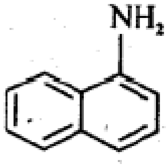
INTEX QUESTIONS

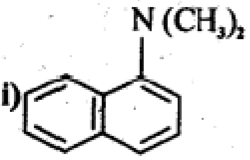
Question 1:

Classify the following amines as primary, secondary and tertiary:

(i)



(ii)



(iii) $(C_2H_5)_2\ CHNH_2$

(iv) $(C_2H_5)_2\ NH$

Solution 1:

(i) 1° (ii) 3° (iii) 1°(iv) 2°

Question 2:

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

(ii) Write IUPAC names of all the isomers.

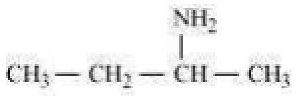
(iii) What type of isomerism is exhibited by different pairs of amines?

Solution 2:

(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-CH_2-CH_2-CH_2-NH_2 Butanamine (1^0)

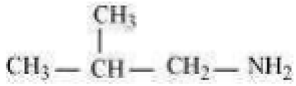
(b)



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

Butan-2-amine (1^0)

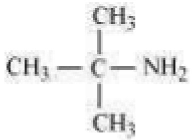
(c)



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

2-Methylpropanamine (1^0)

(d)



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

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

(e) $CH_3-CH_2-CH_2-NH-CH_3$

N-Methylpropanamine (2^0)

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

N-Ethylethanamine (2^0)

(g)

$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-NH-CH_3$

N-Methylpropan-2-amine (2^0)

(h)

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

N,N-Dimethylethanamine (3°)

(iii) Position isomers : (a) and (b); (e) and (g)
Chain isomers: (a) and (c); (a) and (d); (b)and(c); (b)and(d)
Metamers: (e) and (f). (f) and (g)
Functional isomers: All 1^0 amines are functional isomers of 2^0 and 3^0 amines and vice-versa

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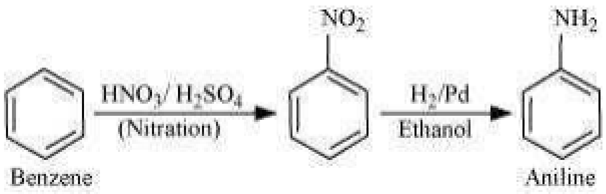
Question 3:

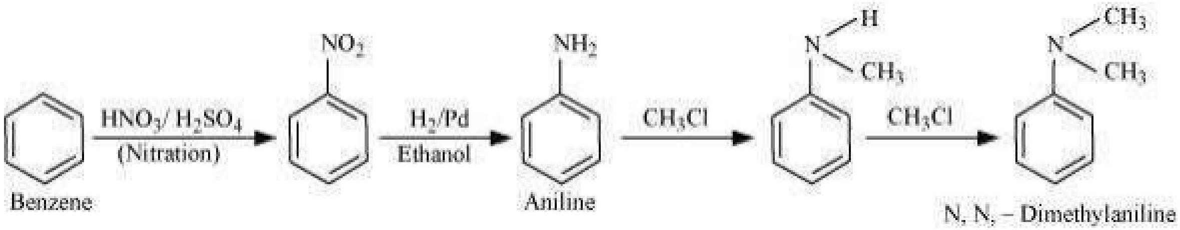
How will you convert:
(i)Benzene into aniline
(ii)Benzene into N,N-dimethylaniline
(iii) $Cl-(CH_2)_4-Cl$ into Hexane -1, 6- diamine

Solution 3:

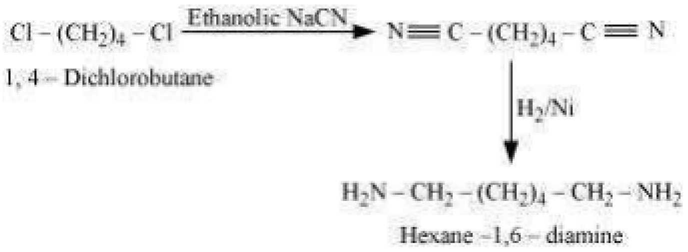
(i)



(ii)



(iii)



Question 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) $C_2H_5NH_2$, $(C_2H_5)_2$ NH, $(C_2H_5)_3N$, $C_6H_5NH_2$

(iii) CH_3NH_2, $(CH_3)_2$ NH, $(CH_3)_3N$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$

Solution 4:

(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.

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

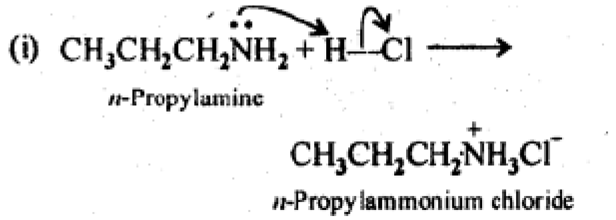
Question 5:

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

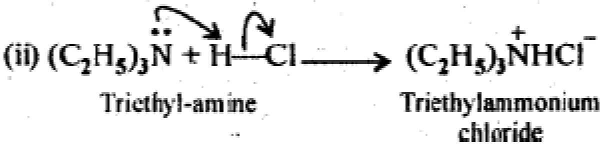
(i) $CH_3CH_2CH_2NH_2 + HCl \longrightarrow$

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

Solution 5:



(i) $CH_3CH_2CH_2\ddot{N}H_2 + H{-}Cl \longrightarrow CH_3CH_2CH_2\overset{+}{N}H_3Cl^-$



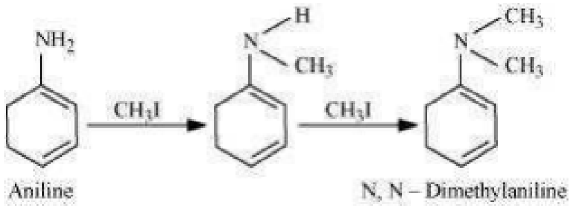
(ii) $(C_2H_5)_3\ddot{N} + H{-}Cl \longrightarrow (C_2H_5)_3\overset{+}{N}HCl^-$

Question 6:

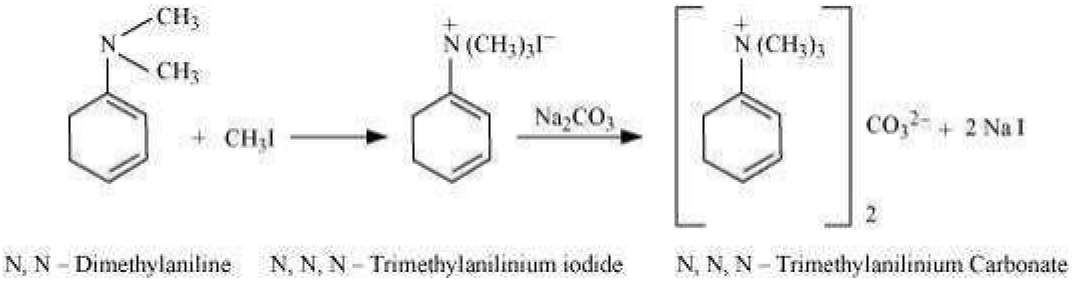
Write reactions of the final alkylation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.

Solution 6:

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



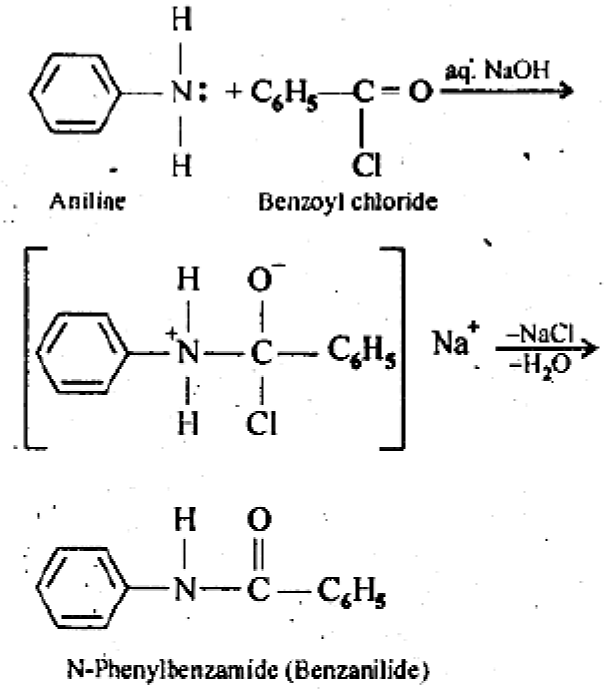
With excess methyl iodide, in the presence of Na_2CO_3 solution, N, N-dimethylaniline produces N, N, N−trimethylanilinium carbonate.



Question 7:

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

Solution 7:



N-Phenylbenzamide (Benzanilide)

Question 8:

Write structures of different isomers corresponding to the molecular formula, C_3H_9N. Write IUPAC names of the isomers which will liberate N_2 gas on treatment with nitrous acid.

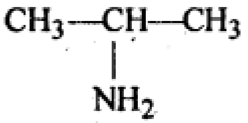
Solution 8:

In all, four structural isomers are possible. These are:

1° amines :

$CH_3CH_2CH_2NH_2$

Propan-1-amine



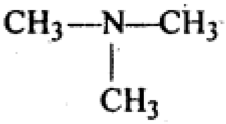
$CH_3-\underset{NH_2}{\underset{|}{CH}}-CH_3$

Propan-2-amine

2° amine : $CH_3-NH-C_2H_5$

N–Methyl ethanamine

3° amine :

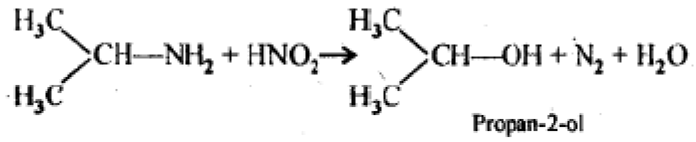


$CH_3-\underset{CH_3}{\underset{|}{N}}-CH_3$

N, N–Dimethyl methanamine

only 1° amines react with HNO_2 to liberate N_2 gas

$$\underset{\text{Propan-1-amine}}{CH_3CH_2CH_2NH_2}+HNO_2\longrightarrow\underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH}+N_2+H_2O$$



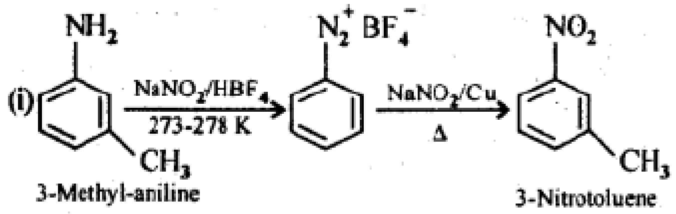
Question 9:

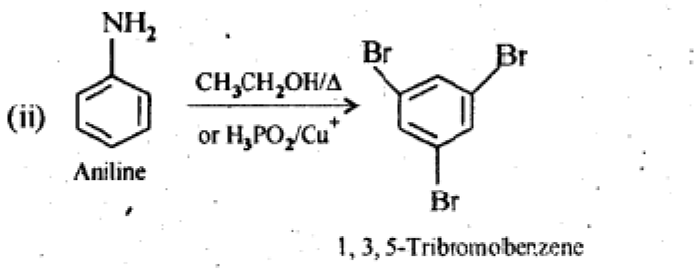
Convert:

(i)3-Methylaniline into 3-nitrotoluene

(ii)Aniline into 1,3,5- Tribromo benzene

Solution 9:





NCERT EXERCISES

Question 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 $(CH_2)_2$ NH_2

(iii) CH_3 $NHCH$ $(CH_3)_2$

(iv) $(CH_3)_3$ CNH

(v) C_6 H_5 $NHCH$

(vi) $(CH_3$ $CH_2)_2$ NCH_3

(vii) m-BrC_6 H_4 NH_2

Solution 1:

(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 2:

Give one chemical test to distinguish between the following pairs of compounds:
(i) Methylamine and dimethylamine
(ii) Secondary and tertiary amines
(iii) Ethylamine and aniline
(iv) Aniline and benzylamine
(v) Aniline and N-Methylaniline.

Solution 2:

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

$$\underset{1^\circ\text{ Amine}}{CH_3NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\substack{\text{Methylisocyanide}\\\text{(offencive smell)}}}{CH_3NC} + 2KCl + 3H_2O$$

$$(CH_3)_2NH \xrightarrow{CHCl_3/KOH(alc)} No\ reaction$$

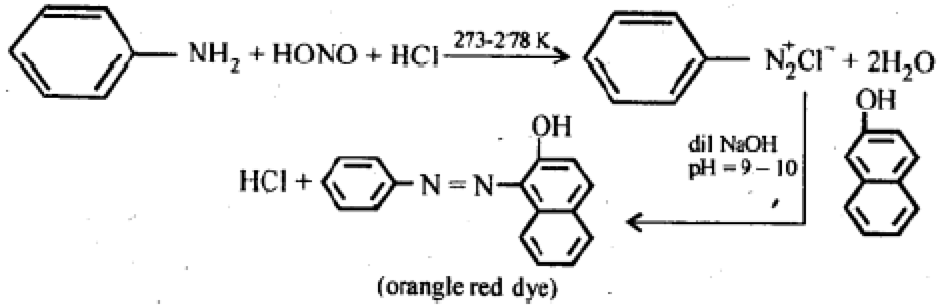
(ii) Secondary and tertiary amine can be distinguished by Liebermann's nitroamine test. Secondary amines gives Liebermann nitroamine test while tertiary amines do not.

$$\underset{\substack{\text{Diethylamine}\\(2^\circ\text{ Amine})}}{(CH_3CH_2)_2NH} + HO-N=O \xrightarrow{HCl+NaNO_2} \underset{\textit{Yellow colour}}{(CH_3CH_2)_2N-N=O} + H_2O$$

$$\underset{\substack{\text{Triethylamine}\\(3^\circ\text{ Amine})}}{(CH_3CH_2)_3N} + HNO_2 \longrightarrow \underset{\substack{\textit{Triethylammonium nitrite}\\\text{(Soluble)}}}{[(CH_3CH_2)_3NH]^+\ NO_2^-}$$

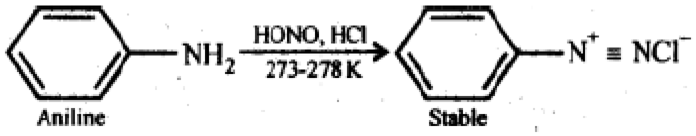
(iii) Ethylamine and aniline can be distinguished by azo test:

$$C_2H_5NH_2 + HONO + HCl \xrightarrow{273-278K} C_2H_5OH + CH_2 = CH_2 + CH_3CH_2Cl + N_2$$



(iv) Aniline and benzylamine can be distinguished by nitrous acid test:

$$\underset{\text{Benzylamine}}{C_6H_5CH_2NH_2} \xrightarrow[HCl]{HONO} \left[\underset{\textit{Unstable}}{C_6H_5CH_2N_2^+Cl-}\right] \xrightarrow[Decomposes]{H_2O} C_6H_5CH_2OH + N_2\uparrow + HCl$$



(v) Aniline and N-methylaniline can be distinguished by carbylamines test:

$$\underset{Aniline}{C_6H_5NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{Offensive\ smaell}{C_6H_5NC} + 3KCl + 3H_2O$$

$$C_6H_5-NH-CH_3 \xrightarrow{CHCl_3+3KOH} No\ reaction$$

Question 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 and p — directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.

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

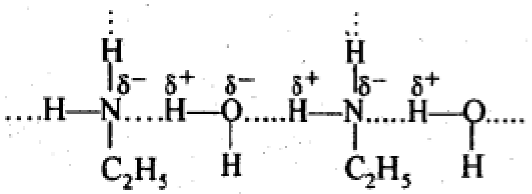
(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

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

Solution 3:

(i) In aniline, the lone pair of electrons on the N-atom is delocalised over the benzene ring. As a result, electron density on the nitrogen atom decreases. Whereas in CH_3NH_2,+ I-effect of $–CH_3$ group increases the electron density on the N-atom. Therefore, aniline is a weaker base than methylamine and hence its pKb value is higher than that of methylamine.

(ii) Ethylamine dissolves in water due to intermolecular H-bonding. However, in case of aniline, due to the large hydrophobic part, i.e., hydrocarbon part, the extent of H-bonding is very less therefore aniline is insoluble in water.



(iii) Methylamine being more basic than water, accepts a proton from water liberating OH^- ions.

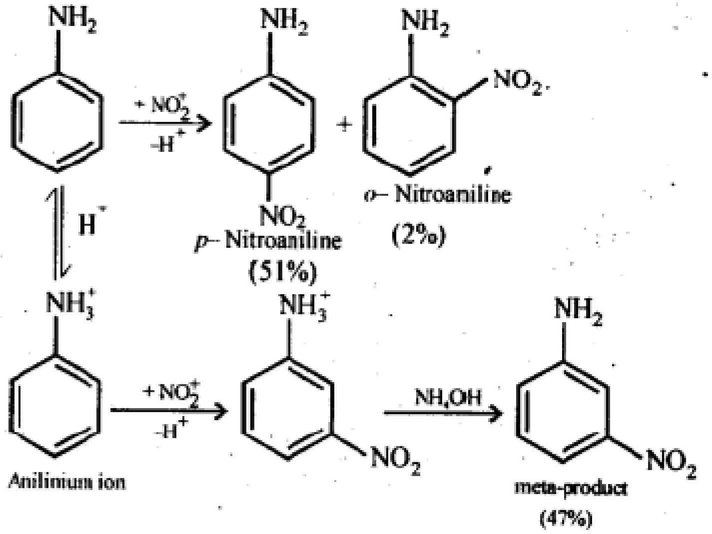
$$CH_3\ddot{N}H_2 + H-OH \longrightarrow CH_3-\overset{+}{N}H_3 + OH^-$$

These OH^- ions combine with Fe^{3+} ions present in H_2O to form brown precipitate of hydrated ferric oxide.

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

$$2Fe^{3+} + 6OH^- \longrightarrow \underset{(Brown\ ppt.)}{2Fe(OH)_3\ or\ Fe_2O_3.3H_2O}$$

(iv) Nitration is usually carried out with a mixture of conc HNO_3+ conc H_2SO_4. In presence of these acids, most of aniline gets protonated to form anilinium ion. Therefore, in presence of acids, the reaction mixture consist of aniline and anilinium ion. Now, $-NH_2$ group in aniline is activating and o, p-directing while the $+NH_3$ group in anilinium ion is deactivating and m-directing: Nitration of aniline (due to steric hindrance at o-position) mainly gives p-nitroaniline, the nitration of anilinium ion gives m-nitroaniline. In actual practice, approx a 1:1 mixture of p-nitroaniline and m-nitroaniline is obtained. Thus, nitration of aniline gives a substantial amount of m-nitroaniline due to protonation of the amino group.

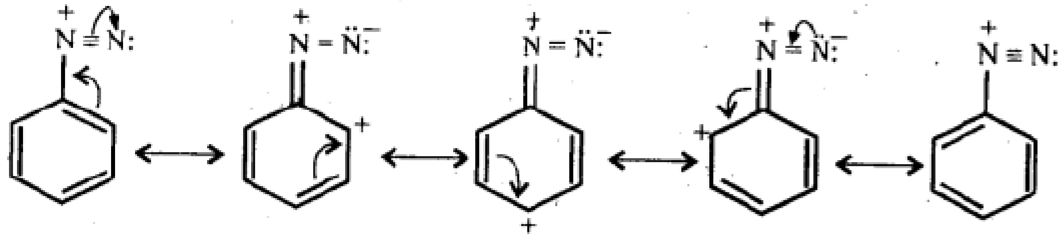


(v) Aniline being a Lewis base reacts with Lewis acid $AlCl_3$ to form a salt.

$$C_6H_5NH_2 + AlCl_3 \longrightarrow C_6H_5NH_2^+AlCl_3^-$$

As a result, N of aniline acquires positive charge and hence it acts as a strong deactivating group for electrophilic substitution reactions. Consequently, aniline does not undergo Fridel Crafts reaction.

(vi) The diazonium salts of aromatic amines are more stable than those of aliphatic amines due to dispersal of the positive charge on benzene ring as a result of resonance.



(vii) Gabriel phthalimide reaction gives pure primary amines without any contamination of secondary and tertiary amines. Therefore, it is preferred for synthesising primary amines.

Question 4:

Arrange the following:
(i) In decreasing order of pKb values:.
$C_6H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ 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:
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3
(v) In increasing order of boiling point:
C_5H_5OH, $(CH_3)_2$ NH, $C_2H_5NH_2$
(vi) In increasing order of solubility in water:
$C_6H_5NH_2$, $(C_5H_5)_2NH$, $C_2H_5NH_2$

Solution 4:

(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 +I 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 pKb values.
$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

(ii) Among CH_3CH_2 and $(C_2H_5)_2NH$, primarily due to the greater +1-effect of the two $–C_2H_5$ groups over one $–CH_3$ group, $(C_2H_5)_2NH$ is more basic than CH_3NH_2. In both $C_6H_5NH_2$ and $C_6H_5N(CH_3)_2$ lone pair of electrons present on N-atom is delocalized over the benzene ring but $C_6H_5N(CH_3)_2$ is more basic due to +1 effect of two $–CH_3$ groups.
$\therefore\ (C_2H_5)_2NH > CH_3NH_2 > C_6H_5N(CH_3)_2 > C_6H_5NH_2$
$\longrightarrow$ Decreasing basic strength
(iii) (a) The presence of electron donating $–CH_3$ group increases while the presence of electron withdrawing NO_2 group decreases the basic strength of amines.
$\therefore$ p-nitroaniline< aniline < p-toluidine
$\longrightarrow$Increasing basic strength
(b) In $C_6H_5NH_2$ and$C_6H_5NHCH_3$, N is directly attached to the benzene ring. As a result, the lone pair of electrons on the N-atom is delocalised over the benzene ring. Therefore, both $C_6H_5NH_2$

and $C_6H_5NHCH_3$ are weaker base in comparison to $C_6H_5CH_2NH_2$. Among $C_6H_5NH_2$ and $C_6H_5NHCH_3$, due to +1 effect of $-CH_3$ group $C_6H_5NHCH_3$ is more basic.

$\therefore\ C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

$\longrightarrow$ Increasing basic strength

(iv) In gas phase or in non-aqueous solvents such as chlorobenzene etc, the solvation effects i. e. the stabilization of the conjugate acid due to H-bonding are absent. Therefore, basic strength depends only upon the +1-effect of the alkyl groups. The +1-effect increases with increase in number of alkyl groups. Thus correct order of decreasing basic strength in gas phase is,

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

$\longrightarrow$ Decreasing basic strength

(v) Since the electronegativity of O is higher than that of N, therefore, alcohols form stronger H-bonds than amines. Also, the extent of H-bonding depends upon the number of H-atoms on the N-atom, thus the extent of H-bonding is greater in primary amine than secondary amine.

$\therefore\ (CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

$\longrightarrow$ Increasing boiling point

(vi) Solubility decreases with increase in molecular mass of amines due to increase in the size of the hydrophobic hydrocarbon part and with decrease in the number of H-atoms on the N-atom which undergo H-bonding.

$\therefore\ C_6H_5NH_2 < (C_6H_5)_2NH < C_2H_5NH_2$

$\longrightarrow$ Increasing solubility

Question 5:

How will you convert:

(i) Ethanoic acid into methanamine
(ii) Hexanenitrile into 1-aminopentane
(iii) Methanol to ethanoic acid.
(iv) Ethanamine into methanamine
(v) Ethanoic acid into propanoic acid
(vi) Methanamine into ethanamine
(vii) Nitromethane into dimethylamine
(viii) Propanoic acid into ethanoic acid

Solution 5:

$$(i)\ CH_3COOH \xrightarrow[-SO_2,\,-HCl]{SOCl_2} CH_3COCl \xrightarrow[NH_4Cl]{NH_3\,(excess)} CH_3CONH_2 \xrightarrow{Br_2\,/\,NaOH} CH_3NH_2$$

$$(ii)\ CH_3(CH_2)_4CN \xrightarrow{H_3O^+} CH_3(CH_2)_4COOH \xrightarrow[-SO_2,\,-HCl]{SOCl_2} CH_3(CH_2)_4COCl \xrightarrow[-NH_4Cl]{NH_3\,(excess)} CH_3(CH_2)_4CONH_2$$

$$CH_3(CH_2)_4NH_2 \xleftarrow{Br_2\,/\,NaOH}$$

(iii) $CH_3OH \xrightarrow[-POCl_3]{PCl_5} CH_3Cl \xrightarrow{KCN(alc)} CH_3CN \xrightarrow{H_3O^+} CH_3COOH$

(iv)
$$\begin{tikzcd}
CH_3CH_2NH_2 \arrow[r, "HONO", "-N_2,-H_2O"'] & CH_3CH_2OH \arrow[r, "K_2Cr_2O_7/H_2SO_4"] & CH_3CHO \arrow[d, "K_2Cr_2O_7/H_2SO_4"] \\
CH_3CONH_2 \arrow[dr, "Br_2/NaOH"] & CH_3COONH_4 \arrow[l, "-H_2O"'] & CH_3COOH \arrow[l, "NH_3"'] \\
 & CH_3NH_2 &
\end{tikzcd}$$

(v)
$$\begin{tikzcd}
CH_3COOH \arrow[r, "LiAlH_4"] & CH_3CH_2OH \arrow[r, "P+I_2", "or\ PI_3"'] & CH_3CH_2I \arrow[r, "KCN", "-KI"'] & CH_3CH_2CN \arrow[dl, "H^+/H_2O"] \\
 & & CH_3CH_2COOH &
\end{tikzcd}$$

(vi)
$$\begin{tikzcd}
CH_3NH_2 \arrow[r, "HONO", "-N_2,-H_2O"'] & CH_3OH \arrow[r, "P+I_2", "or\ PI_3"'] & CH_3I \arrow[r, "KCN", "-KI"'] & CH_3CN \arrow[dl, "Na/C_2H_5OH"] \\
 & & CH_3CH_2NH_2 &
\end{tikzcd}$$

(vii) $CH_3NO_2 \xrightarrow{Sn/HCl} CH_3NH_2 \xrightarrow{CHCl_3.KOH\Delta} CH_3NC \xrightarrow{LiAlH_4} CH_3NHCH_3$

(viii)
$$\begin{tikzcd}
CH_3CH_2COOH \arrow[r, "NH_3", "\Delta"'] & CH_3CH_2CONH_2 \arrow[r, "Br_2/NaOH"] & CH_3CH_2NH_2 \arrow[d, "HNO_2"] \\
 & CH_3COOH & CH_3CH_2OH \arrow[l, "Alk.\ KMnO_4"']
\end{tikzcd}$$

Question 6:

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

Solution 6:

The three type of amines can be distinguished by Hinsberg test. In this test, the amine is shaken with benzenesulphonyl chloride ($C_6H_5SO_2Cl$) in the presence of excess of aqueous NaOH or KOH. A primary amine reacts to give a clear solution, which on acidification yields an insoluble compound.

$$RNH_2 + C_6H_5SO_2Cl \xrightarrow[-HCl]{OH^-} C_6H_5SO_2NHR \xrightarrow{KOH} \underset{\text{(Clear solution)}}{C_6H_5SO_2N^-RK^+} \xrightarrow{H^+} \underset{\text{(Insoluble)}}{C_6H_5SO_2NHR}$$

A secondary amine forms an insoluble compound, which remains insoluble even on acidification.

$$R_2NH + C_6H_5SO_2Cl \xrightarrow[-HCl]{OH^-} \underset{\text{(Insoluble)}}{C_6H_5SO_2NR_2} \xrightarrow{H^+} \text{No reaction}$$

A tertiary amine does not react with the reagent, but dissolves is acid.

$$C_6H_5SO_2Cl + R_3N \xrightarrow{OH^+} No\ reaction$$

$$R_3N + H^+ \longrightarrow \underset{\text{(Clear solution)}}{[R_3NH]^+}$$

Question 7:

Write short notes on the following:

(i) Carbylamine reaction
(ii) Diazotisation
(iii) 'Hofmann's bromamide reaction
(iv) Coupling reaction
(v) Ammonolysis
(vi) Acetylation
(vii) Gabriel phthalimide synthesis

Solution 7:

(i) **Carbylamine reaction:** Both aliphatic and aromatic primary amines when warmed with chloroform and an alcoholic solution of KOH, produces isocyanides or carbylamines which have very unpleasant odours. This reaction is called carbylamine reaction.

$$R-NH_2 + CHCl_3 + 3KOH\,(alc) \longrightarrow R-N \equiv C + 3KCl + 3H_2O$$

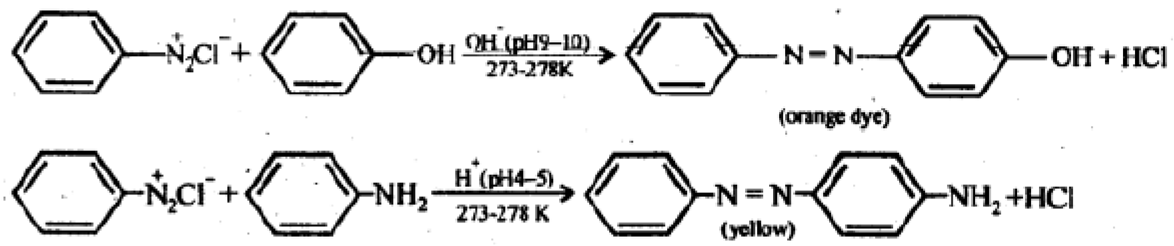
(ii) **Diazotisation:** The process of conversion of a primary aromatic amino compound into a diazonium salt, is known as diazotisation. This process is carried out by adding an aqueous solution of sodium nitrite to a solution of primary aromatic amine (e.g., aniline) in excess of at a temperature below 5°C. HCl

$$\underset{1^\circ\text{ amine}}{ArNH_2} + NaOH_2 + 2HX \xrightarrow{273-278K} \underset{\text{Arene Diazonium salt}}{Ar\overset{+}{N}_2 X^-} + NaX + 2H_2O$$

(iii) **Hoffmann's bromamide reaction:** When an amide is treated with bromine in alkali solution, it is converted to a primary amine that has one carbon atom less than the starting amide. This reaction is known as Hoffmann's bromamide degradation reaction.

$$C_6H_5CONH_2 \xrightarrow{Br_2 + NaOH} C_6H_5NH_2$$

(iv) **Coupling reaction:** In this reaction, arenediazonium salt reacts with aromatic amino compound (in acidic medium) or a phenol (in alkaline medium) to form brightly coloured azo compounds. The reaction generally takes place at para position to the hydroxy or amino group. If para position is blocked, it occurs at ortho position and if both ortho and para positions are occupied, than no coupling takes place.

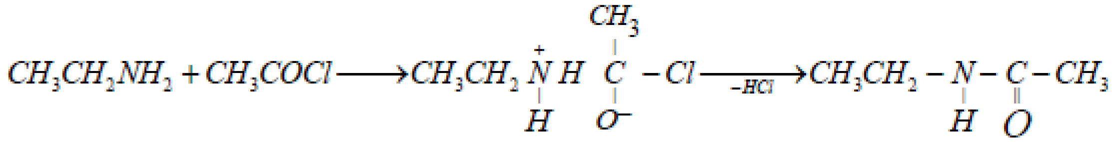


(v) **Ammonolysis:** It is a process of replacement of either halogen atom in alkyl halides (or aryl halides) or hydroxyl group in alcohols (or phenols) by amino group. The reagent used for ammonolysis is alcoholic ammonia. Generally, a mixture of primary, secondary and tertiary amine is formed.

$$ROH + NH_3 \xrightarrow[\text{Hightemp. Prerssure}]{Al_2O_3.\Delta} RNH_2 + H_2O$$

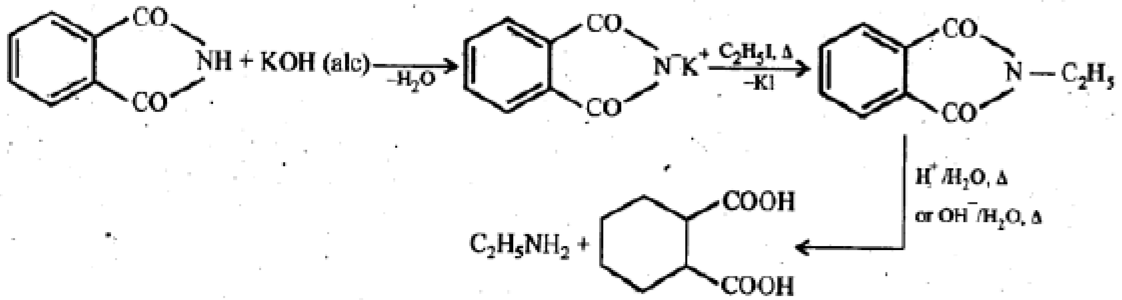
$$\underset{(1°)}{R-NH_2} \xrightarrow[-H_2O]{+R-OH} \underset{(2°)}{R_2NH} \xrightarrow[-H_2O]{+R-OH} \underset{(3°)}{R_3N} \xrightarrow{+R-OH} R_4N^+OH^-$$

(vi) **Acetylation:** The process of introducing an acetyl (CH_3CO-) group into molecule using acetyl chloride or acetic anhydride is called acetylation.



$$CH_3CH_2NH_2 + CH_3COCl \longrightarrow CH_3CH_2\underset{H}{\overset{+}{N}}H\ \underset{O^-}{\overset{CH_3}{C}} - Cl \xrightarrow[-HCl]{} CH_3CH_2 - \underset{H}{N} - \underset{\overset{\|}{O}}{C} - CH_3$$

(vii) **Gabriel phthalimide synthesis:** It is a method of preparation of pure aliphatic and aralkyl primary amines. Phthalimide on treatment with ethanolic KOH gives potassium phathalimide which on heating with a suitable alkyl or aralkyl halides gives N-substituted phthalimides, which on hydrolysis with dil HCl or with alkali give primary amines.



Question 8:

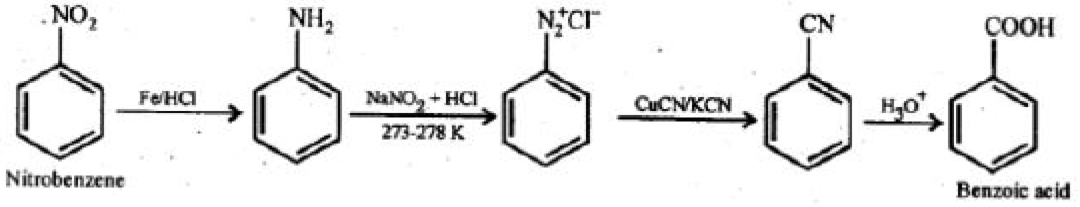
Accomplish the following conversions:

(i) Nitrobenzene to benzoic acid
(ii) Benzene to m-bromophenol
(iii) Benzoic acid to aniline
(iv) Aniline to 2,4,6-tribromofluorobenzene
(v) Benzyl chloride to 2-phenylethanamine
(vi) Chlorobenzene to p-chloroaniline

(vii) Aniline to p-bromoaniline
(viii)Benzamide to toluene
(ix) Aniline to benzyl alcohol.

Solution 8:

(i)



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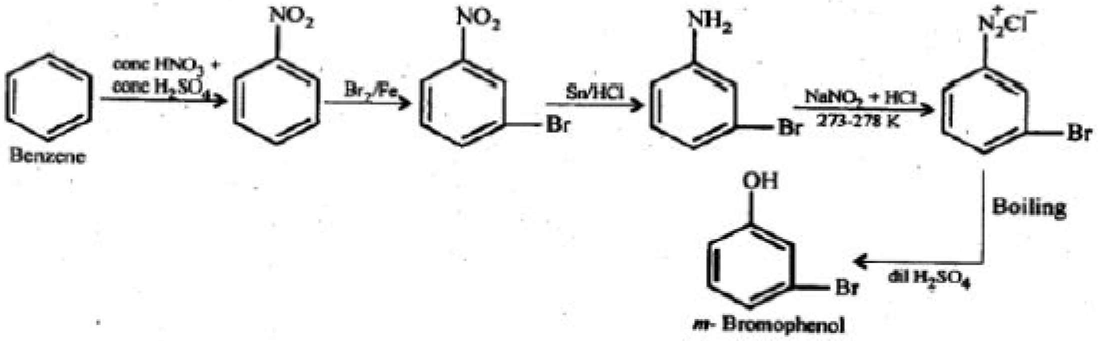

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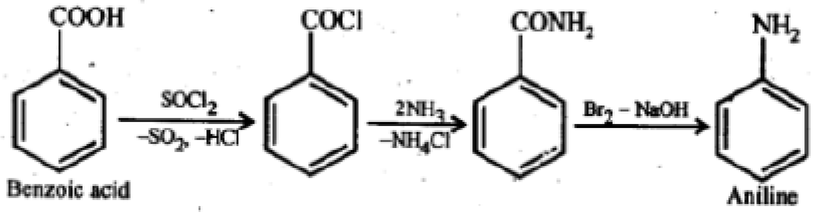

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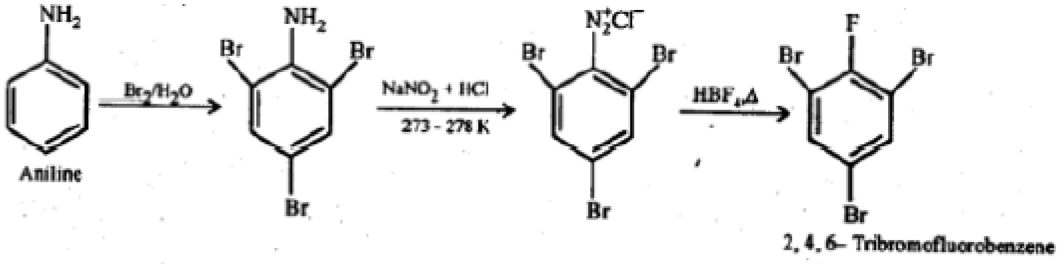

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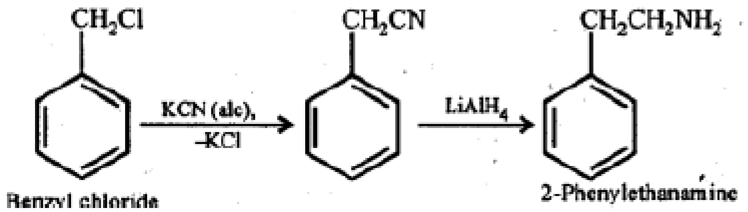

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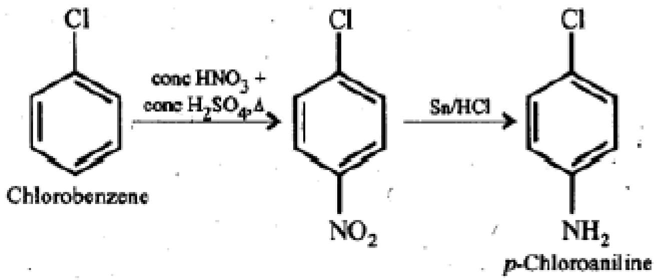

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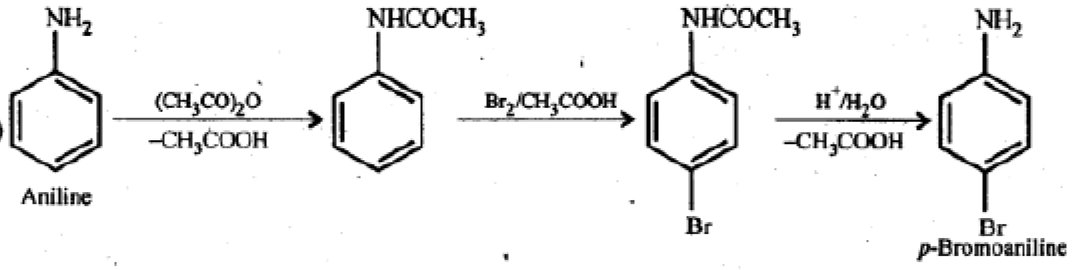

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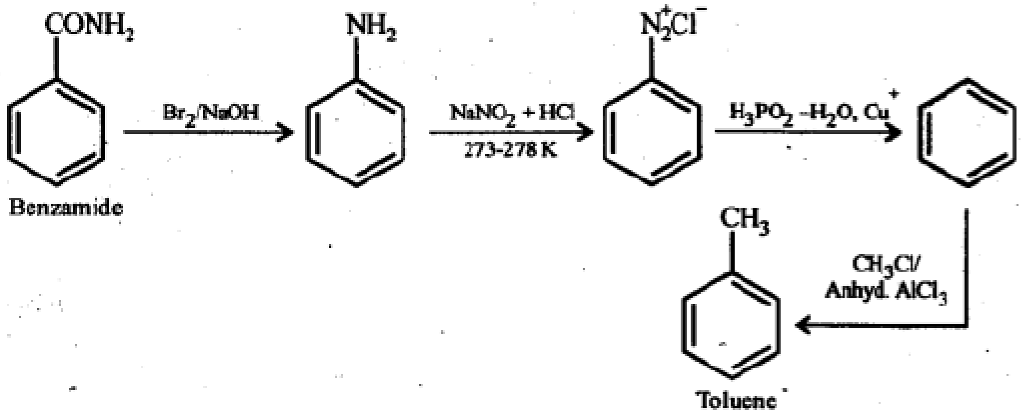

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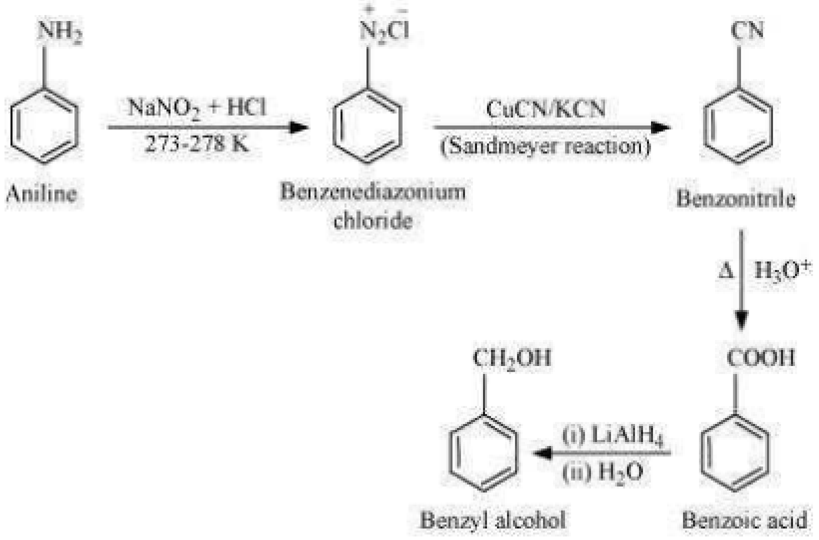


Question 9:

Give the structures of A, B and C in the following reaction:

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

(ii) $C_6H_5Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

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

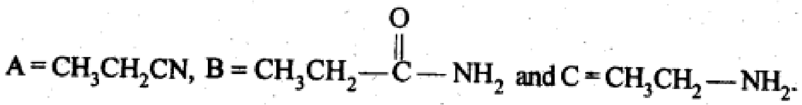
(iv) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{NaNO_2+HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$

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

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

Solution 9:

(i)



$A = CH_3CH_2CN$, $B = CH_3CH_2-\overset{\overset{O}{\|}}{C}-NH_2$ and $C = CH_3CH_2-NH_2$.

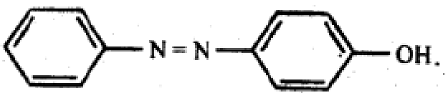
(ii) $A = C_6H_5CN$, $B = C_6H_5COOH$ and $C = C_6H_5CONH_2$

(iii) $A = CH_3CH_2CN$, $B = CH_3CH_2CH_2NH_2$ and $C = CH_3CH_2CH_2OH$

(iv) $A = C_6H_5NH_2$, $B = C_6H_5N^+ \equiv NCl^- = C_6H_5OH$

(v) $A = CH_3CONH_2$, $B = CH_3NH_2$ and $C = CH_3OH$

(vi) $A = C_6H_5NH_2$, $B = C_6H_5N^+ \equiv NCl^-$ and C =



Question 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.

Solution 10:

Since the compound C with molecular formula C_6H_7N is formed from compound B on treatment with Br_2 and KOH ,therefore, compound ‘B’ must be an amide and ‘C’ must be an amine. The only amine having the molecular formula C_6H_7N, i.e., $C_6H_5NH_2$ is aniline. Since ‘C is aniline, therefore, the amide from which it is formed must be benzamide ($C_6H_5CONH_2$). Thus, compound ’B’ is benzamide. Since compound ‘B is formed from compound with aqueous ammonia and heating, therefore, compound ‘A’ must be benzoic acid.

Question 11:

Complete the following reactions:

(i) $C_6H_5NH_2 + CHCl_3 + alc\ KOH \longrightarrow$

(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$

(iii) $C_6H_5NH_2 + H_2SO_4\,(conc) \longrightarrow$

(iv) $C_6H_5N_2Cl + C_2H_5OH \longrightarrow$

(v) $C_6H_5NH_2 + Br_2(aq) \longrightarrow$

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

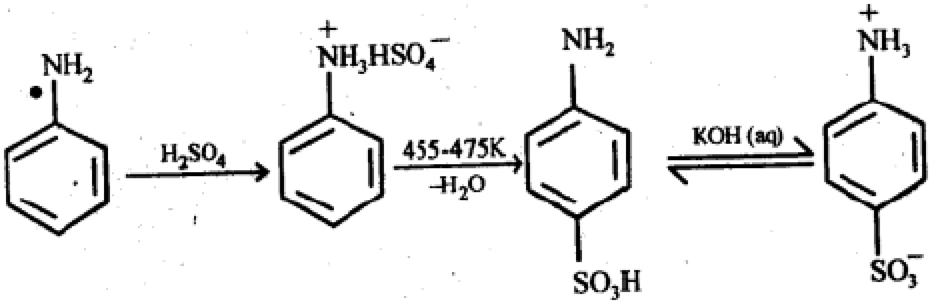
(vii) $C_6H_5N_2Cl \xrightarrow[(ii)\ NaNO_2/Cu.\Delta]{(i)\ HBF_4}$

Solution 11:

(i) $C_6H_5NH_2 + CHCl_3 + 3KOH(alc) \xrightarrow{\Delta} C_6H_5N \equiv C + 3KCl + 3H_2O$

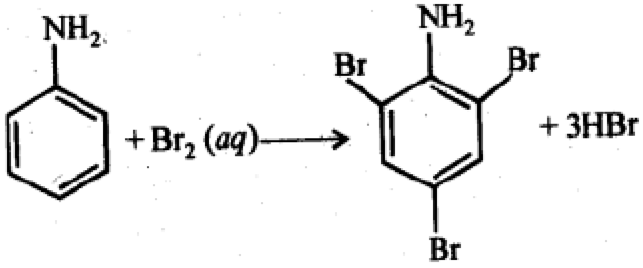
(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \xrightarrow{Cu^+} C_6H_6 + N_2 + H_3PO_3 + HCl$

(iii)



(iv) $C_6H_5N_2Cl + C_2H_5OH \xrightarrow{Reduction} C_6H_6 + CH_3CHO + N_2 + HCl$

(v)



(vi) $C_6H_5NH_2 + CH_3CO{-}O{-}COCH_3 \xrightarrow{CH_3COOH} C_6H_5NHCOCH_3 + CH_3COOH$

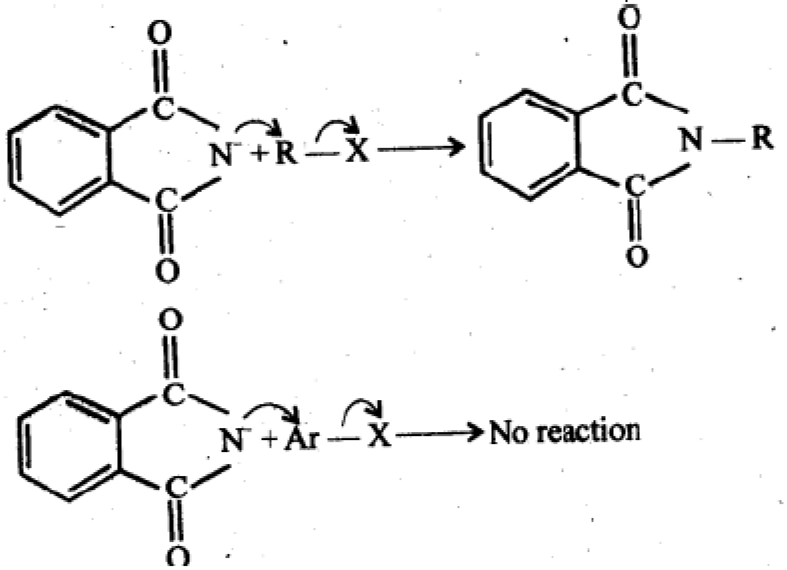
(vii) $C_6H_5N_2Cl \xrightarrow[-HCl]{HBF_4} C_6H_5N_2^+BF_4^- \xrightarrow[\Delta]{NaNO_2/Cu} C_6H_5NO_2 + N_2 + NaBF_4$

Question 12:

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

Solution 12:

The success of Gabriel phthalimide reaction depends upon the nucleophilic attack by the phthalimide anion on the organic halogen compound. Since aryl halides do not undergo nucleophilic substitution reactions easily, therefore, arylamines, i.e. aromatic, primary amines cannot be prepared by Gabriel phthalimide reaction.

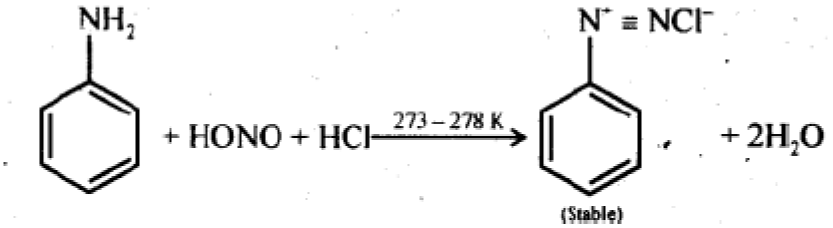


Question 13:

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

Solution 13:

Both aromatic and aliphatic primary amines react with HNO_2 at 273-278 K to form aromatic and aliphatic diazonium salts respectively. But aliphatic diazonium salts are unstable even at this low temperature and thus decompose readily to form a mixture of compounds. Aromatic and aliphatic primary amines react with HNO_2as follows



$$CH_3CH_2NH_2 + HONO + HCl \xrightarrow[-H_2O]{273-278K} \left[\underset{(Unstable)}{CH_3\ CH_2 - N^+ \equiv NCl^-}\right] \xrightarrow[273-278K]{Decomposes} CH_3CH_2OH + CH_2 = CH_2 + CH_3CH_2Cl + N_2$$

Question 14:

Give plausible explanation for each of the following:

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

(ii) Why do primary amines have higher boiling point than tertiary amines?
(iii)Why are aliphatic amines stronger bases than aromatic amines?

Solution 14:

i) Loss of proton from an amine gives an amide ion while loss of a proton from alcohol give an alkoxide ion.

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

$$R-O-H \rightarrow R-O^- + H^+$$

Since O is more electronegative than N, so it will attract positive species more strongly in comparison to N. Thus, RO is more stable than RNH^-. Thus, alcohols are more acidic than amines. Conversely, amines are less acidic than alcohols.

(ii) Due to the presence of two H-atoms on N-atom of primary amines, they undergo extensive intermolecular H-bonding while tertiary amines due to the absence of H-atom on the N-atom do not undergo H-bonding. As a result, primary amines have higher boiling points than tertiary amines of comparable molecular mass.

(iii) Aromatic amines are far less basic than ammonia and aliphatic amines because of following reasons:

(a)Due to resonance in aniline and other aromatic amines, the lone pair of electrons on the nitrogen atom gets delocalized over the benzene ring and thus it is less easily available for protonation. Therefore, aromatic amines are weaker bases than ammonia and aliphatic amines.

(b)Aromatic amines are more stable than corresponding protonated ion; Hence, they have very less tendency to combine with a proton to form corresponding protonated ion, and thus they are less basic.