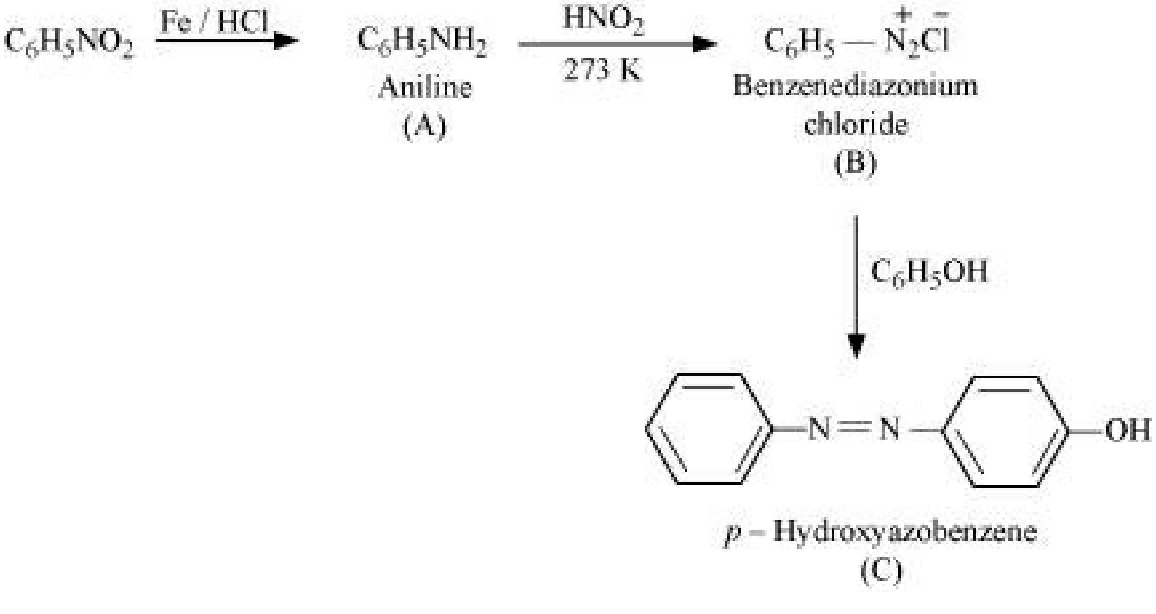
(iv)


$C_6H_5NO_2$
Fe / HCl
$C_6H_5NH_2$
Aniline
(A)
$NaNO_2 + HCl$
273 K
$C_6H_5 - \overset{+}{N}_2\overset{-}{Cl}$
Benzenediazonium chloride
(B)
Δ
H_2O / H^+
C_6H_5OH
Phenol
(C)

(v)

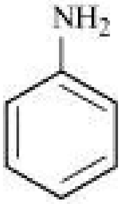

CH_3COOH
NH_3
Δ
CH_3CONH_2
Ethanamide
(A)
NaOBr
CH_3NH_2
Methanamine
(B)
$NaNO_2 / HCl$
CH_3OH
Methanol
(C)

(vi)


$C_6H_5NO_2$
Fe / HCl
$C_6H_5NH_2$
Aniline
(A)
HNO_2
273 K
$C_6H_5 - \overset{+}{N}_2\overset{-}{Cl}$
Benzenediazonium chloride
(B)
C_6H_5OH
N = N
OH
p – Hydroxyazobenzene
(C)

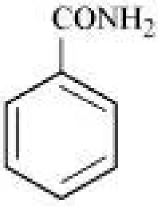
13. An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with $\mathrm{Br_2}$ and KOH forms a compound 'C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

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



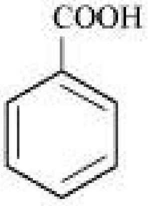
Aniline

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



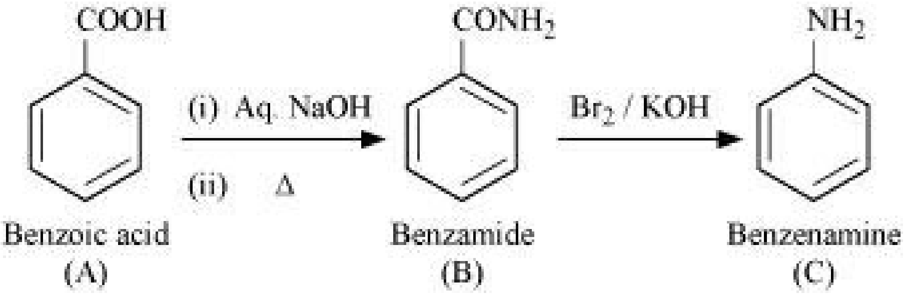
Benzamide

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:



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

Ans. (i)

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

(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)

$$C_6H_5NH_2 + \text{conc.}H_2SO_4 \rightarrow C_6H_5\overset{+}{N}H_3H\overset{-}{SO_4}$$

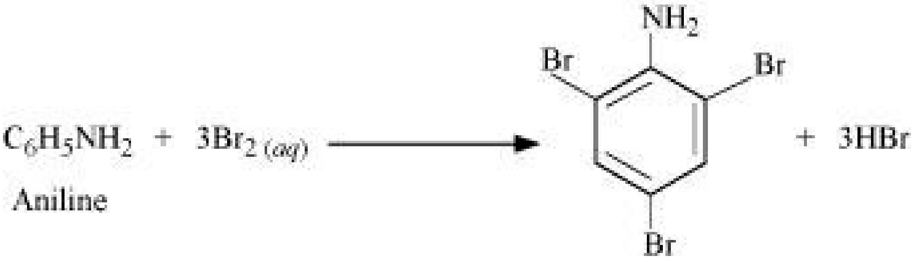
Aniline — Anilinium hydrogen sulphate

(iv)

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

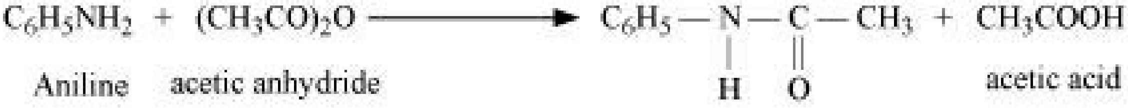
Benzenediazonium chloride — Ethanol — Benzene — Ethanal

(v)



2,4,6 – Tribromoaniline

(vi)



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

Aniline — acetic anhydride — acetic acid

N – Phenylethanamide

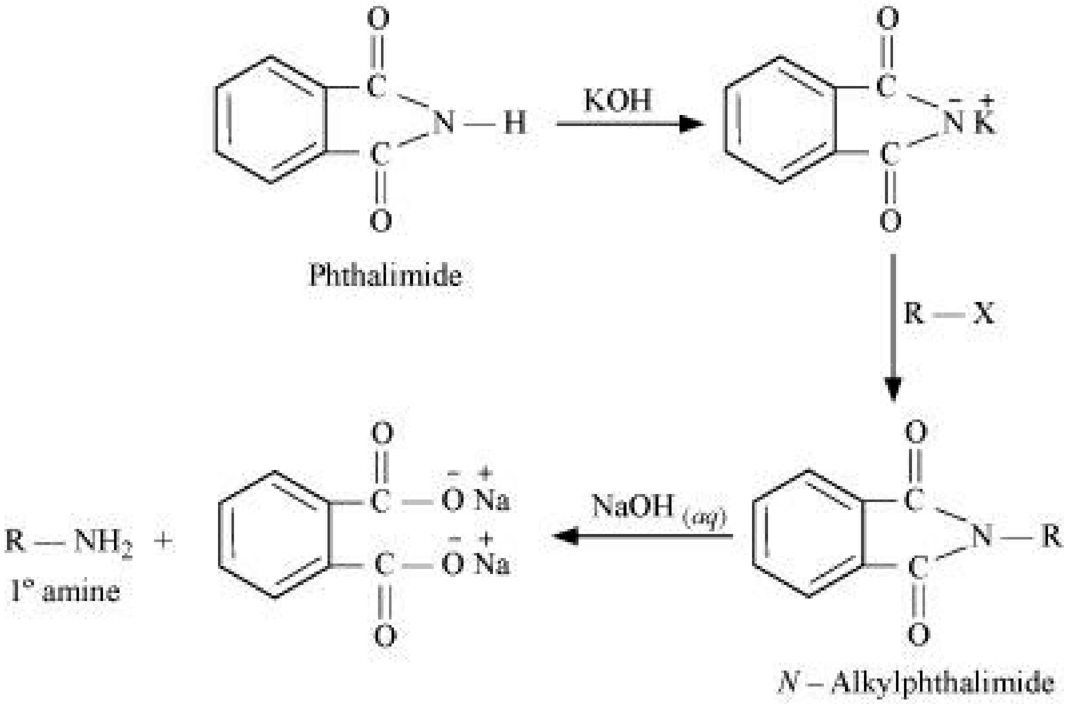
(vii)

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

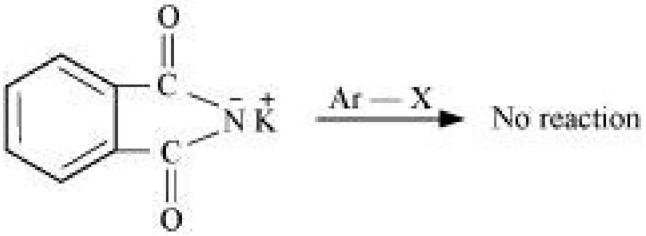
Benzenediazonium chloride — Nitrobenzene

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

Ans. Gabrielphthalimide synthesis is used for the preparation of aliphatic primary amines. It involves nucleophilic substitution $\left(S_N^2\right)$ of alkyl halides by the anion formed by the phthalimide.



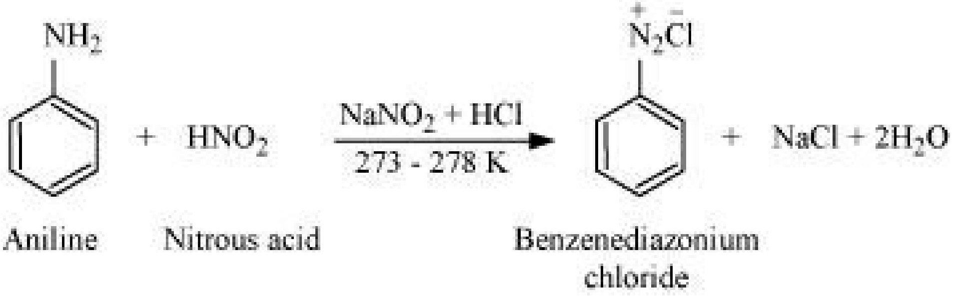
But aryl halides do not undergo nucleophilic substitution with the anion formed by the phthalimide.



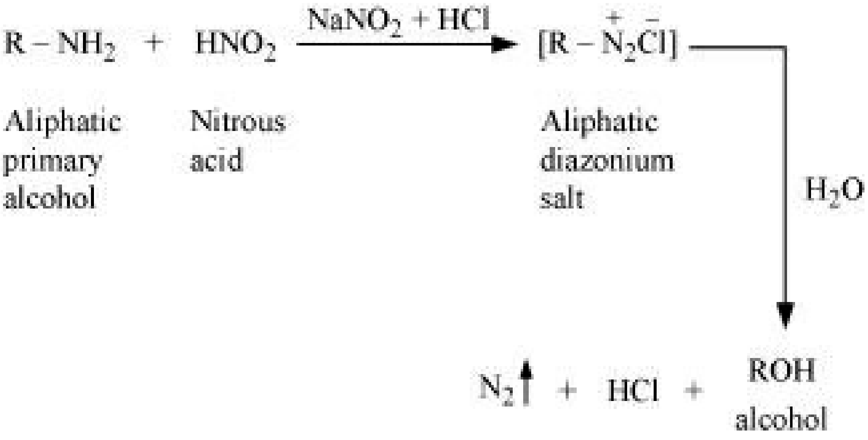
Hence, aromatic primary amines cannot be prepared by this process.

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

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

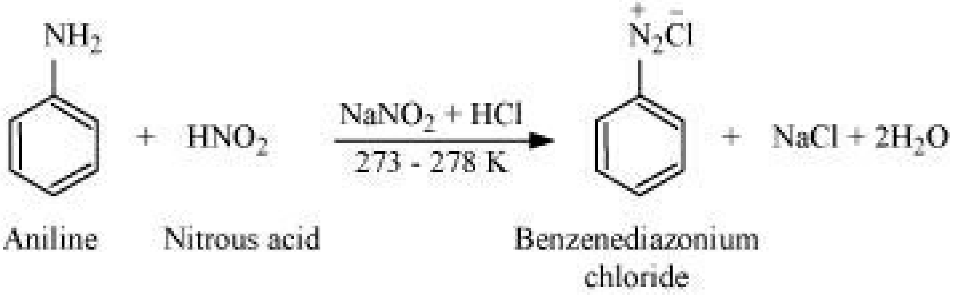


(ii) Aliphatic primary amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) to form unstable aliphatic diazonium salts, which further produce alcohol and HCl with the evolution of N_2 gas.



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

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



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