CHAPTER

12

ORGANIC COMPOUNDS CONTAINING NITROGEN

Syllabus

- *Amines : Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines.*
- *Cyanides and isocyanides - will be mentioned at relevant places in text.*
- *Diazonium salts : Preparation, chemical reactions and importance in synthetic organic chemistry.*

Chapter Analysis

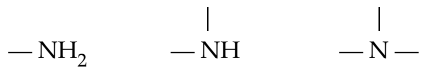
List of Topics	2016		2017		2018
	D	OD	D	OD	D/OD
IUPAC Name	**1Q (1 mark)**	**–**	**1Q (1 mark)**	**1Q (1 mark)**	**–**
Name Reaction	**–**	**1Q (2 marks)**	**1Q (2 marks)**	**–**	**1Q (5 marks)***
Properties	**–**	**–**	**–**	**–**	**1Q (5 marks)***
Writing the structure of compounds/products in a reaction	**1Q (3 marks)***	**–**	**–**	**–**	**1Q (5 marks)***
Give reason	**–**	**1Q (3 marks)**	**1Q (3 marks)**	**1Q (3 marks)**	**1Q (5 marks)***
Chemical test to distinguish between	**–**	**–**	**–**	**–**	**1Q (5 marks)**

- * One question of 5 marks with two choices was asked. First choice has a question of 3 marks on Name Reactions and a question of 2 marks of give reason. Second choice has a question of 3 marks on writing the structure of main products in the reactions, a question of 1 mark on chemical test to distinguish between pair of compounds and a question of 1 mark on arranging given compounds in their increasing order of ${}_pK_b$ values.

On the basis of above analysis, it can be said that from exam point of view, IUPAC name, Name reactions, writing the structure of products for the reactions and give reason are the most important types of questions from the chapter.

Revision Notes

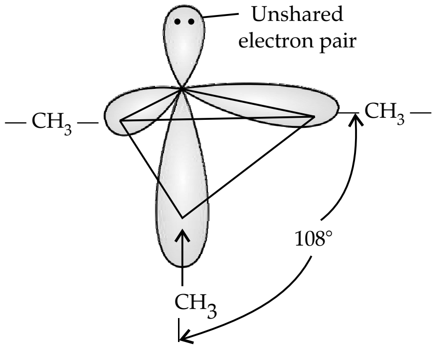
- **Amines :** Amines are considered as amino derivatives of hydrocarbons or alkyl derivatives of ammonia. In these compounds, one, two or three hydrogen atoms are replaced by alkyl or aryl groups. Aliphatic amino compounds are called amino alkanes and aromatic amines are called amino arenes. *e.g.*, CH_3NH_2, $C_2H_5NH_2$, $C_6H_5NH_2$ etc.
- **Classification of amines :**



$-NH_2$ $\quad -\overset{|}{N}H \quad -\overset{|}{N}-$

Primary (1°) Secondary (2°) Tertiary (3°)

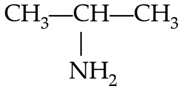
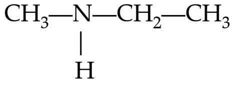
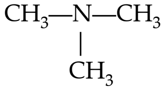
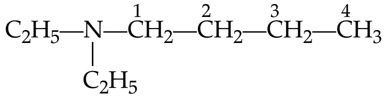
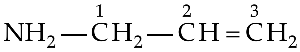
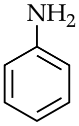
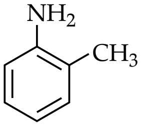
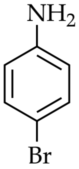
- **Structure of amines :**

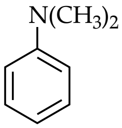


Pyramidal shape of trimethylamine

Nitrogen orbitals in amines are sp^3 hybridised and the geometry is pyramidal. Due to the presence of unshared pair of electrons, the angle C—N—E is less than 109.5°.

- **Nomenclature of some Alkylamines and Arylamines :**

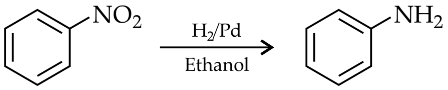
Amine	Common name	IUPAC name
$CH_3—CH_2—NH_2$	Ethylamine	Ethanamine
$CH_3—CH_2—CH_2—NH_2$	*n*-Propylamine	Propan-1-amine
 $CH_3—\underset{\underset{NH_2}{\vert}}{CH}—CH_3$	Isopropylamine	Propan-2-amine
 $CH_3—\underset{\underset{H}{\vert}}{N}—CH_2—CH_3$	Ethylmethylamine	N-Methylethanamine
 $CH_3—\underset{\underset{CH_3}{\vert}}{N}—CH_3$	Trimethylamine	N, N-Dimethylmethanamine
 $C_2H_5—\underset{\underset{C_2H_5}{\vert}}{N}—\overset{1}{C}H_2—\overset{2}{C}H_2—\overset{3}{C}H_2—\overset{4}{C}H_3$	N, N-Diethylbutylamine	N, N-Diethylbutan-1-amine
 $NH_2—\overset{1}{C}H_2—\overset{2}{C}H=\overset{3}{C}H_2$	Allylamine	Prop-2-en-1-amine
$NH_2—(CH_2)_6—NH_2$	Hexamethylenediamine	Hexane-1, 6-diamine
	Aniline	Aniline or Benzenamine
	*o*-Toluidine	2-Aminotoluene
	*p*-Bromoaniline	4-Bromobenzylamine or 4-Bromoaniline

	N, N-Dimethylaniline	N, N-Dimethylbenzenamine

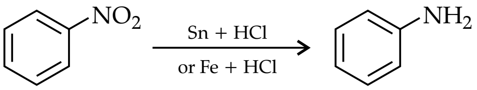
- **Preparation of Amines :**

(i) By reduction of nitro compounds :

(a)



(b)



(c)

$$R-NO_2 + 3H_2 \xrightarrow{Ni} \underset{1^\circ \text{ amine}}{R-NH_2} + 2H_2O$$

(ii) By ammonolysis of alkyl halides :

$$R\text{–}X + NH_3 \rightarrow \underset{(1^\circ)}{RNH_2} \xrightarrow{RX} \underset{(2^\circ)}{R_2NH} \xrightarrow{RX} \underset{(3^\circ)}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary ammonium salt}}{R_4\overset{+}{N}\overset{-}{X}}$$

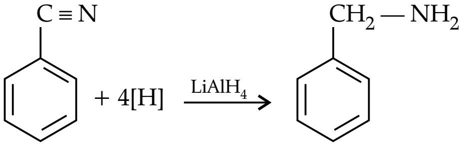
The free amine can be obtained from the ammonium salt by treatment with a strong base :

$$R-\overset{+}{N}H_3\overset{-}{X} + NaOH \rightarrow R-NH_2 + H_2O + \overset{+}{Na}\overset{-}{X}$$

(iii) By reduction of nitriles :

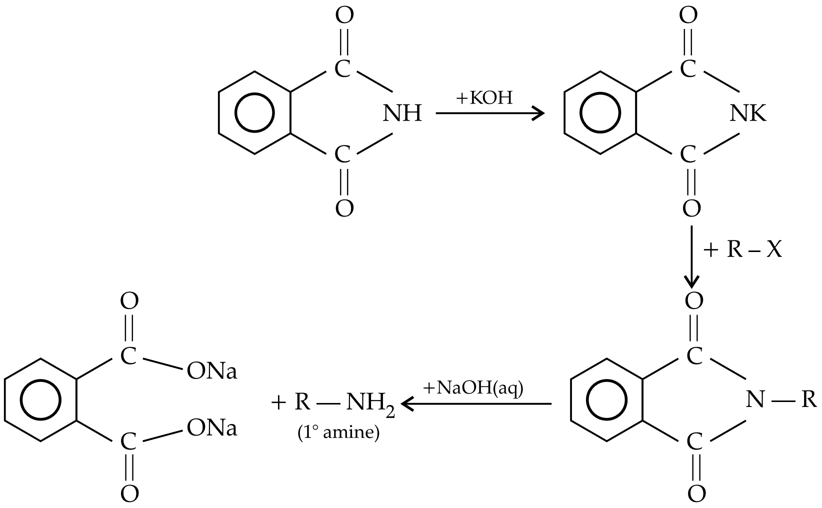
$$2H_2 + R-C\equiv N \xrightarrow{Ni} R-CH_2-NH_2$$

$$R-C\equiv N + 4\,[H] \xrightarrow[\text{or } LiAlH_4]{Na(Hg)/C_2H_5OH} \underset{1^\circ \text{ amine}}{R-CH_2-NH_2}$$

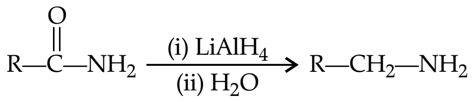


Benzylamine

(iv) Gabriel phthalimide synthesis :



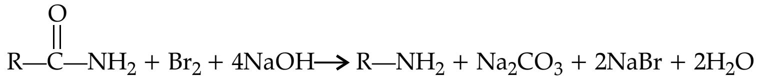
(v) By reduction of amides :



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} R-CH_2-NH_2$$

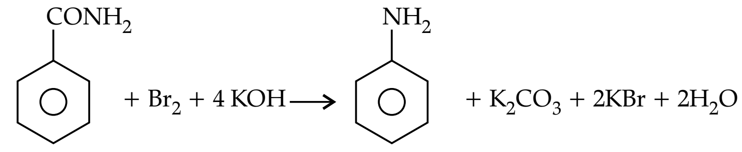
Amine

(vi) By Hoffmann bromamide degradation reaction :



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

1° amine



Benzamide Aniline

- **Physical properties :**

(i) Lower members are combustible gases, members from C_3 to C_{11} are volatile liquids and C_{12} onwards are gaseous. Lower aromatic amines are liquids.

(ii) Pure amines are colourless but develop colour on keeping in air for long time.

(iii) Boiling point increases with an increase in molecular weight. The order of boiling points of isomeric amines :

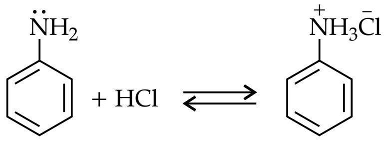
Primary > Secondary > Tertiary.

(vi) Lower members are readily soluble in water which decreases in water and increases in organic solvents with an increase in molecular weight.

- **Chemical properties :**

Reactions due to alkyl group :

$$R-\ddot{N}H_2 + \underset{\text{acid}}{HX} \rightleftharpoons R-\overset{+}{N}H_3\overset{-}{X} \text{ (Salt)}$$



Aniline Anilinium chloride

$$\underset{\text{Amine salts}}{R\overset{+}{N}H_3\overset{-}{X}} + \underset{\text{Base}}{\overset{-}{O}H} \longrightarrow \underset{\text{Parent amine}}{R\ddot{N}H_2} + H_2O + \overset{-}{X}$$

Due to presence of the alkyl group, reaction of amines with proton helps to share the proton of the acid and the ammonium ion formed is stabilized by dispersal of positive charge by +I effect of alkyl group. Thus, alkylamines are stronger bases than ammonia. The basic nature of aliphatic amines should increase with increase in the number of alkyl groups. The order of basicity of amines in the gaseous phase follows the expected order :

Tertiary amine > Secondary amine > Primary amine > NH_3.

The inductive effect, solvation effect and steric hindrance of the alkyl group decides the basic strength of alkyl amines in the aqueous state. The order of basic strength in case of methyl substituted amines and ethyl substituted amines in aqueous solution is as follows :

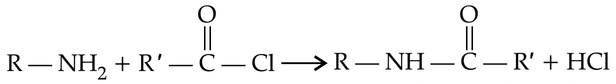
$$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$$
$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$$

As the $—NH_2$ group is attached directly to the benzene ring in aryl amines, this results in the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation. Thus, proton acceptability or the basic nature of aniline or other aromatic amines would be less than that of ammonia. In case of substituted aniline, it is observed that electron releasing groups like $—OCH_3$, $—CH_3$ increase basic strength whereas electron withdrawing groups like $—NO_2$, $—SO_3H$, —COOH, —X decrease it.

(i) Alkylation :

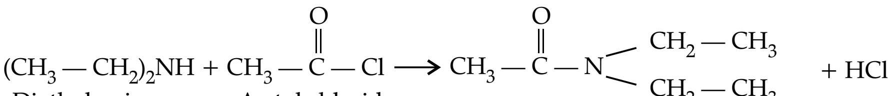
$$\begin{tikzcd}
\underset{\text{Ethylamine}}{CH_3-CH_2-NH_2} \arrow[r, "+CH_3-CH_2-Br", "-HBr"'] & (CH_3-CH_2)_2NH \arrow[d, "-HBr", "+CH_3-CH_2-Br"'] \\
\underset{\text{Tetraethyl ammonium bromide}}{(CH_3-CH_2)_4\overset{+}{N}Br^-} & \underset{\text{Triethylamine}}{(CH_3-CH_2)_3N} \arrow[l, "+CH_3-CH_2-Br"']
\end{tikzcd}$$

(ii) Acylation :



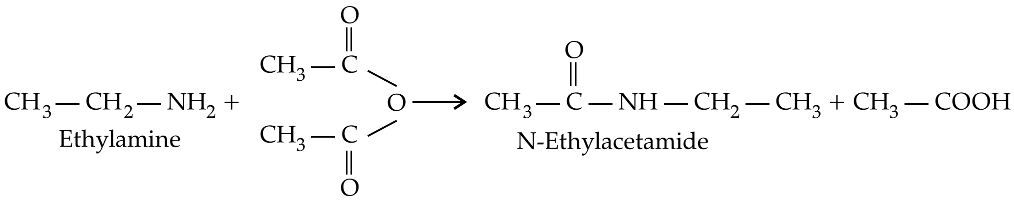
$$R-NH_2 + R'-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow R-NH-\overset{\overset{O}{\|}}{C}-R' + HCl$$

N-substituted amide



$$(CH_3-CH_2)_2NH + CH_3-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-N\begin{matrix} CH_2-CH_3 \\ CH_2-CH_3 \end{matrix} + HCl$$

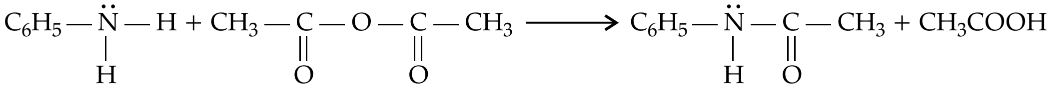
Diethylamine Acetyl chloride N, N—Diethylacetamide



$$CH_3-CH_2-NH_2 + \begin{matrix} CH_3-\overset{\overset{O}{\|}}{C} \\ CH_3-\underset{\underset{O}{\|}}{C} \end{matrix} \!\!>\! O \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-NH-CH_2-CH_3 + CH_3-COOH$$

Ethylamine N-Ethylacetamide

Acetic anhydride



$$C_6H_5-\underset{\underset{H}{|}}{\ddot{N}}-H + CH_3-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow C_6H_5-\underset{\underset{H}{|}}{\ddot{N}}-\underset{\underset{O}{\|}}{C}-CH_3 + CH_3COOH$$

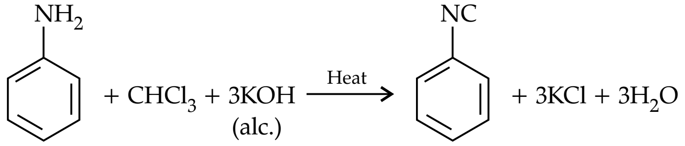
Benzenamine Ethanoic anhydride N-Phenylethanamide or Acetanilide

Benzoylation :

$$\underset{\text{Methlamine}}{CH_3NH_2} + \underset{\text{Benzoyl chloride}}{C_6H_5COCl} \rightarrow \underset{\text{N–Methylbenzamide}}{CH_3NHCOC_6H_5} + HCl$$

(iii) Carbylamine reaction : Secondary and tertiary amines do not give this reaction. This reaction is used as a test for primary amines.

$$R-NH_2 + CHCl_3 + \underset{(alc.)}{3KOH} \xrightarrow{\text{Heat}} R-NC + 3KCl + 3H_2O$$



$$C_6H_5NH_2 + CHCl_3 + \underset{(alc.)}{3KOH} \xrightarrow{\text{Heat}} C_6H_5NC + 3KCl + 3H_2O$$

(iv) Reaction with nitrous acid :

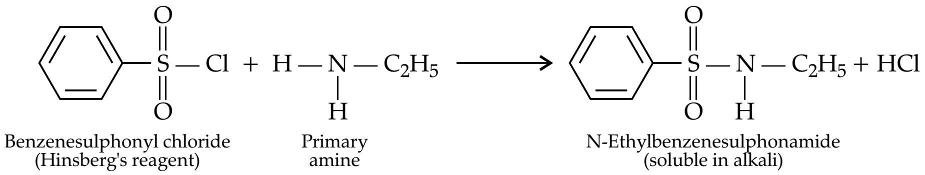
$$\underset{1^\circ \text{ amine}}{R-NH_2} + HNO_2 \xrightarrow{NaNO_2+HCl} [R-\overset{+}{N_2}\overset{-}{Cl}] \xrightarrow{H_2O} ROH + N_2 + HCl$$

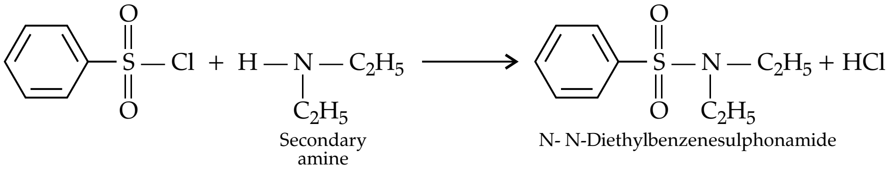
$$\underset{2^\circ \text{ amine}}{R_2NH} + HNO_2 \longrightarrow \underset{\text{N-Nitrosamine}}{R_2N-N=O} + H_2O$$

$$\underset{3^\circ \text{ amine}}{R_3N + HNO_2} \longrightarrow \underset{\text{Trialkyl ammonium nitrite}}{R_3NHNO_2}$$

$$\underset{\text{Aromatic amine}}{C_6H_5-NH_2} \xrightarrow[273-278K]{NaNO_2+2HCl} \underset{\text{Benzenediazonium chloride}}{C_6H_5-\overset{+}{N_2}\overset{-}{Cl}} + NaCl + 2H_2O$$

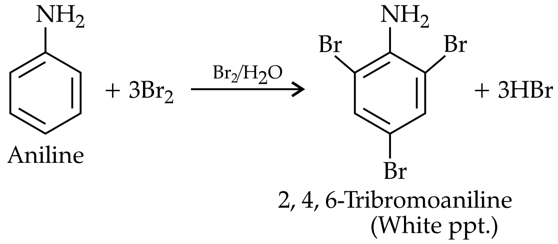
(v) Reaction with arylsulphonyl chloride :

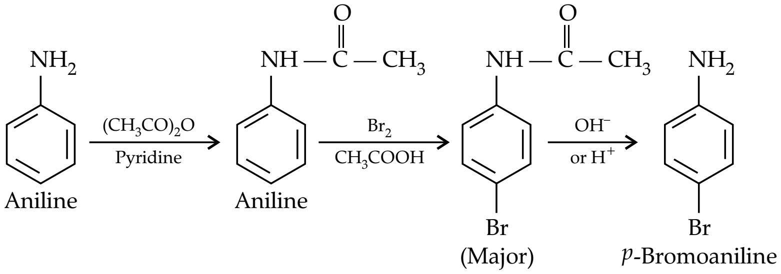




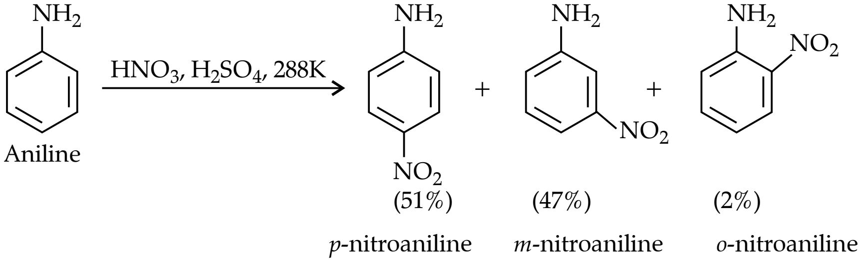
Tertiary amines do not react with benzenesulphonyl chloride.

(vi) Bromination :

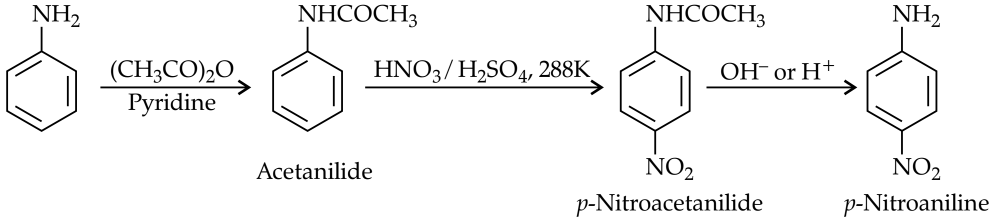




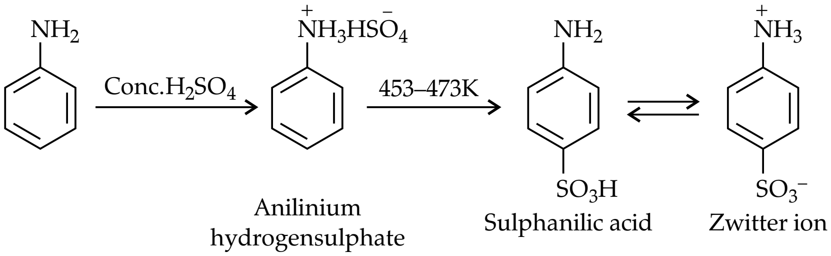
(vii) Nitration :



(viii) Preparation of monosubstituted aniline derivative by acetylation of —NH_2 group :



(ix) Sulphonation :

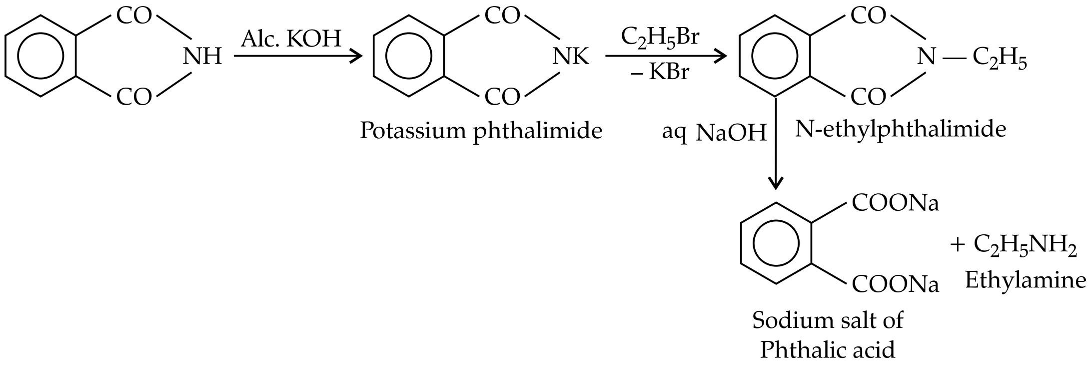


Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to salt formation with aluminium chloride.

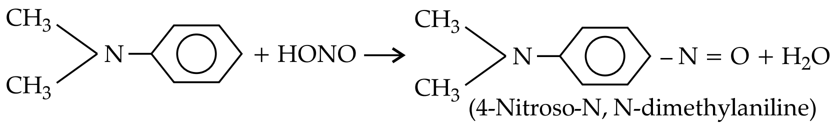
(x) Ammonolysis : Alkyl halide reacts with ammonia to form primary amine. The reaction of ammonia with alkyl halide is known as ammonolysis.

$$C_2H_5I \xrightarrow[-HI]{NH_3/343K} C_2H_5NH_2 \xrightarrow[-HI]{C_2H_5I} (C_2H_5)_2NH \xrightarrow[-HI]{C_2H_5I} (C_2H_5)_3N \xrightarrow{C_2H_5I} [(C_2H_5)_4N^+]I^-$$

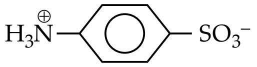
(xi) Gabriel phthalimide synthesis : In Gabriel phthalimide synthesis, pure primary aliphatic amines can be prepared by this process. In this process, phthalimide is reacted with alcoholic KOH to get potassium phthalimide which reacts with alkyl halide to form N-alkyl phthalimide which on basic hydrolysis gives primary amine.



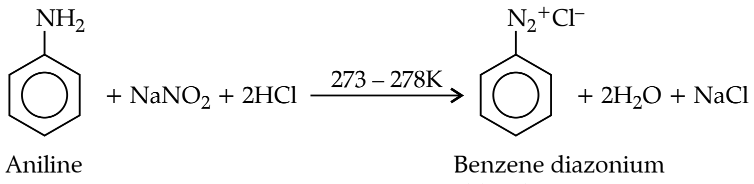
(xii) Nitrosation : Nitrosation is a process of reacting aromatic amines with nitrous acid to introduce nitroso group in it. *e.g.*,



(xiii) Zwitter ion formation : Zwitter ion is the ion which contains both positive and negative ions. It contains acidic as well as basic groups in the same molecule e.g.,



(xiv) Diazotisation : Diazotisation is a process of treating primary aromatic amines with nitrous acid at 273 – 278 K to get diazonium salts which are very useful compounds.



Aniline

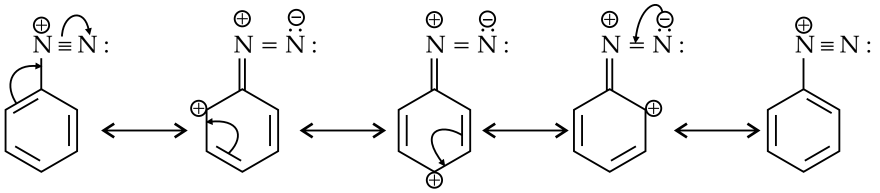
Benzene diazonium chloride

(xv) Friedel-Crafts reaction : Aniline does not undergo Friedel-Crafts reaction as it forms a salt with $AlCl_3$ which is a Lewis acid.

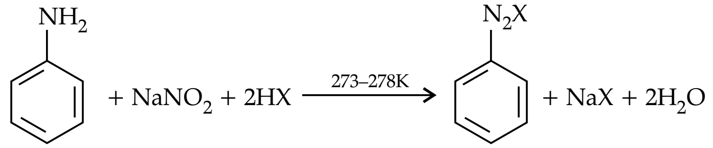
➢ **Diazonium salts :**

(i) General formula : $R\overset{+}{N_2}\overset{-}{X}$ where R stands for an aryl group and X^- ion may be Cl^-, Br^-, HSO_4^-, BF_4^- etc.

(ii) Stability of diazonium salts : Arenediazonium salts are more stable than alkyl diazonium salts due to the dispersal of the positive charge over the benzene ring.



(iii) Preparation of diazonium salts :



Aniline   Benzene diazonium salt

(iv) Chemical properties :

(a) Reactions involving displacement of nitrogen :

(i) Replacement by halide or cyanide ion–

$$Ar\overset{+}{N}_2\overset{-}{X} \xrightarrow{CuCl/HCl} ArCl + N_2$$
$$Ar\overset{+}{N}_2\overset{-}{X} \xrightarrow{CuBr/HBr} ArBr + N_2$$
$$Ar\overset{+}{N}_2\overset{-}{X} \xrightarrow{CuCN/KCN} ArCN + N_2$$

} Sandmeyer's reaction

$$Ar\overset{+}{N}_2\overset{-}{X} \xrightarrow{Cu/HCl} ArCl + N_2 + CuX$$
$$Ar\overset{+}{N}_2\overset{-}{X} \xrightarrow{Cu/HBr} ArBr + N_2 + CuX$$

} Gattermann's reaction

(ii) Replacement by iodide ion–

$$Ar\overset{+}{N_2}\overset{-}{Cl} + KI \longrightarrow ArI + KCl + N_2$$

Benzene diazonium chloride   Iodobenzene

(iii) Replacement by fluoride ion–

(a) $ArN_2{}^+Cl^- + HBF_4 \longrightarrow ArN_2{}^+BF_4^-$

(b) $Ar\overset{+}{N_2}\overset{-}{BF_4} \xrightarrow{\Delta} Ar — F + BF_3 + N_2$

(iv) Replacement by H—

(a) $Ar\overset{+}{N_2}\overset{-}{Cl} + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl$

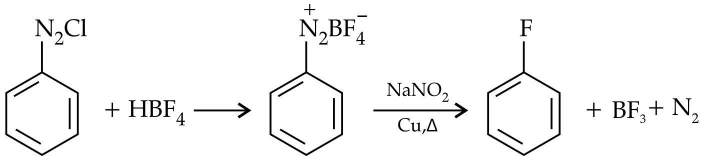
(b) $Ar\overset{+}{N_2}\overset{-}{Cl} + CH_3CH_2OH \longrightarrow ArH + N_2 + CH_3CHO + HCl$

(v) Replacement by hydroxyl group–

$$Ar\overset{+}{N_2}\overset{-}{Cl} + H_2O \xrightarrow{\Delta} ArOH + N_2 + HCl$$

Phenol

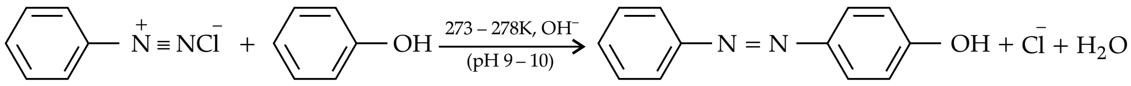
(vi) Replacement by — NO$_2$ group—(Balz-Schiemann reaction)



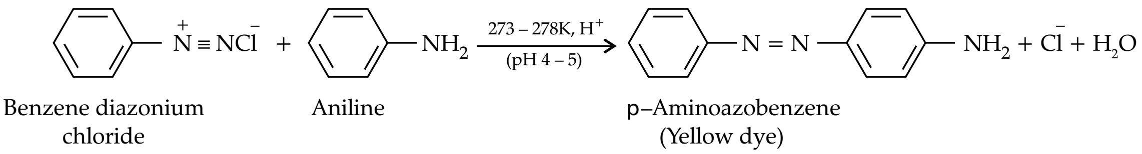
Fluoroboric acid   Nitrobenzene

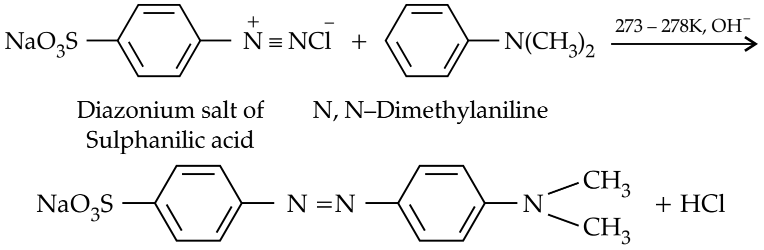
(b) Reactions involving retention of diazo group :

(i) Coupling reaction : The reaction of diazonium salts with phenols and aromatic amines to form azo compounds with the general formula, Ar — N = N — Ar is known as coupling reaction.



Benzene diazonium chloride   Phenol   p–Hydroxyazobenzene (Orange dye)

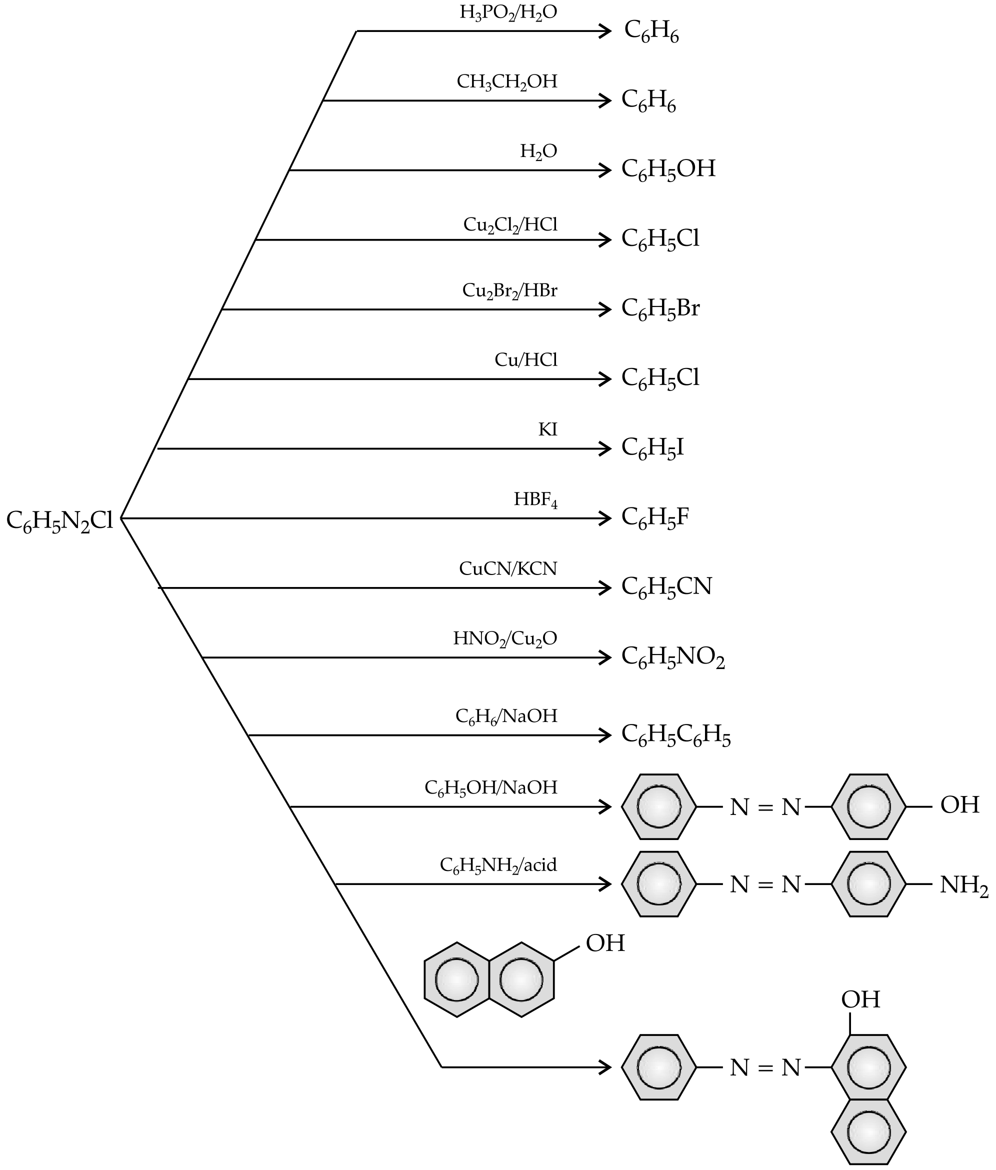




Methyl orange

(v) Importance of Diazonium salts : They are very good intermediates for the introduction of –F, –Cl, –Br, –I, –CN, –OH, $-NO_2$ groups into aromatic ring. Cyanobenzene can be prepared from diazonium salts.

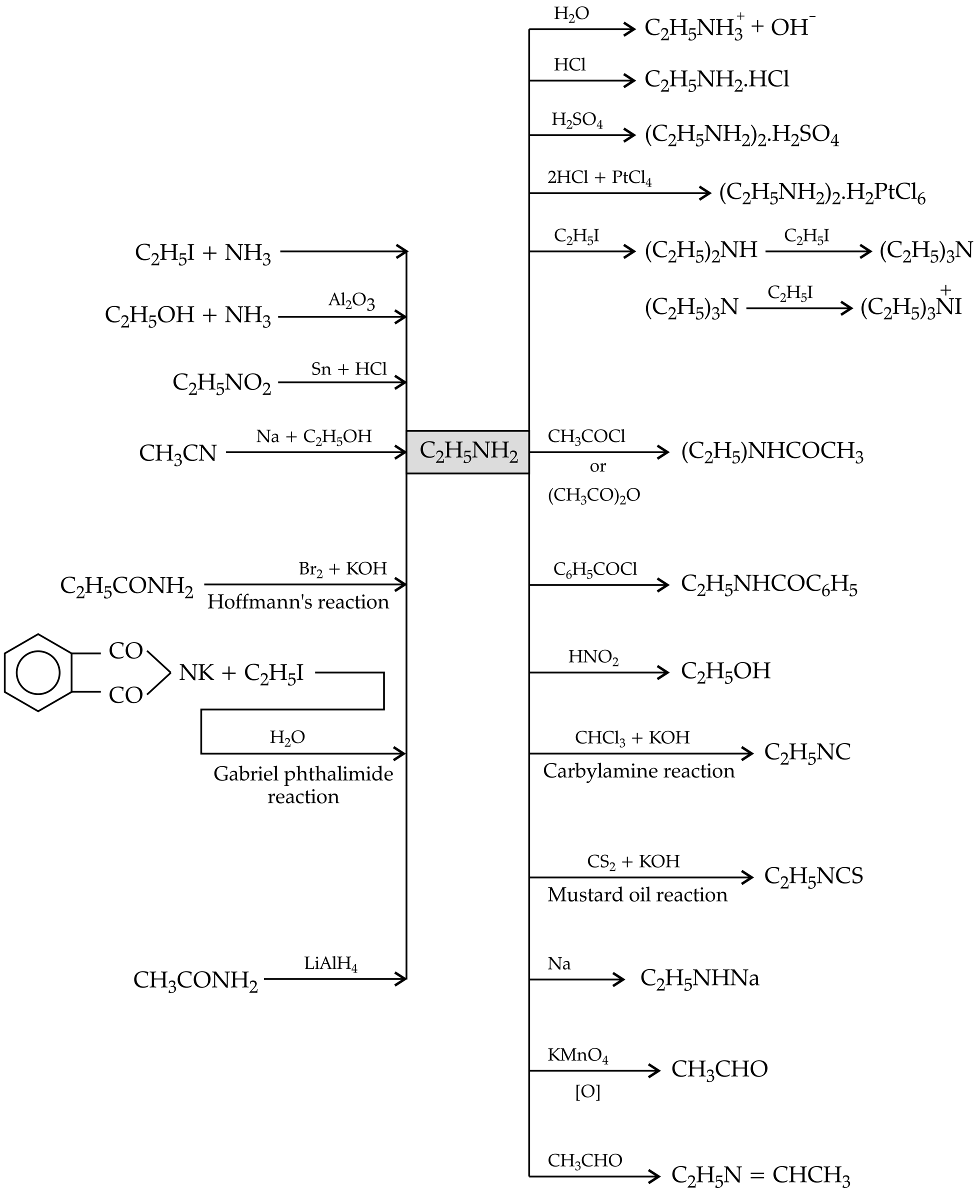
➢ **Synthesis of organic compounds form diazonium salts :**



- **Identification of primary, secondary and tertiary amines :**

S.No.	Test	Primary amine	Secondary amine	Tertiary amine
(i)	Reaction with nitrous acid.	Gives alcohol with effervescence of N_2 gas.	Gives oily nitrosoamine which gives Liebermann's nitrosoamine test.	Forms nitrite in cold soluble in water and on heating gives nitrosoamine
(ii)	Reaction with benzene sulphonyl chloride (Hinsberg's reagent).	Gives N-alkyl benzene-sulphonamide which is soluble in alkali.	Gives N, N-dialkyl benzene sulphonamide which is insoluble in alkali.	No reaction.
(iii)	**Carbylamine test** : Reaction with chloroform and alcoholic KOH.	Forms carbylamine or isocyanide (RNC) with characteristic unpleasant odour.	No reaction.	No reaction.
(iv)	**Hoffmann's mustard oil reaction :** Reaction with CS_2 and $HgCl_2$.	Forms N-substituted isothiocyanate with characteristic unpleasant smell of mustard oil.	No reaction.	No reaction.

- **Methods of preparation and reactions of ethylamine :**



Know the Terms

- **Gomberg-Bachmann reaction :** In the alkaline medium of sodium hydroxide, benzene diazonium chloride reacts with aromatic compound like benzene. When the diazo group is replaced by phenyl or aryl group. The reaction is called Gomberg-Bachmann reaction.
- **Baker-Mulliken test :** The hydroxyl amines when warmed with Tollen's reagent convert it to metallic silver. This reaction is used as a test for nitro compound and known as Baker-Mulliken test.
- **Schotten Baumann reaction :** Benzoylation of amines with benzoyl chloride is known as Schotten Baumann reaction.
- **Cope elimination :** It is quite useful to determine the structure of tertiary amines. It involves the treatment of a tertiary amine in which one of the alkyl group contains at least one β-hydrogen atom with hydrogen peroxide to get an amine oxide which later upon heating forms an alkane and a dialkyl hydroxyl amine.

Very Short Answer-Objective Type Questions (1 mark each)

A. Multiple choice Questions:

Q. 1. Which of the following is a 3° amine?

(a) 1-methylcyclohexylamine

(b) Triethylamine

(c) *tert*-butylamine

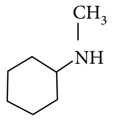
(d) N-methylaniline

U **[NCERT Exemp. Q. 1, Page 180]**

Ans. Correct option : (b)

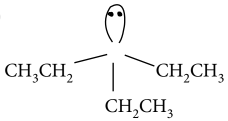
Explanation :

(a)



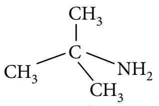
l-Methyl cyclohexylamine
(2°amine)

(b)



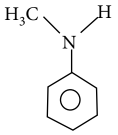
Triethylamine
(3°amine)

(c)



***tert*-Butylamine**
(1°amine)

(d)



N-methylaniline

Q. 2. The correct IUPAC name for $CH_2=CHCH_2\,NHCH_3$ is

(a) Allylmethylamine

(b) 2-amino-4-pentene

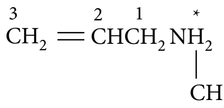
(c) 4-aminopent-1-ene

(d) N-methylprop-2-en-1-amine

A **[NCERT Exemp. Q. 2, Page 180]**

Ans. Correct option : (d)

Explanation :



$$\overset{3}{CH_2} = \overset{2}{C}H\overset{1}{C}H_2\,\underset{\displaystyle CH_3}{\overset{*}{N}H_2}$$

N-Methylprop-2-en-1-amine

Q. 3. Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine?

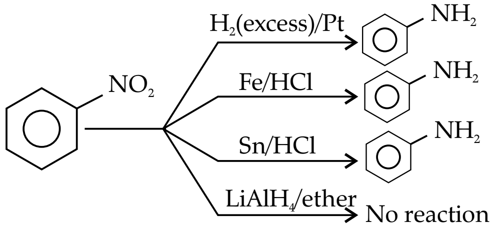
(a) H_2(excess)/Pt **(b) $LiAlH_4$ in ether**

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

R **[NCERT Exemp. Q. 6, Page 181]**

Ans. Correct option : (b)

Explanation :



Q. 4. 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 ___________.

(a) Sodium amide, $NaNH_2$

(b) Sodium azide, NaN_3

(c) Potassium cyanide, KCN

(d) Potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

R **[NCERT Exemp. Q. 7, Page 181]**

Ans. Correct option : (c)

Explanation : KCN is used to increase number of carbon atoms.

$$RX + KCN \rightarrow R - CN + KX$$

$$R - CN + 4H \xrightarrow{H_2/\text{Raney Ni}} R - CH_2NH_2$$

Q. 5. The source of nitrogen in Gabriel synthesis of amines is _____________.

(a) Sodium azide, NaN_3

(b) Sodium nitrite, $NaNO_2$

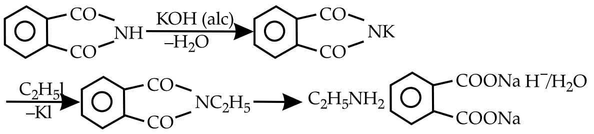
(c) Potassium cyanide, KCN

(d) Potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

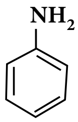
R **[NCERT Exemp. Q. 8, Page 181]**

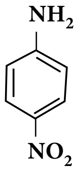
Ans. Correct option : (a)

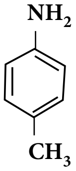
Explanation : Potassium phthalimide is the source of nitrogen in Gabriel synthesis.



Q. 6. The correct increasing order of basic strength for the following compounds is __________.

(I)


(II)


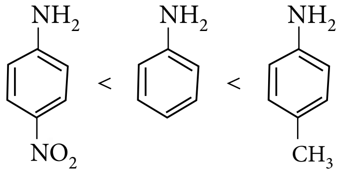
(III)


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

U [NCERT Exemp. Q. 13, Page 182]

Ans. Correct option : (d)

Explanation :



II I III

Electron withdrawing group decreases the basic strength while electron releasing groups increases the basic strength of aniline.

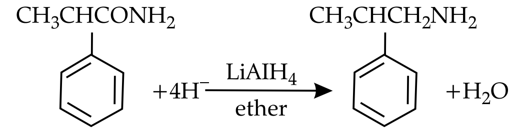
Q. 7. The best reagent for converting 2–phenylpropanamide into 2-phenylpropanamine is _____.

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

U [NCERT Exemp. Q. 10, Page 182]

Ans. Correct option : (d)

Explanation :



2–Phenylpropanamide 2–Phenylpropanamide

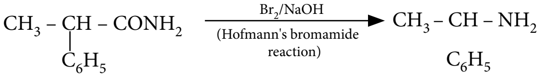
Q. 8. The best reagent for converting, 2-phenylpropanamide into 1- phenylethanamine is ____.

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

R [NCERT Exemp. Q. 11, Page 182]

Ans. Correct option : (b)

Explanation :



$$\underset{C_6H_5}{CH_3-CH}-CONH_2 \xrightarrow[\text{(Hofmann's bromamide reaction)}]{Br_2/NaOH} \underset{C_6H_5}{CH_3-CH}-NH_2$$

2-Phenylpropanamide 1-Phenylethanamine

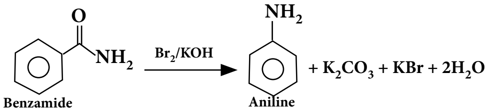
Q. 9. Hoffmann Bromamide Degradation reaction is shown by __________.

(a) $ArNH_2$ **(b) $ArCONH_2$**
(c) $ArNO_2$ **(d) $ArCH_2NH_2$**

R [NCERT Exemp. Q. 12, Page 182]

Ans. Correct option : (b)

Explanation : Hoffmann Bromamide degradation reaction is shown by $ArCONH_2$ by which amide is converted into amine via undergoing intramolecular migration of phenyl group.



Q. 10. Acid anhydrides on reaction with primary amines give ___________.

(a) amide **(b) imide**
(c) secondary amine **(d) imine**

R [NCERT Exemp. Q. 19, Page 183]

Ans. Correct option : (a)

Explanation :

$$C_2H_5NH_2+(CH_3CO)_2O \longrightarrow \underset{\text{N-Ethylacetamide}}{CH_3CONHC_2H_5}+CH_3COOH$$

B. Match the following :

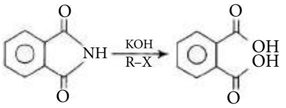
Q. 1. Match the species given in Column I with those mentioned in Column II.

S No.	Column I	S. No.	Column II
(i)	Ammonolysis	(a)	Amine with lesser number of carbon atoms
(ii)	Gabriel phthalimide synthesis	(b)	Detection test for primary amines
(iii)	Hoffmann Bromamide reaction	(c)	Reaction of phthalimide with KOH and R—X
(iv)	Carbylamine reaction	(d)	Reaction of alkylhalides with NH_3

[NCERT Exemp. Q. 66, Page 191]

Ans. (i) → (d), (ii) → (c), (iii) → (a), (iv) → (b)

Explanation :

Column I		Column II	
(i)	Ammonolysis	(d)	Reaction of alkyl halides with NH_3 $R-X \rightarrow RNH_2 + HCl$
(ii)	Gabriel phthalimide synthesis	(c)	Reaction of phthalimide with KOH and R—X 
(iii)	Hoffmann Bromamide reaction	(a)	Amine with lesser number of carbon atoms $RCONH_2 \xrightarrow{Br_2+NaOX} RNH_2$
(iv)	Carbylamine reaction	(b)	Detection test for primary amines

C. Answer the following:

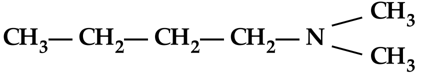
Q. 1. Write IUPAC name of the following compound:
$(CH_3CH_2)_2\ NCH_3$ A **[CBSE Delhi Set-1 2017]**

Ans. N–Ethyl–N-methylethanamine. **1**
[CBSE Marking Scheme 2017]

Q. 2. Write IUPAC name of the following compound:
$(CH_3)_2\ N–CH_2CH_3$ A **[CBSE Delhi Set-3 2017]**

Ans. N,N–Dimethylethylamine **1**

Q. 3. Write IUPAC name of the following compound:

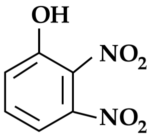


$CH_3—CH_2—CH_2—CH_2—N\begin{matrix}CH_3\\CH_3\end{matrix}$

A **[CBSE Comptt. OD Set 1, 2, 3 2017]**

Ans. N, N–dimethylbutan-1-amine **1**
[CBSE Marking Scheme 2017]

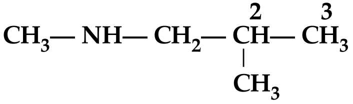
Q. 4. Write IUPAC name of the following compound:



A **[CBSE Comptt. Delhi Set 1, 2, 3 2017]**

Ans. 2, 3–dinitro phenol **1**
[CBSE Marking Scheme 2017]

AI **Q. 5. Write IUPAC name of the given compound:**

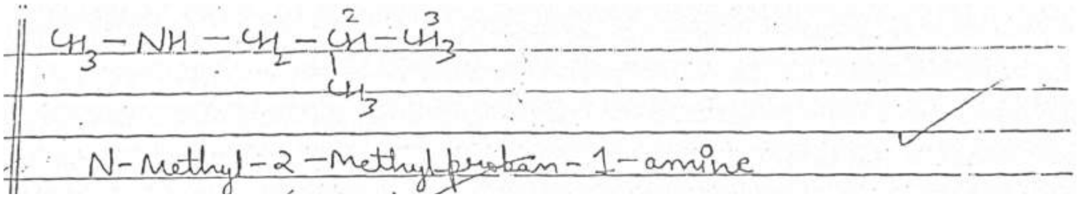


$CH_3—NH—CH_2—\underset{\displaystyle CH_3}{\overset{2}{CH}}—\overset{3}{CH_3}$

A **[CBSE OD Set-2 2017]**

Ans. N–Methyl-2-Methylpropan-1-amine **1**

OR



$CH_3 - NH - CH_2 - \underset{CH_3}{\overset{2}{CH}} - \overset{3}{CH_3}$

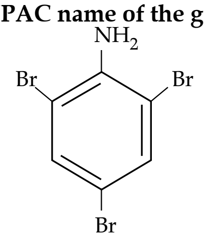
N-Methyl-2-Methyl-~~propan~~ propan-1-amine ✓

1
[Topper's Answer 2017]

Q. 6. Give the IUPAC name of $H_2N — CH_2 — CH_2 — CH = CH_2$. A **[CBSE Comptt. Delhi 2013]**

Ans. But-3-en-1-amine. **1**
[CBSE Marking Scheme 2013]

Q. 7. Write the IUPAC name of the given compound :



A **[CBSE Delhi 2016]**

Ans. 2, 4, 6 – Tribromoaniline / 2, 4, 6 – Tribromobenzenamine. **1**
[CBSE Marking Scheme 2016]

Q. 8. The conversion of primary aromatic amines into diazonium salts is known as ....
R **[CBSE OD 2014]**

Ans. Diazotisation reaction. **1**

Q. 9. Give the IUPAC name and structure of the amine obtained when 3-chlorobutanamide undergoes Hoffmann-bromamide reaction.
A **[CBSE SQP 2016]**

Ans. 3-Chloropropanamine, $CH_3CH(Cl)CH_2NH_2$. **1**

Q. 10. Arrange the following in increasing order of basic strength : Aniline, p-Nitroaniline and p-Toluidine
U **[CBSE Comptt. OD 2015]**

Ans. p-Nitroaniline < Aniline < *p*-Toluidine. **1**
[CBSE Marking Scheme 2015]

Q. 11. Arrange the following in the decreasing order of their basic strength in aqueous solutions :
CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$ and NH_3
U **[CBSE Delhi 2012]**

Ans. $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$. **1**
[CBSE Marking Scheme 2012]

Q. 12. Complete the following reaction equation :
$C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$ ....
R **[CBSE Comptt. Delhi 2015]**

Ans. $Ar\overset{+}{N_2}\overset{-}{Cl} + H_3PO_2 + H_2O \longrightarrow \underset{\text{Benzene}}{ArH} + N_2 + H_3PO_3 + HCl$ (where Ar is C_6H_5) **1**
[CBSE Marking Scheme 2015]

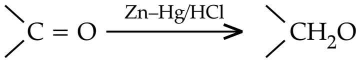
Commonly Made Error

- Some students only write benzene. All the products formed are not mentioned.

Short Answer Type Questions (2 marks each)

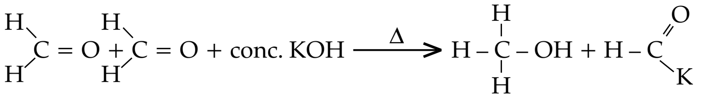
AI Q. 1. Write the reactions involved in the following reactions:
(i) Clemmensen reduction
(ii) Cannizzaro reaction R **[CBSE Delhi Set-3 2017]**

Ans. (i)



1

(ii)



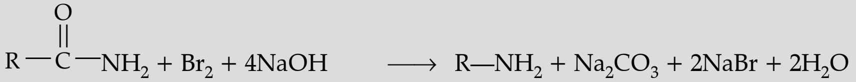
1

Commonly Made Error

- For Clemmensen's reduction, the correct condition for the reaction is not given by many students.

AI Q. 2. Write the chemical equations involved in the following reactions :
(i) Hoffmann-bromamide degradation reaction,
(ii) Carbylamine reaction. R **[CBSE OD 2016; Delhi 2012]**

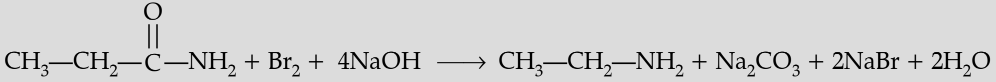
Ans. (i) Hoffmann-bromamide degradation reaction : When an amide is treated with bromine in aqueous or ethanolic solution of sodium hydroxide, a primary amine with one carbon atom less than the original amide is produced. This degradation is known as Hoffmann bromamide degradation reaction.



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

(Aqueous or alcoholic) 1° Amine 1

Example,



$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow CH_3-CH_2-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

Propanamide (Aqueous or alcoholic) Ethanamine

(ii) Carbylamine reaction : It is used as a test for detection of primary amines. When aliphatic or aromatic primary amines are heated with chloroform and alcoholic potassium hydroxide, carbylamine or isocyanides having foul smell are formed. Secondary and tertiary amines do not respond to this test.

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R-NC + 3KCl + 3H_2O$$

(Alcoholic) Alkyl isocyanide 1

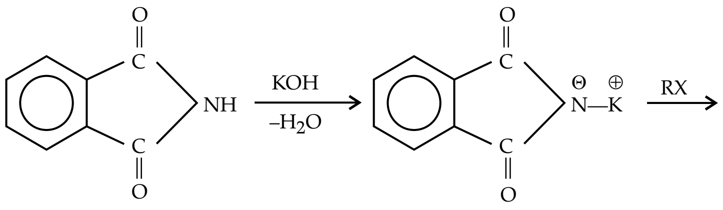
[CBSE Marking Scheme 2016]

Commonly Made Errors

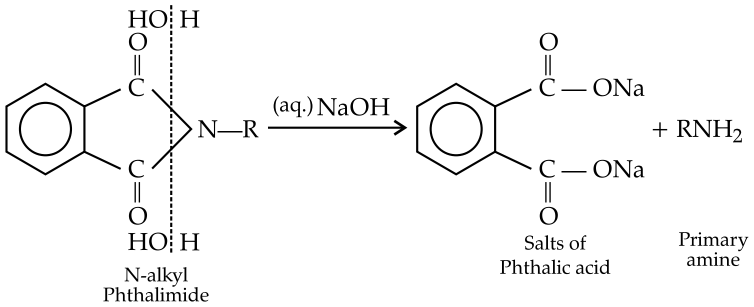
- **(i)** Hoffmann's degradation reaction : Some students are not able to write this equation correctly. On the product side, only alkyl amine was written in several cases; all the products formed were not mentioned by candidates.
- **(ii)** A number of students do not mention alcoholic KOH. Some give incomplete equations and some do not mention by products.

AI Q. 3. Explain the following reactions :
(i) Gabriel phthalimide reaction
(ii) Coupling reaction R **[CBSE Comptt. Delhi 2013]**

Ans. (i) Gabriel's phthalimide synthesis : Phthalimide when treated with alcoholic potassium hydroxide is easily converted into potassium phthalimide which on treatment with alkyl halide followed by hydrolysis with acid or alkali yields phthalic acid and a primary amine.

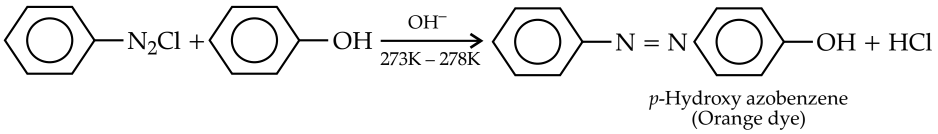


Phthalimide Potassium phthalimide



1

(ii) Coupling reaction : It involves the reaction of benzene diazonium salts with phenols or aryl amines. Coupling of phenol takes place in mild alkaline solution while with aromatic 1° amines in mild acidic medium.



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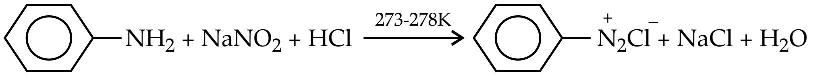
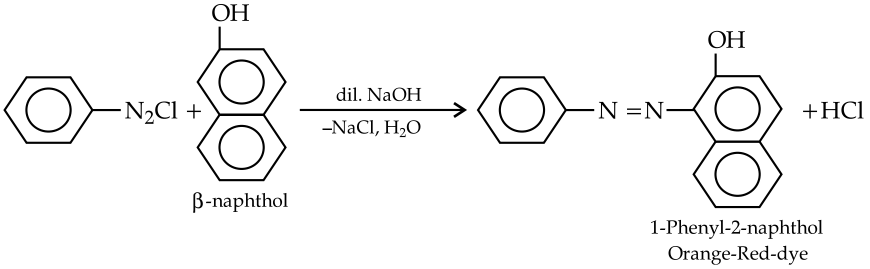
Q. 4. Give chemical tests to distinguish between the following pairs of compounds :

(i) Aniline and Ethylamine

(ii) Ethylamine and Dimethylamine A **[CBSE Comptt. Delhi 2013]**

Ans. (i) Aniline forms diazonium salt with $NaNO_2$/HCl which gives orange red dye with β-naphthol. Ethylamine does not give this test.





1

(ii) Ethylamine gives foul smelling ethyl isocyanide on heating with chloroform and potassium hydroxide solution. Dimethylamine does not give this test. 1

$$C_2H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_2H_5NC + 3KCl + 3H_2O$$

Commonly Made Errors

- Some students give those chemical tests which are given by both the compounds hence the compounds could not be distinguished.
- In several cases, only the name of the test is given, the reagents used and the observations are not written.

Q. 5. Give reasons :

(i) Aniline is a weaker base than cyclohexylamine.

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

A&E **[CBSE Comptt. OD 2013]**

Ans. (i) Cyclohexylamine is more basic than aniline because aniline is a resonance hybrid of various resonance structures. As a result, in aniline the electron donating capacity of nitrogen for protonation is considerably decreased. 1

(ii) Ammonolysis of alkyl halides does not give single amine but gives a mixture of primary, secondary and tertiary amines.

$$C_2H_5I \xrightarrow[-HI]{NH_3/343K} C_2H_5NH_2 \xrightarrow[-HI]{C_2H_5I} (C_2H_5)_2NH$$

$$\xrightarrow[-HI]{C_2H_5I} (C_2H_5)_3N \xrightarrow{C_2H_5I} [(C_2H_5)_4N^+]I^-$$

1

Q. 6. Give reasons :

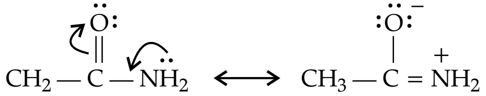
(i) Electrophilic substitution in aromatic amines takes place more readily than benzene.

(ii) CH_3CONH_2 is a weaker base than $CH_3CH_2.NH_2$.

A&E **[CBSE Comptt. OD 2013]**

Ans. (i) —NH_2 group of aromatic amines strongly activates the aromatic ring through delocalization of the lone pair of electrons of the N-atom over the aromatic ring. Due to the strong activating effect of the —NH_2 group, aromatic amines undergo electrophilic substitution reactions readily than benzene. **1**

(ii) Due to resonance, the lone pair of electrons on the nitrogen atom in CH_3CONH_2 is delocalized over the keto group.



As a result, electron density on the N-atom in CH_3CONH_2 decreases. On the other hand, in $C_2H_5NH_2$, due to +I effect of the ethyl group, the electron density on the N-atom increases consequently, CH_3CONH_2 is a weaker base than $CH_3CH_2NH_2$. **1**

Q. 7. A primary amine, RNH_2 can be reacted with CH_3—X to get secondary amine, R—$NHCH_3$ but the only disadvantage is that 3° amine and quaternary ammonium salts are also obtained as side products. Can you suggest a method where RNH_2 forms only 2° amine?

C [NCERT Exemp. Q. 54, Page 189]

Ans. $R—NH_2+CHCl_3+3KOH$

$$\longrightarrow \underset{\text{Alkyl isocyanide}}{R—NC} \xrightarrow[\text{(Reduction)}]{H_2/Pd} \underset{\text{2° Amine}}{R—NH—CH_3}$$

Carbylamine reaction is shown by 1° amine only which results in the replacement of two hydrogen atoms attached to nitrogen atom of NH_2 group by one carbon atom. On catalytic reduction, the isocyanide will give a secondary amine with one methyl group. **2**

Long Answer Type Questions-I

(3 marks each)

Q. 1. Write the structures of A, B and C in the following :

(i) $C_6H_5–CONH_2 \xrightarrow{Br_2/aq.KOH} A \xrightarrow[0\text{-}5°C]{NaNO_2+HCl} B \xrightarrow{KI} C$

(ii) $CH_3–Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow{CHCl_3+alc.KOH} C$.

A [CBSE Delhi 2016; DDE]

Ans. (i) $C_6H_5–CONH_2 \xrightarrow{Br_2/KOH} C_6H_5NH_2$

$[A] \xrightarrow{NaNO_2+HCl} C_6H_5N_2^+Cl^-$ [B] $\xrightarrow{KI} C_6H_5I$ [C]

1½

(ii) $CH_3Cl \xrightarrow{KCN} CH_3CN$ [A] $\xrightarrow{LiAlH_4}$

$CH_3CH_2NH_2$ [B] $\xrightarrow[\Delta]{CHCl_3+KOH} CH_3CH_2NC$ [C]

[CBSE Marking Scheme 2016] 1½

Q. 2. Give the structures of A, B and C in the following reaction : **A [CBSE SQP 2016]**

(i) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{HNO_2;273K} B \xrightarrow{C_6H_5OH} C$

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

Ans. (i) A—$C_6H_5NH_2$, B— $C_6H_5N_2^+Cl^-$, C— $C_6H_5–N_2—C_6H_4–OH$ ½+½+½

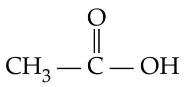
(ii) A—C_6H_5CN, B— C_6H_5COOH, C— $C_6H_5CONH_2$ ½+½+½

AI Q. 3. Give the structure of A, B and C in the following reactions :

(i) $C_6H_5NO_2 \xrightarrow{Sn+HCl} A \xrightarrow[273K]{NaNO_2+HCl} B \xrightarrow{H_2O} C$

(ii) $CH_3CN \xrightarrow{H_2O/H^+} A \xrightarrow[\Delta]{NH_3} B \xrightarrow{Br_2+KOH} C$ **A [CBSE Delhi 2014]**

Ans. (i) $C_6H_5NO_2 \xrightarrow{Sn+HCl} \underset{(A)}{C_6H_5NH_2} \xrightarrow[273K]{NaNO_2+HCl} \underset{(B)}{C_6H_5N_2^+Cl^-} \xrightarrow{H_2O} \underset{(C)}{C_6H_5OH}$ 1½



(ii) $CH_3CN \xrightarrow{H_2O/H^+} \underset{(A)}{CH_3—\overset{\overset{O}{\|}}{C}—OH} \xrightarrow[\Delta]{NH_3} \underset{(B)}{CH_3CONH_2} \xrightarrow{Br_2+KOH} \underset{(C)}{CH_3NH_2}$ 1½

Q. 4. Give the structure of A, B and C in the following reactions :

(i) $CH_3Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[273K]{HNO_2} C$

(ii) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{Br_2+KOH} B \xrightarrow{CHCl_3+NaOH} C$ **A [CBSE Delhi 2014]**

Ans. (i) $CH_3Br \xrightarrow{KCN} \underset{(A)}{CH_3CN} \xrightarrow{LiAlH_4} \underset{(B)}{CH_3CH_2NH_2} \xrightarrow[273\ K]{HNO_2} \underset{(C)}{CH_3CH_2-OH}$ ½ + ½ + ½

(ii) $CH_3COOH \xrightarrow[\Delta]{NH_3} \underset{(A)}{CH_3CONH_2} \xrightarrow{Br_2+KOH} \underset{(B)}{CH_3NH_2} \xrightarrow{CHCl_3+NaOH} \underset{(C)}{CH_3NC}$ ½ + ½ + ½

[CBSE Marking Scheme 2014]

Q. 5. Identify A, B and C in the following reactions:

(i) $CH_3CH_2Cl \xrightarrow{KCN} A \xrightarrow{H_2/Ni} B \xrightarrow{CH_3COCl/Base} C$

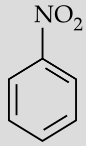
(ii) $C_6H_5N^+_2Cl^- \xrightarrow{HBF_4} A \xrightarrow[\Delta]{NaNO_2/Cu} B \xrightarrow{Sn/HCl} C$

A [CBSE Comptt. OD Set-1, 2, 3 2017]

Ans. (i) A: CH_3-CH_2CN; B $CH_3-CH_2-CH_2-NH_2$; C: $CH_3-CH_2-CH_2-NH-COCH_3$ ½ × 3

(ii)

A: $Ar-\overset{+}{N_2}\overset{-}{B}F_4$; B:



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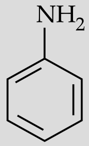


½ × 3

[CBSE Marking Scheme 2017]

Q. 6. Identify A, B and C in the following:

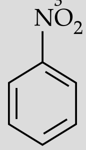
(i) $CH_3CH_2Cl \xrightarrow[NaCN]{Ethanolic} A \xrightarrow{H_2/Ni} B \xrightarrow{CH_3COCl/Base} C$

(ii) $C_6H_5N^+_2Cl^- \xrightarrow{HBF_4} A \xrightarrow[\Delta]{NaNO_2/Cu} B \xrightarrow{Sn/HCl} C$

A [CBSE Comptt. Delhi Set-1, 2, 3 2017]

Ans. (i) A: CH_3- CH_2CN; B CH_3- CH_2- CH_2NH_2 ; C: CH_3-CH_2- CH_2-NH-$COCH_3$ ½ × 3

A: $Ar-\overset{+}{N_2}\overset{-}{B}F_4$; B:



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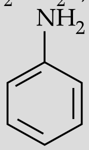


½ × 3

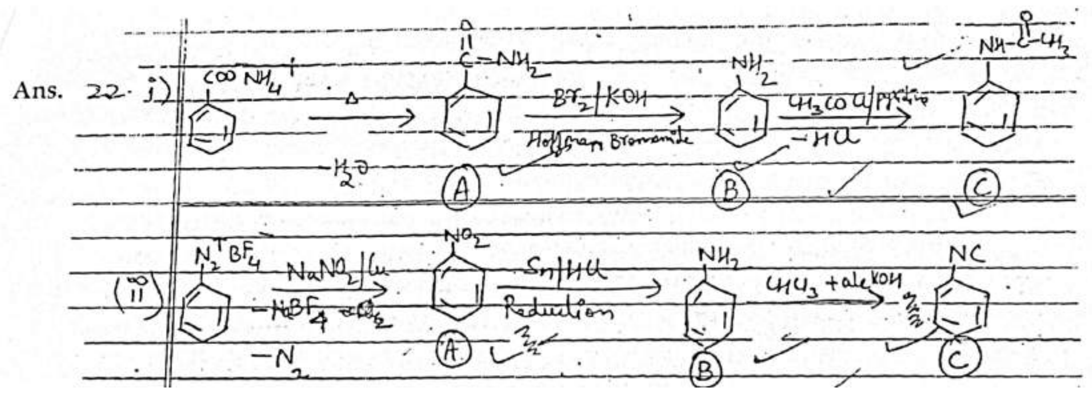
[CBSE Marking Scheme 2017]

Q. 7. Write the structures of A, B, C in the following reactions:

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

(ii) $C_6H_5\overset{+}{N_2}\overset{-}{B}F_4 \xrightarrow[\Delta]{NaNO_2/Cu} A \xrightarrow{Sn/HCl} B \xrightarrow{CHCl_3+alc.\ KOH} C$

A [CBSE OD Set-2 2016]



3

[Topper's Answer 2016]

Detailed Answer:

(i) A ⇒ $C_6H_5–CO–NH_2$

B ⇒ $C_6H_5–NH_2$

C ⇒ $C_6H_5–NH–CO–CH_3$

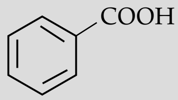
(ii) A ⇒ $C_6H_5–NO_2$

B ⇒ $C_6H_5–NH_2$

C ⇒ $C_6H_5–N{\equiv}C$ 3

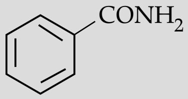
Q. 8. An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C. A **[CBSE Comptt. Delhi 2015]**

Ans. A–



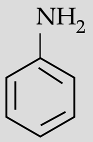
Benzoic acid ½ + ½

B–



Benzamide ½ + ½

C–



Aniline ½ + ½

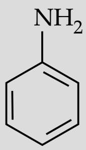
[CBSE Marking Scheme 2015]

Q. 9. An organic aromatic compound 'A' with the molecular formula C_6H_7N is sparingly soluble in water. 'A' on treatment with dil HCl gives a water soluble compound 'B'. 'A' also reacts with chloroform in presence of alcoholic KOH to form an obnoxious smelling compound 'C'. 'A' reacts with benzene sulhponyl chloride to form and alkali soluble compound 'D'. 'A' reacts with $NaNO_2$ and HCl to form a compound 'E' which on reaction with phenol forms an orange dye 'F'. Elucidate the structures of the organic compounds from 'A' to 'F'.

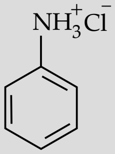
A **[CBSE SQP 2017]**

Ans.

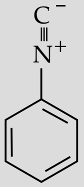
A



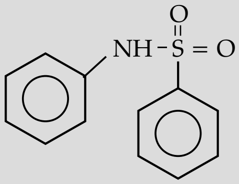
B



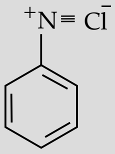
C



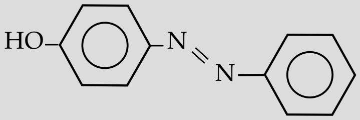
D



E



F



½ each

[CBSE Marking Scheme 2017]

Q. 10. Do as directed :

(i) Arrange the following compounds in the increasing order of their basic strength in aqueous solution : CH_3NH_2, $(CH_3)_3N$, $(CH_3)_2NH$.

(ii) Identify 'A' and 'B' :

$$C_6H_5NH_2 \xrightarrow{NaNO_2/HCl:273K} A \xrightarrow{H_2O/H^+} B$$

(iii) Write equation of carbylamine reaction. U + A + R **[CBSE Comptt. Delhi/OD 2018]**

Ans. (i) $(CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$ 1

(ii) A : $C_6H_5N_2^+Cl^-$ B : C_6H_5OH 1

(iii) $RNH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R-NC + 3KCl + 3H_2O$ 1

[CBSE Marking Scheme 2018]

AI Q. 11. 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 give a significant amount of m-nitroaniline.

A&E **[CBSE OD/Delhi Set-1, 2, 3 2017]**

Ans. (i) Due to the resonance, the electron pair of nitrogen atom gets delocalised towards carbonyl group/resonating structures. **1**

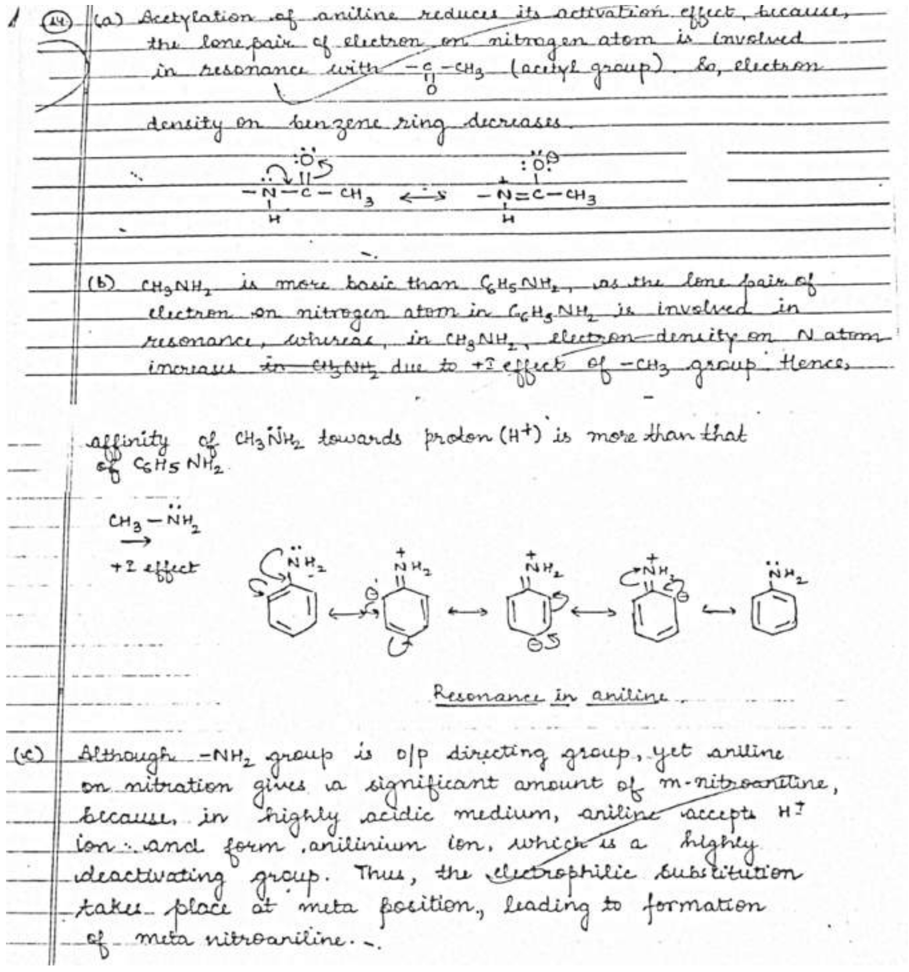
(ii) Because of +I effect in methylamine electron density at nitrogen increases whereas in aniline resonance takes place and electron density on nitrogen decreases/resonating structures. **1**

(iii) Due to protonation of aniline/formation of anilinium ion. **[CBSE Marking Scheme 2017] 1**

Answering Tip

- Draw the resonating structures and chemical reactions to support the answer wherever necessary.

OR



(14) (a) Acetylation of aniline reduces its activation effect, because, the lone pair of electron on nitrogen atom is involved in resonance with $-\underset{O}{\overset{\|}{C}}-CH_3$ (acetyl group). So, electron density on benzene ring decreases.

∴ $-\underset{H}{\underset{|}{\ddot{N}}}-\overset{:\ddot{O}}{\overset{\|}{C}}-CH_3 \longleftrightarrow -\underset{H}{\underset{|}{\overset{+}{N}}}=\overset{:\ddot{O}^{\ominus}}{\overset{|}{C}}-CH_3$

(b) CH_3NH_2 is more basic than $C_6H_5NH_2$, as the lone pair of electron on nitrogen atom in $C_6H_5NH_2$ is involved in resonance, whereas, in CH_3NH_2, electron density on N atom increases ~~in CH_3NH_2~~ due to +I effect of $-CH_3$ group. Hence, affinity of $CH_3\ddot{N}H_2$ towards proton (H^+) is more than that of $C_6H_5NH_2$.

$CH_3-\ddot{N}H_2$
$\longrightarrow$
+I effect

Resonance in aniline

(c) Although $-NH_2$ group is o/p directing group, yet aniline on nitration gives a significant amount of m-nitroaniline, because, in highly acidic medium, aniline accepts H^+ ion and form anilinium ion, which is a highly deactivating group. Thus, the electrophilic substitution takes place at meta position, leading to formation of meta nitroaniline.

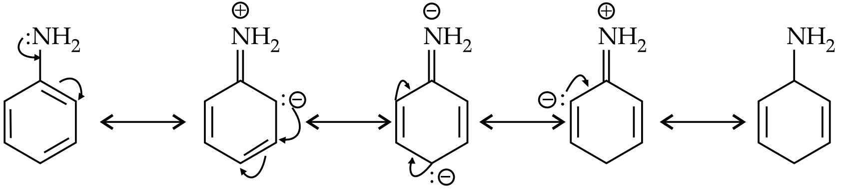
3

[Topper's Answer 2017]

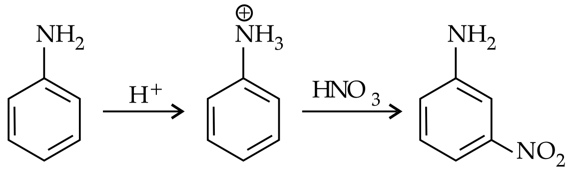
Detailed Answer:

(i) Acetylation of aniline reduces its activation effect as it decreases the electron density on nitrogen. Because of resonance, the electron pair of nitrogen atom gets delocalised towards carbonyl group thereby reducing the activation effect.

(ii) Due to +I effect in CH_3NH_2, electron density in methylamine at nitrogen increases whereas in $C_6H_5NH_2$ resonance takes place and electron density on nitrogen decreases.



(iii) Nitration of aniline occurs in an acidic medium i.e, in the presence of a mixture of concentrated HNO_3 and concentrated H_2SO_4. In acidic medium, aniline is protonated to give anilinium ion. As anilinium ion is meta-directing, it forms a significant amount of m-nitroaniline.



Aniline Anilinium ion m-Nitroaniline (47%) 3

Q. 12. How will you convert the following :

(i) Nitrobenzene into aniline,

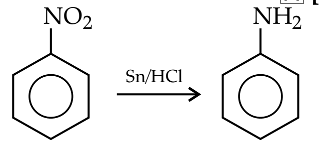
(ii) Ethanoic acid into methanamine,

(iii) Aniline to N-phenylethanamide.

(Write the chemical equations involved.)

A [CBSE Delhi 2014]

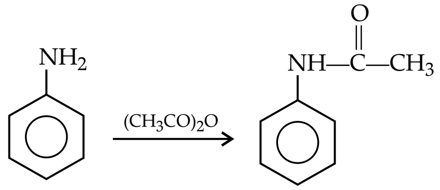
Ans. (i)



1

(ii) $CH_3COOH \xrightarrow[NH_3]{} CH_3CONH_2 \xrightarrow[+KOH]{Br_2} CH_3NH_2$ **1**

(iii)



1

Q. 13. Give reasons for the following :

(i) Aniline does not undergo Friedel-Crafts reaction,

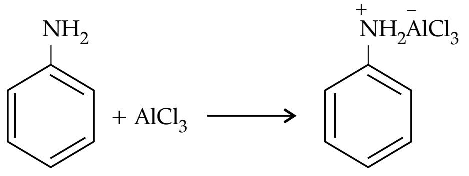
(ii) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution,

(iii) Primary amines have higher boiling point than tertiary amines. A&E [CBSE OD 2016; Delhi 2014]

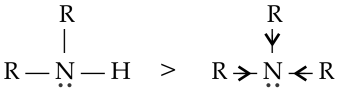
Ans. (i) A Friedel–Crafts reaction is carried out in the presence of $AlCl_3$. But $AlCl_3$ used as catalyst is acidic in nature *i.e.*, Lewis acid whereas aniline is a strong Lewis base. Thus, aniline reacts with $AlCl_3$ to form a salt.

Due to the positive charge on the N–atom, electrophilic substitution in the benzene ring is deactivated. Hence, aniline does not undergo Friedel–Crafts reaction. 1

(ii) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution. +I effect will increase in alkyl group that results in increasing the ease of donation of lone pair electron. Amine accepts a proton and form cation which will be stabilised in water by solvation. Higher the solvation by hydrogen bonding, higher will be the basic strength.

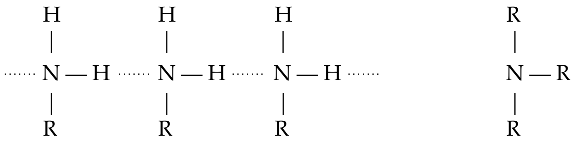


Aniline Salt



Therefore, with increase in methyl group, hydrogen bonding and stabilisation by solvation decreases. This net effect results in decrease of basic strength from secondary to tertiary amine. 1

(iii) In tertiary amine there are no H-atoms whereas in primary amines, two H-atoms are present. Due to the presence of H-atoms, primary amines undergo extensive intermolecular H-bonding.



Primary amine Tertiary amine

As a result, extra energy is required to separate the molecules of primary amine. Therefore, primary amines have higher boiling point than tertiary amine. 1

Long Answer Type Questions-II (5 marks each)

Q. 1. (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 :

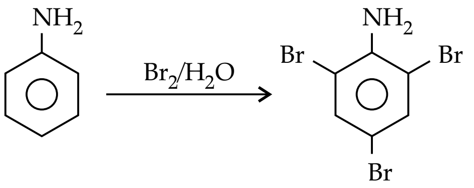
$C_2H_5NH_2$, C_2H_5OH, $(CH_3)_3N$

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

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

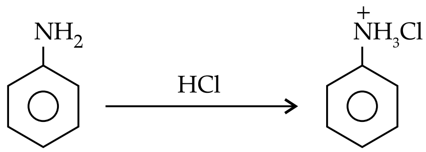
A + U [CBSE Delhi 2015]

Ans. (i) (a)



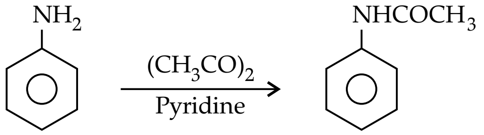
2,4,6-Tribromoaniline 1

(b)



Anilinium chloride **1**

(c)

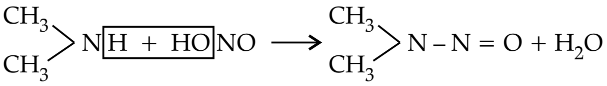


Acetanilide **1**

(ii) $$\underset{\text{increasing order of b. p.}}{\overrightarrow{(CH_3)_3N < C_2H_5NH_2 < C_2H_5OH}}$$

This order is due to H-bonding. **1**

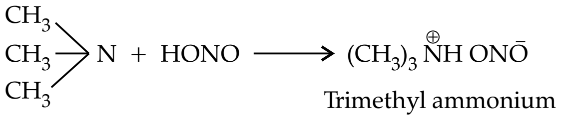
(iii) $(CH_3)_2NH$ reacts with nitrous acid to form an oily layer of N-nitrosamines, which are insoluble in aqueous mineral acids.



$$(CH_3)_2N\boxed{H + HO}NO \longrightarrow (CH_3)_2N-N=O + H_2O$$

N-nitrosamine (yellow ppt)

Whereas $(CH_3)_3N$ reacts with nitrous acid to form soluble nitrite salts with no ppt.



$$(CH_3)_3N + HONO \longrightarrow (CH_3)_3\overset{\oplus}{N}H\ ON\bar{O}$$

Trimethyl ammonium nitrite **1**

Commonly Made Error

- Some students only mention the reagents but the observations are not given.

Q. 2. (i) Write the structures of main products when benzenediazonium chloride reacts with the following reagents :

(a) $H_3PO_2 + H_2O$

(b) CuCN/KCN

(c) H_2O

(ii) Arrange the following in the increasing order of their basic character in an aqueous solution :

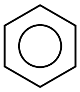
$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$

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

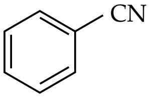
$C_6H_5-NH_2$ and $C_6H_5-NH-CH_3$

A + U **[CBSE OD 2015]**

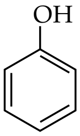
Ans. (i) (a)



(b)



(c)



1 + 1 + 1

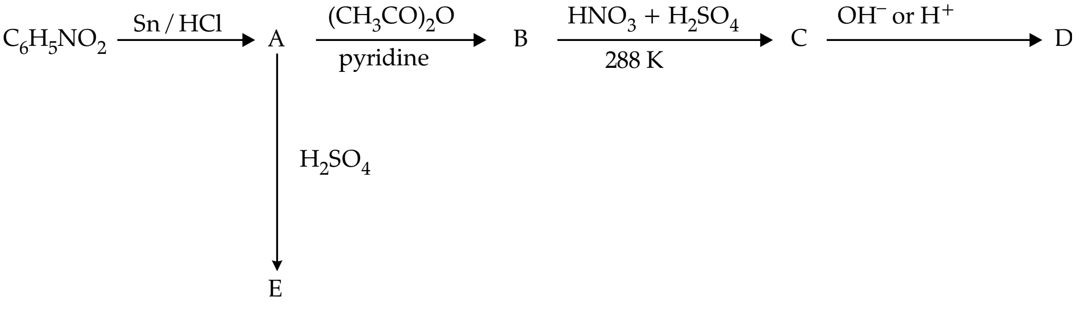
(ii) $C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$ **1**

(iii) Add $CHCl_3$ and alc. KOH, C_6H_5–NH_2 gives foul smell of isocyanide whereas C_6H_5–NH–CH_3 does not (or any other correct test). **1**

Commonly Made Error

- (ii) Some students give incorrect sequence of compounds.

Q. 3. Write the structure of A, B, C, D and E in the following reactions:



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

A

OR

(i) Write the structures of the main products when benzene diazonium chloride reacts with the following reagents:

(a) CuCN

(b) CH_3CH_2OH

(c) Cu / HCl

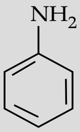
(ii) Arrange the following in the increasing order of their basic strength:

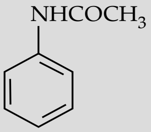
CH_3NH_2, $(CH_3)_2NH$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$

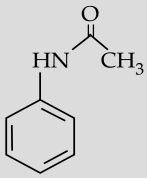
(iii) Write one chemical test to distinguish between Aniline and Ethyl amine.

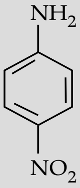
A + U **[CBSE Foreign Set-1, 2, 3 2017]**

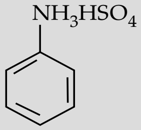
Ans.

A 

B 

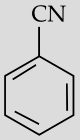
C 

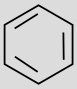
D 

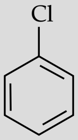
E 

1 × 5=5

OR

(i) (a) 

(b) 

(c) 

1 + 1 + 1

(ii) $C_6H_5NH_2 < C_6H_5CH_2NH_2 < CH_3NH_2 < (CH_3)_2NH$ **1**

(iii) Add $NaNO_2$+ HCl to both the compounds at 273K followed by addition of phenol. Aniline gives orange dye.**1**

(Or any other correct test) [CBSE Marking Scheme 2017]

Commonly Made Error

- Students write just the name of the test and not the reagent i.e., NaOH and I_2.

Answering Tips

- Specify the reagents involved in distinguishing each compound followed by the response of each.
- Be careful while writing the structures, as the answer must correspond to the question.

AI **Q. 4. 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 :**

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

A **[CBSE Delhi 2015]**

Ans.

$$\begin{tikzcd}
 & & \begin{matrix}\text{Benzene}\\ (C)\ C_6H_6\end{matrix} \\
\begin{matrix}C_6H_5CONH_2\\ (A)\\ \text{Benzamide}\end{matrix} \arrow[r, "Br_2 + KOH"] & \begin{matrix}C_6H_5NH_2\\ \text{Aniline}\end{matrix} \arrow[r, "NaNO_2 + HCl", "273\ K"'] \arrow[d, "CuCl_3 + NaOH"'] & C_6H_5N_2Cl\ (B) \arrow[u, "CH_3CH_2OH"'] \arrow[d, "KI"] \\
 & \begin{matrix}C_6H_5NC\\ (D)\\ \text{Phenyl isocyanide}\end{matrix} & \begin{matrix}C_6H_5I\\ (E)\\ \text{Phenyl}\\ \text{iodide}\end{matrix}
\end{tikzcd}$$

5

Q. 5. (i) Account for the following:

(a) CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN.

(b) 2-Fluorobutanoic acid is a stronger acid than 3-Fluorobutanoic acid.

(ii) Write the chemical equation to illustrate the following name reactions:

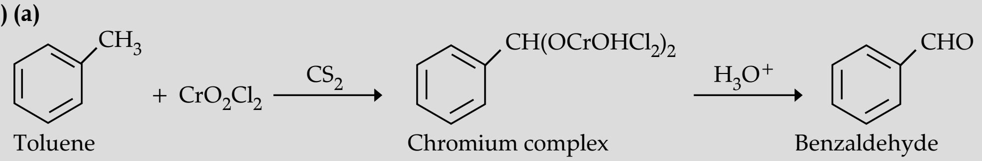
(a) Etard reaction. (b) Rosenmund's reaction.

(iii) Give the mechanism of cyanohydrin formation when carbonyl compounds react with HCN in the presence of alkali. A&E + R + A **[CBSE SQP 2017]**

Ans. (i) (a) Steric and electronic factor. ½+ ½

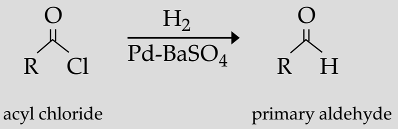
(b) Inductive effect decreases with distance and hence the conjugate base of 2-Fluorobutanoic acid is more stable. **1**

(ii) (a)



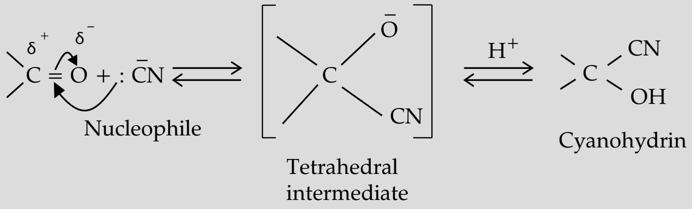
1

(b)



1

(iii) $HCN + \bar{O}H \rightleftharpoons :\bar{C}N + H_2O$



1

[CBSE Marking Scheme 2017]

Commonly Made Error

(ii) Students write only the reaction taking place.

(iii) Write incorrect shifting of electron.

Answering Tip

(iii) Show the electron transfer through arrows.

Detailed Answer :

(i) (a) CH_3COCH_3 is more sterically hindered than CH_3CHO because of the presence of alkyl group on both the sides of carbonyl carbon, making it less reactive due to -I effect. **1**

(b) Because the electronegative fluorine atom closer to the –COOH group is exerting stronger inductive effect. **1**

Q. 6. (a) Write the reactions involved in the following :

(i) Hoffmann bromamide degradation reaction

(ii) Diazotisation

(iii) Gabriel phthalimide synthesis

(b) Give reasons :

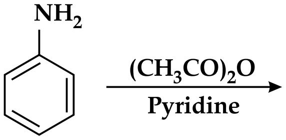
(i) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution.

(ii) Aromatic diazonium salts are more stable than aliphatic diazonium salts. R + A&E

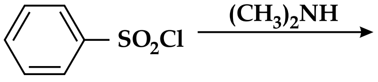
OR

(a) Write the structures of the main products of the following reactions :

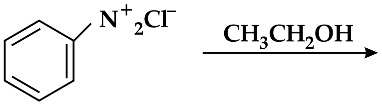
(i)



(ii)



(iii)



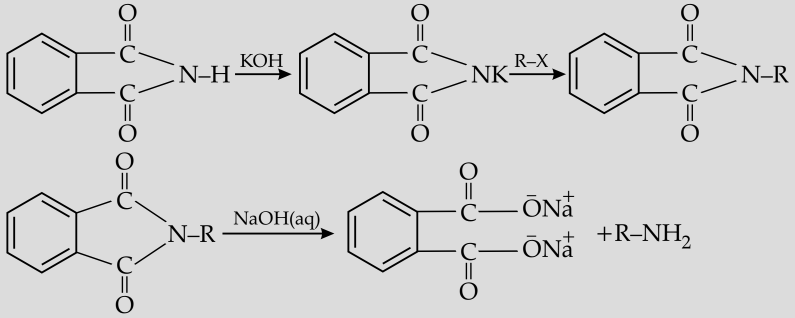
(b) Give a simple chemical test to distinguish between Aniline and N,N-dimethylaniline.

(c) Arrange the following in the increasing order of their ${}_pK_b$ values :
$C_6H_5NH_2$, $C_2H_5NH_2$, $C_6H_5NHCH_3$ A + U **[CBSE Delhi/OD 2018]**

Ans. (i) $Ar/R–CONH_2 + Br_2 + 4NaOH \rightarrow Ar/R–NH_2 + 2NaBr + Na_2CO_3 + 2H_2O$ 1

(ii) $C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{-}278k} C_6H_5N_2Cl + NaCl + 2H_2O$ (or any other correct equation) 1

(iii)



1

(b) (i) Because of the combined factor of inductive effect and solvation or hydration effect. 1

(ii) Due to resonance stabilisation or structural representation/resonating structures. 1

OR

(a) (i) $C_6H_5NHCOCH_3$ 1

(ii) $C_6H_5SO_2N(CH_3)_2$ 1

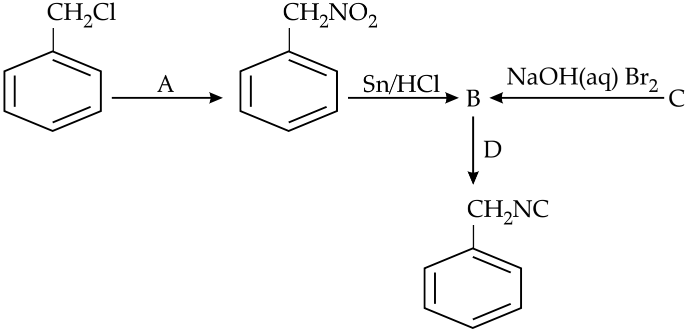
(iii) C_6H_6 1

(b) Add chloroform in the presence of KOH and heat, Aniline gives a offensive smell while N, N dimethylaniline does not. (or any other correct test) 1

(c) $C_2H_5NH_2 < C_6H_5NHCH_3 < C_6H_5NH_2$ 1

[CBSE Marking Scheme 2018]

Q. 7. (a) Identify A-D



(b) Distinguish between the following pair of compounds:

(i) Aniline and Benzylamine.

(ii) Methylamine and Dimethylamine.

(c) Complete the following:

$$CH_3CH_2CN \xrightarrow[\text{OR}]{LiAlH_4} A \xrightarrow{0°C/HNO_2} B$$

A

OR

AI **(a) Account for the following:**

(i) Direct nitration of aniline yields significant amount of meta derivative.

(ii) Primary aromatic amines cannot be prepared by Gabriel phthalimide synthesis.

(b) Carry out the following conversions:

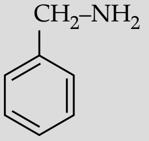
(i) Ethanoic acid into methanamine.

(ii) Aniline to p-Bromoaniline.

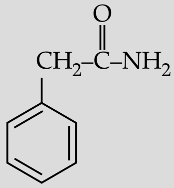
(c) Arrange the following in increasing order of basic strength:
Aniline, p-nitroaniline and p-toludine. A&E + A + U **[CBSE SQP 2018-2019]**

Ans. (a) A = $AgNO_2$ ½

B=



½

C=  ½

D=$CHCl_3$+KOH, Heat. ½

(b) (i)

Experiment	Aniline	Benzylamine
Azo dye test : Dissolve the amine in HCl, cool it and then add cold aqueous solution of $NaNO_2$ and then solution of β-naphthol	A brilliant orange red dye is observed.	No dye is formed.

1

(ii)

Experiment	Methylamine	Dimethylamine
Carbylamine test : To the organic compund add chloroform and ethanolic potassium hydroxide and heat	A foul smelling substance (isocyanide)	No dye is formed.

1

(or any other suitable test)

(c) A = $CH_3CH_2CH_2NH_2$ ½

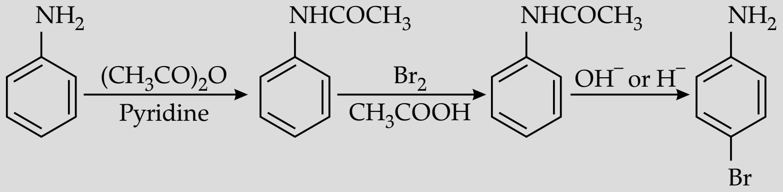
B = $CH_3CH_2CH_2OH$ ½

OR

(a) (i) In strongly acidic medium, aniline is protonated to form the anilium ion which is meta directing. **1**

(ii) Aryl halides do not undergo nucleophile substitution with the anion formed by phathalimide. **1**

(b) (i) $CH_3\text{–}COOH \xrightarrow{NH_3,\ \Delta} CH_3\text{–}CO\text{–}NH_2 \xrightarrow{NaOH\ +\ Br_2} CH_3NH_2$ **1**

(ii)  **1**

(c) p-Nitoraniline < Aniline < p-Toludine. **1**

[CBSE Marking Scheme 2018]