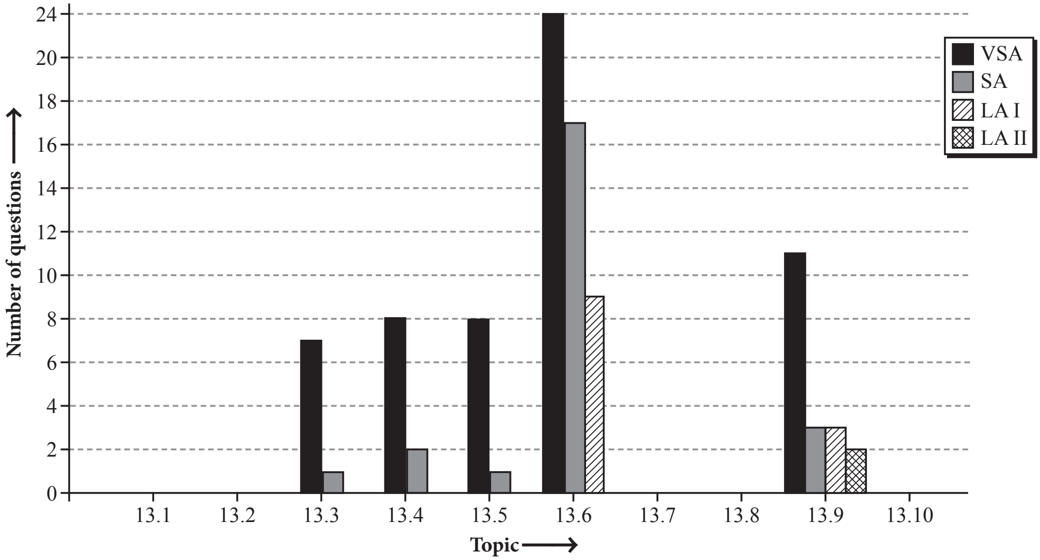
CHAPTER

13

Amines

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2020-2011)



- Maximum total weightage is of *Chemical Reactions of Amines.*
- Maximum VSA type questions were asked from *Chemical Reactions of Amines.*
- Maximum SA and LA I type questions were asked from *Chemical Reactions of Amines.*

QUICK RECAP

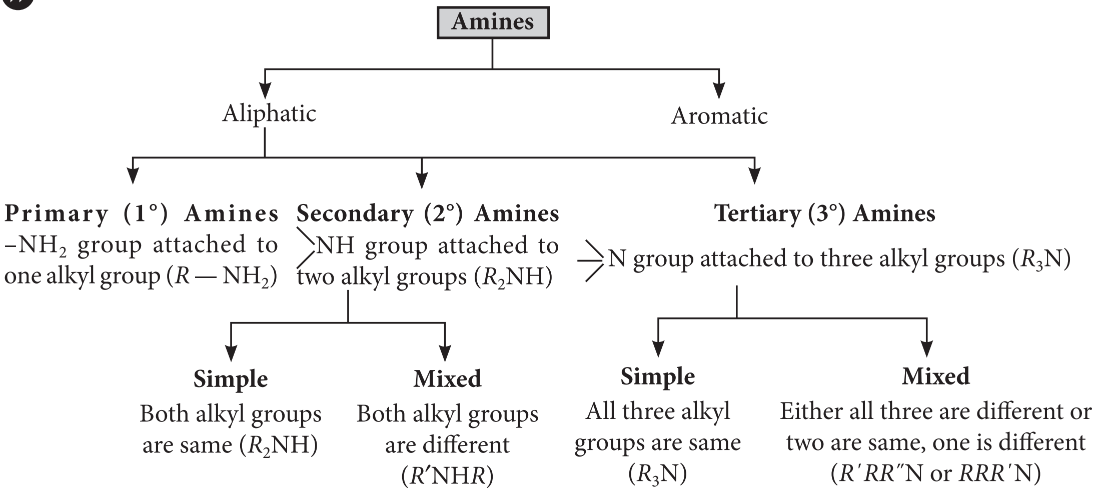
AMINES

- **Amines :** These are alkyl or aryl derivatives of ammonia and are obtained by replacing one, two or three hydrogen atoms by alkyl/aryl groups.

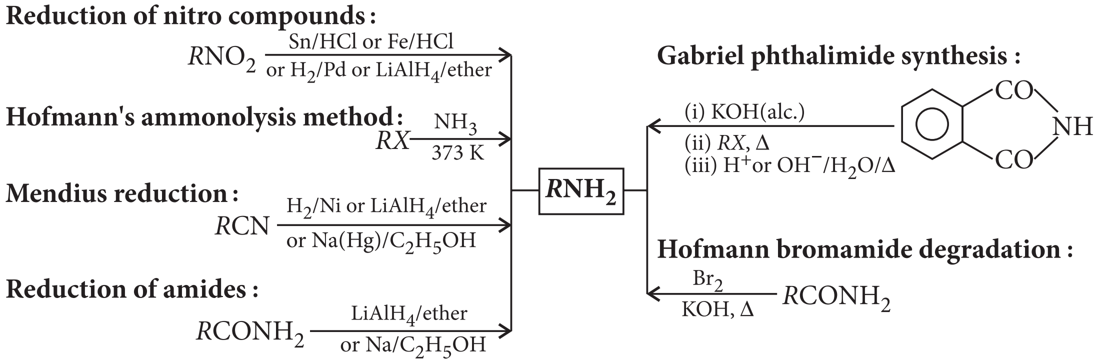
Nomenclature : In common system, an aliphatic amine is named by prefixing alkyl group to amine, *i.e.*, *alkylamine*. In IUPAC system, amines are named as *alkanamines*. In secondary and tertiary amines, when two or more groups are the same, the prefix *di* or *tri* is appended before the name of alkyl group.

Structure : Nitrogen orbitals in amines are sp^3-hybridised and the geometry of amines is pyramidal. Due to the presence of unshared pair of electrons, the angle $C-N-E$, (where E is C or H) is less than 109.5°.

Classification :



Preparation :



- **Limitations of Gabriel phthalimide synthesis :**
  - It is used for the preparation of only 1° amines. *tert*-Butylamine is a 1° amine, but cannot be prepared by this method. In this case, elimination takes place.
  - Aromatic 1° amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution reaction with potassium phthalimide under mild conditions.

Physical properties :

- Lower amines are gases and liquids but higher amines are solids.
- Primary and secondary amines have higher boiling points than other organic compounds due to hydrogen bonding.
- Primary and secondary amines are soluble in water due to hydrogen bonding between $>NH_2$ and H_2O molecules.

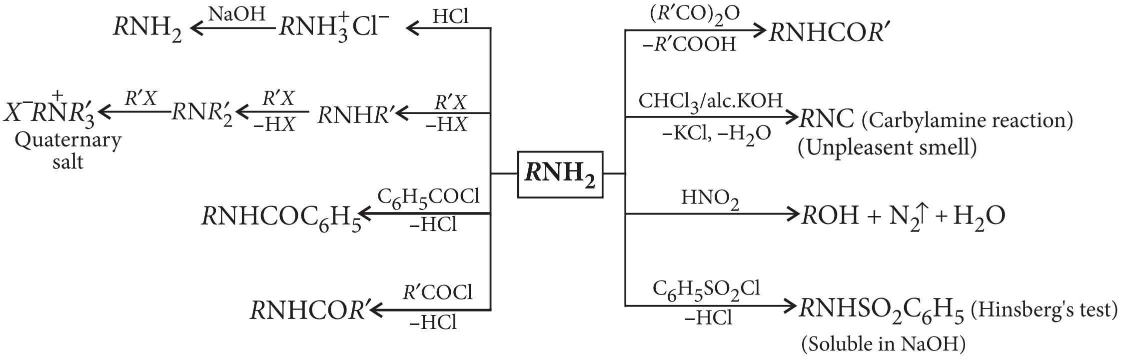
Chemical properties :

Basic character of amines :

- Amines are basic in nature due to the presence of lone pair of electrons on nitrogen atom.
- Aliphatic amines are stronger bases than ammonia due to +*I* effect of alkyl groups present in amines.
- Aromatic amines are weaker bases than ammonia due to –*I* effect of aryl group.
- Beside inductive effect, there are other effects like steric effect, solvation effect, resonance effect which affect the basic strength of amines.
- In gaseous phase, the order of basicity of amines is 3° amine > 2° amine > 1° amine > NH_3.
- In aqueous phase, despite of inductive effect, solvation effect and steric hindrance also play an important role. Thus, the order of basicity of amines is

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

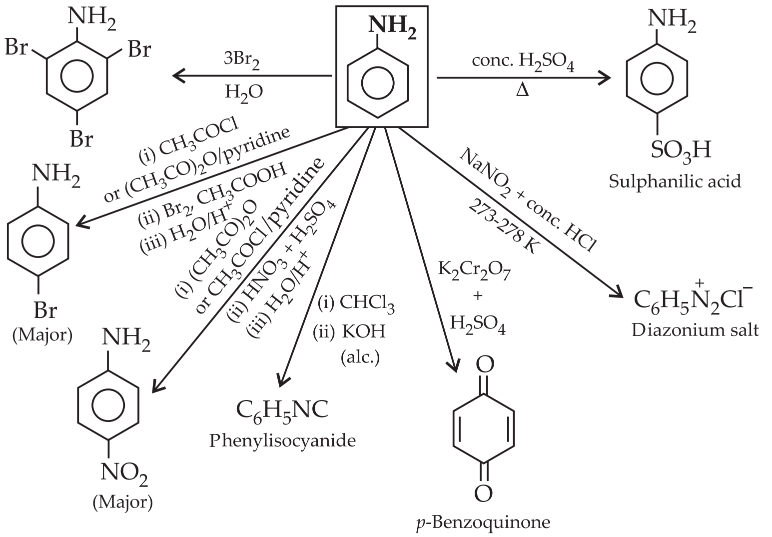
Chemical reactions :



Identification of primary, secondary and tertiary amines :

	Test	Primary amine	Secondary amine	Tertiary amine
1.	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 which is soluble in water and on heating gives nitrosoamine.
2.	Reaction with benzene sulphonyl chloride (*Hinsberg's reagent*)	Gives *N*-alkylbenzene-sulphonamide which is soluble in alkali.	Gives *N*,*N*-dialkylbenzene sulphonamide which is insoluble in alkali.	No reaction
3.	*Carbylamine test* : Reaction with chloroform and alcoholic KOH	Forms carbylamine or isocyanide (*R*NC) with characteristic unpleasant odour.	No reaction	No reaction
4.	*Hofmann's mustard oil reaction* : Reaction with CS_2 and $HgCl_2$.	Forms *N*-substituted isothiocyante with characteristic unpleasant smell of mustard oil.	No reaction	No reaction

Electrophilic substitution reactions of arylamines : Aniline undergoes electrophilic substitution reactions. —NH_2 group is *ortho*- and *para*-directing and a powerful activating group.



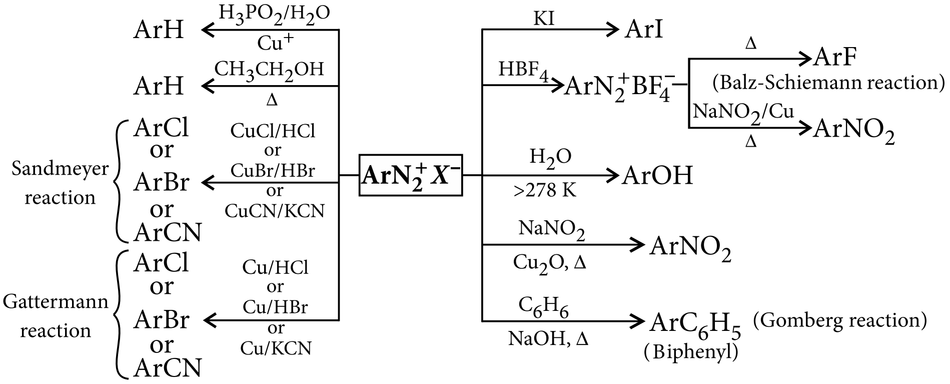
DIAZONIUM SALTS

- **Arenediazonium salts :** They have the general formula $ArN_2^+ X^-$, Ar stands for the aryl ($-C_6H_5$) group and X^- is Cl^-, Br^-, NO_3^-, HSO_4^-, BF_4^-.
- **Nomenclature :** They are named by suffixing diazonium to the name of parent hydrocarbon followed by anion.
- **Preparation :** Benzenediazonium chloride is prepared by the reaction of aniline with nitrous acid (sodium nitrite and hydrochloric acid) at 0-5 °C.

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{0-5^\circ C} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$$

- **Stability :** Arenediazonium salts are more stable (for short time) than alkanediazonium salts due to dispersal of positive charge over the benzene ring.
- **Physical properties :** These are generally colourless, crystalline solids, which are soluble in water. They are unstable and explode in dry state.
- **Chemical properties :**

- **Reactions involving displacement of nitrogen (diazo group) :**



- **Reactions involving retention of diazo group (coupling reactions) :**

$$ArN{=}NC_6H_4NH_2 \xleftarrow[pH\ =\ 4\text{-}5,\ 0\text{-}5^\circ C]{C_6H_5NH_2/H^+} \boxed{ArN_2^+X^-} \xrightarrow[pH\ =\ 9\text{-}10,\ 0\text{-}5^\circ C]{C_6H_5OH/OH^-} ArN{=}NC_6H_4OH$$

Previous Years' CBSE Board Questions

13.3 Nomenclature

VSA (1 mark)

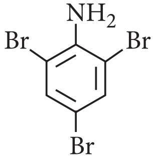
1. Write IUPAC name of the following compound: $(CH_3CH_2)_2NCH_3$ *(Delhi 2017)*

2. Write the structure of 2, 4-dinitrochlorobenzene. *(Delhi 2017)*

3. Write the IUPAC name of the following compound : $CH_3NHCH(CH_3)_2$ *(Delhi 2017)*

4. Write IUPAC name of the following compound: $(CH_3)_2N — CH_2CH_3$ *(Delhi 2017)*

5. Write the IUPAC name of the given compound:



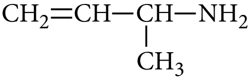
(Delhi 2016)

6. Write the structure of *N*-methylethanamine. *(AI 2013)*

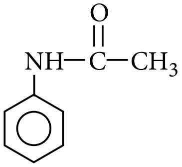
7. Write the structure of 2-aminotoluene. *(AI 2013)*

SA (2 marks)

8. Give IUPAC names of the following compounds:

(a) 

$CH_2{=}CH{-}\underset{\substack{|\\ CH_3}}{CH}{-}NH_2$

(b) 

(Delhi 2012C)

13.4 Preparation of Amines

VSA (1 mark)

9. Ammonolysis of alkyl halides is not a good method to prepare pure primary amines. *(1/5, 2020)*

10. Write the structures of *A* and *B* in the following reaction :

$$CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B$$

(1/5, 2020)

11. Carry out the following conversion: Benzoic acid to aniline. *(1/5, AI 2019)*

12. Write the chemical equation involved in the following reaction : Hofmann bromamide degradation reaction *(AI 2019, 1/5, 2018, 1/2, AI 2016, 2012, 1/3, Foreign 2011)*

13. State and illustrate the following : Gabriel synthesis *(1/5, 2018, 1/2, AI 2013C, 1/3, Foreign 2011)*

14. How do you convert the following : Ethanenitrile to ethanamine *(1/3, AI 2015)*

15. Write chemical equation for the following conversion : Benzyl chloride to 2-phenylethanamine. *(1/3, Delhi 2012)*

16. Why cannot primary aromatic amines be prepared by Gabriel phthalimide synthesis? *(1/2, AI 2011C)*

SA (2 marks)

17. How will you convert the following :
  (i) Nitrobenzene into aniline
  (ii) Ethanoic acid into methanamine
(2/3, Delhi 2014)

18. How are the following conversions carried out?
  (i) CH_3CH_2Cl to $CH_3CH_2CH_2NH_2$
  (ii) Benzene to aniline *(Delhi 2012C)*

13.5 Physical Properties

VSA (1 mark)

19. Out of CH_3NH_2 and CH_3OH, which has higher boiling point? *(2020)*

20. Arrange the following compounds in decreasing order of their boiling points :

Butanol, Butanamine, Butane *(1/3, 2020)*

21. Propanamine and *N*,*N*-dimethylmethanamine contain the same number of carbon atoms, even though propanamine has higher boiling point than *N,N*-dimethylmethanamine. Why? *(AI 2019)*

22. Give reasons for the following :
Primary amines have higher boiling point than tertiary amines. *(1/3, AI 2016, 2014, 2011)*

23. Arrange the following in the increasing order of their boiling points :
$C_2H_5NH_2$, C_2H_5OH, $(CH_3)_3N$ *(1/5, Delhi 2015)*

24. Arrange the following compounds in increasing order of solubility in water :
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$ *(Delhi 2014, AI 2011C)*

25. Out of CH_3NH_2 and $(CH_3)_3N$, which one has higher boiling point? *(Delhi 2014C)*

26. Account for the following :
Ethylamine is soluble in water whereas aniline is not. *(1/3, Delhi 2014C, AI 2011)*

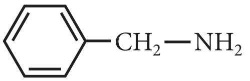
SA (2 marks)

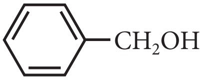
27. Arrange the following compounds as directed :
(i) In increasing order of solubility in water :
$(CH_3)_2NH$, CH_3NH_2, $C_6H_5NH_2$
(ii) In increasing order of boiling point :
$(C_2H_5)_2NH$, $(C_2H_5)_3N$, $C_2H_5NH_2$ *(2/3, 2020)*

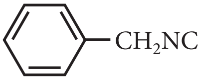
13.6 Chemical Reactions (Amines)

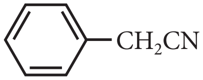
VSA (1 mark)

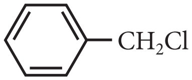
28. Out of the following, the strongest base in aqueous solution is
(a) methylamine (b) dimethylamine
(c) trimethylamine (d) aniline. *(2020)*

29.  on heating with $CHCl_3$ and alcoholic KOH gives foul smell of

(a) 

(b) 

(c) 

(d)  *(2020)*

30. Arrange the following compounds as directed :
In decreasing order of basic strength in aqueous solution :
$(CH_3)_3N$, $(CH_3)_2NH$, CH_3NH_2 *(1/3, 2020)*

31. Give the structures of *A* and *B* in the following sequence of reactions :

$$C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[0°-5°C]{NaNO_2+HCl} B$$

(2/3, 2020)

32. Arrange the following in increasing order of base strength in gas phase.
$(C_2H_5)_3N$, $C_2H_5NH_2$, $(C_2H_5)_2NH$ *(Delhi 2019)*

33. Carry out the following conversion :
Bromomethane to ethanol. *(1/5, AI 2019)*

34. Give reason :
$(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution. *(1/5, 2018)*

35. 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 *(1/3, 2018C, Delhi 2012)*

36. Describe the following by giving the relevant chemical equation :
Carbylamine reaction *(1/3, 2018C, 1/2, AI 2012)*

37. Give a simple chemical test to distinguish between the following pair of compounds :
$(CH_3)_2NH$ and $(CH_3)_3N$ *(1/5, Delhi 2015)*

38. Arrange the following in increasing order of basic strength :
Aniline, *p*-nitroaniline and *p*-toluidine *(1/2, AI 2015, AI 2015C)*

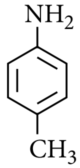
39. Arrange the following in increasing order of basic strength :
$C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$ *(1/2, AI 2015, Delhi 2014)*

40. How will you convert the following :
Aniline into *N*-phenylethanamide
(Write the chemical equations involved.) *(1/3, Delhi 2014)*

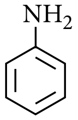
41. Arrange the following in increasing order of basic strength :
$C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5N(CH_3)_2$
(Delhi 2014)

42. Which of the two is more basic and why?
CH_3NH_2 or NH_3 *(Foreign 2014)*

43. Which of the two is more basic and why?



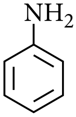
and



(Foreign 2014)

44. Which of the two is more basic and why?

CH_3NH_2 or



(Foreign 2014)

45. Arrange the following in increasing order of their basic strength in aqueous solution :
CH_3NH_2, $(CH_3)_3N$, $(CH_3)_2NH$ *(Delhi 2013)*

46. Complete the following reaction equation :
$C_6H_5NH_2 + Br_{2(aq)} \rightarrow$ *(1/2, AI 2012)*

47. Rearrange the following in an increasing order of their basic strengths :
$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_6H_5)_2NH$ and CH_3NH_2 *(AI 2011)*

48. State reasons for the following :
pK_b value for aniline is more than that for ethylamine. *(1/3, AI 2011)*

49. How will you differentiate between aniline and ethylamine? *(AI 2011)*

50. Why is an alkylamine more basic than ammonia? *(Foreign 2011)*

51. How will you bring about the following conversion :
Ethanamine to ethanoic acid *(Delhi 2011C)*

SA (2 marks)

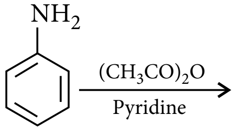
52. How will you distinguish between the following pairs of compounds :
(i) Aniline and ethanamine
(ii) Aniline and *N*-methylaniline
(2/3, 2020)

53. Distinguish between the following :
(i) $CH_3CH_2NH_2$ and $(CH_3CH_2)_2NH$
(ii) Aniline and CH_3NH_2 *(2/5, 2020)*

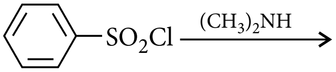
54. Give reasons :
(i) Although $-NH_2$ group is *o*/*p* directing in electrophilic substitution reactions, yet aniline, on nitration gives good yield of *m*-nitroaniline.
(ii) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution. *(2/5, 2020)*

55. Write the structures of the main products of the following reactions :

(i)



(ii)



(2/5, 2018)

56. (a) Give a simple chemical test to distinguish between aniline and *N*, *N*-dimethylaniline.
(b) Arrange the following in the increasing order of their pK_b values :
$C_6H_5NH_2$, $C_2H_5NH_2$, $C_6H_5NHCH_3$
(2/5, 2018)

57. 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.
(2/3, AI 2016, 2014)

58. How do you convert the following :
(i) $C_6H_5CONH_2$ to $C_6H_5NH_2$
(ii) Aniline to phenol
(2/3, AI 2015)

59. Illustrate the following reactions giving suitable example in each case :
(i) Ammonolysis
(ii) Acetylation of amines
(2/5, Foreign 2015)

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

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

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

(2/3, Delhi, AI 2014)

61. Account for the following :
(i) Aniline does not give Friedel–Crafts reaction.
(ii) pK_b of methylamine is less than that of aniline. *(2/3, Delhi 2014C)*

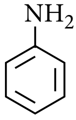
62. (i) Arrange the following compounds in an increasing order of basic strength : $C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2

(ii) Arrange the following compounds in a decreasing order of pK_b values : $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

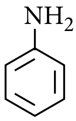
(Delhi 2014C)

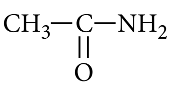
63. Complete the following reactions :

(i) $CH_3CH_2NH_2 + CHCl_3 + \text{alc. KOH} \longrightarrow$

(ii)  + $HCl_{(aq)} \longrightarrow$ *(2/3, AI 2013)*

64. Write the main products of the following reactions :

(i)  $\xrightarrow{Br_{2(aq)}}$?

(ii) 
$CH_3-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow{Br_2 + NaOH}$?

(2/3, AI 2013)

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

(i) Aniline and ethylamine

(ii) Ethylamine and dimethylamine

(Delhi 2013C)

66. Give reasons :

(i) Aniline is a weaker base than cyclohexyl amine.

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

(AI 2013C)

67. Give reasons :

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

(ii) CH_3CONH_2 is weaker base than $CH_3CH_2NH_2$. *(AI 2013C)*

68. How would you account for the following :

(i) Aniline is a weaker base than cyclohexylamine.

(ii) Methylamine in aqueous medium gives reddish-brown precipitate with $FeCl_3$.

(AI 2012C)

LA I (3 marks)

69. (a) Write the chemical reaction of methyl amine with benzoyl chloride and write the IUPAC name of the product obtained.

(b) Arrange the following in the increasing order of their pK_b values : $C_6H_5NH_2$, NH_3, $C_2H_5NH_2$, $(C_2H_5)_2NH$

(3/5, 2020)

70. (a) Give one chemical test to distinguish between the compounds of the following pairs :

(i) CH_3NH_2 and $(CH_3)_2NH$

(ii) Aniline and ethanamine

(b) Why aniline does not undergo Friedel–Crafts reaction? *(AI 2019)*

71. 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.

(Delhi 2017)

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

(i)
$$\begin{tikzcd}
C_6H_5-CONH_2 \arrow[rr, "Br_2/aq.\ KOH"] & & A \arrow[d, "NaNO_2 + HCl"', "0\text{-}5°C"] \\
C & B \arrow[l, "KI"'] & \arrow[l]
\end{tikzcd}$$

(ii)
$$\begin{tikzcd}
CH_3-Cl \arrow[r, "KCN"] & A \arrow[r, "LiAlH_4"] & B \arrow[d] \\
& C & \arrow[l, "CHCl_3 + alc.\ KOH", "\Delta"']
\end{tikzcd}$$

(Delhi 2016)

73. Write the structures of main products when aniline reacts with the following reagents :

(i) Br_2 water (ii) HCl

(iii) $(CH_3CO)_2O$/pyridine *(3/5, Delhi 2015)*

74. Write the chemical equations involved when aniline is treated with the following reagents :

(i) Br_2 water (ii) $CHCl_3$ + KOH

(iii) HCl *(AI 2015)*

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

(i)
$$\begin{tikzcd}
C_6H_5NO_2 \arrow[r, "Sn + HCl"] & A \arrow[r, "NaNO_2 + HCl", "273\ K"'] & B \arrow[d, "H_2O", "\Delta"'] \\
& & C
\end{tikzcd}$$

(ii) $CH_3Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[273\ K]{HNO_2} C$

(3/5, Foreign 2015)

76. 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*. *(Delhi 2015C)*

77. Give the structures of products *A*, *B* and *C* in the following reactions :

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

(ii) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOH + Br_2} B \xrightarrow{CHCl_3 + \text{Alc. NaOH}} C$

(Delhi 2014, 2013)

13.9 Chemical Reactions (Diazonium salts)

VSA (1 mark)

78. Write the structures of *A* and *B* in the following reactions :

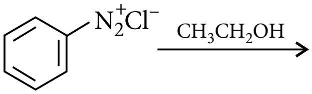
$C_6H_6N_2^+Cl^- \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B$

(1/5, 2020)

79. Carry out the following conversion :
p-nitrotoluene to 2-bromobenzoic acid.

(1/5, AI 2019)

80. Write the structure of the main product of the following reaction :



(1/5, 2018)

81. Complete the following reaction equation :

$C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$

(Delhi 2015C, AI 2013, 2012)

82. The conversion of primary aromatic amines into diazonium salts is known as ____________. *(AI 2014)*

83. Complete the following reaction :

$C_6H_5N_2^+Cl^- \xrightarrow[\text{(Room temp.)}]{H_2O}$ *(1/3, AI 2013)*

84. State and illustrate the following :
Coupling reaction

(1/2, AI 2013C, Foreign 2011)

85. How is the following conversion carried out :
Aniline to *p*-hydroxyazobenzene.

(1/2, Delhi 2012C)

86. How will you bring about the following conversion :

Nitrobenzene to phenol *(1/2, Delhi 2011C)*

87. How will you bring about the following conversion : Aniline to chlorobenzene
Write the chemical equation involved.

(1/2, Delhi 2011C)

88. How will you bring about the following conversion :

Aniline to benzonitrile. *(Delhi 2011C)*

SA (2 marks)

89. (a) Write the reaction involved in the following : Diazotisation

(b) Give reason :
Aromatic diazonium salts are more stable than aliphatic diazonium salts.

(2/5, 2018)

90. Write chemical equations for the following conversions :

(i) Nitrobenzene to benzoic acid.

(ii) Aniline to benzyl alcohol.

(2/3, Delhi 2012)

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

(i) Sandmeyer reaction

(ii) Coupling reaction.

(AI 2012C, Delhi 2011C)

LA I (3 marks)

92. Write the structures of main products when benzene diazonium chloride reacts with the following reagents :

(i) CuCN (ii) CH_3CH_2OH

(iii) KI *(Delhi 2019)*

93. Write the structures of compounds *A*, *B* and *C* in the following reactions :

(a) $CH_3—COOH \xrightarrow{NH_3/\Delta} A \xrightarrow{Br_2/KOH_{(aq)}} B \xrightarrow{CHCl_3 + \text{alc. KOH}} C$

(b) $C_6H_5N_2^+BF_4^- \xrightarrow[\Delta]{NaNO_2/Cu} A \xrightarrow{Fe/HCl} B \xrightarrow{CH_3COCl/pyridine} C$

(AI 2017)

94. Give the structure of *A*, *B* and *C* in the following reactions :

(i) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

(ii)
$$\begin{tikzcd} C_6H_5NO_2 \arrow[r, "Sn + HCl"] & A \arrow[r, "NaNO_2 + HCl", "273\ K"'] & B \arrow[d, "H_2O/H^+"', "\Delta"] \\ & & C \end{tikzcd}$$

(Delhi 2013)

LA II (5 marks)

95. 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 :

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

(Delhi 2015)

96. (i) Write the structures of main products when benzenediazonium chloride ($C_6H_5N_2^+Cl^-$) reacts with the following reagents :

(a) HBF_4/Δ (b) Cu/HBr

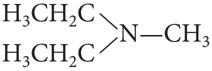
(ii) Write the structures of *A*, *B* and *C* in the following reactions :

(a)
$$\begin{tikzcd} C_6H_5NO_2 \arrow[r, "Sn + HCl"] & A \arrow[r, "NaNO_2 + HCl", "273\ K"'] & B \arrow[d, "H_2O"', "\Delta"] \\ & & C \end{tikzcd}$$

(b) $CH_3Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[273\ K]{HNO_2} C$

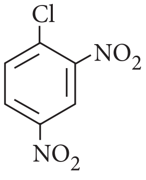
(Foreign 2015)

Detailed Solutions

1.


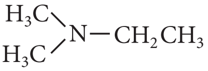
$(H_3CH_2C)_2N{-}CH_3$

IUPAC name : *N*-Ethyl-*N*-methylethanamine

2.


2, 4-Dinitrochlorobenzene

3. *N*-Methylpropan-2-amine (2° amine)

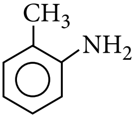
4.


$(H_3C)_2N{-}CH_2CH_3$

N,N-Dimethylethanamine

5. 2, 4, 6-Tribromoaniline

6. $CH_3CH_2NHCH_3$

7.


2-Aminotoluene

8. (a) But-3-*en*-2-amine
(b) *N*-Phenylethanamide

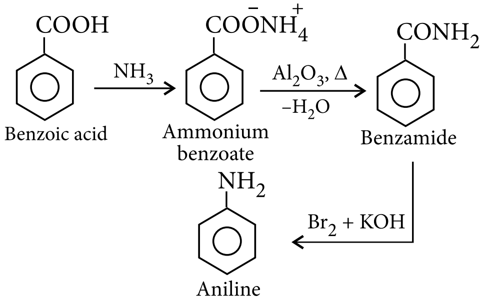
9. The ammonolysis of alkyl halides with ammonia is a nucleophilic substitution reaction in which ammonia acts as a nucleophile by donating the electron pair on nitrogen atom to form primary amine as the initial product. Now, the primary amine can act as a nucleophile and combine with alkyl halide (if available) to give secondary amine and the reaction continues in the same way to form tertiary amine and finally quaternary ammonium salt. Thus, a mixture of products is formed and it is not possible to separate individual amines from the mixture.

$$R-X \xrightarrow[-HX]{NH_2} R-NH_2 \xrightarrow[-HX]{R-X} R_2NH \xrightarrow[-HX]{R-X} R_3N \xrightarrow{R-X} R_4N^+X^-$$

10.

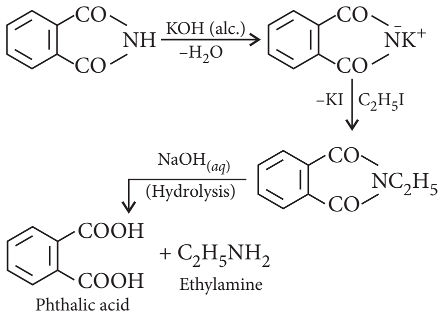
$$CH_3COOH \xrightarrow[\Delta]{NH_3} \underset{(A)}{CH_3CONH_2} \xrightarrow{NaOBr} \underset{(B)}{CH_3NH_2}$$

11.



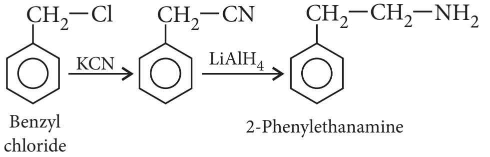
12. $$\underset{\text{Acid amide}}{R\text{—}CONH_2} + Br_2 + 4NaOH \longrightarrow \underset{1^\circ\text{ amine}}{R\text{—}NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

13. Gabriel phthalimide synthesis : In this reaction phthalimide is converted into its potassium salt by treating it with alcoholic potassium hydroxide. Then potassium phthalimide is heated with an alkyl halide to yield an *N*-alkylpthalimide which is hydrolysed to phthalic acid and primary amine by alkaline hydrolysis.



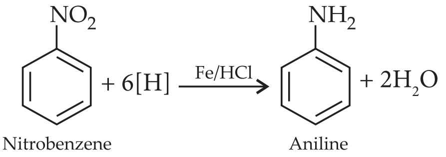
14. $$\underset{\text{Ethanenitrile}}{CH_3CN} + 4[H] \xrightarrow{Na + C_2H_5OH} \underset{\text{Ethanamine}}{CH_3CH_2NH_2}$$

15.

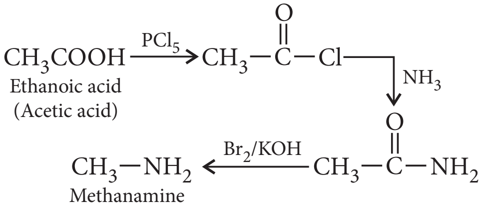


16. Primary aromatic amines cannot be prepared by Gabriel phthalimide synthesis because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

17. (i)



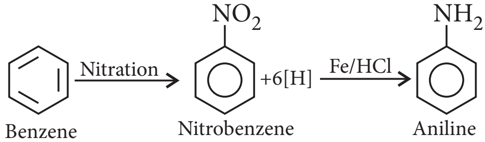
(ii)



$$\underset{\text{Ethanoic acid (Acetic acid)}}{CH_3COOH} \xrightarrow{PCl_5} CH_3-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow{NH_3} CH_3-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{Br_2/KOH} \underset{\text{Methanamine}}{CH_3-NH_2}$$

18. (i) $$\underset{\text{Chloroethane}}{CH_3CH_2Cl} \xrightarrow{\text{alc. NaCN}} \underset{\text{Propane nitrile}}{CH_3CH_2C\equiv N} \xrightarrow[Ni/H_2]{\text{Reduction}} \underset{\text{1-Propanamine}}{CH_3CH_2CH_2NH_2}$$

(ii)



19. CH_3OH has higher boiling point than CH_3NH_2. The hydrogen bonding in alcohols is stronger than that of amines because oxygen is more electronegative than nitrogen.

20. Decreasing order of boiling points of given compounds :

Butanol > butanamine > butane

21. Primary amines ($R - NH_2$) have two hydrogen atoms on nitrogen which can undergo intermolecular hydrogen bonding whereas no such hydrogen bonding is present in tertiary amines (R_3N). So, primary amines boil at a higher temperature than tertiary amines.

22. *Refer to answer 21.*

23. Increasing order of boiling points :

$(CH_3)_3N < C_2H_5NH_2 < C_2H_5OH$

Tertiary amine does not have hydrogen to form hydrogen bonding and hydrogen bonding in alcohol is stronger than that of primary amines because oxygen is more electronegative than nitrogen.

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

1° amines are more soluble in water than 2° amines. Aniline due to large hydrophobic benzene ring is least soluble.

25. *Refer to answer 21.*

26. Ethylamine is soluble in water due to formation of intermolecular hydrogen bonds with water molecules. However, in aniline due to large hydrophobic aryl group the extent of hydrogen bonding decreases considerably and hence aniline is insoluble in water.

27. (i) $C_6H_5NH_2 < (CH_3)_2NH < CH_3NH_2$
1° amines are more soluble in water than 2° amines. Aniline due to large hydrophobic benzene ring is least soluble.
(ii) 1° amines have two, 2° amines have one while 3° amines have no hydrogen linked to nitrogen. The degree of association due to hydrogen bonding and hence the boiling point increase as $(C_2H_5)_3N < (C_2H_5)_2NH < C_2H_5NH_2$

28. (b) : The order of basicity of the given compounds is
$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > C_6H_5NH_2$.
There is a subtle interplay of the inductive effect, solvation effect and steric hindrance of alkyl groups which decides the basic strength of alkyl amines in the aqueous state.

29. (b) : Primary amines when warmed with chloroform and alcoholic solution of KOH produce isocyanides or carbylamines which have foul smell.

30. In case of small alkyl groups like $—CH_3$ the order of basicity is secondary amine > primary amine > tertiary amine due to solvation effect and $+I$ effect of $—CH_3$ group.

$$\begin{array}{lccccc} & (CH_3)_2NH & > & CH_3NH_2 & > & (CH_3)_3N \\ pK_b & 3.27 & & 3.38 & & 4.22 \end{array}$$

31. $$C_6H_5NO_2 \xrightarrow{Fe + HCl} \underset{(A)}{C_6H_5NH_2} \xrightarrow[0\text{-}5°C]{NaNO_2 + HCl} \underset{(B)}{C_6H_5N_2^+Cl^-}$$

32. $C_2H_5NH_2 < (C_2H_5)_2NH < (C_2H_5)_3N$

33. $$\underset{\text{Bromomethane}}{CH_3—Br} \xrightarrow{HCN} CH_3—CN \xrightarrow{Ni/H_2} CH_3CH_2NH_2 \xrightarrow{HNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

34. In aqueous solution, 2°amine is more basic than 3°amine due to the combination of inductive effect, solvation effect and steric hindrance.

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

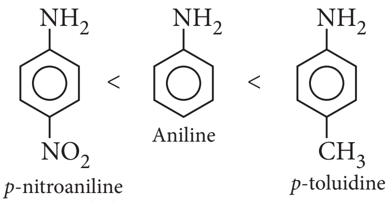
36. Carbylamine reaction is the reaction in which 1° amines produce a bad smelling compound when treated with chloroform in the presence of alkali.

$$RNH_2 + CHCl_3 + 3KOH\ (alc.) \longrightarrow R—N \overset{\rightarrow}{=} C + 3KCl + 3H_2O$$

It is the test for primary amines.

37. When treated with benzenesulphonyl chloride (Hinsberg's reagent), $(CH_3)_2NH$ forms insoluble *N*, *N*-dialkylbenzene sulphonamide which is insoluble in KOH whereas tertiary amine does not react at all.

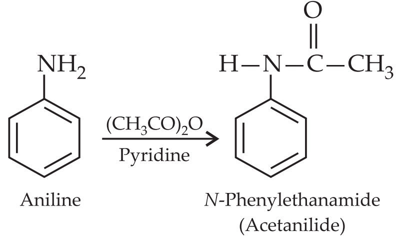
38.



Electron withdrawing group ($–NO_2$) on benzene ring decreases the basicity and electron donating group ($–CH_3$) on benzene ring increases the basicity of compound.

39. $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$
$C_6H_5NH_2$ and $C_6H_5NHCH_3$ are less basic than aliphatic amine $C_6H_5CH_2NH_2$ due to lone pair of nitrogen is in conjugation with benzene ring. But due to $+I$ effect of $—CH_3$ group in $C_6H_5NHCH_3$, it is more basic than $C_6H_5NH_2$.

40.



41. Increasing order of basic strength in gaseous state is as follows :
$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5N(CH_3)_2$
As the number of $—CH_3$ groups ($+I$ effect) attached to nitrogen increases, its basicity will increase.

42. Methyl amine is more basic than ammonia because of the presence of electron donating methyl group ($+I$ effect), which increases the electron density on nitrogen atom.

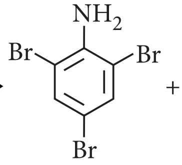
43. $CH_3(C_6H_4)\,NH_2$ is more basic than $C_6H_5NH_2$ due to electron releasing nature of methyl group which pushes electrons towards nitrogen.

44. CH_3NH_2 is more basic than $C_6H_5NH_2$ because in aniline the lone pair of electrons on nitrogen are involved in resonance.

45. In case of small alkyl groups like $—CH_3$ the order of basicity is secondary amine > primary amine > tertiary amine due to solvation effect and +*I* effect of —CH_3 group.

$$(CH_3)_3N \quad < \quad CH_3NH_2 \quad < \quad (CH_3)_2NH$$

46. $C_6H_5NH_2 + Br_{2(aq)} \longrightarrow$



$+ 3HBr$

47. $(C_6H_5)_2NH < C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2$

48. In aniline, the lone pair of electrons on N-atom is delocalised over benzene ring due to resonance. As a result, electron density on the nitrogen atom decreases. In contrast, in ethylamine, +*I*-effect of —C_2H_5 group increases electron density on the nitrogen atom. Therefore, aniline is a weaker base than ethylamine hence, its pK_b value is more than that for ethylamine.

49. Aniline being an aromatic primary amine on treatment with $HNO_2[NaNO_2 + HCl$ (*dil.*)] at 273–278 K followed by treatment with an alkaline solution of β-naphthol gives an orange coloured azo dye. Ethylamine does not give this test.

50. Electron density of N-atom increases due to the +*I* effect of the alkyl group. Hence, alkylamines are stronger bases than ammonia.

$$\ddot{N}H_3, \quad R \rightarrow \ddot{N}H_2$$

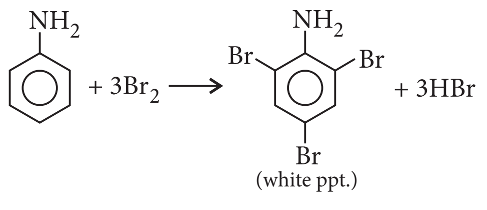
51. $$CH_3CH_2NH_2 \xrightarrow[\text{(ii) } H_2O,\ 273\text{-}278\ K]{\text{(i) } NaNO_2/HCl} CH_3CH_2OH \xrightarrow{K_2Cr_2O_7/H^+} CH_3COOH$$

52. (i) *Refer to answer 49.*

(ii) Aniline gives carbylamine test, *i.e.,* on treatment with alc. KOH and chloroform followed by heating it gives offensive odour of phenylisocyanide but *N*-methylaniline being secondary amine, does not show this test.

53. (i) When heated with an alcoholic solution of KOH and $CHCl_3$, ethylamine gives foul smelling ethyl isocyanide. Diethylamine does not give this test.

(ii) Aniline gives white or brown precipitate with bromine water.



(white ppt.)

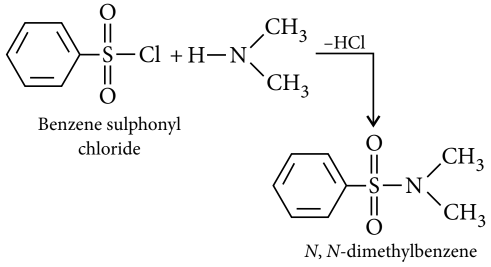
Methylamine does not react with bromine water.

54. (i) Nitration is carried out with conc. HNO_3 in the presence of conc. H_2SO_4. In the presence of these acids, the $-NH_2$ group of aniline gets protonated and is converted into $-\overset{+}{N}H_3$ group. This positively charged group acts as a strong electron withdrawing and *meta*-directing group. Hence, the incoming electrophile goes to *m*-position.

(ii) In aqueous solution, 2°amine is more basic than 3°amine due to the combination of inductive effect, solvation effect and steric reasons.

55. (i) *Refer to answer 40.*

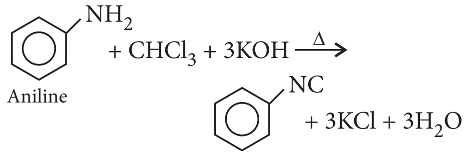
(ii)



Benzene sulphonyl chloride

N, N-dimethylbenzene sulphonamide

56. (a) Aniline undergoes isocyanide test (carbylamine reaction) whereas, *N, N* – dimethylaniline does not.



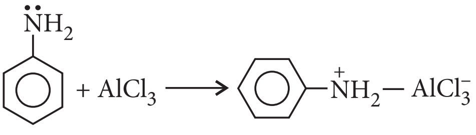
Aniline

Phenyl isocyanide (foul smell)

(b) Stronger the base, lower will be the pK_b value.

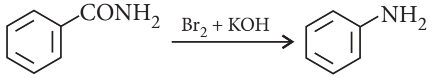
	$C_2H_5NH_2$ <	$C_6H_5NHCH_3$ <	$C_6H_5NH_2$
pK_b	3.29	4.63	9.38

57. (i) In Friedel — Crafts reaction, $AlCl_3$ is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge. This positively charged nitrogen acts as a strong deactivating group, hence aniline does not undergo Friedel — Crafts reaction.



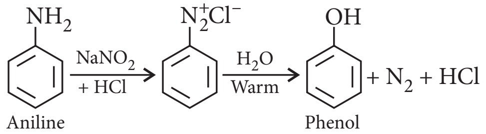
(ii) *Refer to answer 34.*

58. (i)

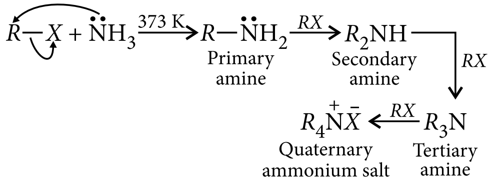


Benzamide

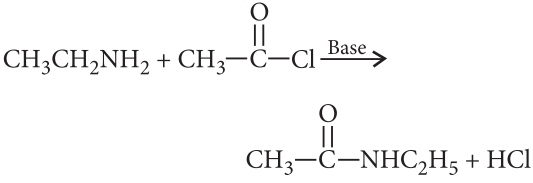
Aniline

(ii) 

59. (i) **Ammonolysis :** Alkyl halides when treated with ethanolic solution of ammonia give a mixture of primary, secondary, tertiary amines and quaternary ammonium salt.



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



$$CH_3CH_2NH_2 + CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{\text{Base}} \underset{N\text{-Ethyl acetamide}}{CH_3-\overset{O}{\overset{\|}{C}}-NHC_2H_5} + HCl$$

N-Ethyl acetamide

60. (i)
$$\begin{tikzcd}
C_6H_5NO_2 \arrow[r, "Sn + HCl"] & \underset{A}{C_6H_5NH_2} \arrow[d, "NaNO_2 + HCl", "273\ K"'] \\
\underset{C}{C_6H_5OH} & \underset{B}{C_6H_5N_2^+Cl^-} \arrow[l, "H_2O"']
\end{tikzcd}$$

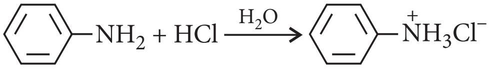
(ii)
$$CH_3CN \xrightarrow{H_2O/H^+} \underset{A}{CH_3COOH} \xrightarrow{NH_3} \underset{B}{CH_3CONH_2} \xrightarrow{Br_2+KOH} \underset{C}{CH_3NH_2}$$

61. (i) *Refer to answer 57(i).*

(ii) In aniline, the lone pair of electrons of N-atom are delocalised over the benzene ring. As a result, electron density on the nitrogen decreases. In contrast, in CH_3-NH_2, $+I$ effect of $-CH_3$ group increases the electron density on the N-atom.
Therefore, aniline is a weaker base than methylamine and hence, its pK_b value is higher than that of methylamine.

62. (i) Increasing order of basic strength is
$C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$
(ii) Stronger the base lower will be its pK_b value hence, the decreasing order of pK_b values :
$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

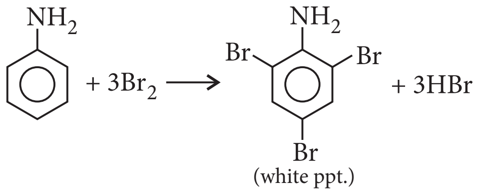
63. (i) $CH_3-CH_2-NH_2 + CHCl_3 + 3KOH \longrightarrow CH_3-CH_2-NC + 3KCl + 3H_2O$

(ii) 

64. (i) *Refer to answer 46.*

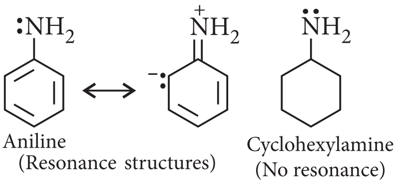
(ii) $CH_3CONH_2 \xrightarrow{Br_2 + NaOH} \underset{\text{Methanamine}}{CH_3-NH_2}$

65. (i) Aniline gives white or brown precipitate with bromine water.



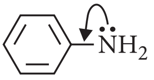
Ethylamine does not react with bromine water.
(ii) When heated with an alcoholic solution of KOH and $CHCl_3$, ethylamine gives foul smelling ethyl isocyanide. Dimethylamine does not give this test.

66. (i) Aniline is weaker base than cyclohexylamine because of resonance. Due to electromeric effect, the lone pair on nitrogen is attracted by benzene ring. Hence, donor tendency of $-\ddot{N}H_2$ group decreases. There is no resonance in cyclohexylamine. Electron repelling nature of cyclohexyl group further increases the donor property of NH_2 group. So, cyclohexylamine is a stronger base.

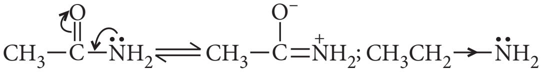


(ii) *Refer to answer 9.*

67. (i) Benzene ring in aromatic amines is highly activated due to the displacement of lone pair of nitrogen towards the ring. It results, increase in the electron density on the ring. This facilitates the electrophilic attack on the ring.



(ii) In CH_3CONH_2, the lone pair of electrons on nitrogen atom is involved in resonance with the carbonyl group. So, the electron pair of nitrogen is not easily available for protonation. Hence, CH_3CONH_2 is a weaker base than $CH_3CH_2NH_2$.



$$CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2 \rightleftharpoons CH_3-\overset{O^-}{\overset{|}{C}}=\overset{+}{N}H_2;\ CH_3CH_2 \rightarrow \ddot{N}H_2$$

68. (i) *Refer to answer 66(i).*

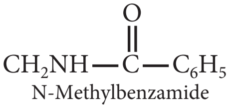
(ii) Methylamine forms hydroxide ions when dissolved in water due to the following acid - base equilibrium.

$$CH_3-NH_2 + H_2O \rightleftharpoons CH_3-\overset{+}{N}H_3 + OH^-$$

These OH^- ions react with Fe^{3+} ions to form ferric hydroxide.

$$2Fe + 6OH^- \longrightarrow 2Fe(OH)_3$$

69. (a) $CH_3NH_2 + C_6H_5COCl \longrightarrow$



$$CH_3NH-\overset{O}{\overset{\|}{C}}-C_6H_5$$

N-Methylbenzamide

(b) Stronger the base, lower will be its pK_b value. Hence increasing order of pK_b values is,
$(C_2H_5)_2NH < C_2H_5NH_2 < NH_3 < C_6H_5NH_2$

70. (a) (i) Methylamine gives carbylamine test, *i.e.,* on treatment with alc. KOH and chloroform, followed by heating it gives offensive odour of methyl isocyanide. Dimethylamine does not give this test.

(ii) *Refer to answer 49.*

(b) *Refer to answer 57 (i).*

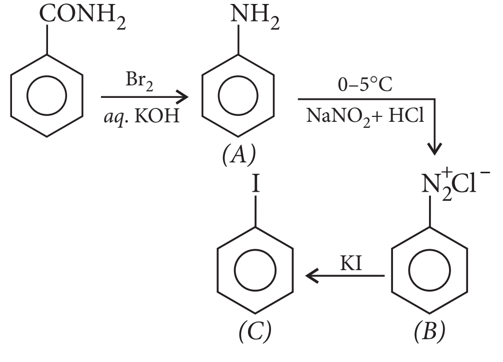
71. (i) After acetylation of aniline, acetanilide is formed in which due to the presence of $-\overset{O}{\overset{\|}{C}}-CH_3$ group having $-I$ effect, electron density on N-atom decreases and hence, activation effect of aniline gets reduced.

(ii) *Refer to answer 44.*

(iii) *Refer to answer 54(i).*

72.

(i)



(ii)

$$CH_3-Cl \xrightarrow{KCN} \underset{(A)}{CH_3CN} \xrightarrow{LiAlH_4} \underset{(B)}{CH_3CH_2NH_2} \xrightarrow[\Delta]{CHCl_3 + alc.\ KOH} \underset{(C)}{CH_3CH_2NC}$$

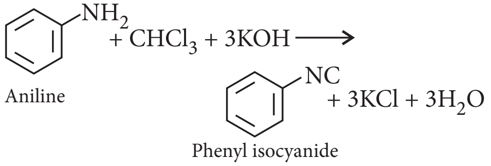
73. (i) *Refer to answer 46.*

(ii) *Refer to answer 63(ii).*

(iii) *Refer to answer 40.*

74. (i) *Refer to answer 46.*

(ii)



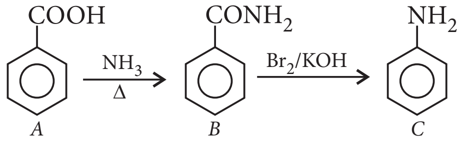
(iii) *Refer to answer 63(ii).*

75. (i) *Refer to answer 60(i).*

(ii)

$$CH_3Cl \xrightarrow{KCN} \underset{A}{CH_3CN} \xrightarrow{LiAlH_4} \underset{B}{CH_3CH_2NH_2} \xrightarrow[273\ K]{HNO_2} \underset{C}{CH_3CH_2OH}$$

76. Formula of the compound '*C*' indicates it is an amine. Since it is obtained by the reaction of Br_2 and KOH with the compound '*B*' so compound '*B*' can be an amide. As '*B*' is obtained from compound '*A*' by reaction with ammonia followed by heating so, compound '*A*' could be an aromatic acid. Formula of compound '*C*' shows it to be aniline, then '*B*' is benzamide and compound '*A*' is benzoic acid. The sequence of reactions can be written as follows :



77. (i)

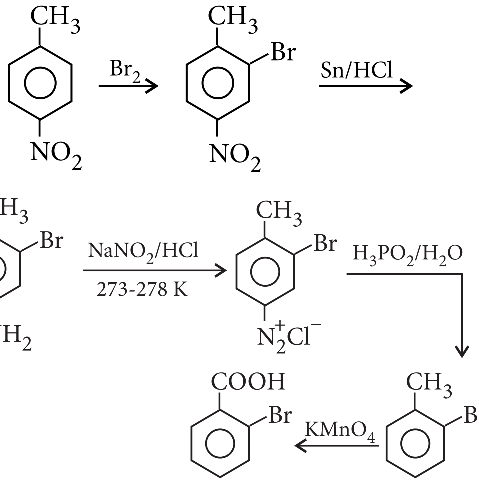
$$CH_3CH_2Br \xrightarrow{KCN} \underset{(A)}{CH_3CH_2CN} \xrightarrow{LiAlH_4} \underset{(B)}{CH_3CH_2CH_2NH_2} \xrightarrow[HNO_2]{273\ K} \underset{(C)}{CH_3CH_2CH_2OH}$$

(ii)

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

78. $$\begin{tikzcd}[column sep=large] C_6H_5\overset{+}{N_2}Cl^- \arrow[r, "CuCN"] & \underset{(A)}{\underset{\text{Benzonitrile}}{C_6H_5CN}} \arrow[d, "H_2O/H^+"] \\ & \underset{(B)}{\underset{\text{Benzoic acid}}{C_6H_5COOH}} \end{tikzcd}$$

79.

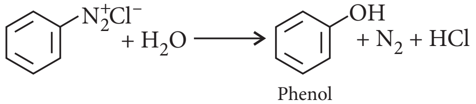


80. $$\underset{\text{Benzenediazonium chloride}}{C_6H_5\overset{+}{N_2}\bar{Cl}} + C_2H_5OH \xrightarrow{\text{Reduction}} \underset{\text{Benzene}}{C_6H_6} + \underset{\text{Ethanal}}{CH_3CHO} + N_2 + HCl$$

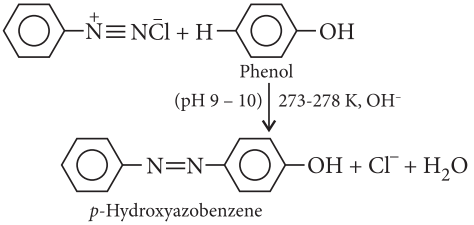
81. $$C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow C_6H_6 + N_2 + H_3PO_3 + HCl$$

82. Diazotisation reaction.

83.

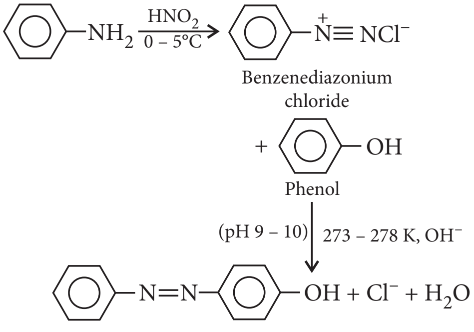


84. Diazonium salts react with aromatic amines in weakly acidic medium and phenols in weakly alkaline medium to form coloured compounds called azo dyes by coupling at *p*-position of amines or phenols.



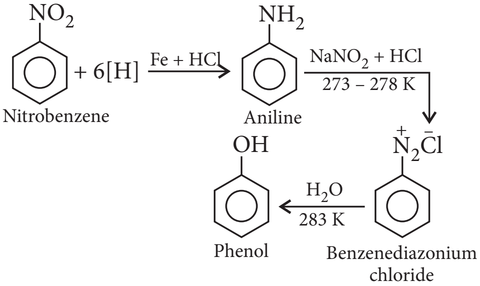
p-Hydroxyazobenzene
(Orange dye)

85.

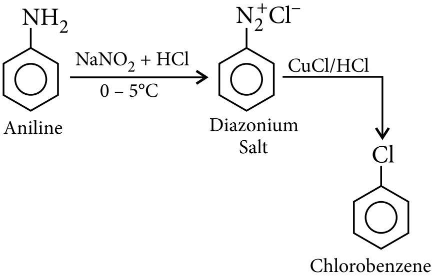


p-Hydroxyazobenzene (orange dye)

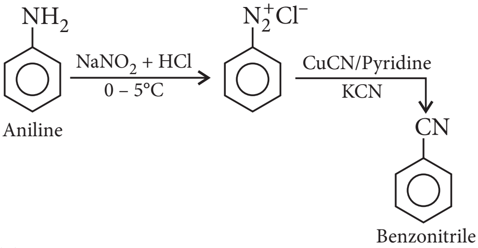
86.



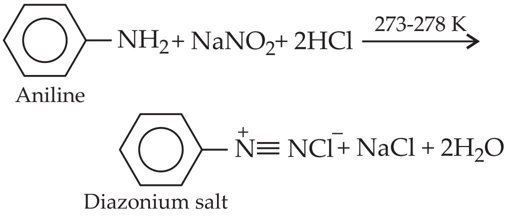
87.



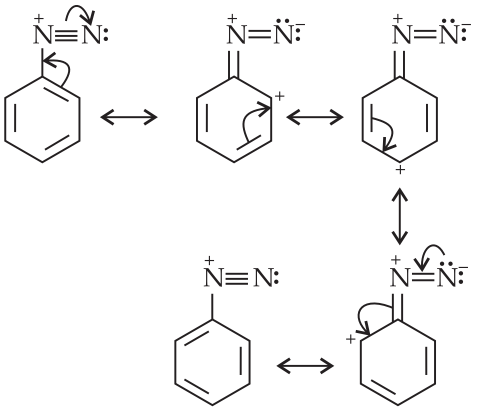
88.



89. (a) Diazotisation :

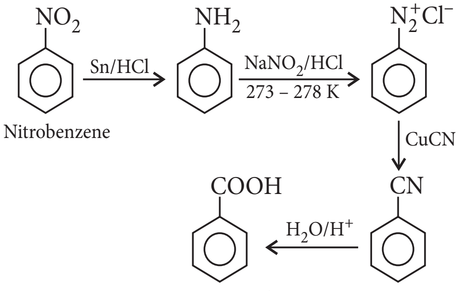


(b) Diazonium salts carry a nitrogen atom with a positive charge. This positive charge is well dispersed in aromatic diazonium salts through resonance as shown below :

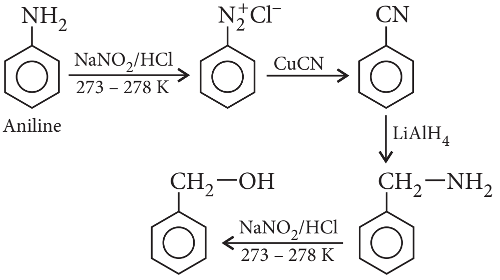


Such a charge delocalisation is not possible in aliphatic diazonium salts and hence they are less stable than aromatic diazonium salts.

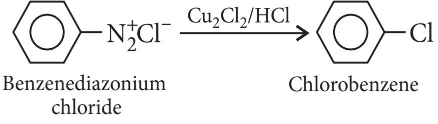
90. (i)



(ii)

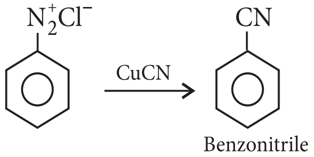


91. (i) **Sandmeyer reaction :** By this reaction nucleophiles like Cl^-, Br^-, CN^- etc. can easily be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of Cu(I) ion.



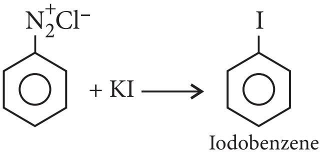
(ii) *Refer to answer 84.*

92. (i)



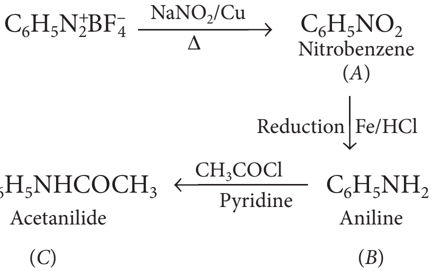
(ii) *Refer to answer 80.*

(iii)

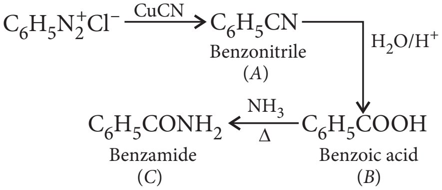


93. (a) *Refer to answer 77 (ii).*

(b)

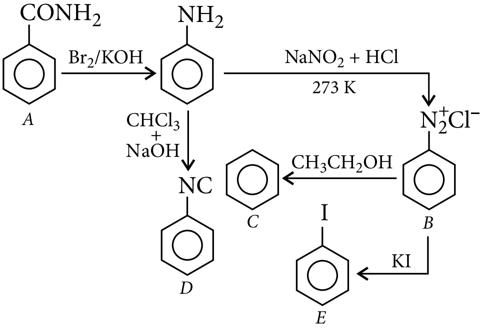


94. (i)

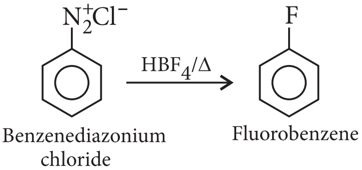


(ii) *Refer to answer 60(i).*

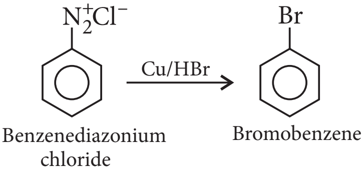
95.



96. (i) (a)



(b)



(ii) (a) *Refer to answer 60(i).*

(b) *Refer to answer 75(ii).*