13

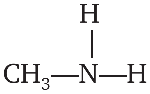
Amines

Facts that Matter

- **Amines:** Derivatives of ammonia obtained by replacement of hydrogen atoms with alkyl or aryl groups.
- **Primary amine:** Characterised by the structure ⟶ RNH_2
- **Secondary amine:** Characterised by the structure ⟶ R_2NH
- **Tertiary amine:** Characterised by the structure ⟶ R_3N
- **Amines behave as Lewis bases:** Amines have one unshared electron pair on the nitrogen atom due to which they behave as Lewis bases.
  - Amines exhibit hydrogen bonding.
  - Alkyl amines are found to be stronger bases than ammonia.
  - Reactivity of aromatic amines can be controlled by acylation process.
  - Aryl diazonium salt usually obtained from arylamines.
  - Coupling reaction of aryl diazonium salts with phenols or arylamines will give rise to the formation of azodyes.

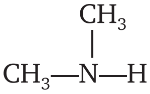
Amines

Amines are the derivatives of ammonia (NH_3) in which one or more hydrogen atoms have been replaced by alkyl groups.



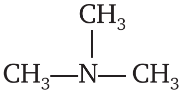
$CH_3-\overset{\overset{H}{|}}{N}-H$

methylamine



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

Dimethylamine



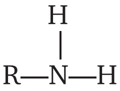
$CH_3-\overset{\overset{CH_3}{|}}{N}-CH_3$

Trimethylamine

Classification of Amines

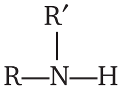
Amines are obtained by the replacement of one or more hydrogen atoms of ammonia by alkyl or aryl groups.

They are classified as primary, secondary or tertiary amines i.e. 1°, 2° and 3° according to the number of alkyl groups attached to the nitrogen atom.



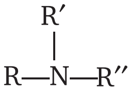
$R-\overset{\overset{H}{|}}{N}-H$

Primary
(1°)



$R-\overset{\overset{R'}{|}}{N}-H$

Secondary
(2°)



$R-\overset{\overset{R'}{|}}{N}-R''$

Tertiary
(3°)

Primary amine (1°): A primary amine has only one alkyl group directly attached to the nitrogen atom.

Secondary amine (2°): A secondary amine has two alkyl groups directly attached to the nitrogen atom.

Tertiary amine (3°): A tertiary amine has three alkyl groups directly attached to the nitrogen atom.

Structure of Amines

Nitrogen atom orbitals in amines are sp^3 hybridised and the geometry of amines is pyramidal. Each of the three sp^3 hybridised orbitals of nitrogen overlaps with the orbital of hydrogen atom or carbon atom depending upon the composition of the amines. The fourth sp^3 hybridised orbital of nitrogen in all amines contains an unshared pair of electrons.

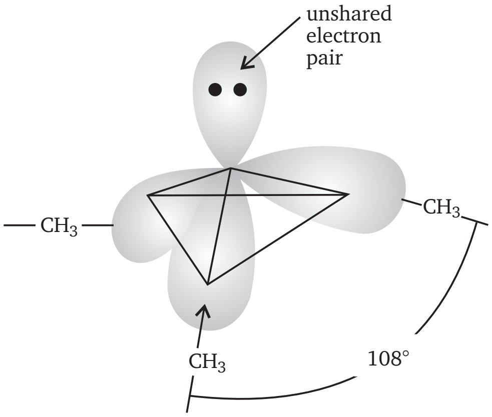


Fig. 13.1 Pyramidal shape of trimethylamine

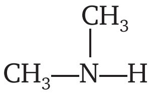
Nomenclature

The following rules are applied in naming amines.

(1) Amines are named by naming the alkyl groups attached to the nitrogen atom followed by the ending amine. Notice that the names are written as one word.

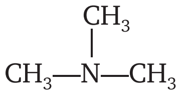
CH_3NH_2 Methylamine $CH_3CH_2-NH_2$ Ethylamine $CH_3CH_2CH_2-NH_2$ *n*-propylamine

(2) When two or three identical alkyl groups are attached to the nitrogen atom, the prefix *di-* or *tri-* is added to the name of the amine.



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

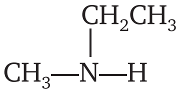
Dimethylamine



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

Trimethylamine

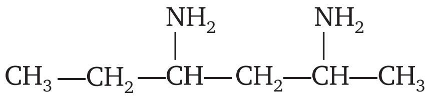
(3) When two or three different alkyl groups are attached to the nitrogen atom, they are named in alphabetical order.



$$CH_3-\overset{\overset{\displaystyle CH_2CH_3}{|}}{N}-H$$

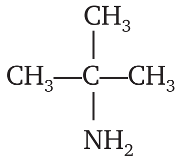
Ethyl methylamine

(4) If the amine is too complex, then the IUPAC system of nomenclature is used. In this system the amino group ($-NH_2$) is considered as a substituent, and its position on the chain is indicated by the lowest possible number.



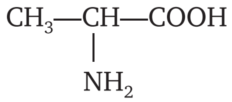
$$CH_3-CH_2-\overset{\overset{\displaystyle NH_2}{|}}{CH}-CH_2-\overset{\overset{\displaystyle NH_2}{|}}{CH}-CH_3$$

5-Methyl-3-aminohexane



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

2-Amino-2-methylpropane



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

2-Aminopropanoic acid

- **Reason based facts:**
  - (*i*) Gabriel phthalimide synthesis is not suitable for the preparation of aromatic primary amines because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.
  - (*ii*) **Basic character of amines:**
    - (*a*) Ammonia is a Lewis base due to the presence of lone pair of electrons. Amines are derivatives of ammonia.
    - (*b*) Basic character depends on the pK_b value. *Larger the value of* pK_b *or smaller the value of* K_b*, weaker is the base and vice-versa.*

Name of amine	**pK_b**
Methanamine	3.38
N–Methylmethanamine	3.27
N, N–Dimethylmethanamine	4.22
Ethanamine	3.29
N–Ethylethanamine	3.00
N–N–Diethylethanamine	3.25
Benzenamine	9.38
Phenylmethanamine	4.70
N–Methylaniline	9.30
N, N–Dimethylaniline	8.92

Basicity Constants

Strong bases (e.g., NaOH or KOH) completely ionise in aqueous solution. Amines are weak bases. They are only partially ionised in aqueous solution and an equilibrium exists between the ionised and unionised forms:

$$R-NH_2 + H_2O \rightleftharpoons R-\overset{+}{N}H_3 + \overset{-}{O}H$$

The extent of ionisation is described by an equilibrium constant K_b, which is known as the basicity constant. It is defined as the concentration of the products of ionisation in moles per litre divided by the concentration of the unionised base.

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

(*c*) **Basic character of Primary, Secondary and Tertiary amines**

Condition No. 1: 3° amine > 2° amine > 1° amine (In vapour phase).

This is due to +*I* effect of alkyl group.

Condition No. 2: In aqueous solution, 1° amine > 2° amine > 3° amine

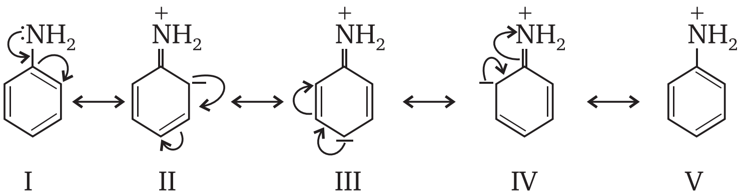
This is due to solvation effect. Greater the size of the ion lesser will be solvation and less stabilised is the ion.

Condition No. 3: In general the basic character of amines in aqueous medium *i.e.,* inductive effect, solvation effect and steric hindrance are in sequence as follows:

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

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

Condition No. 4: In case of aryl amines (aniline): Aniline is less basic than ammonia because the —NH_2 group is attached directly to the benzene ring. Hence the unshared electron pair on the nitrogen atom is less available for protonation due to the resonance.



Condition No. 5: Effect of the substituents on basic strength of aniline:

(*a*) The presence of ERG group increases the basic strength of aniline,

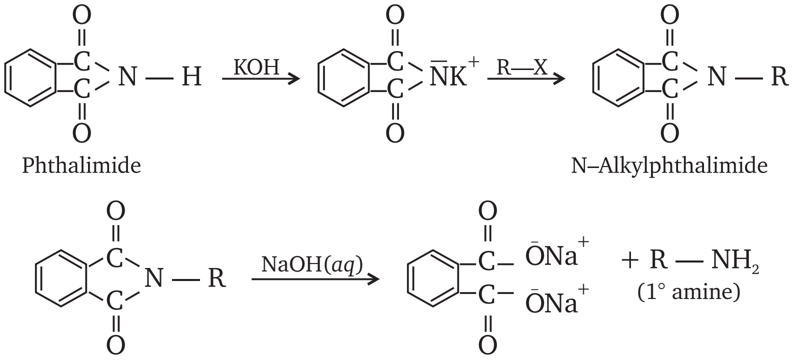
(*b*) The presence of EWG group decreases the basic strength of aniline.

(*iii*) Nitration of aniline gives *ortho*, *para* and *meta* derivatives—In strong acidic medium aniline is protonated to form anilinium ion which is *meta* directing, hence besides *ortho* and *para* derivatives significant amount of *meta* derivative is also formed.

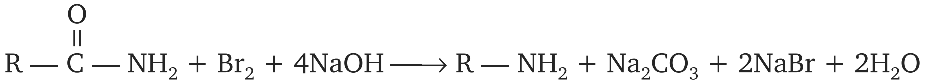
(*iv*) Aniline does not undergo Friedel Crafts reaction—Due to salt formation with aluminium chloride (Lewis acid), nitrogen atom of aniline acquire positive charge and acts as a strong deactivating group for further reaction.

Some Important Name Reactions

- **Gabriel phthalimide synthesis:** Gabriel synthesis is used for the preparation of primary alkyl amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide, which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.



- **Hoffmann bromamide degradation reaction:** Hoffmann developed a method for the preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. The amine so formed contains one carbon less than that present in the amide.

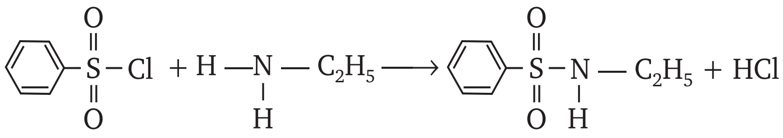


$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

- **Carbylamine reaction:** Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for the identification of primary amines.

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{Heat}} R-NC + 3KCl + 3H_2$$

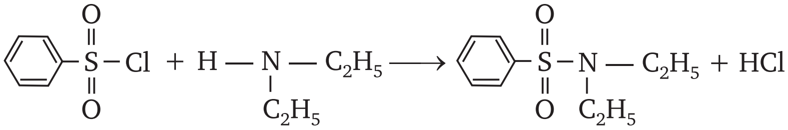
- **Hinsberg Test:** Benzenesulphonyl chloride ($C_6H_5SO_2Cl$), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.
  (*a*) The reaction of benzenesulphonyl chloride with primary amine yields N–ethylbenzenesulphonyl amide.



N–Ethylbenzenesulphonamide
(soluble in alkali)

The hydrogen atom attached to the nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

(*b*) In the reaction with secondary amines, N, N–diethylbenzenesulphonamide is formed



N, N–Diethylbenzenesulphonamide

Since N, N–diethylbenzenesulphonamide does not contain any hydrogen atom attached to the nitrogen atom, thereforce it is not acidic and insoluble in alkali.

(*c*) Tertiary amines do not react with benzenesulphonyl chloride. This property of amines of reacting with benzenesulphonyl chloride in a different manner is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines.

- **Sandmeyer Reaction:** The Cl^-, Br^- and CN^- acting as nucleophiles can easily be introduced in the benzene ring of diazonium salts in the presence of Cu(I) ion as:

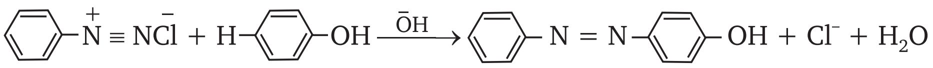
$$\begin{tikzcd} & ArCl + N_2 \\ Ar\overset{+}{N_2}\overset{-}{X} \arrow[ur, "CuCl/HCl"] \arrow[r, "CuBr/HBr"] \arrow[dr, "CuCN/KCN"'] & ArBr + N_2 \\ & ArCN + N_2 \end{tikzcd}$$

- **Gatterman Reaction:** Chlorine or bromine can be introduced in the benzene ring by treating the diazonium salt solution with the corresponding halogen acid in the presence of copper powder.

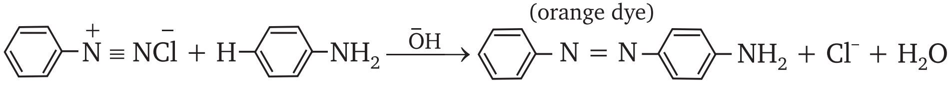
$$\begin{tikzcd} & ArCl + N_2 + CuX \\ Ar\overset{+}{N_2}\overset{-}{X} \arrow[ur, "Cu/HCl"] \arrow[dr, "Cu/HBr"'] & \\ & ArBr + N_2 + CuX \end{tikzcd}$$

- **Coupling reactions:** The azo products obtained have an extended conjugate system having both the aromatic rings joined through the –N = N– bond. These compounds are often coloured and are used as dyes. Benzene diazonium chloride reacts with phenol in which phenol molecule at its para position is coupled with the diazonium salt to form *p*–hydroxyazobenzene. This type of reaction is known as coupling reaction.

  Similarly the reaction of diazonium salt with aniline yields *p*–aminoazobenzene.



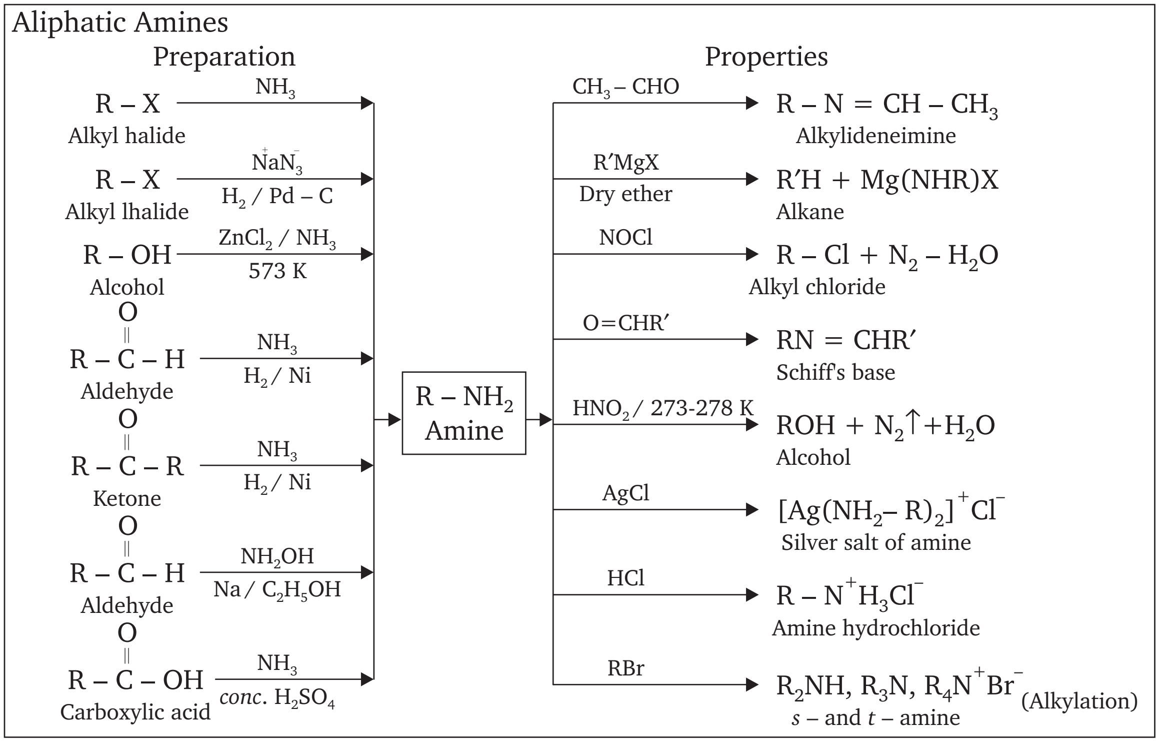
p–Hydroxyazobenzene
(orange dye)



p–Aminoazobenzene
(yellow dye)

Impotant Reaction with Reagents

(Based on Preparation and Properties)



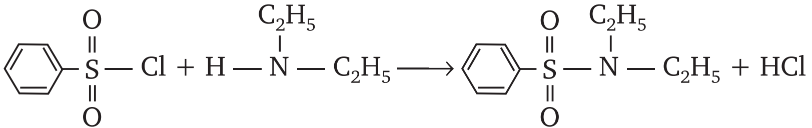
Distinction Between Pairs of Compounds

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

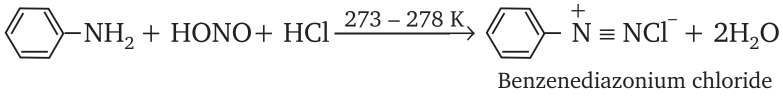
$$\underset{\text{Methylamine }(1^0)}{CH_3—NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\substack{\text{Methylisocyanide}\\ \text{(foul smell)}}}{CH_3—NC} + 3KCl + 3H_2O$$

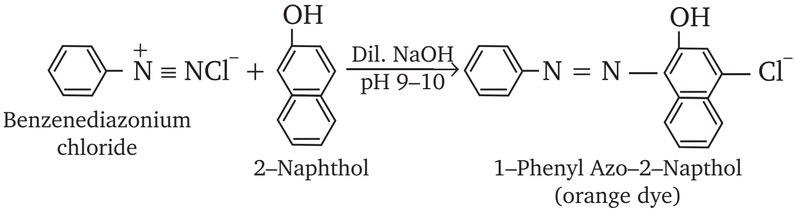
$$(CH_3)_2NH + CHCl_3 + 3KOH \xrightarrow{\Delta} \text{No reaction}$$

(*ii*) **Secondary** and **tertiary amines** can be distinguished by allowing them to react with Hinsberg reagent (benzenesulphonyl chloride, $C_6H_5SO_2Cl$). Secondary amines react with Hinsberg reagent to form a product that is insoluble in an alkali. For example, N, N–diethylamine reacts with Hinsberg reagent to form N, N–diethyl-benzenesulphonamide, which is insoluble in an alkali. Tertiary amines however, do not react with Hinsberg's reagent.



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





$$CH_3CH_2 - NH_2 + HONO \xrightarrow{273\text{-}278\ K} C_2H_5OH + N_2\uparrow + H_2O$$

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

$$C_6H_5CH_2 - NH_2 \xrightarrow[HCl]{NaNO_2+} \underset{\text{(unstable)}}{C_6H_5CH_2 - \overset{+}{N_2}\overset{-}{Cl}} \xrightarrow{H_2O} C_6H_5CH_2OH + HCl + N_2\uparrow$$

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

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

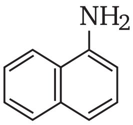
$$\underset{\text{Benzylamine(1°)}}{C_6H_5 - NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\text{Benzyl isocyanide (foul smell)}}{C_6H_5 - NC} + 3KCl + 3H_2O$$

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

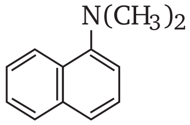
NCERT IN-TEXT QUESTIONS SOLVED

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

(*i*)



(*ii*)



(*iii*) $(C_2H_5)_2CHNH_2$ (*iv*) $(C_2H_5)_2NH$

Ans. (*i*) 1° (*ii*) 3° (*iii*) 1° (*iv*) 2°

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

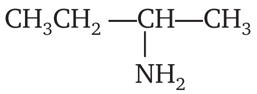
(*ii*) Write IUPAC names of all the isomers?

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

Ans. (*i*), (*ii*) **Primary amines:**

(*a*) $CH_3CH_2CH_2CH_2NH_2$

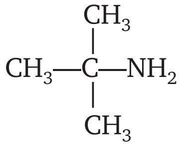
Butanamine

(*b*) 
$CH_3CH_2—CH(NH_2)—CH_3$

Butan-2-amine

(*c*) 
$CH_3—CH(CH_3)—CH_2—NH_2$

2-Methyl propanamine

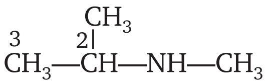
(*d*) 
$CH_3—C(CH_3)_2—NH_2$

2-Methyl propan-2-amine

Secondary amines:

(*e*) $CH_3CH_2CH_2—NH—CH_3$

N-Methylpropanamine

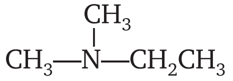
(*f*) 
$CH_3—CH(CH_3)—NH—CH_3$

N-Methylpropane 2-amine

(*g*) $CH_3—CH_2—NH—CH_2CH_3$

N-Ethylethanamine

Tertiary amines:

(*h*) 
$CH_3—N(CH_3)—CH_2CH_3$

N, N-Dimethylethanamine

(*iii*) **Position isomers:** (a) and (b), (e) and (j)

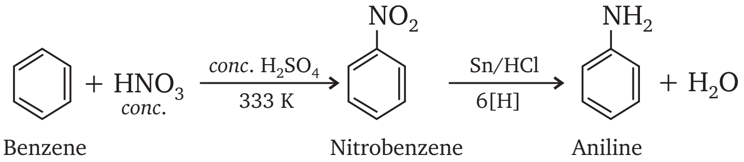
Chain isomers: (a)and (c), (a) and (d), (b) and (c), (b) and (d)

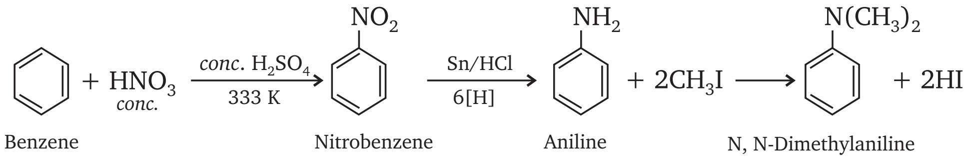
Metamers: (e) and (g), (f) and (g).

13.3. How will you convert

(*i*) Benzene into aniline (*ii*) Benzene into N, N-dimethylaniline

(*iii*) $Cl—(CH_2)_4—Cl$ into hexan-1, 6-diamine?

Ans. (*i*) 

(*ii*) 

(*iii*) $Cl(CH_2)_4Cl \xrightarrow{2KCN} N\equiv C-(CH_2)_4-C\equiv N \xrightarrow{Na/C_2H_5OH} \underset{\text{Hexan-1, 6-diamine}}{H_2NCH_2-(CH_2)_4-CH_2NH_2}$

13.4. Arrange the following in increasing order of their basic strength:

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

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

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

Ans. (*i*) $C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$

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

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

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

(*i*) $CH_3CH_2CH_2NH_2 + HCl \longrightarrow$

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

Ans. (*i*) $\underset{n\text{-Propylamine}}{CH_3CH_2CH_2\ddot{N}H_2} + H-Cl \longrightarrow \underset{n\text{-Propylammonium chloride}}{CH_3CH_2CH_2\overset{+}{N}H_3Cl^-}$

(*ii*) $\underset{\text{Triethylamine}}{(C_2H_5)_3\ddot{N}} + H-Cl \longrightarrow \underset{\text{Triethylammonium chloride}}{(C_2H_5)_3\overset{+}{N}HCl^-}$

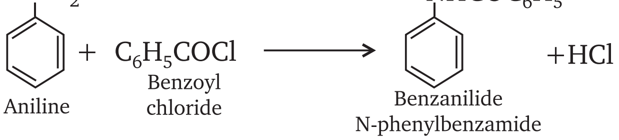
13.6. Write reactions of the final alkylation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.

Ans. $\underset{\text{Aniline}}{C_6H_5\ddot{N}H_2} + CH_3-I \longrightarrow \underset{\text{N-Methylanilinium iodide}}{[C_6H_5\overset{+}{N}H_2CH_3]I^-}$

$2[C_6H_5\overset{+}{N}H_2CH_3]I^- + Na_2CO_3 \longrightarrow \underset{\text{N-Methylaniline}}{2C_6H_5NHCH_3} + CO_2 + 2NaI$

$C_6H_5\ddot{N}HCH_3 \xrightarrow[Na_2CO_3]{CH_3-I} \underset{\text{N, N-Dimethylaniline}}{C_6H_5N(CH_3)_2}$

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

Ans. 

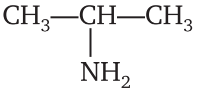
13.8. Write structures of different isomers corresponding to the molecular formula, C_3H_9N. Write IUPAC names of the isomers which will liberate nitrogen gas OH treatment with nitrous acid.

Ans. In all four structural isomers are possible. These are;

1° Amines:

$CH_3CH_2CH_2NH_2$

Propan-1-amine



$CH_3—\underset{\displaystyle NH_2}{\underset{|}{CH}}—CH_3$

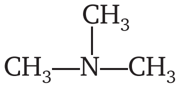
Propan–2–amine

2° Amines:

$CH_3—NH—C_2H_5$

N-Methylethanamine

3° Amines:



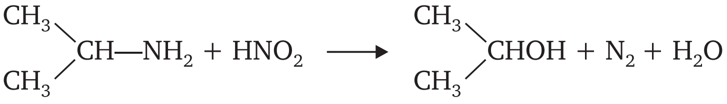
$CH_3—\overset{\displaystyle CH_3}{\overset{|}{N}}—CH_3$

N, N-Dimethylmethanamine

Only 1° amines react with HNO_2 to liberate N_2 gas

$$CH_3CH_2CH_2NH_2 + HNO_2 \longrightarrow CH_3CH_2CH_2OH + N_2 + H_2O$$

Propan–1–amine | Propan–1–ol (major product)



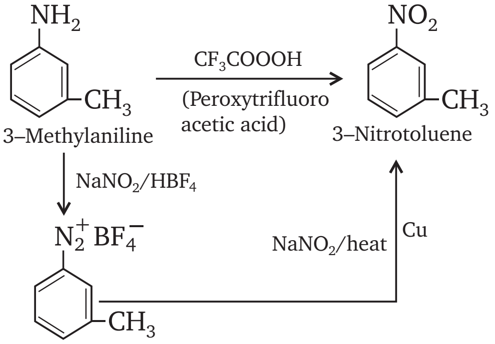
Propan–2–amine | Propan–2–ol (major product)

13.9. Convert

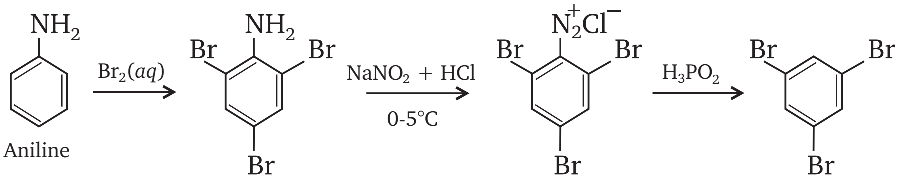
(*i*) 3-Methylaniline into 3-nitrotoluene

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

Ans. (*i*)



(*ii*)



1,3,5-Tribromobenzene

NCERT TEXTBOOK QUESTIONS SOLVED

13.1. 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*-$BrC_6H_4NH_2$. [*Delhi CBSE* 2017]

Ans. (*i*) 1-Methylethanamine (1°), (*ii*) Propan-1-amine (1°), (*iii*) N-Methylpropan-2-amine (2°), (*iv*) 2-Methylpropan-2-amine (3°), (*v*) N-Methylbenzenamine or N-Methylaniline (2°), (*vi*) N-Ethyl-N-methylethanamine (3°), (*vii*) 3-Bromobenzenamine or 3-Bromoaniline (1°).

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

(*i*) Methylamine and dimethylamine (*ii*) Secondary and tertiary amines

(*iii*) Ethylamine and aniline (*iv*) Aniline and benzylamine

(*v*) Aniline and N-methylaniline

Ans. (*i*) These can be distinguished by the carbylamine test.

$$\underset{\substack{\text{Methylamine}\\ \text{(1° Amine)}}}{CH_3NH_2} + CHCl_3 + \underset{(alc)}{3KOH} \xrightarrow{\Delta} \underset{\substack{\text{Methylisocyanide}\\ \text{(offensive smell)}}}{CH_3NC} + 3KCl + 3H_2O$$

$$\underset{\substack{\text{Dimethylamine}\\ \text{(2° Amine)}}}{(CH_3)_2NH} \xrightarrow{CHCl_3/KOH\ (alc)} \text{No reaction}$$

(*ii*) These can be distinguished by Libermann nitrosoamine test, since 2° amines give Libermann nitrosoamine test while 3° amines do not.

$$\underset{\text{Diethylamine}}{(CH_3CH_2)_2NH} + HO{—}N{=}O \longrightarrow \underset{\substack{\text{N-Nitrosodiethylamine}\\ \text{(yellow colour)}}}{(CH_3CH_2)_2N{—}N{=}O} + H_2O$$

Tertiary amines do not give this test.

(*iii*) **Azodye test:** It involves the reaction of any aromatic primary amine with HNO_2 ($NaNO_2$ + *dil.* HCl) at 273-278 K followed by treatment with an alkaline solution of 2-napthol (β-napthol) when a brilliant yellow, orange or red coloured dye is obtained. Aliphatic primary amines like ethylamine under these condition give a brisk evolution of N_2 gas with the formation of primary alcohol.

(*iv*) **Nitrous acid test:** Benzylamine reacts with nitrous acid to form a diazonium salt which being unstable even at low temperature, decomposes with evolution of N_2 gas.

Aniline, on the other hand, reacts with HNO_2 to form benzene diazonium chloride which is stable at 273 - 278 K and hence does not decompose to evolve N_2 gas.

(*v*) **Carbylamine test:** Aniline being a primary amine gives carbylamine test, *i.e.* when heated with an alcoholic solution of KOH and $CHCl_3$, it gives an offensive smell of phenyl isocyanide.

In contrast N-methylaniline being a secondary amine does not give this test.

13.3. Account for the following:

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

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

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

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

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

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

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

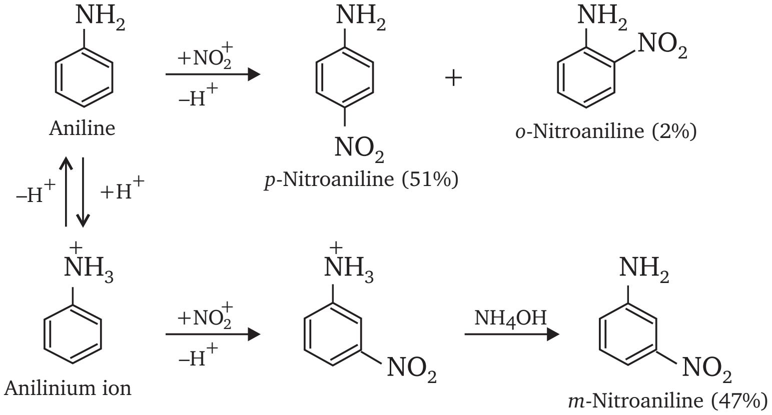
Ans. (*i*) Aniline is a weaker base than methylamine due to the presence of positive charge on nitrogen atom in three out of five resonating structures, that is why its pK_b is more than that of methylamine.

(*ii*) Ethylamine is soluble in water because it can form H-bond with water molecules whereas aniline is insoluble because of greater hydrocarbon part which makes it less polar, therefore it cannot form H-bond with water.

(*iii*) $CH_3NH_2 + H_2O \longrightarrow CH_3\overset{\oplus}{N}H_3 + OH^-$

$FeCl_3 + 3OH^- \longrightarrow \underset{\text{(reddish-brown)}}{Fe(OH)_3} + 3Cl^-$

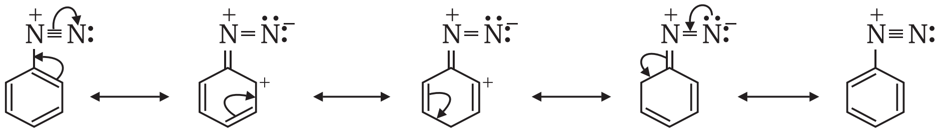
(*iv*)



Thus, nitration of aniline gives a substantial amount of *m*-nitroaniline due to protonation of the amino group.

(*v*) Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst. Due to this, nitrogen atom of aniline acquires some positive charge and hence acts as a strong deactivating group for further reaction.

(*vi*) The diazonium salts of aromatic amines are more stable than those of aliphatic amines due to the dispersal of positive charge on the benzene ring as shown below:



(*vii*) Gabriel synthesis is used for the preparation of primary amines, phthalimide on treatment with ethanolic potassium hydroxide that forms potassium salt of phthalimide, which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine.

13.4. Arrange the following:

(*i*) In decreasing order of the pK_b values:

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

(*ii*) In increasing order of basic strength:

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

(*iii*) In increasing order of basic strength:

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

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

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

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

(*v*) In increasing order of boiling point:

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

(*vi*) In increasing order of solubility in water:

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

Ans. (*i*) $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

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

(*iii*) (*a*) *p*-Nitroaniline < Aniline < *p*-Toluidine

(*b*) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

(*iv*) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$ is decreasing order of basic strength in gas phase.

(*v*) $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$ is increasing order of boiling point.

(*vi*) $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$ is increasing order of solubility in water.

13.5. How will you convert:

(*i*) Ethanoic acid into methanamine [*AI* 2017]

(*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

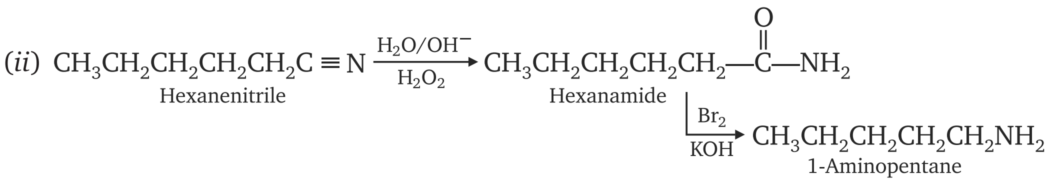
(*viii*) Propanoic acid into ethanoic acid?

Ans. (*i*)

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[\text{heat}]{NH_3} CH_3CONH_2$$

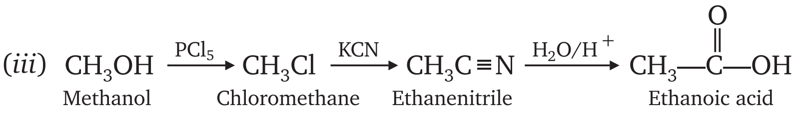
Then, $CH_3CONH_2 + Br_2 + 4KOH \longrightarrow \underset{\text{Methanamine}}{CH_3NH_2} + K_2CO_3 + 2KBr + H_2O.$

(*ii*)



$$\underset{\text{Hexanenitrile}}{CH_3CH_2CH_2CH_2CH_2C\equiv N} \xrightarrow[H_2O_2]{H_2O/OH^-} \underset{\text{Hexanamide}}{CH_3CH_2CH_2CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} \xrightarrow[KOH]{Br_2} \underset{\text{1-Aminopentane}}{CH_3CH_2CH_2CH_2CH_2NH_2}$$

(*iii*)



$$\underset{\text{Methanol}}{CH_3OH} \xrightarrow{PCl_5} \underset{\text{Chloromethane}}{CH_3Cl} \xrightarrow{KCN} \underset{\text{Ethanenitrile}}{CH_3C\equiv N} \xrightarrow{H_2O/H^+} \underset{\text{Ethanoic acid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH}$$

(*iv*) $$\underset{\text{Ethanamine}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[KMnO_4/H_2SO_4\text{ (dil.)}]{[O]} \underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[\text{heat}]{NH_3} \underset{\text{Ethanamide}}{CH_3CONH_2}$$

$$\xrightarrow[KOH]{Br_2} \underset{\text{Methanamine}}{CH_3NH_2}$$

(*v*) $$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{PCl_5} \underset{\text{Chloroethane}}{CH_3CH_2Cl} \xrightarrow{KCN} \underset{\text{Propanenitrile}}{CH_3CH_2C\equiv N} \xrightarrow{H_2O/H^+}$$

$$+ \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

(*vi*) $$\underset{\text{Methanamine}}{CH_3NH_2} \xrightarrow{HNO_2} \underset{\text{Methanol}}{CH_3OH} \xrightarrow{PCl_5} \underset{\text{Chloromethane}}{CH_3Cl} \xrightarrow{KCN} \underset{\text{Ethanenitrile}}{CH_3C\equiv N} \xrightarrow[4[H]]{Na/C_2H_5OH} \underset{\text{Ethanamine}}{CH_3CH_2NH_2}$$

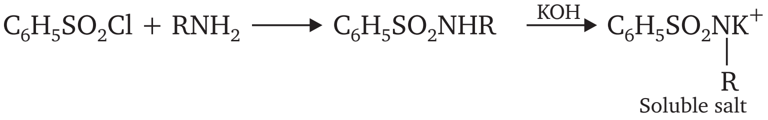
(*vii*) $$\underset{\text{Nitromethane}}{CH_3NO_2} \xrightarrow[6\ [H]]{Sn/HCl} \underset{\text{Methanamine}}{CH_3NH_2} \xrightarrow{CH_3Cl} \underset{\substack{\text{N-Methylmethanamine}\\ \text{(Dimethylamine)}}}{(CH_3)_2NH}$$

(*viii*) $$\underset{\text{Propanoic acid}}{CH_3CH_2COOH} \xrightarrow[\text{heat}]{NH_3} \underset{\text{Propanamide}}{CH_3CH_2CONH_2} \xrightarrow[KOH]{Br_2} \underset{\text{Ethanamine}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

$$\xrightarrow[KMnO_4/H_2SO_4]{[O]} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

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

Ans. Add Hinsberg reagent, $C_6H_5SO_2Cl$: Primary amines will react to form a compound which is soluble in KOH, 2° amines will form a salt which is insoluble in KOH while 3° amines will not react at all.



$$C_6H_5SO_2Cl + RNH_2 \longrightarrow C_6H_5SO_2NHR \xrightarrow{KOH} \underset{\text{Soluble salt}}{C_6H_5SO_2\underset{\underset{\displaystyle R}{|}}{N}K^+}$$

$$C_6H_5SO_2Cl + R_2NH \longrightarrow C_6H_5SO_2NR_2 \xrightarrow{KOH} \text{Insoluble}$$

$$C_6H_5SO_2Cl + R_3N \longrightarrow \text{No reaction}$$

13.7. Write short notes on the following:

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

Ans. (*i*) **Carbylamine reaction:**

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for the identification of primary amines.

$$R\text{—}NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{heat}} R\text{—}NC + 3KCl + 3H_2O$$

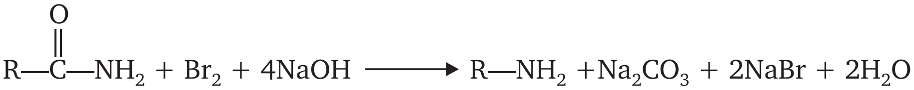
(*ii*) **Diazotisation:**

The process of converting an amine to the corresponding diazonium salt is called diazotisation.

$$\underset{\text{Aniline}}{C_6H_5NH_2} + NaNO_2 + HCl \xrightarrow{0\text{-}5°C} \underset{\substack{\text{Benzene diazonium}\\ \text{chloride}}}{C_6H_5\overset{+}{N}_2Cl^-} + NaCl + 2H_2O$$

(*iii*) **Hoffmann's bromamide reaction:**

Hoffmann's developed a method for the preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. In this degradation reaction, migration of an alkyl or aryl group takes place from the carbonyl carbon of the amide to the nitrogen atom.



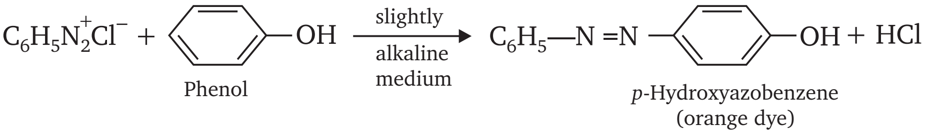
$$R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}NH_2 + Br_2 + 4NaOH \longrightarrow R\text{—}NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

(*iv*) **Coupling reaction:**

Diazonium salts react readily with phenols and dialkylanilines ($C_6H_5NR_2$) to form highly coloured derivatives known as azo compounds.

Ar – N = N – Ar

For example,



Such a reaction in which the diazonium ion is joined or coupled to the ring of a phenol or an aromatic amine are called diazo coupling reactions.

(*v*) **Ammonolysis:**

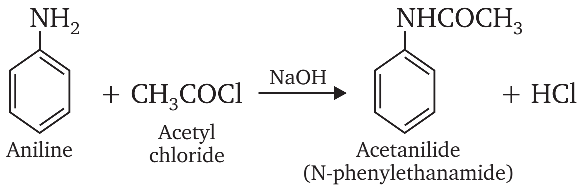
Alkyl halide reacts with ammonia to form primary amines. The reaction of ammonia with alkyl halide is known as ammonolysis.

$$CH_3Cl + NH_3 \longrightarrow CH_3NH_2 : HCl$$

$$CH_3NH_2 . HCl + NH_3 \longrightarrow CH_3NH_2 + NH_4Cl$$

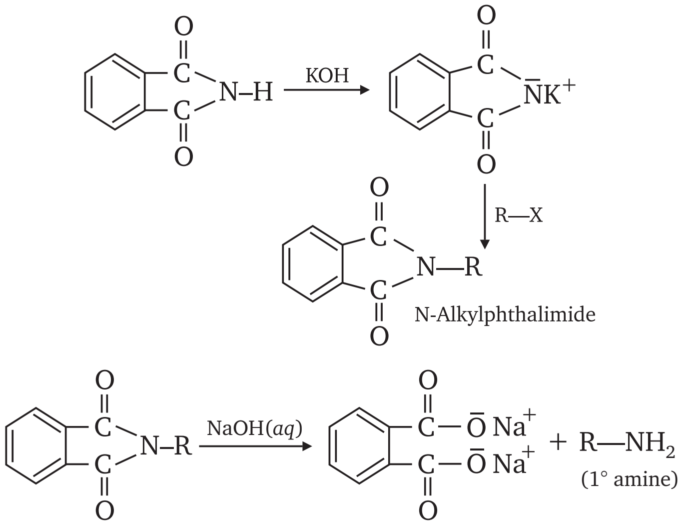
(*vi*) **Acetylation:**

The process in which an acetyl group $(CH_3-\overset{\overset{O}{\|}}{C}-)$ is introduced in an organic compound is called acetylation. It is done by the reaction with acetyl chloride or acetic anhydride.



(*vii*) **Gabriel phthalimide synthesis:**

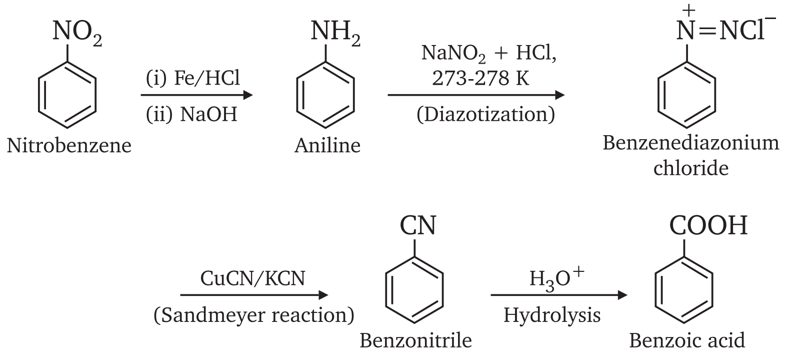
Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms a potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine.



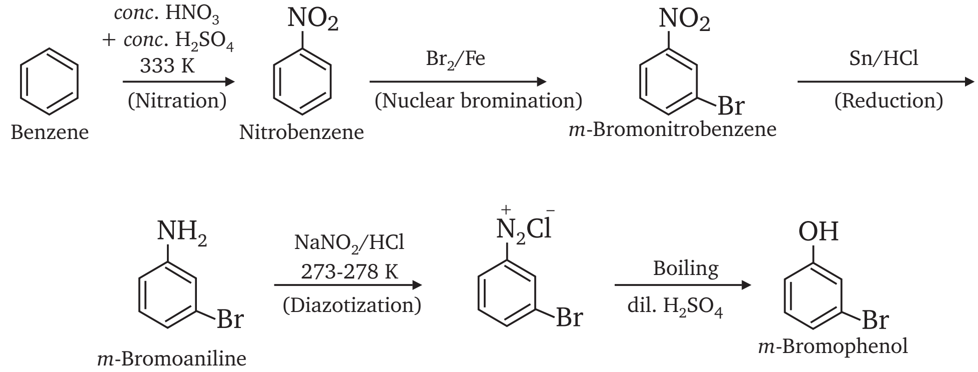
13.8. Accomplish the following conversions:

(*i*) Nitrobenzene to benzoic acid
(*ii*) Benzene to *m*-bromophenol
(*iii*) Benzoic acid to aniline
(*iv*) Aniline to 2, 4, 6-tribromofluorobenzene
(*v*) Benzyl chloride to 2-phenylethanamine
(*vi*) Chlorobenzene to *p*-chloroaniline
(*vii*) Aniline to *p*-bromoaniline
(*viii*) Benzamide to toluene
(*ix*) Aniline to benzyl alcohol.

Ans. (*i*)



(*ii*)



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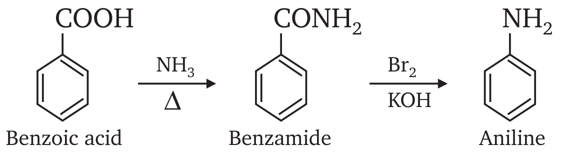

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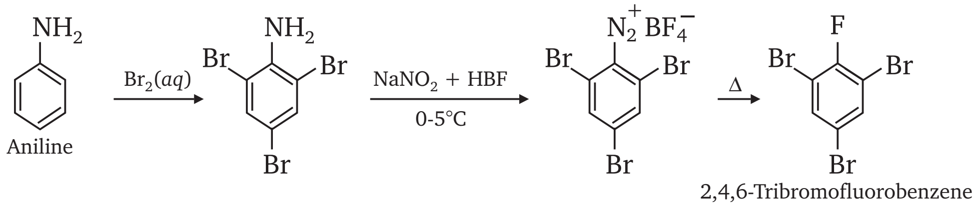

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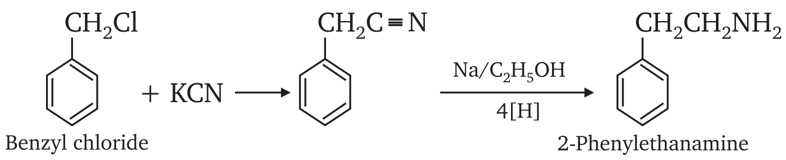
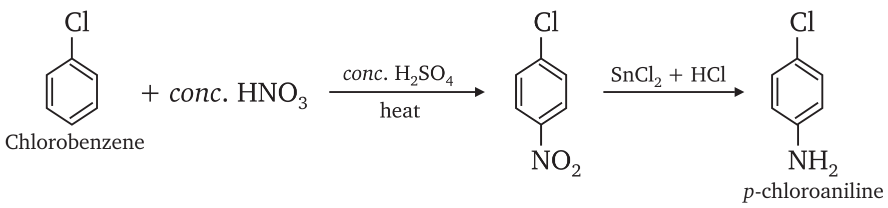
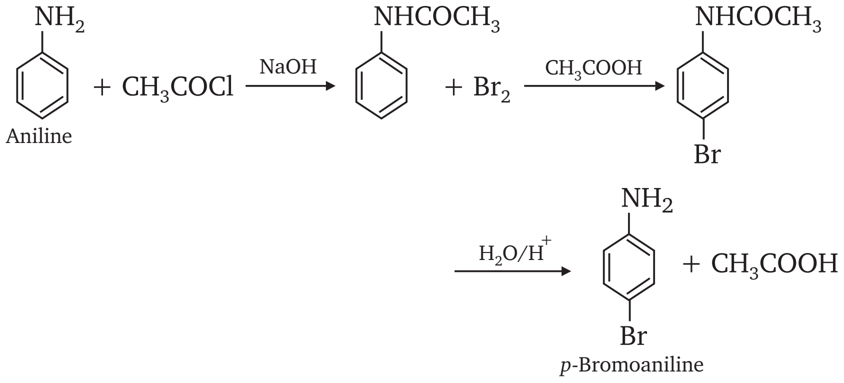


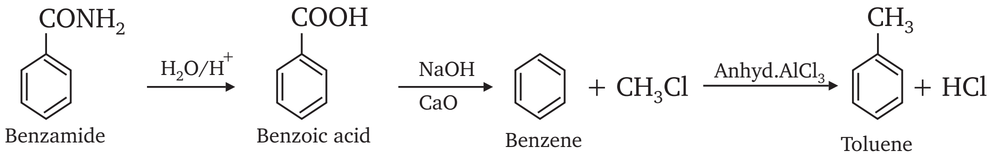
(*vi*)



(*vii*)



(*viii*)



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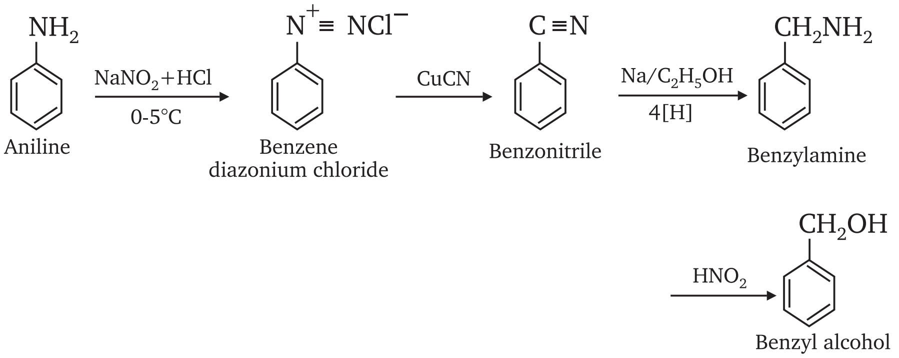


13.9. Give the structures of A, B and C in the following reactions:

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

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

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

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

Ans. (*i*)

$$\underset{\text{Iodoethane}}{CH_3CH_2I} \xrightarrow[-NaI]{NaCN} \underset{\text{Propanenitrile (A)}}{CH_3CH_2CN} \xrightarrow[\text{(Partial hydrolysis)}]{OH^-} \underset{\text{Ethanamide (B)}}{CH_3-\overset{\overset{O}{\|}}{C}-NH_2}$$

$$\xrightarrow[\text{(Hoffmann bromamide reaction)}]{NaOH + Br_2} \underset{\text{Methanamine (C)}}{CH_3-NH_2}$$

(*ii*)

$$\underset{\text{Benzenediazonium chloride}}{C_6H_5N_2Cl} \xrightarrow[\text{(Sandmeyer reaction)}]{CuCN} \underset{\text{Cyanobenzene (A)}}{C_6H_5CN} \xrightarrow[\text{Hydrolysis}]{H_2O/H^+} \underset{\text{Benzoic acid (B)}}{C_6H_5COOH}$$

$$\xrightarrow{NH_3} [C_6H_5COONH_4] \xrightarrow[-H_2o]{\Delta} \underset{\text{Benzamide (C)}}{C_6H_5CONH_2}$$

(*iii*)

$$\underset{\text{Bromoethane}}{CH_3CH_2Br} \xrightarrow{KCN} \underset{\text{Propanenitrile (A)}}{CH_3CH_2CN} \xrightarrow[\text{(Reduction)}]{LiAlH_4} \underset{\text{Propan-1-amine (B)}}{CH_3CH_2CH_2NH_2}$$

$$\xrightarrow[\text{(Diazotisation)}]{HNO_2, 0°C} [CH_3CH_2CH_2\overset{+}{N}\equiv NCl^-] \xrightarrow[-N_2\ \ -HCl]{H_2O} \underset{\text{Propanol (C)}}{CH_3CH_2CH_2OH}$$

(*iv*)

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow[\text{(Reduction)}]{Fe/HCl} \underset{\text{Aniline (A)}}{C_6H_5NH_2} \xrightarrow[273K]{NaNO_2 + HCl} \underset{\text{Benzenediazonium chloride(B)}}{C_6H_5\overset{+}{N}\equiv NCl^-} \xrightarrow[\Delta]{H_2O/H^+} \underset{\text{Phenol (C)}}{C_6H_5OH}$$

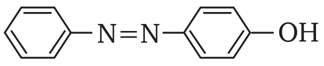
(*v*)

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[\Delta]{NH_3} \underset{\text{Ethanamide (A)}}{CH_3CONH_2} \xrightarrow[\text{(Hoffmann–bromamide reaction)}]{NaOBr} \underset{\text{Methanamine (B)}}{CH_3NH_2} \xrightarrow{NaNO_2\ /\ HCl} \underset{\text{Methanol (C)}}{CH_3OH}$$

(*vi*)

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow{Fe/HCl} \underset{\text{Aniline (A)}}{C_6H_5NH_2} \xrightarrow[273K]{HNO_2} \underset{\text{Benzenediazonium chloride (B)}}{C_6H_5-\overset{+}{N}\equiv NCl^-}$$

$$\xrightarrow[\text{(Coupling reaction)}]{C_6H_5OH}$$



p-Hydroxyazobenzene (C)

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

Ans. Step 1. To find out the structure of compounds 'B' and 'C'.

(*i*) Since compound 'C' with M.F. C_6H_7N is formed from compound 'B' on treatment with Br_2 + KOH (*i.e.*, Hoffmann bromamide reaction). Therefore, compound 'B' must be an amide and 'C' must be an amine. The only amine having the M.F. C_6H_7N is $C_6H_5NH_2$ (i.e. aniline or benzenamine).

(*ii*) Since 'C' is aniline, therefore, the amide from which it is formed must be benzamide ($C_6H_5CONH_2$). Thus, compound 'B' is benzamide:

The chemical equation showing the conversion of 'B' to 'C' is

$$\underset{\substack{\text{Benzamide (B)}\\ \text{(M.F.}=C_7H_7NO)}}{C_6H_5CONH_2} \xrightarrow[\textit{(Hoffmann bromamide reaction)}]{Br_2/KOH} \underset{\substack{\text{Benzenamine(C)}\\ \text{(M.F.}=C_6H_7N)}}{C_6H_5NH_2}$$

Step 2. To find out the structure of compound 'A'.

Since compound 'B' is formed from compound 'A' by treatment with aqueous ammonia and heating. Therefore, compound 'A' must be benzoic acid or benzenecarboxylic acid.

$$\underset{\substack{\text{Benzenecarboxylic acid}\\ \text{or Benzoic acid (A)}}}{C_6H_5COOH} \xrightarrow[(ii)\ \Delta]{(i)\ \text{Aq.}NH_3} \underset{\text{Benzamide (B)}}{C_6H_5CONH_2}$$

13.11. 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*) $C_6H_5NH_2 + H_2SO_4\ \text{(conc.)} \longrightarrow$ (*iv*) $C_6H_5N_2Cl + C_2H_5OH \longrightarrow$

(*v*) $C_6H_5NH_2 + Br_2\ (aq) \longrightarrow$ (*vi*) $C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow$

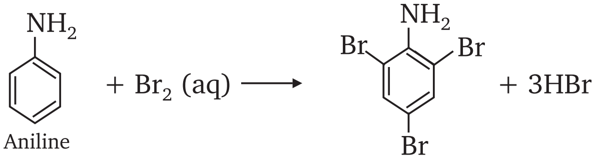
(*vii*) $C_6H_5N_2Cl \xrightarrow[(ii)\ NaNO_2/Cu,\Delta]{(i)\ HBF_4}$

Ans. (*i*) $$\underset{\text{Aniline}}{C_6H_5NH_2} + CHCl_3 + 3KOH(alc.) \xrightarrow[\text{(Carbylamine reaction)}]{\Delta} \underset{\substack{\text{Phenyl isocyanide}\\ \text{(Offensive smell)}}}{C_6H_5N{\equiv}C} + 3KCl + 3H_2OO$$

(*ii*) $$\underset{\substack{\text{Benzenediazonium}\\ \text{chloride}}}{C_6H_5N_2Cl} + H_3PO_2 + H_2O \xrightarrow[(Reduction)]{Cu^+} \underset{\text{Benzene}}{C_6H_6} + N_2 + H_3PO_3 + HCl$$

(*iii*) $$\underset{\text{Aniline}}{C_6H_5NH_2} + H_2SO_4(con\ c) \longrightarrow \underset{\text{Anilinium hydrogen sulphate}}{C_6H_5\overset{+}{N}H_3HSO_4^-}$$

(*iv*) $$\underset{\substack{\text{Benzenediazonium}\\ \text{chloride}}}{C_6H_5N_2Cl} + C_2H_5OH \xrightarrow{\text{Reduction}} \underset{\text{Benzene}}{C_6H_6} + \underset{\text{Ethanal}}{CH_3CHO} + N_2 + HCl$$

(*v*)


Aniline

2, 4, 6-Tribromoaniline

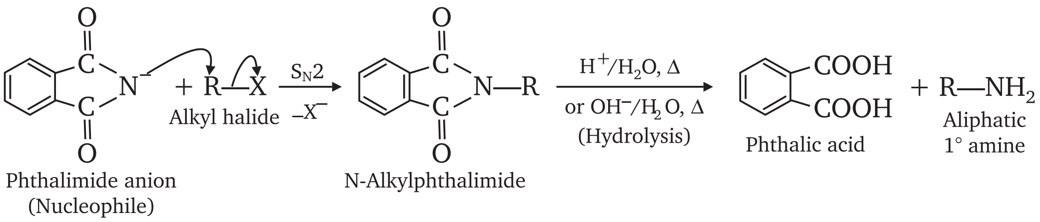
(*vi*) $$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Acetic anhydride}}{CH_3CO{-}O{-}COCH_3} \xrightarrow[\substack{\text{or Pyridine}\\ (Acetylation)}]{CH_3COOH} \underset{\text{Acetanilide}}{C_6H_5CONHCH_3} + CH_3COOH$$

(*vii*) $$\underset{\substack{\text{Benzenediazonium}\\ \text{Chloride}}}{C_6H_5N_2Cl} \xrightarrow[-HCl]{HBF_4} \underset{\substack{\text{Benzenediazonium}\\ \text{fluoroborate}}}{C_6H_5\overset{+}{N}_2BF_4^-} \xrightarrow[\Delta]{NaNO_2/Cu,} \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + BF_3 + NaF$$

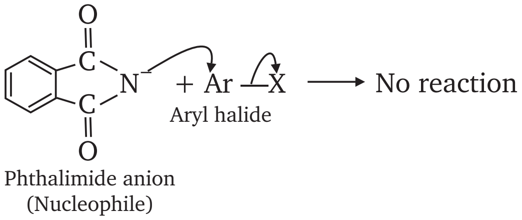
13.12. Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

Ans. The key step in the Gabriel phthalimide synthesis is a S_N2 reaction in which the nucleophile, phthalimide anion displaces the halide ion from alkyl halide to form

N-alkylphthalimide. This upon subsequent acid or alkaline hydrolysis gives the corresponding aliphatic primary amine.



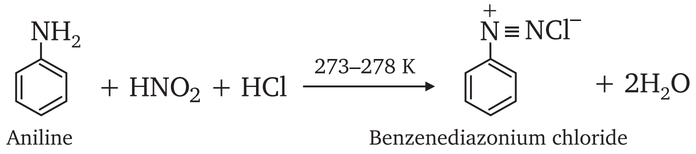
Since aryl halides do not undergo nucleophilic substitution reaction easily, therefore anylamines, *i.e.* aromatic primary amines cannot be prepared by Gabriel phthalimide reaction.



13.13. Write the reactions of

(*i*) aromatic and (*ii*) aliphatic primary amines with nitrous acid.

Ans. Aromatic primary amines react with HNO_2 at 273-278 K to form aromatic diazonium salts.



Aliphatic primary amines also react with HNO_2 at 273-278 K to form aliphatic diazonium salts. But these are unstable even at low temperature and thus decomposes readily to form a mixture of compounds consisting of alkyl chlorides, alkenes and alcohols, out of which alcohols generally predominates.

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} + HNO_2 + HCl \xrightarrow[(-2H_2O)]{273\text{–}278\ K} \underset{\substack{\text{Ethanediazonium chloride}\\(\textit{unstable})}}{[CH_3CH_2 - \overset{+}{N} \equiv N]Cl^-}$$

$$\xrightarrow{H_2O} \underset{\text{Ethanol}}{CH_3CH_2OH} + N_2 + HCl$$

13.14. Give plausible explanation for each of the following:

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

(*ii*) Why do primary amines have higher boiling point than tertiary amines?

(*iii*) Why are aliphatic amines stronger bases than aromatic amines?

Ans. (*i*) It is because $C_2H_5O^{\ominus}$ is more stable than $C_2H_5NH^{\ominus}$ because oxygen is more electronegative than nitrogen.

(*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 a H-atoms on the N-atom do not undergo H-bonding. As a result, primary amines have higher boiling point than tertiary amines of comparable molecular masses.

(*iii*) It is because there is electron withdrawing, C_6H_5 group in aromatic amines which makes them less basic than aliphatic amines in which alkyl group is electron releasing.

13.15. Account for the following: [*CBSE* 2014]

(*i*) Primary amines (R-NH_2)have higher boiling point than tertiary amines (R_3N).

(*ii*) Aniline does not undergo Friedel-Crafts reaction.

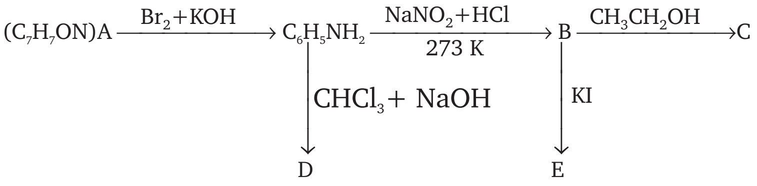
(*iii*) CH_3 $_2$NH is more basic than CH_3 $_3$N in an aqueous solution [*CBSE* 2014]

Ans. (*i*) Due to maximum intermolecular hydrogen bonding in primary amines (due to presence of more number of H-atoms), primary amines have higher boiling point in comparison to tertiary amines.

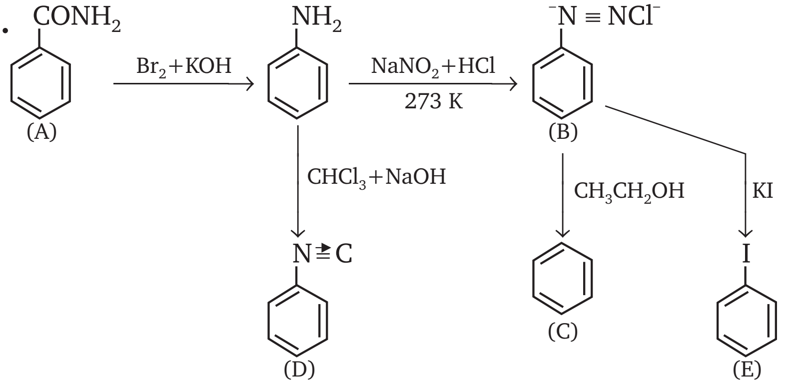
(*ii*) Aniline does not undergo Friedel-Crafts reaction due to acid-base reaction. Aniline and a Lewis Acid/Protic Acid, which is used in Friedel-crafts reaction.

(*iii*) In CH_3 $_3$N there is maximum steric hindrance and least solvation but in $(CH_3)_2$ NH the solvation is more group; di-methyl amine is still a stronger base than tri-methyl amine.

13.16. An aromatic compound 'A' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of A,B,C, D and E in the following reactions. [*CBSE* 2014]



Ans.



13.17. (*a*) Write the structures of main products when aniline reacts with the following reagents:

(*i*) Br_2/water

(*ii*) HCl

(*iii*) $(CH_3CO)_2O$/pyridine [*CBSE* 2015]

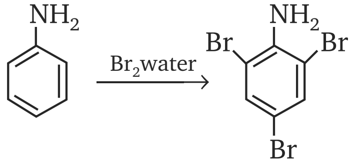
(*b*) Arrange the following in the increasing order of their boiling point:

$C_2H_5NH_2, C_2H_5OH, (CH_3)_3N$

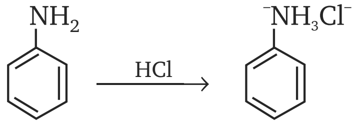
(*c*) Give a simple chemical test to distinguish between the following pair of compounds:

$(CH_3)_2NH$ and $(CH_3)_3N$

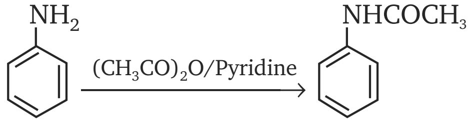
Ans. (*a*) (*i*)



(*ii*)



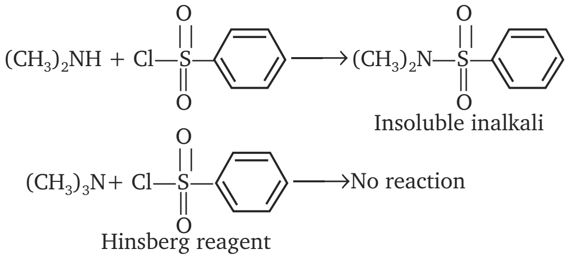
(*iii*)



(*b*) $(CH_3)_3N < C_2H_5NH_2 < C_2H_5OH$

Ethanol has higher boiling point than ethylamine because oxygen forms more extensive H-bond because of its high electronegativity than nitrogen. In trimethylamine, there is no hydrogen atom and hence has the least boiling point.

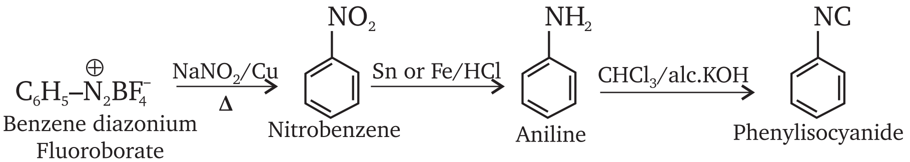
(*c*) **Hinsberg reagent :**



13.18. Write the structures of A,B and C in the following reactions:

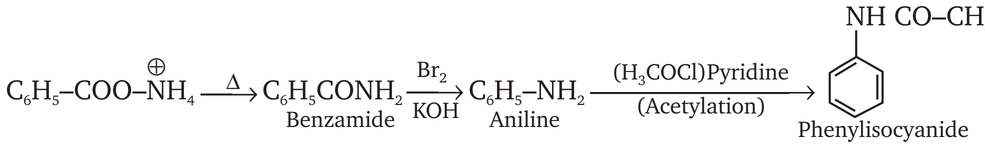
(*i*) $C_6H_5\text{–}COO^-NH_4^+ \xrightarrow{\Delta} A \xrightarrow{Br_2/KOH} B \xrightarrow{CH_3COCl/pyridine} C$

(*ii*)

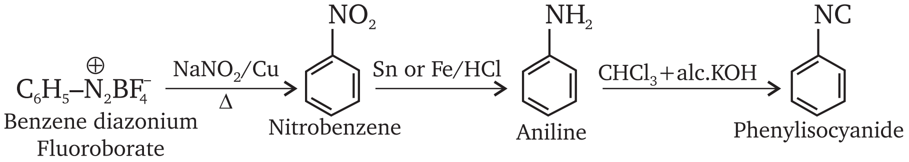


[*CBSE* 2016, 2017 *C*]

Ans. (*i*)



(*ii*)



ADDITIONAL QUESTIONS SOLVED

I. Very Short Answer Type Questions

(1 Mark)

Q1. Direct nitration of aniline is not carried out. Explain why? [*CBSE* 2009]

Ans. Direct nitration of aniline yields various oxidation products in addition to the nitro-derivatives.

Q2. Why do amines react as nucleophiles? [*AI* 2007]

Ans. It is due to the presence of lone pair of electrons on the nitrogen atom which they can donate and thus act as nucleophiles.

Q3. Mention one commercial use of N, N-Dimethyl aniline (DMA) [*AI, Foreign* 2007]

Ans. It is used as a raw material in the preparation of a number of dyes, for example methyl orange, crystal violet, malachite green, etc.

Q4. Arrange the following compounds in an increasing order of basic strength in their aqueous solution. NH_3,CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$ [*AI* 2009]

Ans. $(CH_3)_2NH > CH_3NH_2 > (CH_3)N > NH_3$

Q5. Why is an alkylamine more basic than ammonia? [*AI* 2009]

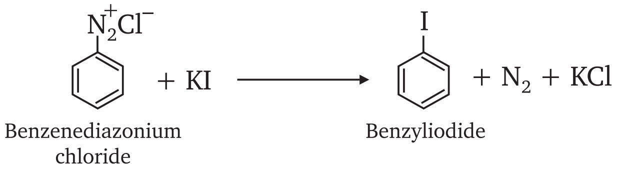
Ans. Due to dispersal of positive charge by the +*I* effect of the alkyl group, alkyl amines are stronger bases than ammonia.

Q6. Primary amines have higher boiling points than tertiary amines why? [*AI* 2008]

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

Q7. Write a chemical reaction in which the iodide ion replaces the diazonium group in a diazonium salt.

Ans. The replacement of diazonium group by iodide ion is done by treating a diazonium salt with potassium iodide as follows:



Q8. Write the chemical equations for the following chemical reaction: A primary amine is prepared from a primary alkyl halide. [*AI, Foreign* 2007]

Ans. $RX + NH_3 \longrightarrow RNH_2 + HX$

Q9. Give a chemical test to distinguish between aniline and N-methyl aniline. [*CBSE* 2006]

Ans. **Carbylamine reaction or isocyanide test:** Primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. On the contrary N-methyl aniline will not react with chloroform and ethanolic potassium hydroxide.

Q10. Give a chemical test to distinguish between aniline and ethylamine. [*AI, Foreign* 2006]

Ans. Add $NaNO_2$ and HCl. Cool it to 0-5°C. Add alkaline solution of β-napthal. Aniline will give an orange red dye whereas ethylamine will not form such a dye.

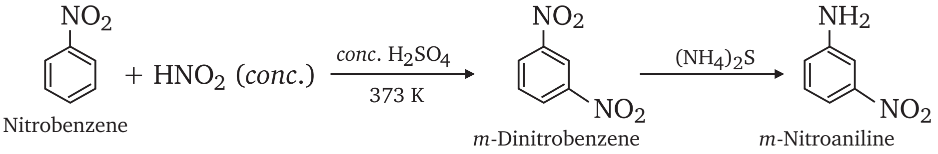
Q11. Why are aqueous solutions of amines basic in nature? [*CBSE* 2006 *C*]

Ans. $RNH_2 + H_2O \longrightarrow R\overset{\oplus}{N}H_3 + OH^-$

It is due to the formation of OH^- ions on hydrolysis of amines.

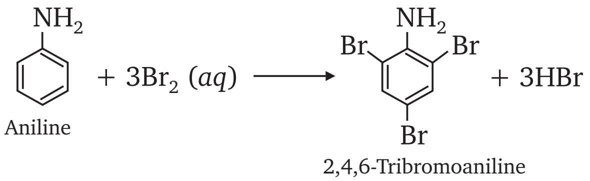
Q12. How is *m*-nitroaniline obtained from nitrobenzene? [*AI* 2006 *C*]

Ans.



Q13. State the reaction taking place when Bromine water is added to the aqueous solution of aniline. [*CBSE* 2005]

Ans.

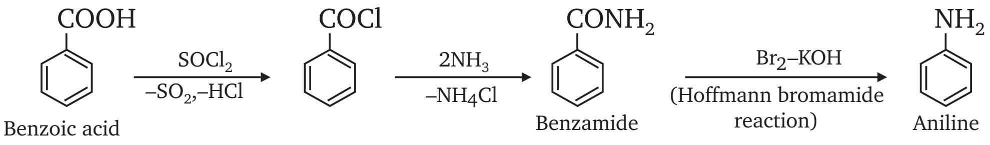


Q14. How is the basic strength of aromatic amines affected by the presence of an electron releasing group on the benzene ring? [*AI* 2005]

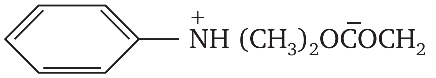
Ans. An electron releasing group increases the electron density on the N-atom. As a result, its tendency to donate an electron pair increases and hence the basicity of amines increases.

Q15. How is aniline obtained from benzoic acid? [*AI* 2005 *C*]

Ans.



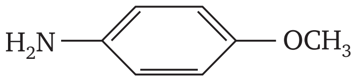
Q16. Write the IUPAC name of the following.



[*AI* 2004]

Ans. N, N-Dimethylanilinium ethanoate

Q17. Write the IUPAC name of the following:



[*AI* 2004]

Ans. 4-Methoxyaniline

Q18. Arrange the following in the order of their increasing basic character in solution: NH_3, $EtNH_2$, Et_2NH, Et_3N [*Foreign* 2004]

Ans. $NH_3 < EtNH_2 < Et_3N < Et_2NH$

Q19. Give chemical test to distinguish between $C_6H_5CH_2NH_2$ and $C_6H_5NH_2$. [*CBSE* 2004]

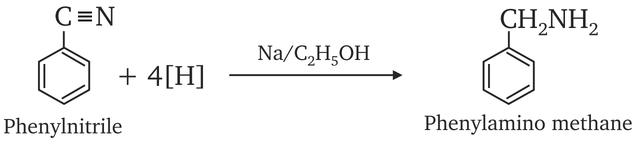
Ans. $C_6H_5CH_2NH_2$ reacts with HNO_2 at 273-278 K to give diazonium salt, which is being unstable and decomposes with brisk evolution of N_2 gas.

$$C_6H_5CH_2NH_2 \xrightarrow[273\text{–}278K]{HNO_2/HCl} \underset{\substack{\text{Benzyldiazonium}\\\text{chloride (unstable)}}}{[C_6H_5CH_2-\overset{+}{N}\equiv N]Cl^-} \xrightarrow{H_2O} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + N_2 + HCl$$

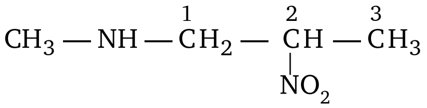
In contrast, $C_6H_5NH_2$ reacts with HNO_2 at 273-278 K to form a stable benzene diazonium chloride salt which upon treatment with an alkaline solution of β-napthol gives an orange dye.

Q20. How is phenylaminomethane have obtained from phenyl nitrile? [*AI* 2004 *C*]

Ans.



Q21. Write IUPAC name of the following:

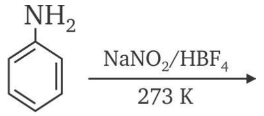


$$CH_3-NH-\overset{1}{C}H_2-\underset{NO_2}{\overset{2}{C}H}-\overset{3}{C}H_3$$

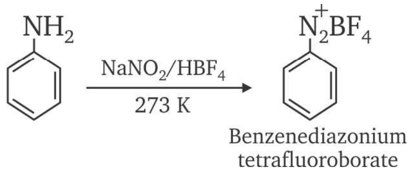
[*CBSE* 2003]

Ans. N-Methyl-2-nitropropane.

Q22. Complete the following reaction: [*AI CBSE* 2003]



Ans.



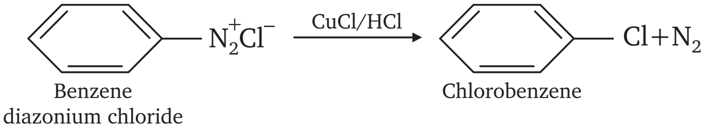
Q23. Wrtie the IUPAC name of the following compound. [*AI* 2003]

$C_6H_5\overset{+}{N}[CH_3]_3Br$

Ans. Trimethyl phenylammonium bromide

Q24. What is Sandmeyer reaction?

Ans. The reaction of a diazonium salt with CuCl/HCl or CuBr/HBr to give the corresponding chloroamine or bromo- amine is called Sandmeyer reaction.



Q25. How will you convert benzene into aniline?

Ans. $$\underset{\text{Benzene}}{C_6H_6} \xrightarrow[333\text{ K}]{conc.\ HNO_3 + conc.\ H_2SO_4} \underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow[\text{Reduction}]{Sn/HCl} \underset{\text{Aniline}}{C_6H_5NH_2}$$

Q26. Name one reagent used for the separation of primary, secondary and tertiary amines.

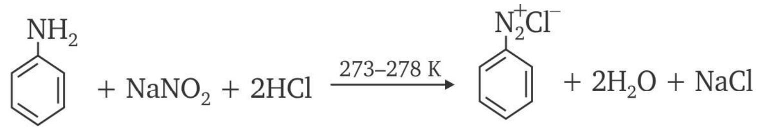
Ans. Hinsberg's reagent ($C_6H_5SO_2Cl$)

Q27. What product is formed when aniline is first diazotised and then reacted with phenol in the alkaline medium.

Ans. *p*-Hydroxyazobenzene

Q28. What is diazotisation?

Ans. The process of conversion of aromatic primary amines by treating with $NaNO_2$/HCl at 273-278 K to diazonium salts is called diazotisation.



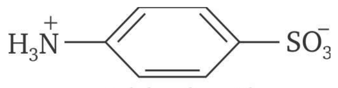
Q29. Mention two important uses of sulphanilic acid.

Ans. Sulphanilic acid is used in the manufacture of

(*i*) Dyes (*ii*) Sulpha drugs.

Q30. Give an example of a zwitter ion.

Ans.



Sulphanilic acid

Q31. Write the chemical reaction for the reduction of nitroethane by $LiAlH_4$.

Ans. $\underset{\text{Nitroethane}}{CH_3CH_2 — NO_2} \xrightarrow[(ii)\,H_3O^+]{(i)\,LiAlH_4/ether} \underset{\text{Ethanamine}}{CH_3CH_2NH_2}$

Q32. What is a coupling reaction?

Ans. Reaction of diazonium salts with phenols in basic medium (pH 9-10) and with amines in acidic medium (pH 4 - 5) to give the corresponding azodyes is called the coupling reaction.

Azodyl
(*p*-Aminoazobenzene)

Q33. Give IUPAC name of sulphanilic acid.

Ans. 4-Aminobenzene sulphonic acid

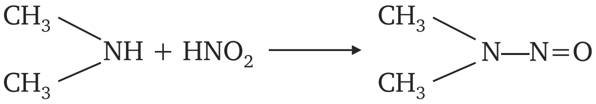
Q34. Write the IUPAC name of the following compound.

$m – NC – C_6H_4 – NH_2$

Ans. 4-Aminobenzenenitrile

Q35. An organic compound 'A' having molecular formula C_2H_7N on treatment with HNO_2 gave an oily yellow substance. Identify 'A'.

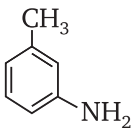
Ans.



('A')

yellow oily compound
(N-methyl-N-nitroso
ethanamine)

Q36. Give the common and IUPAC name of the following compound.



Ans. 3-Methylaniline is the IUPAC name.

Common name of the compound is *m*-Toluidine.

Q37. Name the compounds formed on heating $[(CH_3)_3\,NC_2H_5]^+OH^-$

Ans. $$\underset{\text{Ethyltrimethyl ammonium hydroxide}}{[(CH_3)_3NC_2H_5]^+OH^-} \xrightarrow{\text{heat}} \underset{\text{Ethane}}{CH_2{=}CH_2} + \underset{\text{Trimethylamide}}{(CH_3)_3N} + H_2O$$

Q38. What is Mendius reduction? Give equation.

Ans. $CH_3C{\equiv}N + 4[H] \xrightarrow{Na/C_2H_5OH} CH_3CH_2NH_2$

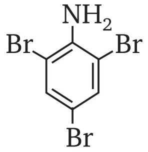
Q39. Write the IUPAC Name: $C_6H_5\,CH_2CH_2NH_2$

Ans. 2-phenylethanamine

Q40. Write the IUPAC name: $CH_3NHC_2H_5$

Ans. N-Methyl the ethanamine

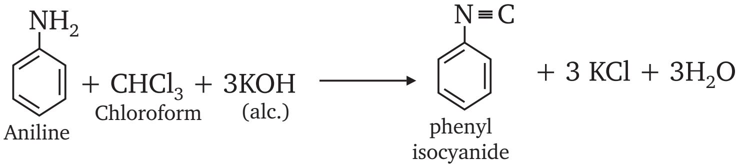
Q41. Write IUPAC name:



Ans. 2, 4, 6-Tribromobenzamine.

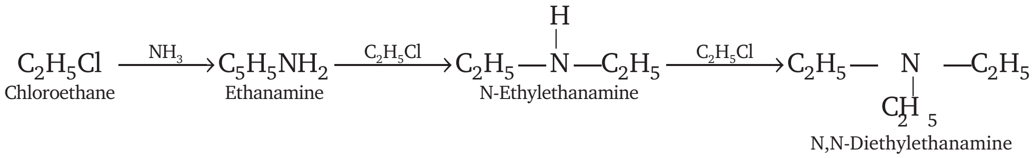
Q42. Convert aniline to phenyl isocyanide.

Ans.



Q43. Convert chloroethane to N, N-Diethylethanamine.

Ans.



$$\underset{\text{Chloroethane}}{C_2H_5Cl} \xrightarrow{NH_3} \underset{\text{Ethanamine}}{C_5H_5NH_2} \xrightarrow{C_2H_5Cl} \underset{\text{N-Ethylethanamine}}{C_2H_5{-}\overset{\overset{H}{|}}{N}{-}C_2H_5} \xrightarrow{C_2H_5Cl} \underset{\text{N,N-Diethylethanamine}}{C_2H_5{-}\underset{\underset{C_2H_5}{|}}{N}{-}C_2H_5}$$

Q44. Identify A and B in each of the following sequence:

$$CH_3COOC_2H_5 \xrightarrow{NH_3} A \xrightarrow{Br_2/KOH} B$$

Ans. $$CH_3COOC_2H_5 \xrightarrow{NH_3} \underset{\substack{\text{'A'}\\ \text{Ethanamide}}}{CH_3CONH_2} \xrightarrow{Br_2/KOH} \underset{\substack{\text{'B'}\\ \text{Methanamine}}}{CH_3NH_2}$$

II. Short Answer Type Questions

(2 or 3 Marks)

Q1. Complete and name the following reactions: [*CBSE* 2009]

(*a*) $RNH_2 + CHCl_3 + 3KOH$

(*b*) $RCONH_2 + Br_2 + 4NaOH$

Ans. (*a*) Carbylamine reaction:

$RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$

(*b*) Hoffmann bromamide degradation reaction:

$RCONH_2 + Br_2 + 4NaOH \longrightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

Q2. Predict, giving reasons the order of basicity of the following compounds:

(*i*) gaseous phase

(*ii*) in aqueous solution

$(CH_3)_3N, (CH_3)_2NH, CH_3NH_2, NH_3$

[*CBSE* 2009, *Delhi* 2012]

Ans. (*i*) In gaseous phase, basic character of amines increases with the increase in the number of electron the releasing alkyl groups due to+I effect so the trend of basic character is

$3° > 2° > 1° > NH_3$

Therefore,

$(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$

(*ii*) In aqueous phase, solvation of ammonium cation occurs by water molecules, greater the size of ion, lesser will be the solvation and lesser will be the stability of ion, So on combining +*I* effect and solvation effect. In aqueous phase trend changes to 2°>1°>3°,

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

Q3. Account for the following:

(*a*) Aniline does not undergo Friedel Crafts alkylation.

(*b*) Although NH_2 group is an ortho and *para*-directing group, nitration of aniline gives *meta* derivative along with ortho and *para* derivatives. [*CBSE* 2009, *AI* 2017]

Ans. (*a*) Aniline does not undergo Friedel Crafts reaction (alkylation and acetylation) due to salt formation with aluminium chloride. The Lewis acid which is used as a catalyst. Due to this, nitrogen of aniline acquires a positive charge and hence acts as a strong deactivating group for further reaction.

(*b*) During nitration, in strongly acidic medium aniline is protonated to form anilinium ion, which is a *meta*-directing group, so along with *o* and *p*-isomers meta isomer is also obtained.

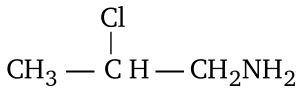
Q4. (*a*) How can you convert an amide into an amine having one carbon less than the starting compound?

(*b*) Name the reaction.

(*c*) Give the IUPAC name and structure of the amine obtained by the above method if the amide is 3-chlorobutanamide. [*CBSE* 2009]

Ans. (*a*) By reacting it with NaOH and Br_2.

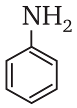
(*b*) Hoffmann bromamide degradation reaction:

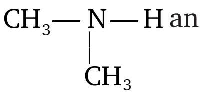
(*c*) 

$CH_3 - \overset{\overset{\displaystyle Cl}{|}}{C}H - CH_2NH_2$

2-chloropropanamine

Q5. How will you distinguish between:

(*a*)  and CH_3NH_2

(*b*) 

$CH_3 - \underset{\underset{\displaystyle CH_3}{|}}{N} - H$ and $(CH_3)_3N$

Ans. (*a*) By reacting with $NaNO_2$ and HCl at the temperature of around 0 to 5°C, Aniline will from diazonium salt. CH_3NH_2 will form methanol and bubbles of N_2 gas will come out of the solution.

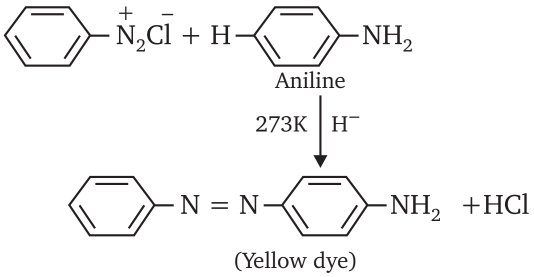
(*b*) By Hinsberg's reagent, $C_6H_5SO_2Cl$ $(CH_3)_3N$ will not react. $(CH_3)_2NH$ will form a product which is insoluble in alkali.

Q6. Explain the following giving suitable examples.

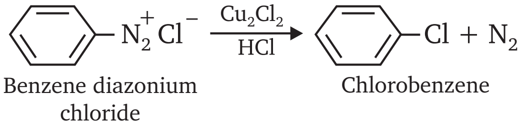
(*i*) Coupling reaction of a diazonium salt

(*ii*) Sandmeyer's reaction.

Ans. (*i*) **Coupling reaction:** It is the reaction of an aromatic diazonium salt with phenol or aromatic amine at low temperature to give a coloured azo compounds.



(*ii*) **Sandmeyer's reaction:** It is a reaction of diazonium salt with cuprous halide and hydrogen halides to get haloarenes.

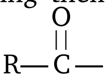


Q7. Account for any two of the following:

(*a*) Amines are basic substances while amides are neutral.

(*b*) Aromatic amines are weaker bases than aliphatic amines.

[*AI* 2007, 2017]

Ans. (*a*) In amines alkyl group is an electron releasing group which increases the electron density on nitrogen thus making them basic whereas in amides  $R-\overset{O}{\overset{||}{C}}-$ group is electron withdrawing, therefore they are neutral.

(*b*) It is because aryl group is an electron withdrawing group which decreases electron density on nitrogen atom, making them less basic whereas alkyl group is electron releasing which makes alkylamines more basic.

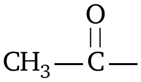
Q8. Give reasons: [*AI* 2006 *C*, 2005 *C*]

(*a*) Methyl amine is a stronger base than ammonia.

(*b*) Reactivity of $-NH_2$ group gets reduced in acetanilide.

[*AI* 2017]

Ans. (*a*) It is because methyl group is an electron releasing group and it increases the electron density on 'N' atom.

(*b*) It is because  $CH_3-\overset{O}{\overset{||}{C}}-$ group is an electron withdrawing group.

Q9. (*a*) Assign a reason for the following statements:
Alkylamines are stronger bases than arylamines.

(*b*) How would you convert methylamine into ethylamine? [*CBSE* 2005]

Ans. (*a*) It is because in arylamines the$-NH_2$ group is attached directly to the benzene ring. It results in the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation whereas alkyl group are electron releasing group.

(*b*)
$$\underset{\text{Methylamine}}{CH_3NH_2} + HNO_2 \longrightarrow CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow{KCN} CH_3C\equiv N$$

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xleftarrow[4[H]]{Na/C_2H_5OH}$$

Q10. (*a*) How will you convert an alkyl halide to a primary amine whose molecule has one carbon atom more than the used alkyl halide molecule?

(*b*) Why are amines more basic than the comparable alcohols. [*Foreign* 2005]

Ans. (*a*) $\underset{\text{Chloromethane}}{CH_3Cl} + KCN \longrightarrow \underset{\text{Ethananitrile}}{CH_3C \equiv N} \xrightarrow[4[H]]{Na/C_2H_5OH} \underset{\text{Ethanamine}}{CH_3CH_2NH_2}$

(*b*) Due less electronegativity of oxygen atom as compared to nitrogen, amines are more basic than alcohols.

Q11. Give reasons:

(*a*) Methylamine in water reacts with ferric chloride to precipitate ferric hydroxide.

(*b*) Aromatic amines are less basic than aliphatic amines.

Ans. (*a*) $CH_3NH_2 + H_3O^+ \longrightarrow CH_3\overset{\oplus}{N}H_3 + OH^-$

$FeCl_3 + 3OH^- \longrightarrow \underset{\text{(Reddish brown ppt)}}{Fe(OH)_3} + 3Cl^-$

From the above set of reactions, we can see that hydronium ion (from water) reacts with methylamine to form $CH_3.\overset{\oplus}{N}H_3$ species, and then $FeCl_3$ reacts with OH^- ions (from water) to give $Fe(OH)_3$ as a reddish brown ppt.

(*b*) **In aromatic amines:** $-NH_2$ group is directly attached to the benzene ring. It results in the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation.

Q12. Give reasons for the following observations:

(*i*) It is difficult to prepare pure amines by ammonolysis of alkyl halides.

(*ii*) Electrophilic substitution in case of aromatic amines takes place more readily than in benzene. [*AI* 2004 *C*]

Ans. (*i*) It is because ammonolysis yields a mixture of primary, secondary and tertiary amines and also a quaternary ammonium salt is formed.

(*ii*) It is because–NH_2 group is electron releasing group and it increases electron density on benzene ring.

Q13. Write one chemical equation each to exemplify the following reactions:

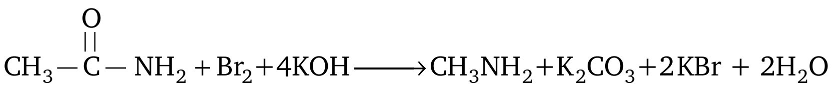
(*i*) Carbylamine reaction

(*ii*) Hoffmann bromamide reaction. [*AI* 2003, 2014]

Ans. (*i*) **Carbylamine reaction:** When primary amines react with $CHCl_3$ and KOH, it gives offensive smelling compounds isocyanide.

$$C_2H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_2H_5N \equiv C + 3KCl + H_2O$$

(*ii*) **Hoffmann's bromamide reaction:** It involves the reaction of Br_2 and *aq*. or ethanolic solution of KOH to form an amine.



$$CH_3-\overset{\overset{\displaystyle O}{||}}{C}-NH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + K_2CO_3 + 2KBr + 2H_2O$$

Q14. Illustrate the following with an example of reaction:

(*i*) Ambidient nucleophile (*ii*) Hinsberg test [*AI* 2003]

Ans. (*i*) $C_2H_5Cl + KCN \longrightarrow C_2H_5-C \equiv N + KCl$

$C_2H_5Cl + AgCN \longrightarrow C_2H_5—N \equiv C + AgCl$

These reactions show that CN^- an ambidient nucleophile.

(*ii*) **Hinsberg test:**

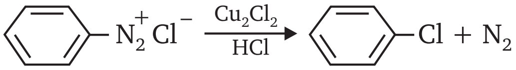
The reaction of benzenesulphonyl chloride (Hinsberg reagent), $C_6H_5SO_2Cl$ with primary amine yields N-ethyl benzenesulphonyl amide which is soluble in an alkali. In the reaction with secondary amines N, N-diethyl benzene sulphonamide is formed which is insoluble in alkali. Tertiary amines do not react with benzene sulphonyl chloride.

Q15. Illustrate the following with an example of reaction in each case.

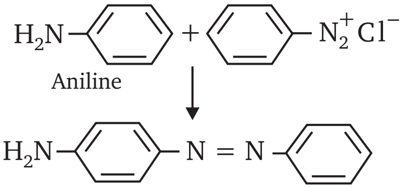
(*i*) Sandmeyer reaction

(*ii*) Coupling reaction [*Foreign* 2003]

Ans. (*i*) **Sandmeyer's reaction:** It is the reaction of arene diazonium salts with cuprous halid and hydrogen halide to form haloarenes.



(*ii*) **Coupling reaction:** It is the reaction of arene diazonium salts with aromatic amines, phenols, etc. to get azodyes.

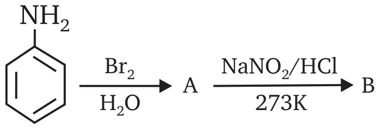


Azodye
(*p*-Aminobenzene)

Q16. Identify A and B in the following reactions:

(*i*) $C_2H_5C\equiv N \xrightarrow{LiAlH_4} A \xrightarrow{HNO_2} B$

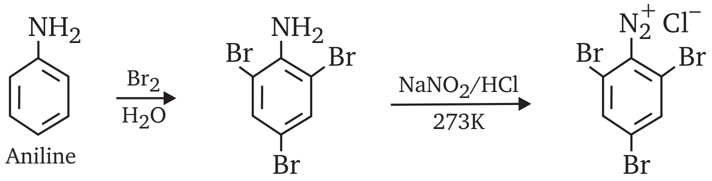
(*ii*)



[*AI, Foreign* 2003]

Ans. (*i*) $\underset{\text{Propenonitrile}}{C_2H_5C\equiv N} \xrightarrow{LiAlH_4} \underset{\text{'A' propanamine}}{C_2H_5CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{'B'Propanol}}{C_2H_5OH}$

(*ii*)



2, 4, 6-Tribromo-aniline

2, 4, 6-Tribromo-benzendiazo chloride

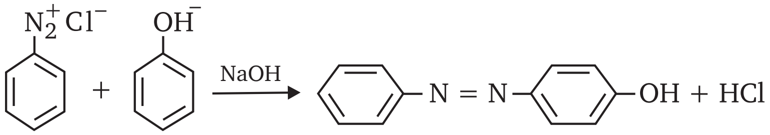
Q17. What happens when: (Write reactions only)

(*i*) Nitroethane is treated with $LiAlH_4$.

(*ii*) Diazonium chloride reacts with phenol in basic medium. [*AI* 2003 *C*]

Ans. (*i*) $\underset{\text{Nitroethane}}{C_2H_5NO_2} \xrightarrow{LiAlH_4} C_2H_5NH_2 + 2H_2O$

(*ii*)



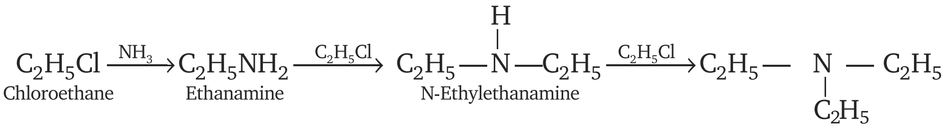
p-Hydroxyazobenzene

Q18. Write chemical equations for the following reactions:

(*i*) Reaction of ethanolic NH_3 with C_2H_5Cl.

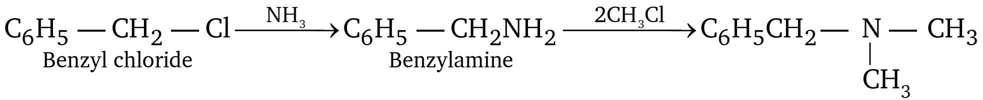
(*ii*) Ammonolysis of benzyl chloride and reaction of amine so formed with two moles of CH_3Cl.

Ans. (*i*)



$$\underset{\text{Chloroethane}}{C_2H_5Cl} \xrightarrow{NH_3} \underset{\text{Ethanamine}}{C_2H_5NH_2} \xrightarrow{C_2H_5Cl} \underset{\text{N-Ethylethanamine}}{C_2H_5-\overset{\displaystyle H}{\overset{|}{N}}-C_2H_5} \xrightarrow{C_2H_5Cl} \underset{\text{N,N-Diethylethanamine}}{C_2H_5-\underset{\underset{\displaystyle C_2H_5}{|}}{N}-C_2H_5}$$

(*ii*)



$$\underset{\text{Benzyl chloride}}{C_6H_5-CH_2-Cl} \xrightarrow{NH_3} \underset{\text{Benzylamine}}{C_6H_5-CH_2NH_2} \xrightarrow{2CH_3Cl} \underset{\text{N, N-Dimethylphenyl Methanamine}}{C_6H_5CH_2-\underset{\underset{\displaystyle CH_3}{|}}{N}-CH_3}$$

Q19. Write chemical equation for the following conversions:

(*i*) $CH_3CH_2—Cl$ into $CH_3CH_2CH_2—NH_2$

(*ii*) $C_6H_5—CH_2—Cl$ into $C_6H_5CH_2CH_2NH_2$

Ans. (*i*) $\underset{\text{Chloroethane}}{CH_3CH_2Cl} \xrightarrow{\text{Ethanolic NaCN}} \underset{\text{Propanenitrile}}{CH_3CH_2C \equiv N} \xrightarrow{\text{reduction}} \underset{\text{Propan-1-amine}}{CH_3CH_2CH_2NH_2}$

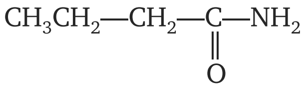
(*ii*) $\underset{\text{(Benzylchloride)}}{\underset{\text{Chloro phenyl methane}}{C_6H_5CH_2Cl}} \xrightarrow{\text{Ethanolic NaCN}} \underset{\text{(Benzyl cyanide)}}{\underset{\text{Phenyl ethane nitrile}}{C_6H_5CH_2C \equiv N}} \xrightarrow{H_2/Ni} \underset{\text{2–Phenyl ethanamine}}{C_6H_5—CH_2—CH_2—NH_2}$

Q20. Write structure and IUPAC names of

(*i*) The amide which gives propana mine by Hoffmann bromamide reaction.

(*ii*) The amine produced by the Hoffmann's degradation of benzamide.

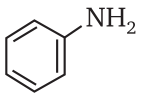
Ans. (*i*) Propanamine contains three carbon atoms. Hence, the amide molecule must contain four carbon atoms. The structure and IUPAC name of the starting amide with four carbon atoms:



$CH_3CH_2—CH_2—\underset{\underset{O}{\|}}{C}—NH_2$

Butanamide

(*ii*) Benzamide is an aromatic amide containing seven carbon atoms. Hence, the amine formed from benzamide is an aromatic primary amine containing six carbon atoms.



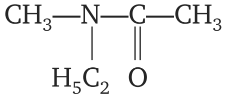
Aniline or benzenamine

Q21. (*a*) Give plausible explanation for each of the following:

(*i*) The presence of a base is needed in the ammonolysis of alkyl halides.

(*ii*) Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis.

(*b*) Write the IUPAC name of:



$CH_3—\underset{\underset{H_5C_2}{|}}{N}—\underset{\underset{O}{\|}}{C}—CH_3$

[*CBSE* 2009]

Ans. (*a*) (*i*) To get free amines the obtained ammonium salt is treated with a strong base.

(*ii*) Aromatic primary amines cannot be prepared by this method because aryl halides does not undergo nucleophilic substitution with the anion formed by phthalimide.

(*b*) (*iii*) N-ethyl—N— methylethana-mide.

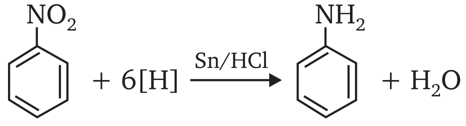
Q22. How would you achieve the following conversions:

(*i*) Nitrobenzene to aniline

(*ii*) An alkyl halide to a quarternary ammonium salt.

(*iii*) Aniline to benzonitrile.

Ans. (*i*)



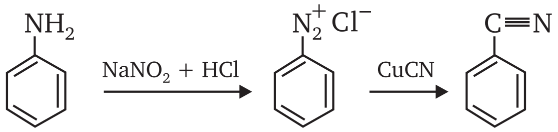
Nitrobenzene Aniline

(*ii*)

$$\underset{\text{Chloroethane}}{C_2H_5Cl+NH_3} \longrightarrow \underset{\text{Ethanamine}}{C_2H_5NH_2} \xrightarrow{C_2H_5Cl} \underset{\text{N-Ethylethanamine}}{(C_2H_5)_2NH} \xrightarrow{C_2H_5Cl}$$

$$\underset{\text{N,N-Diethyl ethanamine}}{(C_2H_5)_3N} \xrightarrow{C_2H_5Cl} \underset{\text{Tetraethyl Ammonium chloride}}{(C_2H_5)_4N^+ Cl}$$

(*iii*)



Aniline Benzonitrile

Q23. What happens when (write reactions only).

(*i*) Nitropropane is treated with $LiAlH_4$.

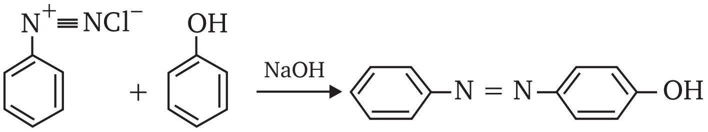
(*ii*) Ethyl isocyanide undergoes hydrolysis.

(*iii*) Benzene diazonium chloride reacts with phenol in basic medium.

Ans. (*i*) $CH_3CH_2CH_2NO_2 \xrightarrow{LiAlH_4} CH_3CH_2CH_2NH_2 + 2H_2O$

(*ii*) $C_2H_5N \quad C + 2H_2O \qquad\qquad C_2H_5NH_2 + HCOOH$

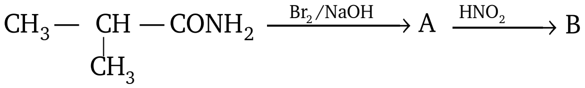
(*iii*)



Phenol p-Hydroxyazobenzene

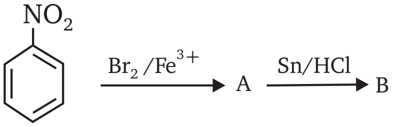
Q24. Identify A and B in the following reactions: [*AI Foreign* 2003]

(*i*)



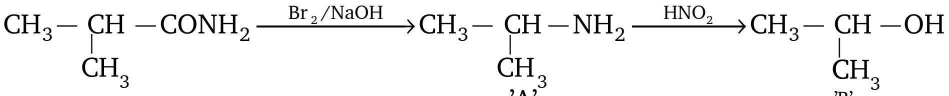
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CONH_2 \xrightarrow{Br_2/NaOH} A \xrightarrow{HNO_2} B$

(*ii*)



(*iii*) $CH_3CN \xrightarrow{H^+/H_2O} A \xrightarrow{LiAlH_4} B \quad \xrightarrow{\rightrightarrows H^+}$

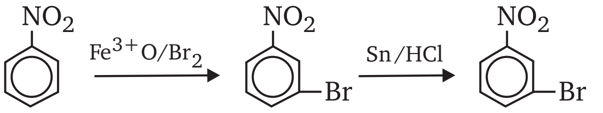
Ans. (*i*)



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CONH_2 \xrightarrow{Br_2/NaOH} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH_2 \xrightarrow{HNO_2} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH$

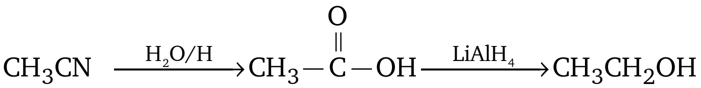
'A' 'B' propan-2-ol

(*ii*)



Nitrobenzene 'A' *m*-Bromoaniline

(*iii*)

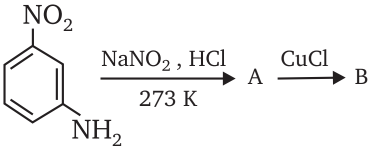


$CH_3CN \xrightarrow{H_2O/H} CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-OH \xrightarrow{LiAlH_4} CH_3CH_2OH$

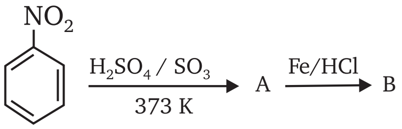
Ethanenitrile Ethanoic acid 'A' Ethanol 'B'

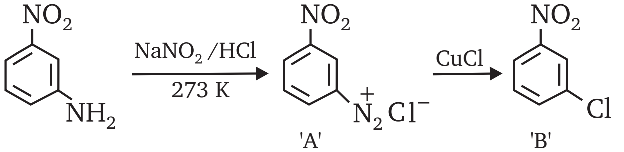
Q25. Identify A and B in the following reactions: [*AI Foreign* 2003]

(*i*)



(*ii*) $CH_3CH_2CH_2Br \xrightarrow{NaCN} A \xrightarrow{LiAlH_4} B$

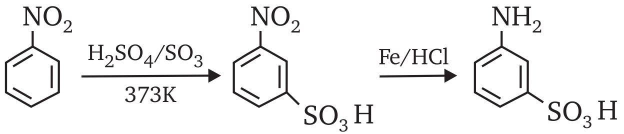
(*iii*) 

Ans. (*i*) 

'A' 'B'

3-Chloronitrobenzene

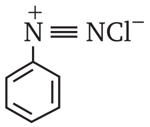
(*ii*) $CH_3CH_2CH_2Br \xrightarrow{NaCN} \underset{'A'}{CH_3CH_2CH_2C \equiv N} \xrightarrow{LiAlH_4} \underset{\text{Butanamine 'B'}}{CH_3CH_2CH_2CH_2NH_2}$

(*iii*) 

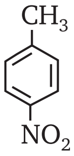
'A' 'B'

Q26. Write structures for the following compounds:

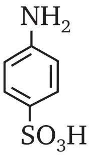
(*a*) Benzene diazonium chloride (*b*) *p*-Nitrotoluene (*c*) Sulphanilic acid.

Ans. (*a*) 

Benzene diazonium chloride

(*b*) 

p-Nitrotoluene

(*c*) 

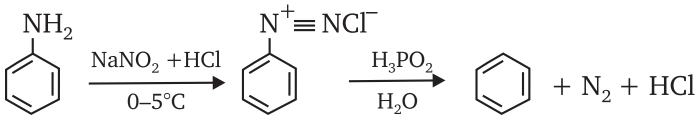
Sulphanilic aicd

Q27. Write reactions and conditions required for the following conversions:

(*i*) Aniline to benzene (*ii*) Methylamine to methylcyanide

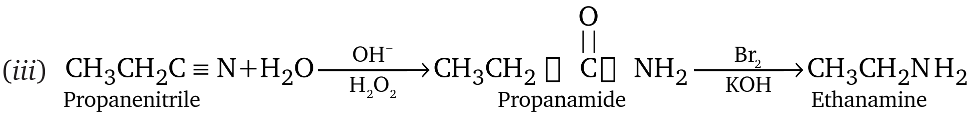
(*iii*) Propanenitrile to ethylamine (*iv*) *m*-Bromoaniline to *m*-bromophenol

(*v*) Nitrobenzene to 2, 4, 6-tribromoaniline.

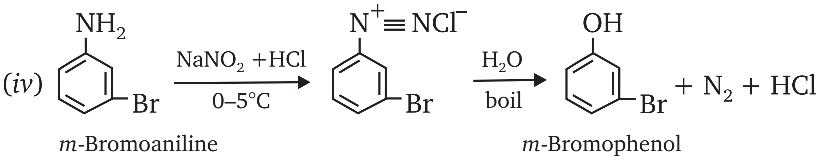
Ans. (*i*) 

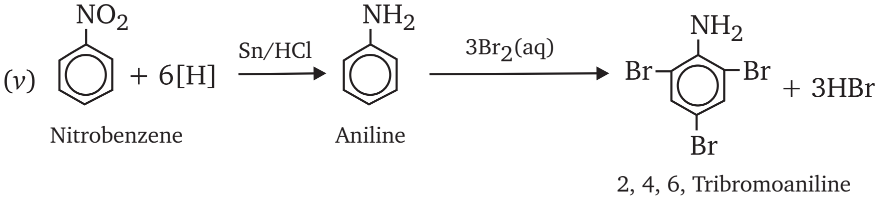
Aniline Benzene

(*ii*) $\underset{\text{Methylamine}}{CH_3NH_2} \xrightarrow{HNO_2} CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow{KCN} \underset{\text{Methyl cyanide}}{CH_3C \equiv N}$



$$(iii)\ \underset{\text{Propanenitrile}}{CH_3CH_2C\equiv N} + H_2O \xrightarrow[H_2O_2]{OH^-} \underset{\text{Propanamide}}{CH_3CH_2-\overset{\overset{\displaystyle O}{||}}{C}-NH_2} \xrightarrow[KOH]{Br_2} \underset{\text{Ethanamine}}{CH_3CH_2NH_2}$$





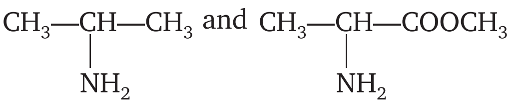
Q28. A compound 'A' of molecular formula $C_3H_7O_2N$ on reaction with Fe and conc. HCl gives a compound 'B' of molecular formula C_3H_9N. Compound 'B' on treatment with $NaNO_2$ and HCl gives another compound 'C' of molecular formula C_3H_8O. The compound 'C' has molecular formula, C_3H_8O. The compound 'C' gives effervescence with Na. On oxidation with CrO_3, the compound 'C' gives a saturated aldehyde containing three carbon atoms. Deduce the structures of A, B and C and write the equations for the reaction involved.

Ans.

$$\begin{tikzcd}
\underset{\substack{\text{'A'}\\ \text{1-Nitropropane}}}{CH_3CH_2CH_2NO_2} \arrow[r, "Fe/HCl"] & \underset{\substack{\text{'B'}\\ \text{1-Propanamine}}}{CH_3CH_2CH_2NH_2} \arrow[r, "NaNO_2/HCl"] & \underset{\substack{\text{'C'}\\ \text{Propan-1-ol}}}{CH_3CH_2CH_2OH} \arrow[d, "Na"] \\
 & & \underset{\text{Sodium propoxide}}{CH_3CH_2CH_2ONa + H_2}
\end{tikzcd}$$

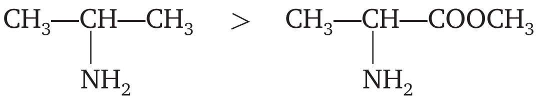
$$\underset{\substack{\text{'C'}\\ \text{1-Propanol}}}{CH_3CH_2CH_2OH} \xrightarrow{CrO_3} \underset{\text{Propanal}}{CH_3CH_3CHO}$$

Q29. Which amine in the following pair is a stronger base? Give reasons.



$$CH_3-\underset{\underset{\displaystyle NH_2}{|}}{CH}-CH_3 \text{ and } CH_3-\underset{\underset{\displaystyle NH_2}{|}}{CH}-COOCH_3$$

Ans.



$$CH_3-\underset{\underset{\displaystyle NH_2}{|}}{CH}-CH_3 > CH_3-\underset{\underset{\displaystyle NH_2}{|}}{CH}-COOCH_3$$

It is because ester group is an electron withdrawing group, it reduces the electron density on the nitrogen atom.

Q30. A compound 'x' having molecular formula C_3H_7NO reacts with Br_2 in the presence of KOH to give another compound 'y'. The compound 'y' reacts with HNO_2 to form ethanol and N_2 gas. Identify the compounds *x* and *y* and write the reactions involved.

Ans. $$\underset{\substack{\text{'x'}\\ \text{Propanamide}}}{CH_3CH_2CONH_2} + Br_2 + 4KOH \longrightarrow \underset{\substack{\text{'y'}\\ \text{Ethanalamine}}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH+N_2+H_2O}$$

Q31. An aliphatic compounds (A) with molecular formula C_2H_3Cl on treatment with AgCN give two isomeric compounds of unequal amounts with the molecular formula C_3H_3N.

The minor among the two products on complete reduction with H_2 in the presence of Ni, gives a compounds 'B' with molecular formula C_3H_3N. Identify the compounds 'A', 'B' and write the reactions involved.

Ans. $$\underset{\substack{\text{Chloroethene}\\ \text{(A)}}}{CH_2{=}CH{-}Cl} + AgCN \longrightarrow \underset{\text{Minor}}{CH_2{=}CH{-}C\equiv N} + \underset{\text{Major}}{CH_2{=}CH{-}\overset{+}{N}\equiv \overset{-}{C}}$$

$$\underset{\text{Propenenitrile}}{CH_2{=}CH - C\quad N} \quad \overset{H_2}{\underset{Ni}{}} \quad \underset{\substack{\text{1 propanamine}\\ \text{'B'}}}{CH_3 - CH_2 - CH_2 - NH_2}$$

Q32. Iodomethane reacts with KCN to form a major product 'A'. Compound 'A' on reduction in the presence of $LiAlH_4$ forms a higher amine 'B'. Compounds B on treatment with $CuCl_2$ forms a blue coloured complex 'C'. Identify the compounds 'A' , 'B' and 'C'.

Ans. $$\underset{\text{Iodomethane}}{CH_3I} + KCN \longrightarrow CH_3C\equiv N \xrightarrow{LiAlH_4} \underset{\substack{\text{Ethylamine}\\ \text{'B'}}}{CH_3CH_2NH_2} + CuCl_2 \; \big\downarrow \; \underset{\text{Blue complex}}{[Cu(CH_3CH_2NH_2)_4]Cl_2}$$

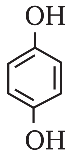
Q33. An organic compound 'A' having molecular formula C_3H_5N on hydrolysis gave another compound 'B'. The compound 'B' on treatment with HNO_2 gave ethyl alcohol. 'B' on warming with $CHCl_3$ and alcoholic caustic potash gave an offensive smelling substance 'C'. Identify 'A', 'B' and 'C'.

Ans. $$\underset{\text{'A'}}{C_2H_5N\equiv C} + 2H_2O \xrightarrow{H^+} \underset{\text{'B'}}{C_2H_5NH_2} \xrightarrow{HNO_2} C_2H_5OH + N_2 + H_2O$$

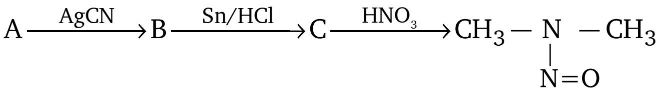
$$\underset{\text{'B'}}{CH_3CH_2NH_2} + CHCl_3 + 3KOH \longrightarrow \underset{\text{'C'}}{CH_3CH_2N\equiv C} + 3KCl + 3H_2O$$

Q34. Identify compounds A, B and C in the following reactions:

(*a*) $A \xrightarrow[NaOH]{Br_2} B \xrightarrow{HNO_2} C \xrightarrow[I_2]{\text{Red P}} CH_3I$

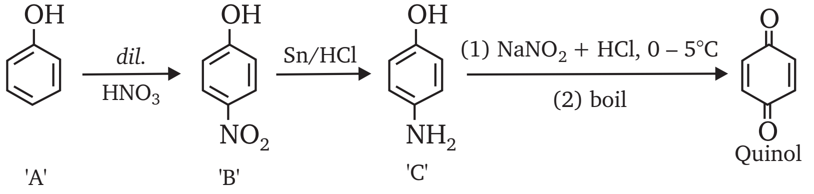
(*b*) $A \xrightarrow{\text{dil.}HNO_3} B \xrightarrow{Sn/HCl} C \xrightarrow[\text{boil}]{NaNO_3+HCl}$ 

(*c*) $A \xrightarrow{\Delta} B \xrightarrow[KOH]{Br_2} C \xrightarrow{HNO_2} C_2H_5OH$

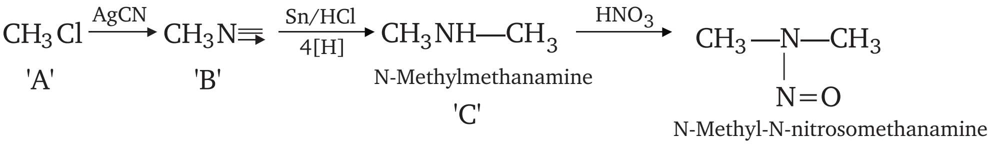
(*d*) 

$A \xrightarrow{AgCN} B \xrightarrow{Sn/HCl} C \xrightarrow{HNO_3} CH_3-\underset{\underset{N=O}{|}}{N}-CH_3$

Ans. (*a*) $\underset{\text{'A'}}{CH_3CONH_2} \xrightarrow[NaOH]{Br_2} \underset{\text{'B'}}{CH_3NH_2} \xrightarrow{HNO_2} \underset{\text{'C'}}{CH_3OH} \xrightarrow[I_2]{\text{Red P}} CH_3I$

(*b*) 

(*c*) $\underset{\text{'A'}}{CH_3CH_2COONH_4} \xrightarrow{\text{heat}} \underset{\text{'B'}}{CH_3CH_2CONH_2} \xrightarrow[KOH]{Br_2} \underset{\text{'C'}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH}$

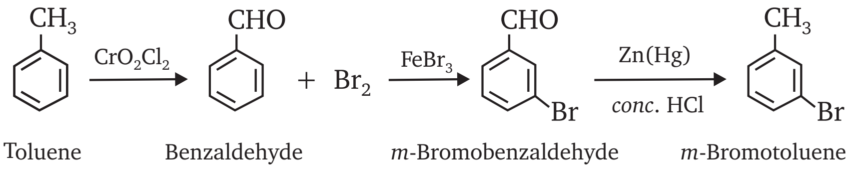
(*d*) 

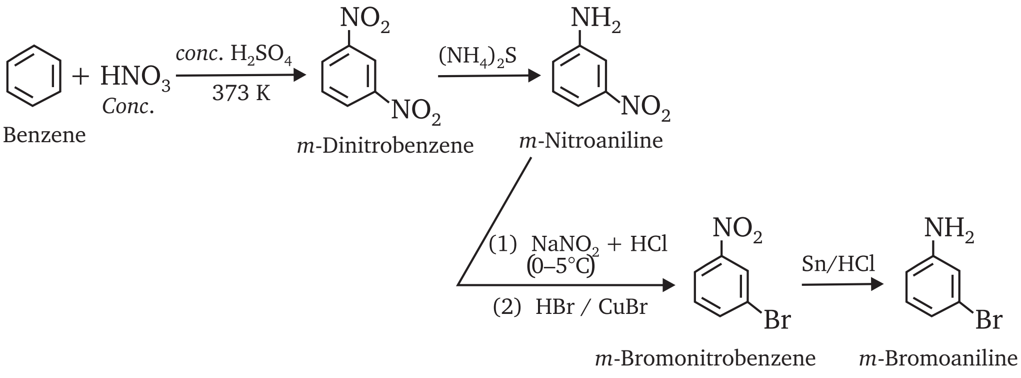
$\underset{\text{'A'}}{CH_3Cl} \xrightarrow{AgCN} \underset{\text{'B'}}{CH_3N\equiv} \xrightarrow[4[H]]{Sn/HCl} \underset{\text{'C'}}{\underset{\text{N-Methylmethanamine}}{CH_3NH—CH_3}} \xrightarrow{HNO_3} \underset{\text{N-Methyl-N-nitrosomethanamine}}{CH_3—\underset{\underset{N=O}{|}}{N}—CH_3}$

Q35. Carry out following conversions:

(*i*) Toluene to *m*-bromotoluene

(*ii*) Benzene to *m*-bromoaniline.

Ans. (*i*) 

(*ii*) 

III. Long Answer Type Questions *(5 Marks)*

Q1. (*a*) How is aniline obtained from benzene?

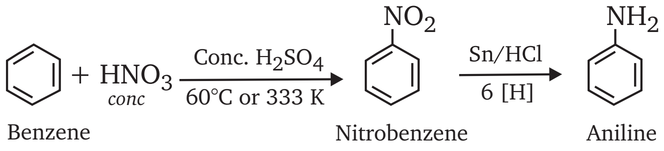
(*b*) Why are the secondary amines more basic than primary amines? Explain.

(*c*) Write the complete chemical set of reactions for the conversion of aniline to sulphanilic acid.

(*d*) Mention two important uses of sulphanilic acid.

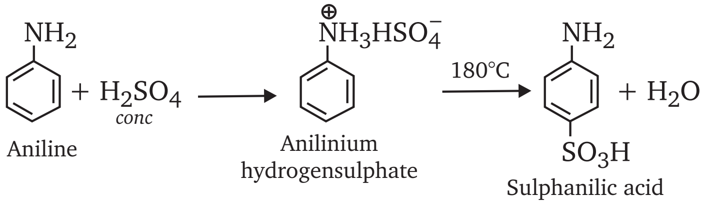
(*e*) Write a chemical reaction of aniline which may distinguish it from ethylamine. [*CBSE* 2003]

Ans. (*a*)



(*b*) In secondary amines, there are two alkyl groups which are electron releasing and increase electron density on nitrogen more than in primary amines in which there is only one alkyl group.

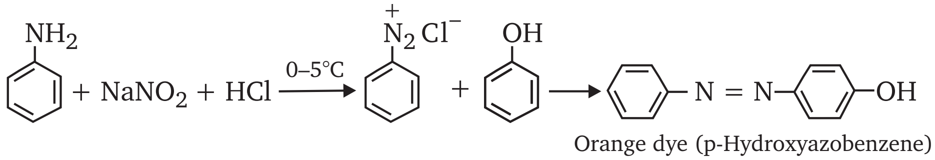
(*c*)



(*d*) (*i*) It is used for the manufactures of dyes.

(*ii*) It is used for the manufacture of sulpha drugs.

(*e*) **Azo dye test.** Aniline diazotises in HNO_2. Diazonium salt forms an orange dye with alkaline solution of phenol.



Ethylamine liberates N_2 gas on reaction with HNO_2 as:

$C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + N_2 + H_2O$

Q2. How is benzenediazonium chloride prepared in solution? Give an account of its coupling reaction with phenols and amines.

Ans. Aromatic diazonium salts are generally prepared by adding a cold aqueous solution of sodium nitrite to the solution or suspension of a primary aromatic amine in an acid at 273-278 K.

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{-}278\text{ K}} \underset{\text{Benzene diazonium chloride}}{C_6H_5N_2^+Cl^-} + NaCl + 2H_2O$$

Arenediazonium salts react with highly reactive (*i.e.*, electron rich) aromatic compounds such as phenols and amines to form brightly coloured azo compounds. Coupling with phenols occurs in basic medium (pH 9-10) while that of amines occurs in faintly acidic medium (pH 4-5) at 273-278 k.

IV. Value Based Questions

Q1. Sushil's friend want to play Holi with synthetic colours, eggs, muddy water, etc. Sunil persuades his friends to play Holi with natural colours. He reminds them that last time one of their friends had developed skin allergy after playing Holi with synthetic colours. It took him a long time to recover. Sushil's friends agreed and prepared natural colours using leaves and flowers.

(*i*) Mention the values shown by Sushil.

(*ii*) Write the names and reaction of preparation of two azo dyes (synthetic).

(*iii*) Write the name of two pigments present in natural colours.

Ans. (*i*) Self awareness, Critical thinking.

(*ii*) Benzenediazoniumchloride reacts with β–napthol to form an azo dye by coupling reaction (Benzene diazonium chloride reacts with phenol to form *p*–hydroxyazobenzene.

(*iii*) Xanthophylls, lutein.

Q2. You are staying near a fertiliser factory. In the middle of night there is a leakage of ammonia which is detected by its smell. Within 10 minutes you find the smell is intolerable.

(*a*) What would you do as first aid against this gas spill accident for self and neighbor?

(*b*) What value do you derive from this?

Ans. (*a*) Ammonia is highly soluble in water. It is detected by its characteristic fishy odor. Hence one needs to keep a wet handkerchief on the nose to stop inhaling the gas. Also one can help his neighbours with his suggestions.

(*b*) Alertness to tackle disasters for society.

V. HOTS Questions

Q1. Aniline gets coloured on standing in air for a long time. Why?

Ans. Due to strong electron-donating effect (+*R* effect) of NH_2 group, the electron density on the benzene ring increases. As a result, aniline is easily oxidised on standing in air for a long time to form coloured products.

Q2. CH_3CONH_2 is a weaker base than $CH_3CH_2NH_2$.

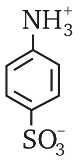
Ans. Due to resonance, the lone pair of electrons on the nitrogen atom in CH_3CONH_2 is delocalised over the keto group. There is no such effect in $CH_3CH_2NH_2$. Due to reduction in electron density on N-atom of CH_3CONH_2, it is a weaker base than $CH_3CH_2NH_2$.

Q3. Aromatic primary amines can't be prepared by Gabriel phthalimide synthesis.

Ans. The preparation of aromatic primary amines (Aniline) by Gabriel phthalimide reaction requires the treatment of potassium. phthalimide with C_6H_5Cl or C_6H_5Br, which is a nucleophilic substituion reaction. Since aryl halides do not undergo nucleophilic substitution under ordinary laboratory conditions, therefore C_6H_5Cl or C_6H_5Br does not react with potassium phthalimide to give N-phenl phthalimide and hence aromatic primary amines can't be prepared by this method.

Q4. Sulphanilic acid has acidic as well as basic group; but it is soluble in alkali but insoluble in mineral acids. Explain.

Ans. Sulphanilic acid exists in the form of a Zwitter ion as:



In the presence of *dil*. NaOH, the weakly acidic —NH$_3^+$ group transfers its H$^+$ to OH$^-$ to form a soluble salt *p* NH$_2$C$_6$H$_4$SO$_3^-$ Na$^+$. On the other hand, —SO$_3^+$ group is a very weak base and does not accept H$^+$ from *dil*. HCl to form NH$_3$C$_6$H$_4$SO$_3$H and therefore it does dissolve in *dil*. HCl.

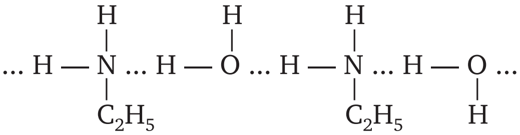
Q5. Explain why:

(*i*) Ethylamine is soluble in water but aniline is not.

(*ii*) Aniline does not undergo Friedel Crafts reaction.

(*iii*) Diazonium salts of aromatic amines are more stable than that of aliphatic amines.

Ans. (*i*) Ethyl amine dissolves in water due to the formation of H-bonding with water molecules:



$$\ldots H - \underset{C_2H_5}{\underset{|}{\overset{\overset{H}{|}}{N}}} \ldots H - \overset{\overset{H}{|}}{O} \ldots H - \underset{C_2H_5}{\underset{|}{\overset{\overset{H}{|}}{N}}} \ldots H - \underset{\underset{H}{|}}{O} \ldots$$

However in aniline due to larger hydrophobic alkyl part, extent of H-bonding decreases considerably and hence insoluble in water.

(*ii*) Aniline being a Lewis base reacts with Lewis acids like AlCl$_3$ or FeCl$_3$ to form a salt. Thus, nitrogen atom of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction which does not undergo Friedel-Crafts reaction.

(*iii*) The diazonium salts of aromatic amines are more stable than those of aliphatic amines due to the dispersal of positive charge on the benzene ring as shown below: