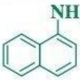
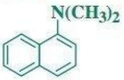
Amines

NCERT Intext Questions

Q. 1. Classify the following amines as primary, secondary or tertiary:

(a) 

(b) 

(c) $(C_2H_5)_2CHNH_2$ **(d)** $(C_2H_5)_2NH$

Ans. (a) Primary (b) Tertiary (c) Primary (d) Secondary

Q. 2. (a) Write structures of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$.

(b) Write IUPAC names of all the isomers.

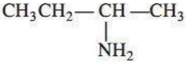
(c) What type of isomerism is exhibited by different pairs of amines?

Ans. (a) and (b)

Primary amines:

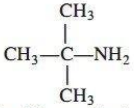
(i) $CH_3CH_2CH_2CH_2NH_2$

Butanamine

(ii) 

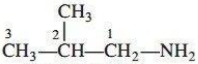
$CH_3CH_2—\underset{\displaystyle NH_2}{\underset{|}{CH}}—CH_3$

Butan-2-amine

(iii) 

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

2-methylpropan-2-amine

(iv) 

$\overset{3}{CH_3}—\overset{\displaystyle CH_3}{\overset{2\,|}{CH}}—\overset{1}{CH_2}—NH_2$

2-Methylpropanamine

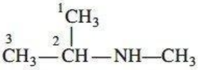
Secondary amines:

(v) $CH_3—CH_2—NH—CH_2CH_3$

N-Ethylethanamine

(vi) $CH_3CH_2CH_2—NH—CH_3$

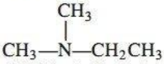
N-Methylpropanamine

(vii) 

$\overset{3}{CH_3}—\overset{\displaystyle {}^{1}CH_3}{\overset{2\,|}{CH}}—NH—CH_3$

N-Methylpropan-2-amine

Tertiary amine:

(viii) 

$CH_3—\overset{\displaystyle CH_3}{\overset{|}{N}}—CH_2CH_3$

N, N-Dimethylethanamine

(c) **Chain isomers:** (i) & (iv), (ii) & (iii)

Position isomers: (i) & (ii), (vi) & (vii)

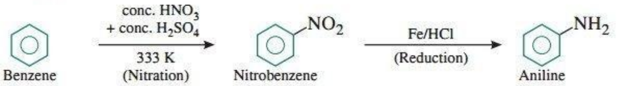
Metamers: (v) & (vi), (v) and (vii)

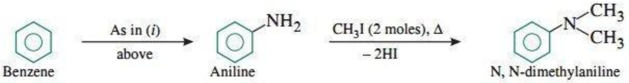
Functional isomers: All primary amines are functional isomers of secondary and tertiary amines and vice-versa.

Q. 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*) $\underset{\text{1,6-Dichlorobutane}}{Cl—(CH_2)_4—Cl} \xrightarrow{\text{Ethanolic NaCN}} N \equiv C—(CH_2)_4—C \equiv N$

$$\xrightarrow{H_2/Ni} \underset{\text{Hexane-1, 6-diamine}}{H_2N—CH_2—(CH_2)_4—CH_2—NH_2}$$

or

$$\underset{\text{Hexane-1, 6-diamine}}{H_2N—(CH_2)_6—NH_2}$$

Q. 4. Arrange the following in increasing order of their basic strength:

(*a*) $C_2H_5NH_2$, $C_6H_5NH_2$, NH_3 , $C_6H_5CH_2NH_2$, $(C_2H_5)_2NH$

(*b*) $C_2H_5NH_2$, $(C_2H_5)_2$ NH, $(C_2H_5)_3N$, $C_6H_5NH_2$

(*c*) CH_3NH_2 , $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$

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

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

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

Q. 5. Complete the following acid–base reactions and name the products:

(*i*) $CH_3CH_2CH_2NH_2$ + HCl ⟶

(*ii*) $(C_2H_5)_3N$ + HCl ⟶

Ans. (*i*) $\underset{n\text{-Propylamine}}{CH_3CH_2CH_2\ddot{N}H_2} + H—Cl \longrightarrow \underset{n\text{-Propylammonium chloride}}{CH_3CH_2CH_2\overset{+}{N}H_3\,Cl^-}$

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

Q. 6. Write the reactions of the final alkylation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.

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

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

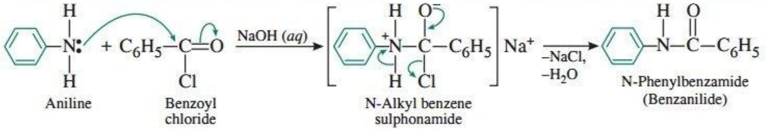
$C_6H_5\ddot{N}HCH_3 \xrightarrow[Na_2CO_3]{+CH_3I} \underset{\text{N, N-Dimethylaniline}}{C_6H_5N(CH_3)_2}$

$C_6H_5\ddot{N}(CH_3)_2 + CH_3—I \longrightarrow \underset{\text{N, N, N-Trimethylanilinium iodide}}{C_6H_5\overset{+}{N}(CH_3)_3I^-}$

$2C_6H_5\overset{+}{N}(CH_3)_3\,I^- + Na_2CO_3 \longrightarrow \underset{\text{N, N, N-Trimethylanilinium carbonate}}{[C_6H_5\overset{+}{N}(CH_3)_3]_2CO_3^{2-}} + 2NaI$

Q. 7. Write chemical reaction of aniline with benzoyl chloride and write the name of the product obtained.

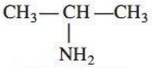
Ans.



Q. 8. Write structures of different isomers corresponding to the molecular formula, C_3H_9N. Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.

Ans. In all, four structural isomers are possible. These are as follows:

Primary amines: $\underset{\text{Propan-1-amine}}{CH_3CH_2CH_2NH_2}$

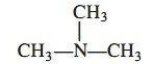


$CH_3—\underset{NH_2}{CH}—CH_3$

Propan-2-amine

Secondary amines: $CH_3—NH—C_2H_5$
N-Methylethanamine

Tertiary amines:



$(CH_3)_3N$
N,N-dimethylmethanamine

Only primary amines react with HNO_2 to liberate N_2 gas

$$\underset{\text{Propan-1-amine}}{CH_3CH_2CH_2NH_2} + HNO_2 \longrightarrow \underset{\substack{\text{Propan-1-ol}\\\text{(Major product)}}}{CH_3CH_2CH_2OH} + H_2O + N_2$$

$$(CH_3)_2CH—NH_2 + HNO_2 \longrightarrow (CH_3)_2CHOH + N_2 + H_2O$$

Propan-2-amine

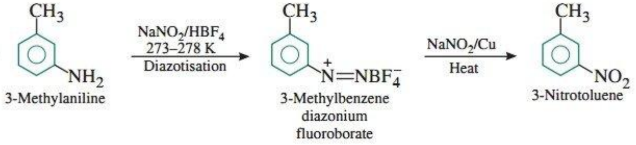
Propan-2-ol
(Major product)

Q. 9. Convert:

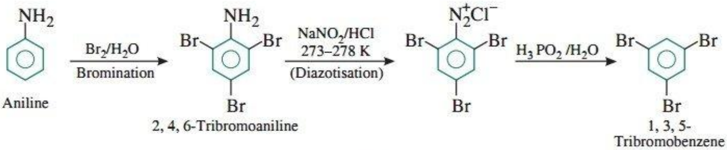
(*i*) 3-Methylaniline into 3-nitrotoluene

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

Ans. (*i*)



(*ii*)



NCERT Exercises

Q. 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*-$BrC_6H_4NH_2$

Ans. (*i*) Propan-2-amine (primary)

(*ii*) Propan-1-amine (primary)

(*iii*) N-Methylpropan-2 amine (secondary)

(*iv*) 2-Methylpropan-2-amine (primary)

(*v*) N-Methylbenzenamine or N-Methylaniline (secondary)

(*vi*) N-Ethyl-N-methylethanamine (tertiary)

(*vii*) 3-Bromobenzenamine or 3-Bromoaniline (primary).

Q. 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*) Methylamine is 1° amine, therefore, it gives carbylamine test, *i.e.*, when heated with an alcoholic solution of KOH and $CHCl_3$ it gives an offensive smell of methyl carbylamine. In contrast, dimethylamine is a secondary amine and hence does not give this test.

$$\underset{\substack{\text{Methylamine}\\(1^\circ\text{ amine})}}{CH_3NH_2} + CHCl_3 + \underset{\text{(alc.)}}{3KOH} \xrightarrow{\text{Heat}} \underset{\substack{\text{Methyl carbylamine}\\\text{(offensive smell)}}}{CH_3NC} + 3KCl + 3H_2O$$

$$\underset{\substack{\text{Dimethylamine}\\(2^\circ\text{ amine})}}{(CH_3)_2NH} \xrightarrow[\text{Heat}]{CHCl_3/KOH(\text{alc.})} \text{No reaction.}$$

(*ii*) By Hinsberg's reagent (benzenesulphonyl chloride). The amine is treated with benzenesulphonyl chloride and shaken with alkali solution when the two amines behave in different ways:

(*a*) Secondary amines form dialkyl benzenesulphonamide which does not react with alkali and hence it remains insoluble.

(*b*) Tertiary amines do not react with benzenesulphonyl chloride at all.

$$C_6H_5SO_2Cl + \underset{\substack{\text{Secondary}\\\text{amine}}}{HNR_2} \longrightarrow \underset{\substack{\text{Dialkyl}\\\text{Benzenesulphonamide}}}{C_6H_5SO_2NR_2} \xrightarrow{KOH} \text{No reaction}$$

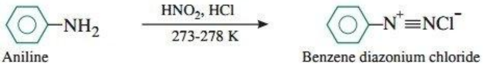
$$C_6H_5SO_2Cl + \underset{\substack{\text{Tertiary}\\\text{amine}}}{R_3N} \longrightarrow \text{No reaction}$$

(*iii*) Ethylamine is primary aliphatic amine while aniline is a primary aromatic amine. These may be distinguished by the azo dye test: Refer to Points to remember 12(*c*).

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

$$\underset{\text{Benzylamine}}{C_6H_5CH_2NH_2} \xrightarrow[HCl]{HNO_2} \underset{\text{Unstable}}{[C_6H_5CH—\overset{+}{N} \equiv NCl^-]} \xrightarrow[\text{Decomposes}]{H_2O} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + N_2\uparrow + HCl$$

Aniline 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*) 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 secondary amine does not give this test.

$$\underset{\substack{\text{Aniline}\\(1^\circ\text{ amine})}}{C_6H_5NH_2} + CHCl_3 + \underset{\text{(alc.)}}{3KOH} \xrightarrow{\Delta} \underset{\substack{\text{Phenyl isocyanide}\\\text{(offensive)}}}{C_6H_5NC} + 3KCl + 3H_2O$$

$$\underset{\text{N-Methylaniline }(2^\circ\text{ amine})}{C_6H_5—NH—CH_3} \xrightarrow{CHCl_3/KOH(\text{alc.})} \text{No reaction.}$$

Q. 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.

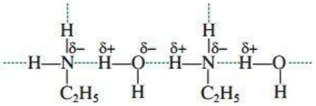
(*v*) Aniline does not undergo Friedel–Crafts reaction. *[CBSE 2020 (56/5/1)]*

(*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*) In aniline due to resonance, the lone pair of electrons on the N-atom are delocalised over the benzene ring. Due to this, electron density on the nitrogen decreases. On the other hand, in CH_3NH_2, +I-effect of CH_3 increases the electron density on the N-atom. Consequently aniline is a weaker base than methylamine and hence its pK_b value is higher than that of methylamine.

(*ii*) Ethylamine dissolves in water because it forms H-bonds with water molecules as shown below:



In aniline, due to the large hydrocarbon part the extent of H-bonding decreases considerably and hence aniline is insoluble in water.

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

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

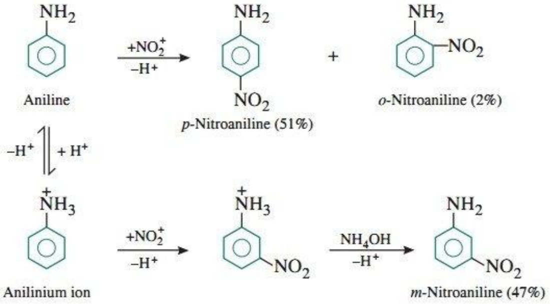
These OH^- ions combine with Fe^{3+} ions present in H_2O to form brown precipitate of hydrated ferric oxide.

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

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

(*iv*) Nitration is usually carried out with a mixture of conc. HNO_3 and conc. H_2SO_4. In presence of these acids, most of aniline gets protonated to form anilinium ion. Thus, in presence of acids, the reaction mixture consists of aniline and anilinium ion. The $—NH_2$ group in aniline is *o, p*-directing and activating while the $—\overset{+}{N}H_3$ group in anilinium ion is *m*-directing and deactivating.

Nitration of aniline mainly gives *p*-nitroaniline. On the other hand, the nitration of anilinium ion gives *m*-nitroaniline.



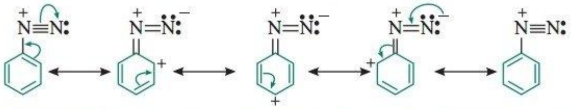
Thus, nitration of aniline gives a substantial amount of *m*-nitroaniline due to protonation of the amino group.

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

$$\underset{\text{Lewis base}}{C_6H_5NH_2} + \underset{\text{Lewis acid}}{AlCl_3} \longrightarrow C_6H_5\overset{+}{N}H_2AlCl_3^-$$

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

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



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

Q. 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:

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2$ NH 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, $(CH_3)_2$ NH, $C_2H_5NH_2$

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

(*v*) $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

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

Q. 5. How will you convert

(*i*) Ethanoic acid to methanamine

(*ii*) Hexanenitrile to 1-aminopentane

(*iii*) Methanol to ethanoic acid

(*iv*) Ethanamine to methanamine

(*v*) Ethanoic acid to propanoic acid

(*vi*) Methanamine to ethanamine

(*vii*) Nitromethane to dimethylamine

(*viii*) Propanoic acid to ethanoic acid?

Ans. (*i*)

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow{SOCl_2} \underset{\text{Ethanoyl chloride}}{CH_3COCl} \xrightarrow{NH_3(\text{excess})} \underset{\text{Ethanamide}}{CH_3CONH_2} \xrightarrow[\text{(Hoffmann bromamide reaction)}]{Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$$

(*ii*)

$$\underset{\text{Hexanenitrile}}{CH_3(CH_2)_4CN} \xrightarrow[\text{Hydrolysis}]{H_3O^+} \underset{\text{Hexanoic acid}}{CH_3(CH_2)_4COOH} \xrightarrow{PCl_5} \underset{\text{Hexanoyl chloride}}{CH_3(CH_2)_4COCl}$$

$$\xrightarrow[\Delta]{NH_3(\text{excess})} CH_3(CH_2)_4CONH_2 \xrightarrow{Br_2/KOH} \underset{\text{Aminopentane}}{CH_3(CH_2)_4NH_2}$$

(*iii*)

$$\underset{\text{Methanol}}{CH_3OH} \xrightarrow{PCl_5} CH_3Cl \xrightarrow{KCN(\text{alc.})} \underset{\text{Ethanenitrile}}{CH_3CN} \xrightarrow{H_3O^+} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

(*iv*)

$$\underset{\text{Ethanamine}}{CH_3CH_2NH_2} \xrightarrow[-N_2,\,-H_2O]{HONO} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

$$\xrightarrow[\text{(oxidation)}]{CrO_3-H_2SO_4} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[\Delta]{NH_3} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[\text{(Hoffmann bromamide reaction)}]{Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$$

(*v*)

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[\text{Reduction}]{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{P/I_2} \underset{\text{Ethyl iodide}}{CH_3CH_2I} \xrightarrow[-\,KI]{+\,KCN} \underset{\text{Ethyl cyanide}}{CH_3CH_2CN}$$

$$\xrightarrow{H_2O/H^+} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

(*vi*)

$$\underset{\text{Methanamine}}{CH_3NH_2} \xrightarrow[-N_2,\,-H_2O]{HONO} \underset{\text{Methanol}}{CH_3OH} \xrightarrow{P/I_2} \underset{\text{Methyl iodide}}{CH_3I} \xrightarrow[-\,KI]{KCN} \underset{\text{Ethanenitrile}}{CH_3CN} \xrightarrow[\text{Reduction}]{Na/C_2H_5OH} \underset{\text{Ethanamine}}{CH_3CH_2NH_2}$$

(*vii*)

$$\underset{\text{Nitromethane}}{CH_3NO_2} \xrightarrow{Sn/HCl} \underset{\text{Methylamine}}{CH_3NH_2} \xrightarrow{CHCl_3\,+\,KOH} \underset{\text{Methyl isocyanide}}{CH_3NC} \xrightarrow[\text{(Reduction)}]{Na/C_2H_5OH} \underset{\text{Dimethylamine}}{CH_3NHCH_3}$$

(*viii*)

$$\underset{\text{Propanoic acid}}{CH_3CH_2COOH} \xrightarrow{NH_3} CH_3CH_2COONH_4 \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{Propionamide}}{CH_3CH_2CONH_2}$$

$$\xrightarrow{Br_2/KOH} \underset{\text{Ethanamine}}{CH_3CH_2NH_2} \xrightarrow[-N_2,\,-H_2O]{HONO} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

$$\xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

Q. 6. **Describe the method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved.**

Ans. Refer to Points to remember 12(*a*).

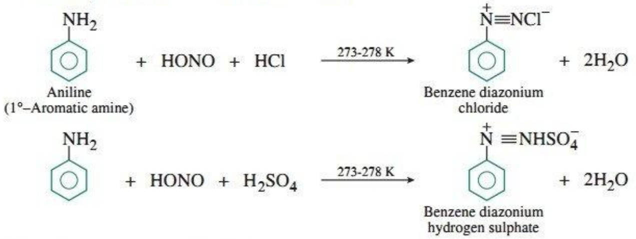
Q. 7. **Write short notes on the following:**

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

Ans. (*i*) Refer to Points to remember 10(*e*).

(*ii*) **Diazotisation reaction:** When a cold solution of a primary aromatic amine in a dilute mineral acid (HCl or H_2SO_4) is treated with a cold solution of nitrous acid (generated *in situ* by the action of dil. HCl or dil. H_2SO_4 on $NaNO_2$) at 273-278 K, arene diazonium salt is formed. This reaction is called diazotization reaction. For example,

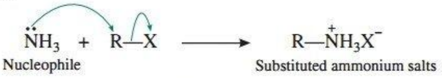
$$NaNO_2 + HCl \longrightarrow HONO + NaCl$$



(*iii*) Refer to Points to remember 10(*b*).

(*iv*) Refer to Points to remember 9(*b*).

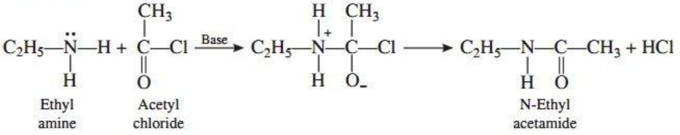
(*v*) **Ammonolysis:** The process of cleavage of the C—X bond by ammonia molecule is known as ammonolysis.



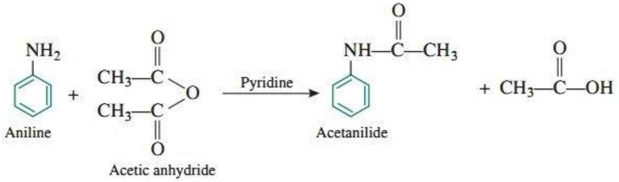
$$\underset{\text{Nucleophile}}{\ddot{N}H_3} + R-X \longrightarrow \underset{\text{Substituted ammonium salts}}{R-\overset{+}{N}H_3X^-}$$

$$\underset{(1°)}{R-NH_2} \xrightarrow{+R-X} \underset{(2°)}{R_2NH} \xrightarrow{+RX} \underset{(3°)}{R_3N} \xrightarrow{+RX} \underset{\substack{\text{Quaternary}\\ \text{ammonium salt}}}{R_4N^+X^-}$$

(*vi*) **Acetylation:** The process of introducing an acetyl group ($CH_3-\overset{\overset{O}{\|}}{C}-$) into a molecule is called acetylation.



$$\underset{\substack{\text{Ethyl}\\ \text{amine}}}{C_2H_5-\underset{H}{\ddot{N}}-H} + \underset{\substack{\text{Acetyl}\\ \text{chloride}}}{\overset{CH_3}{\underset{O}{C}}-Cl} \xrightarrow{\text{Base}} C_2H_5-\overset{H}{\underset{H}{\overset{+}{N}}}-\overset{CH_3}{\underset{O^-}{C}}-Cl \longrightarrow \underset{\substack{\text{N-Ethyl}\\ \text{acetamide}}}{C_2H_5-\underset{H}{N}-\underset{O}{C}-CH_3} + HCl$$

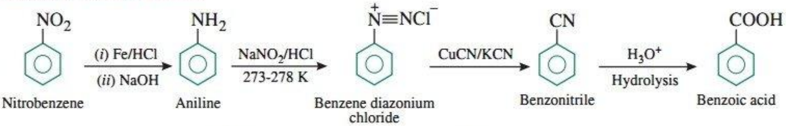


(*vii*) Refer to Points to remember 10(*a*).

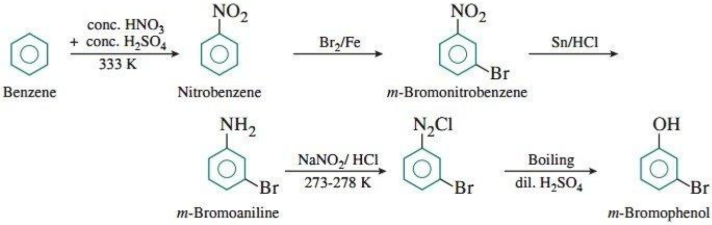
Q. 8. Accomplish the following conversions:

- **(*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**

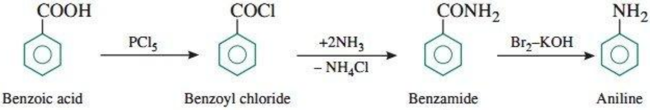
Ans. (*i*)



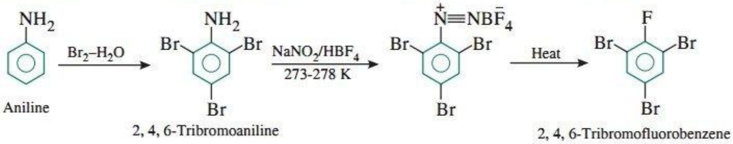
(*ii*)



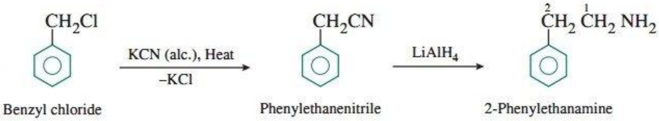
(*iii*)



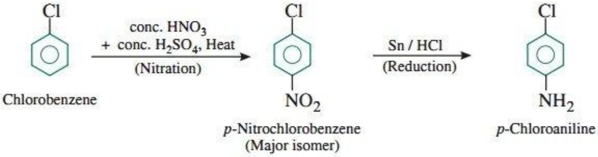
(*iv*)



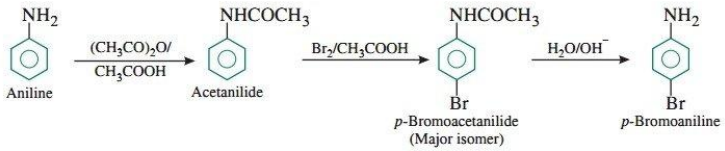
(*v*)



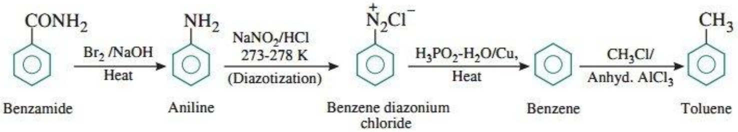
(*vi*)



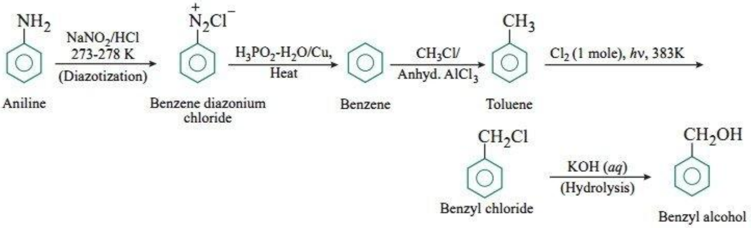
(*vii*)



(*viii*)



(*ix*)



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

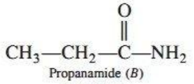
(*iii*) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0°C]{HNO_2} C$

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

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

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

Ans. (*i*)



$$\underset{\text{Iodoethane}}{CH_3CH_2I} \xrightarrow{NaCN} \underset{\text{Propanenitrile }(A)}{CH_3CH_2CN} \xrightarrow[\text{Partial hydrolysis}]{OH^-} \underset{\text{Propanamide }(B)}{CH_3-CH_2-\overset{\overset{O}{\|}}{C}-NH_2}$$

$$\xrightarrow{NaOH + Br_2} \underset{\text{Ethanamine }(C)}{CH_3-CH_2-NH_2}$$

(*ii*)

$$\underset{\text{Benzene diazonium chloride}}{C_6H_5N_2Cl} \xrightarrow{CuCN} \underset{\text{Cyanobenzene }(A)}{C_6H_5CN} \xrightarrow[\text{Hydrolysis}]{H_2O/H^+} \underset{\text{Benzoic acid }(B)}{C_6H_5COOH} \xrightarrow{NH_3}$$

$$C_6H_5COONH_4 \xrightarrow{Heat} \underset{\text{Benzamide }(C)}{C_6H_5CONH_2}$$

(*iii*)

$$\underset{\text{Bromoethane}}{CH_3CH_2Br} \xrightarrow{KCN} \underset{\text{Propane nitrile }(A)}{CH_3CH_2CN} \xrightarrow{LiAlH_4} \underset{\text{Propan-1-amine }(B)}{CH_3CH_2CH_2NH_2}$$

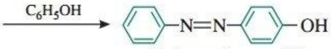
$$\xrightarrow[0°C]{HNO_2} [CH_3CH_2CH_2\overset{+}{N}\equiv NCl^-] \xrightarrow{H_2O} \underset{\text{Propanol }(C)}{CH_3CH_2CH_2OH}$$

(*iv*)

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

(*v*) $$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[\text{Heat}]{NH_3} \underset{\text{Ethanamide }(A)}{CH_3CONH_2} \xrightarrow{NaOBr} \underset{\text{Methanamine }(B)}{CH_3NH_2} \xrightarrow{NaNO_2/HCl} \underset{\text{Methanol }(C)}{CH_3OH}$$

(*vi*) $$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow{Fe/HCl} \underset{\text{Aniline }(A)}{C_6H_5NH_2} \xrightarrow[273\text{ K}]{NaNO_2/HCl} \underset{\text{Benzenediazonium chloride }(B)}{C_6H_5{-}\overset{+}{N}{\equiv}NCl^-}$$



p-Hydroxyazobenzene (*C*)

Q. 10. An aromatic compound '*A*' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound '*C*' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds *A*, *B* and *C*.

Ans. (*i*) To find out the structures of compounds '*B*' and '*C*'.

(*a*) Since compound '*C*' with molecular formula C_6H_7N is formed from compound '*B*' on treatment with Br_2 + KOH compound 'B' must be an amide and '*C*' must be an amine, the only amine having the molecular formula C_6H_7N is $C_6H_5NH_2$ (aniline).

(*b*) Since '*C*' is aniline, the amide from which it is formed must be benzamide. Thus, compound '*B*' is benzamide.

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

$$\underset{\substack{\text{Benzamide }(B)\\(\text{M.F.} = C_7H_7NO)}}{C_6H_5CONH_2} \xrightarrow{Br_2/KOH} \underset{\substack{\text{Aniline }(C)\\(\text{M.F.} = C_6H_7N)}}{C_6H_5NH_2}$$

(*ii*) To find out the structure of compound '*A*'.

As compound '*B*' is formed from compound '*A*' with aqueous ammonia and heating, therefore, compound '*A*' must be benzoic acid.

$$\underset{\text{Benzoic acid }(A)}{C_6H_5COOH} \xrightarrow[(ii)\text{ Heat}]{(i)\text{ aq. }NH_3} \underset{\text{Benzamide }(B)}{C_6H_5CONH_2}$$

Q. 11. Complete the following reactions:

(*i*) $C_6H_5NH_2 + CHCl_3 + \text{alc.}KOH \longrightarrow$

(*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*) $$\underset{\text{Aniline}}{C_6H_5NH_2} + CHCl_3 + \underset{(\text{alc.})}{3KOH} \xrightarrow[\text{(Carbylamine reaction)}]{\text{Heat}} \underset{\substack{\text{Phenyl isocyanide}\\(\text{Offensive smell})}}{C_6H_5N \equiv C} + 3KCl + 3H_2O$$

(*ii*) $$\underset{\substack{\text{Benzene diazonium}\\\text{chloride}}}{C_6H_5N_2Cl} + H_3PO_2 + H_2O \xrightarrow{\text{Reduction}} \underset{\text{Benzene}}{C_6H_6} + N_2 + H_3PO_3 + HCl$$

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

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

Aniline

2, 4, 6-Tribromoaniline

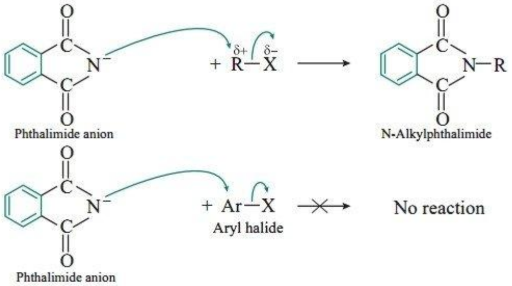
(*vi*) $$\underset{\text{Aniline}}{C_6H_5NH_2} + (CH_3CO)_2O \longrightarrow \underset{\text{Acetanilide}}{C_6H_5NHCOCH_3} + CH_3COOH$$

(*vii*) $$\underset{\text{Benzene diazonium chloride}}{C_6H_5\overset{+}{N}_2\overset{-}{Cl}} \xrightarrow{HBF_4} \underset{\text{Benzene diazonium tetrafluoroborate}}{C_6H_5\overset{+}{N}_2BF_4^-} \xrightarrow[\text{Heat}]{NaNO_2/Cu} \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + BF_3 + NaF$$

Q. 12. Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

[*CBSE 2020 (56/5/1)*]

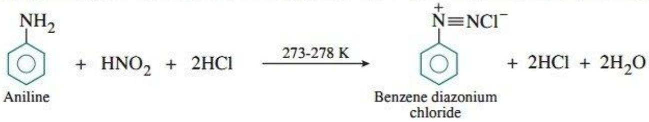
Ans. The success of Gabriel phthalimide reaction depends upon the nucleophilic attack by the phthalimide anion on the organic halogen compound.



Aryl halides do not undergo nucleophilic substitution reactions easily because the carbon–halogen bond acquires partial double bond character due to resonance, therefore aromatic primary amines cannot be prepared by Gabriel phthalimide reaction.

Q. 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 this low temperature and thus decompose readily to form a mixture of compounds consisting of alkyl chlorides, alkenes and alcohols, out of which alcohols generally predominate.

$$CH_3CH_2NH_2 + HNO_2 + HCl \xrightarrow{273-278\text{ K}} \underset{\substack{\text{Ethane diazonium chloride}\\ \text{(unstable)}}}{[CH_3CH_2—\overset{+}{N}\equiv N]Cl^-} \xrightarrow{H_2O} \underset{\text{Ethanol}}{CH_3CH_2OH} + N_2 + HCl$$

Q. 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? **[*CBSE 2020 (56/5/1)*]**

Ans. (*i*) Loss of a proton from an amine gives amide ion while loss of a proton from alcohol gives an alkoxide ion as shown below:

$$\underset{\text{Amine}}{R—NH_2} \longrightarrow \underset{\text{Amide ion}}{R—NH^-} + H^+$$

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

As O is more electronegative than N, RO^- can accommodate the negative charge more easily than the RNH^- can accommodate the negative charge.

RO^- is more stable than RNH^-. Therefore, amines are less acidic than alcohols.

(*ii*) In primary amines, two hydrogen atoms are present on N-atom and they undergo extensive intermolecular hydrogen bonding which results in association of molecules while in tertiary amines, no hydrogen atom is present on N-atom. Hence there is no hydrogen bonding in tertiary amines. As a result of this primary amines have higher boiling point than tertiary amines.

(*iii*) Aliphatic amines are stronger bases than aromatic amines because:

(*a*) due to resonance in aromatic amines, the lone pair of electrons on the nitrogen atom gets delocalised over the benzene ring and thus is less easily available for protonation.

(*b*) the aryl amine ions have lower stability than the corresponding alkyl amines, *i.e.*, protonation of aromatic amines is not favoured.

Multiple Choice Questions

Choose and write the correct option(s) in the following questions.

1. The correct IUPAC name for $CH_2{=}CHCH_2NHCH_3$ is [*NCERT Exemplar*]

(*a*) Allylmethylamine
(*b*) 2-amino-4-pentene
(*c*) 4-aminopent-1-ene
(*d*) N-methylprop-2-en-1-amine

2. In order to prepare a 1° amine from an alkyl halide with simultaneous addition of one CH_2 group in the carbon chain, the reagent used as source of nitrogen is ___________. [*NCERT Exemplar*]

(*a*) Sodium amide, $NaNH_2$
(*b*) Sodium azide, NaN_3
(*c*) Potassium cyanide, KCN
(*d*) Potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

3. The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is ___________. [*NCERT Exemplar*]

(*a*) excess H_2
(*b*) Br_2 in aqueous NaOH
(*c*) iodine in the presence of red phosphorus
(*d*) $LiAlH_4$ in ether

4. Which of the following would not be a good choice for reducing nitrobenzene to aniline? [*CBSE 2023(56/5/2)*]

(*a*) $LiAlH_4$
(*b*) H_2/Ni
(*c*) Fe and HCl
(*d*) Sn and HCl

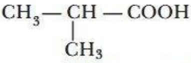
5. Amongst the given set of reactants, the most appropriate for preparing 2° amine is ___________. [*NCERT Exemplar*]

(*a*) 2° R—Br + NH_3
(*b*) 2° R—Br + NaCN followed by H_2/Pt
(*c*) 1° R—NH_2 + RCHO followed by H_2/Pt
(*d*) 1° R—Br (2 mol) + potassium phthalimide followed by H_3O^+/heat

6. The best reagent for converting, 2-phenylpropanamide into 1-phenylethanamine is ___________. [*NCERT Exemplar*]

(*a*) excess H_2/Pt
(*b*) $NaOH/Br_2$
(*c*) $NaBH_4$/methanol
(*d*) $LiAlH_4$/ether

7. An organic compound '*A*' on treatment with NH_3 gives '*B*' which on heating gives '*C*'. '*C*' when treated with Br_2 in the presence of KOH produces ethylamine. Compound '*A*' is

(*a*) $CH_3—CH_2—CH_2—COOH$
(*b*) CH_3COOH
(*c*) 
$CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—COOH$
(*d*) $CH_3—CH_2—COOH$

8. The source of nitrogen in Gabriel synthesis of amines is ___________. [*NCERT Exemplar*]

(*a*) Sodium azide, NaN_3
(*b*) Sodium nitrite, $NaNO_2$
(*c*) Potassium cyanide, KCN
(*d*) Potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

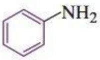
9. Out of the following, the strongest base in aqueous solution is [*CBSE 2020(56/1/1)*]

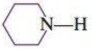
(*a*) Methylamine
(*b*) Dimethylamine
(*c*) Trimethylamine
(*d*) Aniline

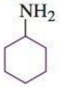
10. CH_3CONH_2 on reaction with NaOH and Br_2 in alcoholic medium gives: *[CBSE 2023(56/1/1)]*

(*a*) CH_3COONa (*b*) CH_3NH_2 (*c*) CH_3CH_2Br (*d*) $CH_3CH_2NH_2$

11. Which of the following is the weakest Brönsted base? *[NCERT Exemplar]*

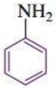
(*a*) 

(*b*) 

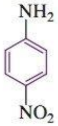
(*c*) 

(*d*) CH_3NH_2

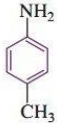
12. The correct increasing order of basic strength for the following compounds is ___________. *[NCERT Exemplar]*



(I)



(II)



(III)

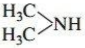
(*a*) II < III < I (*b*) III < I < II (*c*) III < II < I (*d*) II < I < III

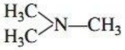
13. Which of the following is least basic? *[CBSE 2023 (56/1/1)]*

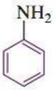
(*a*) $(CH_3)_2NH$ (*b*) NH_3 (*c*) —NH_2 (*d*) $(CH_3)_3N$

14. The most reactive amine towards dilute hydrochloric acid is ___________. *[NCERT Exemplar]*

(*a*) $CH_3—NH_2$

(*b*) 
$(H_3C)_2NH$

(*c*) 
$(H_3C)_2N—CH_3$

(*d*) 

15. The order of reactivity of halides with amines is

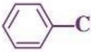
(*a*) RBr > RI > RCl (*b*) RI > RBr > RCl (*c*) RCl > RBr > RI (*d*) RI > RCl > RBr

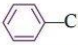
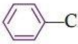
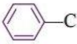
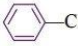
16. Benzylamine may be alkylated as shown in the following equation:

$$C_6H_5CH_2NH_2 + R—X \longrightarrow C_6H_5CH_2NHR$$

Which of the following alkylhalides is best suited for this reaction through S_N1 mechanism? *[NCERT Exemplar]*

(*a*) CH_3Br (*b*) C_6H_5Br (*c*) $C_6H_5CH_2Br$ (*d*) C_2H_5Br

17.  **—CH_2—NH_2 on heating with $CHCl_3$ and alcoholic KOH gives foul smell of** *[CBSE 2020(56/3/1)]*

(*a*) —CH_2OH (*b*) —CH_2NC (*c*) —CH_2CN (*d*) —CH_2Cl

18. Which of the following compounds will dissolve in an alkali solution after it undergoes reaction with Hinsberg's reagent?

(*a*) $(CH_3)_3N$ (*b*) CH_3NH_2 (*c*) $(C_2H_5)_2NH$ (*d*) $C_6H_5NHC_6H_5$

19. Methylamine reacts with HNO_2 to form ___________. *[NCERT Exemplar]*

(*a*) $CH_3—O—N{=}O$ (*b*) $CH_3—O—CH_3$ (*c*) CH_3OH (*d*) CH_3CHO

20. In the nitration of benzene using a mixture of conc. H_2SO_4 and conc. HNO_3, the species which initiates the reaction is ___________. *[NCERT Exemplar]*

(*a*) NO_2 (*b*) NO^+ (*c*) NO_2^+ (*d*) NO_2^-

21. Which of the following will be most stable diazonium salt $R\overset{+}{N}_2\bar{X}$?

(*a*) $CH_3CH_2\overset{+}{N}_2\bar{X}$ (*b*) $C_6H_5\overset{+}{N}_2\bar{X}$ (*c*) $CH_3\overset{+}{N}_2\bar{X}$ (*d*) $C_6H_5CH_2\overset{+}{N}_2\bar{X}$

22. Reduction of nitrobenzene by which of the following reagent does not give aniline?

(*a*) Sn/HCl (*b*) Fe/HCl (*c*) H_2-Pd (*d*) Sn/NH_4OH

23. Which of the following cannot be prepared by Sandmeyer's reaction?
(*a*) Chlorobenzene (*b*) Bromobenzene (*c*) Iodobenzene (*d*) All of these

24. Match the following:

Reactions	Products
(*i*) $(CH_3CH_2)_2NH + CH_3CH_2Br$	A. $CH_3CONHC_2H_5$
(*ii*) $(CH_3CO)_2O + C_2H_5NH_2$	B. C_6H_5NC
(*iii*) $CH_3CH_2NH_2 + HONO$	C. $(CH_3CH_2)_3N$
(*iv*) $C_6H_5NH_2 + CHCl_3 + KOH$	D. CH_3CH_2OH

(*a*) (*i*) — A, (*ii*) — C, (*iii*) — D, (*iv*) — B (*b*) (*i*) — C, (*ii*) — A, (*iii*) — D, (*iv*) — B
(*c*) (*i*) — B, (*ii*) — A, (*iii*) — C, (*iv*) — D (*d*) (*i*) — D, (*ii*) — C, (*iii*) — A, (*iv*) — B

25. Complete the following analogy:
Nitrating mixture : A :: Schiff's base : B
(*a*) A : conc. HNO_3 + conc. H_2SO_4 ; B : $RN=CHR$
(*b*) A : dil. HNO_3 + conc. H_2SO_4 ; B : $R_2N=CHR$
(*c*) A : conc. HNO_3 + conc. H_2SO_4; B : $NaBH_4$
(*d*) A : dil. HNO_3 + dil. H_2SO_4 ; B : $RN=CHR$

26. The action of nitrous acid on ethylamine gives mainly : [*CBSE 2023(56/4/2)*]
(*a*) ethyl nitrite (*b*) ethyl alcohol (*c*) nitroethane (*d*) ethane

Answers

1. (*d*)	**2.** (*c*)	**3.** (*d*)	**4.** (*b*)	**5.** (*c*)	**6.** (*b*)	**7.** (*d*)	**8.** (*d*)	**9.** (*b*)	**10.** (*b*)
11. (*a*)	**12.** (*d*)	**13.** (*c*)	**14.** (*b*)	**15.** (*b*)	**16.** (*c*)	**17.** (*b*)	**18.** (*b*)	**19.** (*c*)	**20.** (*c*)
21. (*b*)	**22.** (*d*)	**23.** (*c*)	**24.** (*b*)	**25.** (*b*)	**26.** (*a*)				

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement.

1. **Assertion (*A*) :** Hoffmann's bromamide reaction is given by primary amines.
Reason (*R*) : Primary amines are more basic than secondary amines.

2. **Assertion (*A*) :** In order to convert R–Cl to pure $R–NH_2$, Gabriel-phthalimide synthesis can be used.
Reason (*R*) : With proper choice of alkyl halides, phthalimide synthesis can be used to prepare 1°, 2° or 3° amines.

3. **Assertion (*A*) :** Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis.
Reason (*R*) : Aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

4. **Assertion (*A*) :** Butan-1-ol is more soluble in water than butan-1-amine.
Reason (*R*) : Alcohols are less polar than amines.

5. **Assertion** (*A*) : Only a small amount of HCl is required in the reduction of nitro compounds with iron scrap and HCl in the presence of steam.
Reason (*R*) : $FeCl_2$ formed gets hydrolysed to release HCl during the reaction.

6. **Assertion** (*A*) : Acetanilide is less basic than aniline.
Reason (*R*) : Acetylation of aniline results in decrease of electron density on nitrogen.

7. **Assertion** (A) : Acetylation of aniline gives a monosubstituted product.
Reason (*R*) : Activating effect of $—NHCOCH_3$ group is more than that of amine group. [*CBSE 2023(56/1/1)*]

8. **Assertion** (*A*) : $—NH_2$ group is *o*- and *p*-directing in electrophilic substitution reactions.
Reason (*R*) : Aniline cannot undergo Friedel-Crafts reaction. [*CBSE 2023(56/1/1)*]

9. **Assertion** (*A*) : Reduction of *m*-dinitrobenzene with ammonium sulphide gives *m*-nitroaniline.
Reason (*R*) : *m*-nitroaniline formed gets precipitated and hence further reduction is prevented.

10. **Assertion** (*A*) : N-Ethylbenzene sulphonamide is soluble in alkali.
Reason (*R*) : Hydrogen attached to nitrogen in sulphonamide is strongly acidic.

11. **Assertion** (*A*) : N, N-Diethylbenzene sulphonamide is insoluble in alkali.
Reason (*R*) : Sulphonyl group attached to nitrogen atom is strong electron withdrawing group.

Answers

1. (*a*) **2.** (*c*) **3.** (*a*) **4.** (*c*) **5.** (*d*) **6.** (*d*) **7.** (*c*) **8.** (*b*) **9.** (*c*) **10.** (*d*) **11.** (*b*)

Passage-based/Case-based/ Source-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

Amines have a lone pair of electrons on nitrogen atom due to which they behave as Lewis base. Larger the value of K_b or smaller the value of pK_b stronger is the base. Amines are more basic than alcohols, ethers, esters, etc. The basic character of aliphatic amines should increase with the increase of alkyl substitution. But it does not occur in a regular manner as a secondary aliphatic amine is unexpectedly more basic than a tertiary amine in solutions. Aromatic amines are weaker bases than ammonia and aliphatic amines. Electron-donating groups such as $—CH_3$, $—OCH_3$, $—NH_2$, etc., increase the basicity while electron-withdrawing substituents such as $—NO_2$, —CN, halogens. etc. decrease the basicity of amines. The effect of these substituents is more at *p*- than at *m*-positions.

1. **Arrange the following in increasing order of their basic strength:**
   $C_2H_5NH_2$, $C_6H_5NH_2$, NH_3, $C_6H_5CH_2NH_2$, $(C_2H_5)_2NH$
2. **Arrange the following compounds in increasing order of their acidic strength:**
   Methylamine, dimethylamine, aniline, N-methylaniline
3. **$(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution. Give reason.**

OR

Which is more acidic, aniline or ammonia?

Answers

1. $C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$
2. dimethylamine < methylamine < N-methylaniline < aniline
3. The basicity of amine in aqueous solution depends upon the stability of the substituted ammonium cation. Here the combination of three factors, +ve I effect of CH_3 groups, hydrogen bonding and steric hindrance favour greater stability for ammonium cation of dimethyl amine than ammonium cation of trimethyl amine. Hence, dimethylamine is stronger base than trimethyl amine.

OR

Due to delocalization of the lone pair of electrons of the N-atom of aniline over the benzene ring, aniline is more acidic than ammonia.

PASSAGE–2

Amines are usually formed from nitro compounds, halides, amides, imides, etc. They exhibit hydrogen bonding which influences their physical properties. In alkyl amines, a combination of electron releasing, steric and hydrogen bonding factors influence the stability of the substituted ammonium cations in protic polar solvents and thus affect the basic nature of amines. In aromatic amines, electron releasing and withdrawing groups, respectively increase and decrease their basic character. Influence of the number of hydrogen atoms at nitrogen atom on the type of reactions and nature of products is responsible for identification and distinction between primary, secondary and tertiary amines. Presence of amino group in aromatic ring enhances reactivity of the aromatic amines. Aryl diazonium salts provide advantageous methods for producing aryl halides, cyanides, phenols and arenes by reductive removal of the diazo group. [*CBSE 2023(56/4/2)*]

Answer the following questions :

1. **Arrange the following in the increasing order of their pK_b, values in aqueous solution:**

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

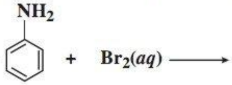
2. **Aniline on nitration gives a substantial amount of *m*-nitroaniline, though amino group is *o/p* directing. Why?**

3. **An aromatic compound 'A' of molecular formula $C_7H_6O_2$ on treatment with aqueous ammonia and heating forms compound 'B'. Compound 'B' on heating with Br_2 and aqueous KOH gives a compound 'C' of molecular formula C_6H_7N. Write the structures of A, B and C.**

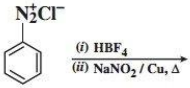
OR

Complete the following reactions giving main products:

1.



2.



Answers

1. In aqueous phase, the substituted ammonium cations (formed by the amines, on accepting protons) are stabilized by two factors:–

   (*a*) + I effect of the alkyl group substituted.

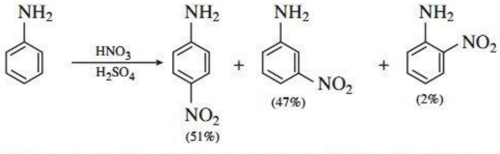
   (*b*) Solvation by the solvent molecules.

   The base strength of an amine is determined by the above mentioned two effects as well as the steric effect of the alkyl chain.

   Taking all three effects into consideration the pK_b of the given bases follows the order in the aqueous phase.

   $(C_2H_5)_2NH_2 > (C_2H_5)_3N > C_2H_5NH_2$

2.



   Nitration of aniline in strongly acidic medium results in protonation of $-\ddot{N}H_2$ group. The anilinium ion thus formed is meta-directing in nature. Therefore, we obtain substantial amount of meta products.

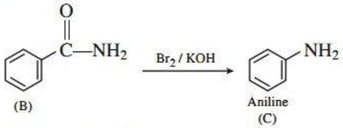
3. $C_7H_6O_2$, an aromatic compound, with degree of unsaturation = 5 is becoming 'B' on treatment with aqueous NH_3. The compound 'B' on treating with Br_2 and *aq*.KOH is forming C.

   We know that the reagent Br_2/KOH is Hoffman Bromamide reagent. So, B must be an aromatic amide.

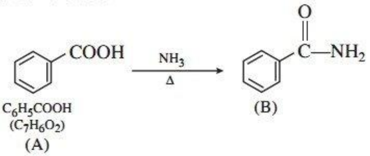
The degree of unsaturation (D.U) of ‘C’ is

$$(\text{D.U}) = \frac{2C + 2 + N - X - H}{2} = \frac{2(6) + 2 + 1 - 7}{2} = 4$$

The loss of 1 Du can be attributed to the loss of CO_2 from the aromatic amide ‘B’. From the above clues it becomes clear that B is an aromatic amide with 7 carbon atoms, with D.U. = 5. So, ‘B’ is Benzamide and ‘C’ is aniline.

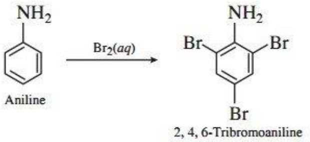


Benzamide is formed when NH_3 is heated with carboxylic acid with D.U = 5 and having 7-carbon atoms. So, ‘A’ is benzoic acid.



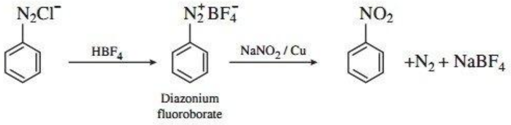
OR

(*a*)



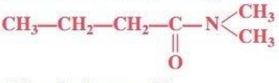
Aniline has $—\ddot{N}H_2$ group which is ortho and para directing in nature. So, the incoming electrophile is directed towards 2nd, 4th and the 6th positions.

(*b*)



CONCEPTUAL QUESTIONS

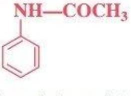
Q. 1. Write the IUPAC name of the given compound: **[*CBSE (F) 2016*]**



$$CH_3—CH_2—CH_2—\overset{\displaystyle O}{\overset{\|}{C}}—N\begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

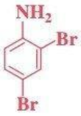
Ans. N, N – Dimethylbutanamide

Q. 2. Write the IUPAC name of the given compound: **[*CBSE East 2016*]**



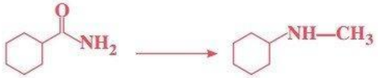
Ans. N- Phenylethanamide

Q. 3. Write the IUPAC name of the given compound: [*CBSE South 2016*]



Ans. 2,4-Dibromobenzenamine or 2,4-Dibromoaniline

Q. 4. Suggest a route by which the following conversion can be accomplished. [*NCERT Exemplar*] [*HOTS*]



Ans.

Q. 5. Why do amines behave as nucleophiles?

Ans. Due to the presence of a lone pair of electrons on nitrogen atom, amines behave as nucleophiles.

Q. 6. What is the role of pyridine in the acylation reaction of amines? [*NCERT Exemplar*]

Ans. Pyridine and other bases are used to remove the side product, *i.e.*, HCl from the reaction mixture.

Q. 7. What is the role of HNO_3 in the nitrating mixture used for nitration of benzene? [*NCERT Exemplar*]

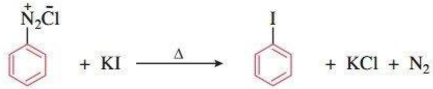
Ans. HNO_3 acts as a base in the nitrating mixture and provides the electrophile NO_2^+.

Q. 8. The conversion of primary aromatic amines into diazonium salts is known as __________ . [*CBSE (AI) 2014*]

Ans. Diazotisation

Q. 9. Write a chemical reaction in which the iodide ion replaces the diazonium group in a diazonium salt.

Ans.



Benzene diazonium chloride

Iodobenzene

Q. 10. Why is benzene diazonium chloride not stored and is used immediately after its preparation? [*NCERT Exemplar*]

Ans. Benzene diazonium chloride is very unstable.

Q. 11. What are the reactions involved in the reductive removal of nitro group from an aromatic compound? [*HOTS*]

Ans.

$$\underset{\text{Nitrobenzene}}{C_6H_5{-}NO_2} \xrightarrow[\text{Reduction}]{\text{Sn/HCl}} \underset{\text{Aniline}}{C_6H_5{-}NH_2} \xrightarrow[\text{(Diazotisation)}]{\substack{NaNO_2/HCl\\ 273-278}} \underset{\text{Benzenediazonium chloride}}{C_6H_5{-}\overset{+}{N}{\equiv}NCl^-} \xrightarrow[\text{(Reduction)}]{\text{Aq. } H_3PO_2} \underset{\text{Benzene}}{C_6H_6}$$

Short Answer Questions–I

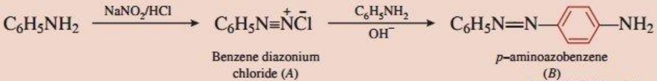
Each of the following questions are of 2 marks.

Q. 1. Identify *A* and *B* in each of the following processes: [*CBSE (AI) 2010*]

(*i*) $CH_3CH_2Cl \xrightarrow{NaCN} A \xrightarrow[Ni/H_2]{\text{Reduction}} B$

(*ii*) $C_6H_5NH_2 \xrightarrow{NaNO_2/HCl} A \xrightarrow[OH^-]{C_6H_5NH_2} B$

Ans. (*i*) $CH_3CH_2Cl \xrightarrow{NaCN} \underset{\substack{\text{Ethyl cyanide}\\(A)}}{CH_3CH_2CN} \xrightarrow[Ni/H_2]{\text{Reduction}} \underset{\substack{n\text{-Propyl amine}\\(B)}}{CH_3CH_2CH_2NH_2}$ 1

(*ii*)


1

[*CBSE Marking Scheme 2010*]

Q. 2. Arrange the following: [*CBSE Guwahati 2015*]

(*i*) **In increasing order of their basic strength**

$C_6H_5—NH_2, CH_3—CH_2—NH_2, CH_3—NH—CH_3$

(*ii*) **In increasing order of solubility in water**

$CH_3—NH_2, (CH_3)_3N, CH_3—NH—CH_3$

Ans. (*i*) $C_6H_5NH_2 < CH_3—CH_2—NH_2 < CH_3NHCH_3$

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

Q. 3. Account for the following:

(*i*) **Aniline gets coloured on standing in air for a long time.**

(*ii*) **MeNH$_2$ is stronger base than MeOH.** [*NCERT Exemplar*]

Ans. (*i*) Due to 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.

(*ii*) Nitrogen is less electronegative than oxygen therefore lone pair of electrons on nitrogen is readily available for donation. Hence, MeNH$_2$ is more basic than MeOH.

Q. 4. Account for the following: [*CBSE (AI) 2014*] [*HOTS*]

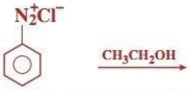
(*i*) **pK_b of aniline is more than that of methylamine.**

(*ii*) **Although trimethylamine and *n*-propylamine have the same molecular weight, but the former boils at a lower temperature (276 K) than the latter (322 K). Explain.**

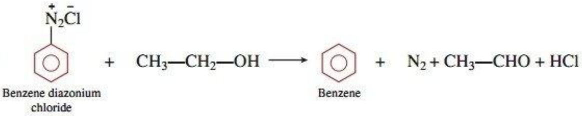
Ans. (*i*) Refer to Ans. 3(*i*) NCERT Exercises.

(*ii*) *n*-Propylamine has two H-atoms on the N-atom and hence undergoes intermolecular H-bonding, thereby raising its boiling point. Trimethylamine, $(CH_3)_3N$, being a tertiary amine does not have any H-atom on the N-atom. As a result, it does not undergo H-bonding and hence its boiling point is low.

Q. 5. (*i*) **Complete the reaction with the main product formed:**



(*ii*) **Convert Bromoethane to Propanamine.** [*CBSE 2023(56/5/2)*]

Ans. (*i*)


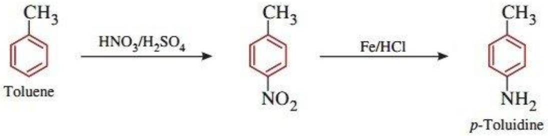
(*ii*) $\underset{\text{Bromoethane}}{CH_3CH_2—Br} \xrightarrow{KCN(alc)} CH_3—CH_2—CN \xrightarrow[\text{or } LiAlH_4]{Na(Hg)/C_2H_5OH} \underset{\text{Propanamine}}{CH_3—CH_2—CH_2—NH_2}$

Q. 6. How will you carry out the following conversions?

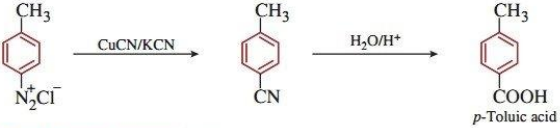
(*i*) toluene ⟶ *p* - toluidine

(*ii*) *p* - toluidine diazonium chloride ⟶ *p* - toluic acid [*NCERT Exemplar*]

Ans. (*i*)



(*ii*)

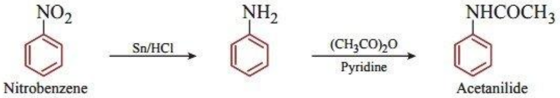


Q. 7. Write the following conversions:

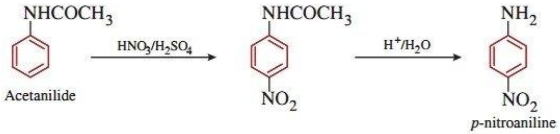
(*i*) nitrobenzene ⟶ acetanilide

(*ii*) acetanilide ⟶ *p*-nitroaniline [*NCERT Exemplar*]

Ans. (*i*)



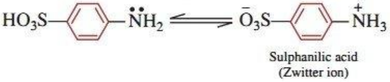
(*ii*)



Q. 8. (*i*) Draw the zwitter ion structure for sulphanilic acid.

(*ii*) How can the activating effect of —NH_2 group in aniline be controlled?

Ans. (*i*)



(*ii*) Due to strong activating effect of —NH_2 group, aniline readily undergoes electrophilic substitution reaction to give 2, 4, 6 trisubstituted aniline and it is difficult to stop the reaction at monosubstitution stage. If we wish to stop the reaction at monosubstitution stage, the activating effect of the —NH_2 group is reduced by acylation.

The lone pair of electrons on nitrogen of acetanilide interacts with oxygen atom due to resonance as shown above. Hence, the lone pair of electrons on nitrogen is less available for donation to benzene ring by resonance. Therefore the activating effect of —NH_2 group is reduced.

Short Answer Questions–II

Each of the following questions are of 3 marks.

Q. 1. **(*i*) Arrange the following compounds in increasing order of dipole moment.**

$CH_3CH_2CH_3$, $CH_3CH_2NH_2$, CH_3CH_2OH [*NCERT Exemplar*]

(*ii*) Give possible explanation for each of the following:

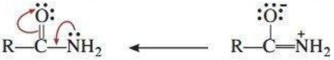
(*a*) The presence of a base is needed in the ammonolysis of alkyl halides.

(*b*) Amides are more acidic than amines.

Ans. (*i*) $CH_3CH_2CH_3 < CH_3CH_2NH_2 < CH_3CH_2OH$

(*ii*) (*a*) To remove HX formed so that the reaction shifts in the forward direction.

(*b*)



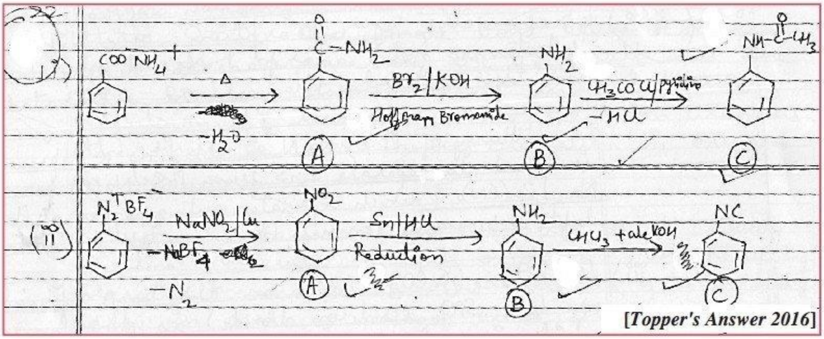
Due to +R effect, availability of lone pair of electron on N of —NH_2 group decreases. As a result, acid amide is much weaker base than amines. Because of the positive charge on N, as a result of resonance, N can easily lose a proton and behaves, as a weak acid.

Q. 2. **Write the structures of *A*, *B* and *C* in the following:**

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

(*ii*) $C_6H_5N_2^+BF_4^- \xrightarrow{NaNO_2/Cu} A \xrightarrow{Sn/HCl} B \xrightarrow[\Delta]{CHCl_3+alc.KOH} C$ [*CBSE (F) 2016*]

Ans.



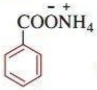
[*Topper's Answer 2016*]

Q. 3. **Complete the following reactions:**

(*i*) $C_6H_5—COOH \xrightarrow{NH_3} A \xrightarrow{Heat} B \xrightarrow{Br_2/KOH} C$

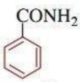
(*ii*) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273-278K]{NaNO_2+HCl} B \xrightarrow{CuCN} C$ [*CBSE East 2016*]

Ans. (*i*) *A* =



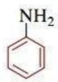
Ammonium benzoate

, *B* =



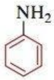
Benzamide

, *C* =



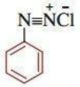
Aniline

(*ii*) *A* =



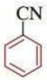
Aniline

, *B* =



Benzene diazonium chloride

, *C* =

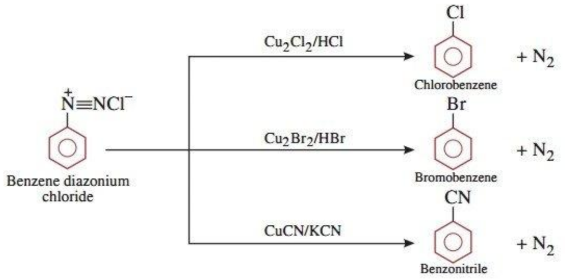


Benzonitrile

Q. 4. **(*i*) Illustrate Sandmeyer's reaction with an equation.**

(*ii*) Explain, why $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in aqueous solution. **[*CBSE 2023(56/5/2)*]**

Ans. (*i*) Sandmeyer's reaction:



(*ii*) Greater the stability of the substituted ammonium cation, stronger is the base. Due to the combination of the factors: +I effect of methyl groups, solvation effect and steric hindrance of methyl groups, the substituted ammonium cation of $(CH_3)_2NH$ is more stable than $(CH_3)_3N$ in aqueous solutions therefore $(CH_3)_2NH$ is more basic than $(CH_3)N$ in aqueous solutions.

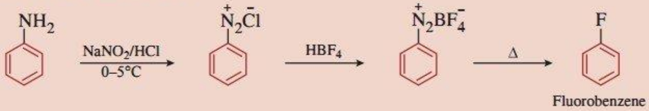
Q. 5. **How are the following conversions carried out:**

(*i*) Aniline to fluorobenzene

(*ii*) Benzene diazonium chloride to benzene

(*iii*) Methyl chloride to ethylamine **[*CBSE (F) 2013*]**

Ans. (*i*) Aniline to fluorobenzene



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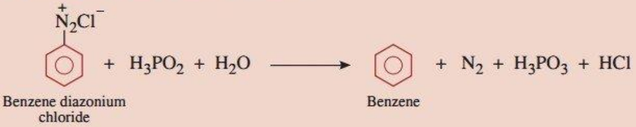
(*ii*) Benzene diazonium chloride to benzene



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(*iii*) Methyl chloride to ethylamine

$$\underset{\text{Methyl chloride}}{CH_3{-}Cl} \xrightarrow{\text{alc. KCN}} CH_3{-}CN \xrightarrow{LiAlH_4} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

1

[*CBSE Marking Scheme 2013*]

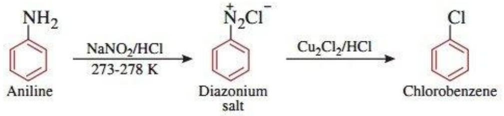
Q. 6. **How will you convert the following:**

(*i*) Aniline to chlorobenzene

(*ii*) Ethanoic acid to methanamine

(*iii*) Benzene diazonium chloride to phenol **[*CBSE (F) 2013*]**

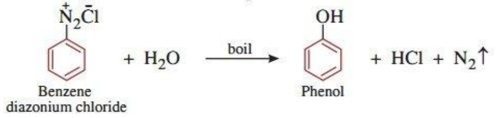
Ans. (*i*) Aniline to chlorobenzene



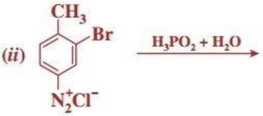
(*ii*) Ethanoic acid to methanamine

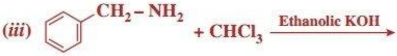
$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[\Delta]{NH_3} \underset{\text{Ethanamide}}{CH_3CONH_2} \xrightarrow[\text{(Hoffmann bromamide reaction)}]{Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$$

(*iii*) Benzene diazonium chloride to phenol

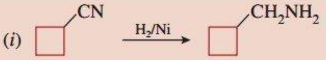


Q. 7. Complete the following reactions: **[*CBSE 2019 (56/2/1)*]**





Ans.



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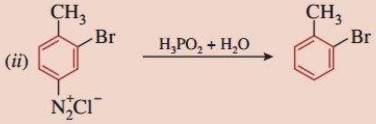

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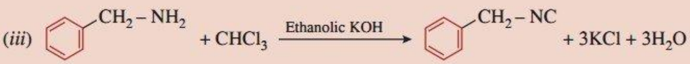

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[*CBSE Marking Scheme 2019 (56/2/1)*]

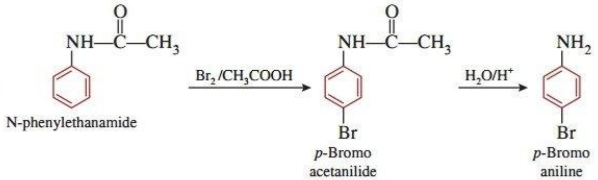
Q. 8. How do you convert the following:

(*i*) N-phenylethanamide to *p*-bromoaniline

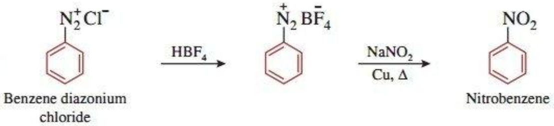
(*ii*) Benzene diazonium chloride to nitrobenzene

(*iii*) Benzoic acid to aniline **[*CBSE 2019 (56/2/1)*]**

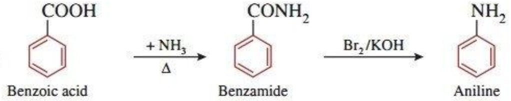
Ans. (*i*)



(*ii*)



(*iii*)



Q. 9. Account for the following:

(*i*) Aniline cannot be prepared by the ammonolysis of chlorobenzene under normal conditions.

(*ii*) N-ethylethanamine boils at 329.3K and butanamine boils at 350.8K, although both are isomeric in nature.

(*iii*) Acylation of aniline is carried out in the presence of pyridine. (*CBSE Sample Paper 2022*)

Ans. (*i*) In case of chlorobenzene, the C—Cl bond is quite difficult to break as it acquires a partial double bond character due to conjugation.

So, Under the normal conditions, ammonolysis of chlorobenzene does not yield aniline.

(*ii*) Primary and secondary amines are engaged in intermolecular association due to hydrogen bonding between nitrogen of one and hydrogen of another molecule. Due to the presence of three hydrogen atoms, the intermolecular association is more in primary amines than in secondary amines as there are two hydrogen atoms available for hydrogen bond formation in it.

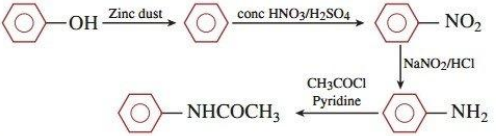
(*iii*) During the acylation of aniline, stronger base pyridine is added. This is done in order to remove the HCl so formed during the reaction and to shift the equilibrium to the right hand side.

Q. 10. Convert the following:

(*i*) Phenol to N-phenylethanamide. **(*ii*) Chloroethane to methanamine.**

(*iii*) Propanenitrile to ethanol. **(*CBSE Sample Paper 2022*)**

Ans. (*i*) Phenol into N-phenylethanamide



(*ii*) Chloroethane to methanamine

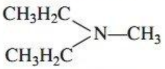
$$C_2H_5Cl \xrightarrow{\text{Aq NaOH}} C_2H_5OH \xrightarrow{KMnO_4} CH_3COOH \xrightarrow{NH_3/\text{ heat}} CH_3CONH_2 \xrightarrow{Br_2/\text{ KOH}} CH_3NH_2$$

(*iii*) Propanenitrile to ethanal

$$\begin{tikzcd}
CH_3CH_2CN \arrow[r, "H_3O^+"] & CH_3CH_2CONH_2 \arrow[r, "Br_2/NaOH"] & CH_3CH_2NH_2 \arrow[d, "HNO_2"] \\
& CH_3CHO & CH_3CH_2OH \arrow[l, "PCC"']
\end{tikzcd}$$

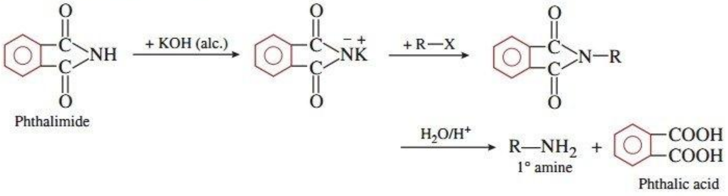
Q. 11. **(*i*) Write the IUPAC name for the following organic compound:**
$(CH_3CH_2)_2NCH_3$
(*ii*) Write the equations for the following:
(*a*) Gabriel phtalimide synthesis
(*b*) Hoffmann bromamide degradation ***[CBSE 2022 (56/4/2)]***

Ans. (*i*)



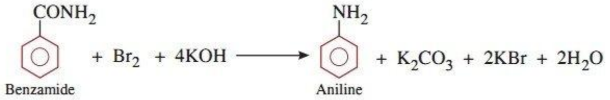
N-ethyl-N-methylethanamine

(*ii*) (*a*) Gabriel phthalimide synthesis



(*b*) Hoffmann bromamide degradation

$$\underset{\text{Acid amide}}{R-CONH_2} + Br_2 + 4NaOH \longrightarrow \underset{1^\circ \text{ amine}}{R-NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$



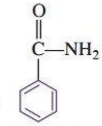
Long Answer Questions

Each of the following questions are of 5 marks.

Q. 1. **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 Delhi 2015*] [*HOTS*]**

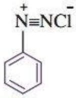
$$\begin{tikzcd}
\underset{A}{C_7H_7ON} \arrow[r, "Br_2 + KOH"] & C_6H_5NH_2 \arrow[r, "NaNO_2 + HCl", "273\text{ K}"'] \arrow[d, "CHCl_3 + NaOH"] & B \arrow[r, "CH_3CH_2OH"] \arrow[d, "KI"] & C \\
 & D & E &
\end{tikzcd}$$

Ans. *A* =



Benzamide

; *B* =

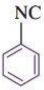


Benzene diazonium chloride

; *C* =

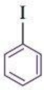
Benzene

; *D* =



Phenyl isocyanide

; *E* =

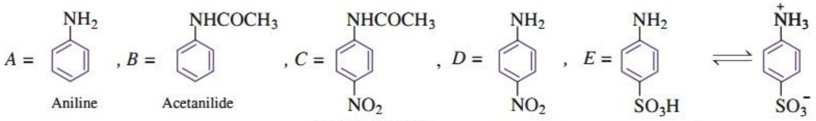


Iodobenzene

Q. 2. Write the structures of *A*, *B*, *C*, *D* and *E* in the following reactions: **[*CBSE (F) 2017*]**

$$\begin{tikzcd}
C_6H_5NO_2 \arrow[r, "Sn/HCl"] & A \arrow[r, "(CH_3CO)_2O"', "pyridine"] \arrow[d, "H_2SO_4"] & B \arrow[r, "HNO_3 + H_2SO_4", "288\ K"'] & C \arrow[r, "\bar{O}H \text{ or } \overset{+}{H}"] & D \\
 & E & & &
\end{tikzcd}$$

Ans.



Aniline, Acetanilide, *p*-Nitroacetanilide, *p*-Nitroaniline, Sulphanilic acid

Q. 3. **(*i*) Write the structures of main products when aniline reacts with the following reagents:**

(*a*) Br_2 water **(*b*) HCl** **(*c*) $(CH_3CO)_2O$/pyridine**

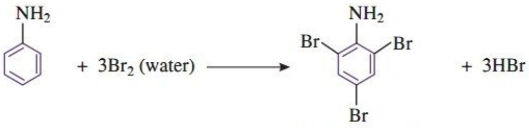
(*ii*) Arrange the following in the increasing order of their boiling point:

$C_2H_5NH_2$, C_2H_5OH, $(CH_3)_3N$

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

$(CH_3)_2NH$ and $(CH_3)_3N$ **[*CBSE Delhi 2015*]**

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

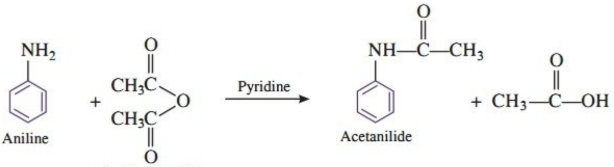


2,4,6-Tribromoaniline

(*b*)

Aniline Anilinium chloride

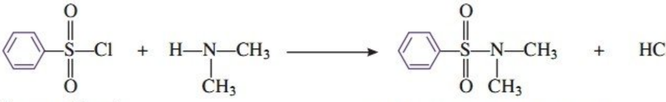
(*c*)



Aniline Acetic anhydride Acetanilide

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

(*iii*) Dimethyl amine and trimethyl amine can be distinguished by using Hinsberg's reagent, *i.e.*, $C_6H_5SO_2Cl$. When treated with Hinsberg's reagent dimethylamine being a 2° amine gives N, N-dimethyl benzene sulphonamide which is insoluble in aqueous KOH solution while trimethyl amine being a 3° amine does not react with Hinsberg's reagent.



Benzene sulphonyl chloride

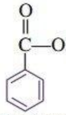
N,N-Dimethyl benzene sulphonamide (insoluble in KOH)

Q. 4. **An aromatic compound 'A' of molecular formula $C_7H_6O_2$ undergoes a series of reactions as shown below. Write the structures of *A*, *B*, *C*, *D* and *E* in the following reactions:**

[*CBSE Allahabad 2015*]

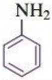
$$\begin{tikzcd}
\underset{A}{(C_7H_6O_2)} \arrow[r, "NH_3/heat"] & C_6H_5CONH_2 \arrow[r, "Br_2 + NaOH"] \arrow[d, "LiAlH_4/ether"] & B \arrow[r, "(CH_3CO)_2O"] \arrow[d, "Br_2(aq)"] & C \\
 & D & E &
\end{tikzcd}$$

Ans. $A =$



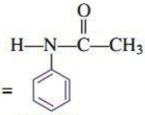
Benzoic acid

; $B =$



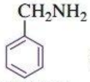
Aniline

; $C =$



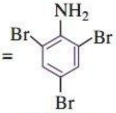
N-Phenyl ethanamide

; $D =$



Benzylamine

; $E =$



2,4,6-Tribromo aniline

Q. 5. **(*i*) How will you bring about the following conversions?**

(*a*) Ethanamine into methanamine (*b*) Aniline into 1, 3, 5-tribromobenzene

(*c*) Aniline into 4-bromoaniline

(*ii*) Account for the following:

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

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

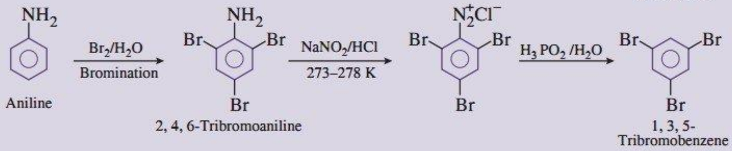
[*CBSE 2019 (56/5/2)*]

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

$$\begin{tikzcd}
\underset{\text{Ethanamine}}{CH_3CH_2NH_2} \arrow[r, "HNO_2"] & CH_3CH_2OH \arrow[r, "CrO_3/H_2SO_4", "{[O]}"'] & CH_3COOH \arrow[d, "\Delta\ NH_3"] & \\
 & & CH_3CONH_2 \arrow[r, "+Br_2/KOH"] & \underset{\text{Methanamine}}{CH_3NH_2}
\end{tikzcd}$$

1

(*b*)



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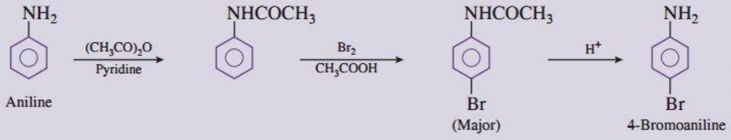
(*c*)



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(*ii*) (*a*) Refer to Ans. 3(*iii*) of NCERT Exercises. 1

(*b*) Refer to Ans. 3(*vi*) of NCERT Exercises. 1

[*CBSE Marking Scheme 2019 (56/5/2)*]

Q. 6. A hydrocarbon '*A*', (C_4H_8) on reaction with HCl gives a compound '*B*', (C_4H_9Cl), which on reaction with 1 mol of NH_3 gives compound '*C*', ($C_4H_{11}N$). On reacting with $NaNO_2$ and HCl followed by treatment with water, compound '*C*' yields an optically active alcohol, '*D*'. Ozonolysis of '*A*' gives 2 moles of acetaldehyde. Identify the compounds '*A*' to '*D*'. Explain the reactions involved. [*HOTS*]

Ans. $(A) \xrightarrow{\text{Ozonolysis}} 2CH_3CHO$

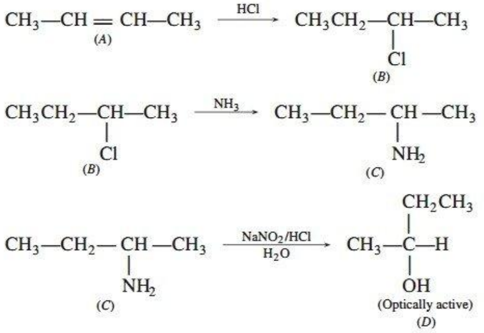
$\underset{(A)}{C_4H_8} \xrightarrow{HCl} \underset{(B)}{C_4H_9Cl}$ Addition of HCl has occurred on '*A*'. This implies '*A*' is an alkene.

$\underset{(B)}{C_4H_9Cl} \xrightarrow{NH_3} \underset{(C)}{C_4H_{11}N}$ Cl in compound '*B*' is substituted by NH_2 to give '*C*'.

$(C) \xrightarrow[H_2O]{NaNO_2/HCl} (D)$ '*C*' gives a diazonium salt with $NaNO_2$/HCl that liberates N_2 to give optically active alcohol. This means that '*C*' is a primary amine. Number of carbon atoms in amine is same as compound '*A*'.

Since products of ozonolysis of compound '*A*' are $CH_3—CH=O$ and $O=CH—CH_3$. Therefore, the compound '*A*' is $CH_3—CH=CH—CH_3$.

On the basis of structure of '*A*', the reactions can be explained as follows:



$$\underset{(A)}{CH_3—CH=CH—CH_3} \xrightarrow{HCl} \underset{(B)}{CH_3CH_2—\underset{\underset{Cl}{|}}{CH}—CH_3}$$

$$\underset{(B)}{CH_3CH_2—\underset{\underset{Cl}{|}}{CH}—CH_3} \xrightarrow{NH_3} \underset{(C)}{CH_3—CH_2—\underset{\underset{NH_2}{|}}{CH}—CH_3}$$

$$\underset{(C)}{CH_3—CH_2—\underset{\underset{NH_2}{|}}{CH}—CH_3} \xrightarrow[H_2O]{NaNO_2/HCl} \underset{\underset{(D)}{\text{(Optically active)}}}{CH_3—\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{OH}{|}}{C}}—H}$$

Q. 7. (*i*) Give reason:

(*a*) Aniline on nitration gives good amount of *m*-nitroaniline, though $—NH_2$ group is *o*/*p* directing in electrophilic substitution reactions.

(*b*) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution.

(*c*) Ammonolysis of alkyl halides is not a good method to prepare pure primary amines.

(*ii*) Write the reaction involved in the following:

(*a*) Carbylamine test

(*b*) Gabriel phthalimide synthesis [*CBSE 2023(56/2/1)*]

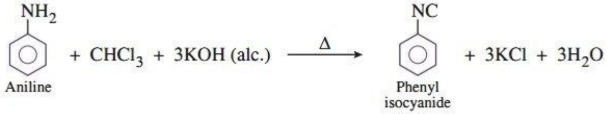
Ans. (*i*) (*a*) In a strong acidic medium aniline is protonated to form anilinium ion which is meta directing. That is why besides the ortho and para derivatives good amount of meta-nitroaniline is also obtained.

(*b*) Greater the stability of the substituted ammonium cation, stronger is the base. Due to the combination of the factors +I effect of methyl groups, solvation effect and steric hinderance of methyl groups the substituted ammonium cation of $(CH_3)_2NH$ is more stable than $(CH_3)_3N$ in aqueous solutions, therefore $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in aqueous solutions.

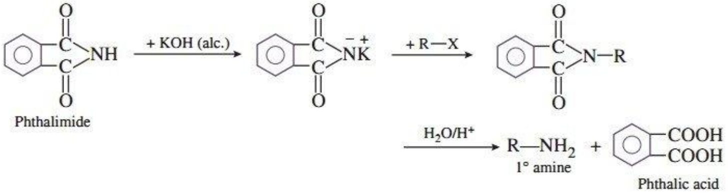
(*c*) Ammonolysis of alkyl halides gives a mixture of primary, secondary and tertiary amines along with some quaternary ammonium salts. If excess of alcoholic ammonia is used primary amine is the major product if excess of halide is used quaternary ammonium salt is the major product. As the mixtures obtained are very complex and difficult to separate therefore this is not good method to prepare pure primary amines.

(*ii*) (*a*) **Carbylamine test:**

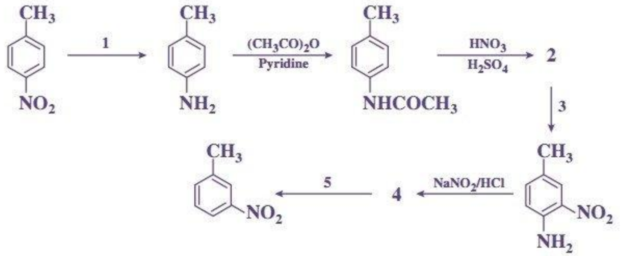
$$\underset{\text{1° amine}}{R\text{—}NH_2} + CHCl_3 + 3KOH\ (\text{alc.}) \xrightarrow{\Delta} \underset{\substack{\text{Alkyl}\\ \text{isocyanide}}}{R\text{—}NC} + 3KCl + 3H_2O$$



(*b*) **Gabriel phthalimide synthesis:**

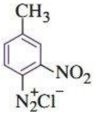


Q. 8. Predict the reagents or the products in the following reaction sequence: **[*HOTS*]**



Ans. 1. Sn–HCl (conc.) 2.

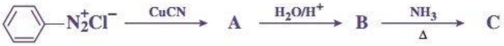
3. H_2O/H^+ 4.



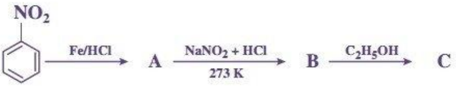
5. H_3PO_2/H_2O

Q. 9. (*i*) **Write the structures of A, B and C in the following reactions:**

(*a*)



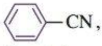
(*b*)



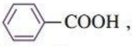
(ii) Why aniline does not undergo Friedal-Crafts reaction?

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

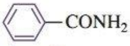
C_2H_5OH, $C_2H_5NH_2$, $(C_2H_5)_3N$ **[*CBSE 2023(56/2/1)*]**

Ans. (*i*) (*a*) A =  ,

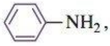
Benzonitrile

B =  ,

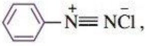
Benzoic acid

C = 

Benzamide

(*b*) A =  ,

Aniline

B =  ,

Benzene diazonium chloride

C = 

Benzene

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

$$\underset{\text{Lewis base}}{C_6H_5NH_2} + \underset{\text{Lewis acid}}{AlCl_3} \longrightarrow C_6H_5\overset{+}{N}H_2AlCl_3^-$$

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

(*iii*) $C_2H_5NH_2 < C_2H_5OH < (C_2H_5)_3N$

Questions for Practice

Choose and write the correct answer for each of the following.

1. **Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine?** [*NCERT Exemplar*]

(*a*) H_2 (excess)/Pt (*b*) $LiAlH_4$ in ether

(*c*) Fe and HCl (*d*) Sn and HCl

2. **Which of the following compound will not undergo azo coupling reaction with benzene diazonium chloride?**

(*a*) Aniline (*b*) Phenol

(*c*) Anisole (*d*) Nitrobenzene

3. **Amongst the following, the strongest base in aqueous medium is __________.** [*NCERT Exemplar*]

(*a*) CH_3NH_2 (*b*) $NCCH_2NH_2$

(*c*) $(CH_3)_2NH$ (*d*) $C_6H_5NHCH_3$

4. **Complete the following analogy:**

Nitrating mixture : A :: Schiff's base : B

(*a*) A : conc. HNO_3 + conc. H_2SO_4 ; B : $RN{=}CHR$

(*b*) A : dil. HNO_3 + conc. H_2SO_4 ; B : $R_2N{=}CHR$

(*c*) A : conc. HNO_3 + conc. H_2SO_4 ; B : $NaBH_4$

(*d*) A : dil. HNO_3 + dil. H_2SO_4 ; B : $RN{=}CHR$

5. **Which of the following has highest pK_b value?**

(*a*) $CH_3CH_2NH_2$ (*b*) NH_3

(*c*) CH_3NH_2 (*d*) $C_6H_5NH_2$

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement.

6. **Assertion (*A*) :** Ethanamide on treatment with bromine and potassium hydroxide gives ethanamine.

   Reason (*R*) : During this reaction one carbon of amide is lost as carbonate ion.

7. **Assertion (*A*) :** Acylation of amines gives a monosubstituted product whereas alkylation of amines gives polysubstituted product.

   Reason (*R*) : Acyl group sterically hinders the approach of further acyl groups.

8. **Assertion (*A*) :** Tertiary amines have lower boiling points than those of primary and secondary amines of comparable molecular masses.

   Reason (*R*) : Tertiary amines are unable to form intermolecular hydrogen bonds.

9. **Assertion (*A*) :** In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.

   Reason (*R*) : The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance.

10. **Assertion (*A*) :** Aromatic diazonium salts are more stable than aliphatic diazonium salts.

    Reason (*R*) : Aromatic diazonium salts undergo coupling reactions with phenols and amines.

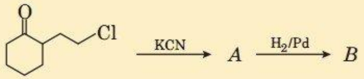
Answer the following questions:

11. Explain the observed K_b order:

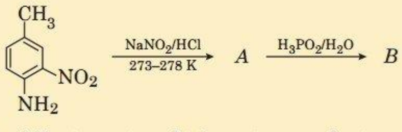
    $Et_2NH > Et_3N > EtNH_2$ in aqueous solution

12. Identify A and B in the following reaction.

(*i*)

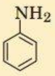


(*ii*)

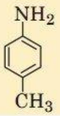


13. In the following pairs which one is more basic and why?

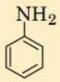
(*i*) CH_3NH_2 or



(*ii*)



or



14. How are the following conversions carried out?

(*i*) Ethanamine to N-ethylethanamide

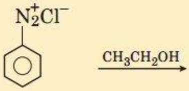
(*ii*) Chloroethane to propan-1-amine

15. Predict, giving reasons, the order of basicity of the following compounds in

(*i*) gaseous phase and

(*ii*) in aqueous solutions $(CH_3)_3N$, $(CH_3)_2NH$, CH_3NH_2, NH_3.

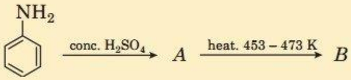
16. (*i*) Complete the reaction with the main product formed:



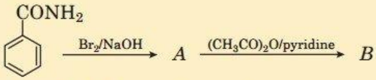
(*ii*) Convert Bromoethane to Propanamine. **[*CBSE 2023(56/5/2)*]**

17. Write structures of compounds A and B in each of the following reactions: **[*CBSE 2019(56/3/2)*]**

(*i*)



(*ii*)



18. Complete the following chemical equations: **[*CBSE Delhi 2010*]**

(*i*) $C_6H_5N_2Cl + C_6H_5NH_2 \xrightarrow{OH^-}$

(*ii*) $C_6H_5N_2Cl + CH_3CH_2OH \longrightarrow$

(*iii*) $RNH_2 + CHCl_3 + KOH \longrightarrow$

19. Give reasons:

(*i*) Acetylation of aniline reduces its activation effect.

(*ii*) CH_3NH_2 is more basic than $C_6H_5NH_2$.

(*iii*) Although $—NH_2$ is *o*/*p* directing group, yet aniline on nitration gives a significant amount of *m*-nitroaniline. **[*CBSE Delhi 2017*]**

20. Write equations involved in the following reactions:

(*i*) Ethanamine reacts with acetyl chloride.

(*ii*) Aniline reacts with bromine water at room temperature.

(*iii*) Aniline reacts with chloroform and ethanolic potassium hydroxide. **[*CBSE 2022(56/4/2)*]**

21. How will you carry out the following conversions:

(*i*) Nitrobenzene to Aniline

(*ii*) Ethanamide to Methanamine

(*iii*) Ethanenitrile to Ethanamine **[*CBSE 2022(56/4/2)*]**

22. (*i*) Illustrate the following reactions:

(*a*) Sandmeyer's reaction (*b*) Gattermann's reaction.

(*ii*) Write a chemical test to distinguish between aniline and methylamine.

[*CBSE Sample Paper 2017*]

23. (*i*) Write reasons for the following:

(*a*) Ethylamine is soluble in water whereas aniline is insoluble.

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

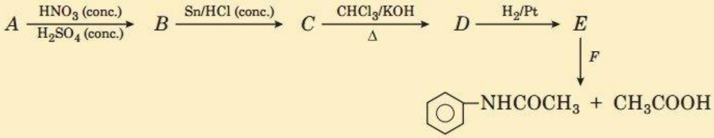
(*c*) Amines behave as nucleophiles.

(*ii*) Explain briefly:

(*a*) Carbylamine reaction

(*b*) Gabriel Phthalimide synthesis [*CBSE 2023(56/1/1)*]

24. Write structures of reagents/organic compounds (A to F) in the following sequence of reactions:



Answers

1. (*b*) **2.** (*d*) **3.** (*c*) **4.** (*a*) **5.** (*d*) **6.** (*d*) **7.** (*c*) **8.** (*a*) **9.** (*d*) **10.** (*b*)