13

Amines

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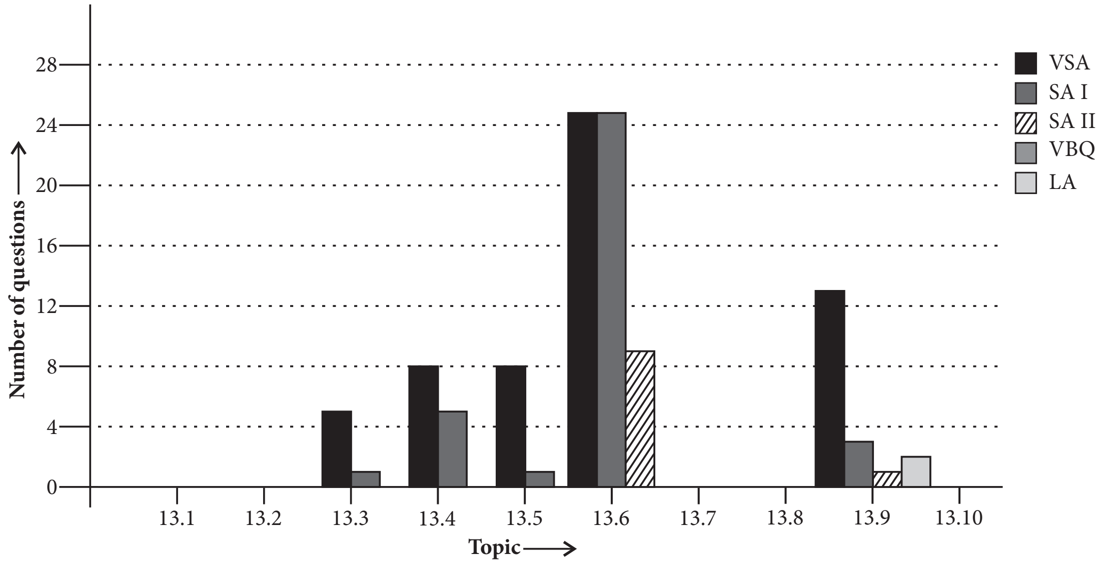
Topicwise Analysis of Last 10 Years' CBSE Board Questions



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

QUICK RECAP

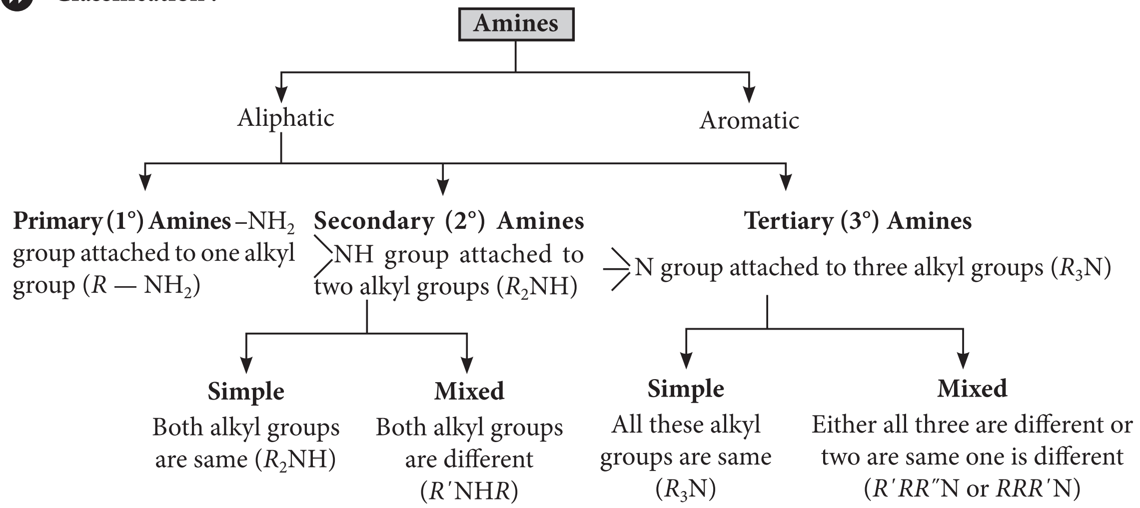
AMINES

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

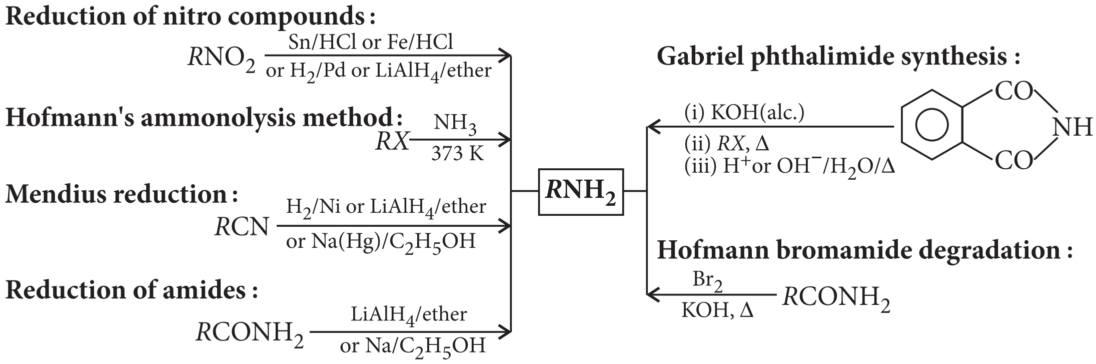
Nomenclature : In common system, an aliphatic amine is named by prefixing alkyl group to amine, *i.e.*, *alkylamine*. In IUPAC system, amines are named as *alkanamines*. In secondary and tertiary amines, when two or more groups are the same, the prefix *di* or *tri* is appended before the name of alkyl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

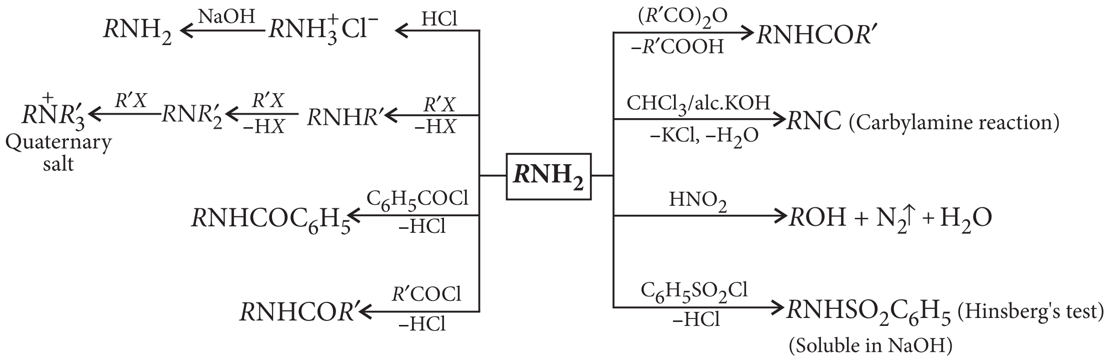
- Lower amines are gases and liquids but higher amines are solids.
- Primary and secondary amines have higher boiling points than other organic compounds due to hydrogen bonding.
- Primary and secondary amines are soluble in water due to hydrogen bonding between $-NH_2$ and H_2O molecules.

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.
  - Besides inductive effect, there are other effects like steric effect, solvation effect, resonance effect which effect 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 $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

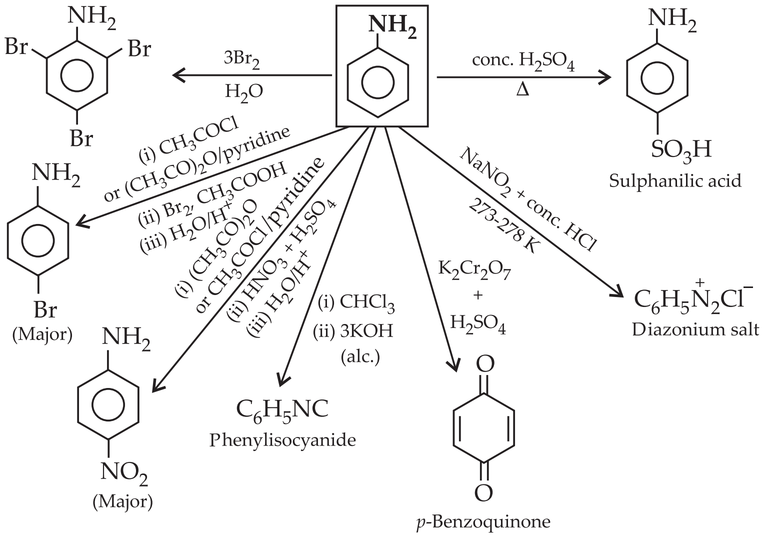
- **Chemical reactions :**



- **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.



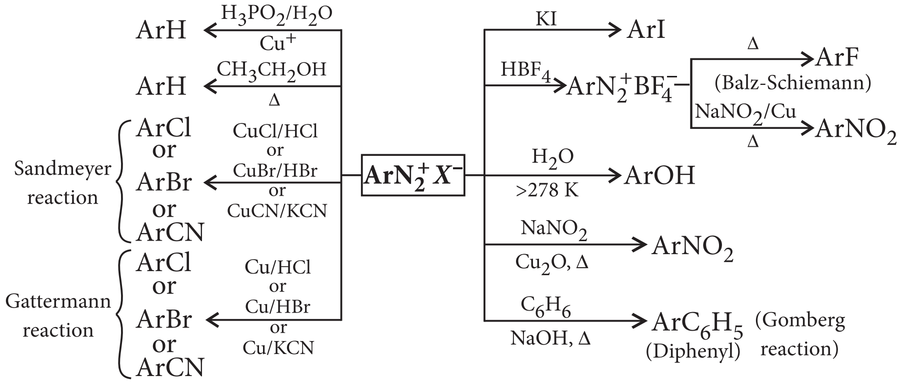
DIAZONIUM SALTS

- **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.

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

- **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) :**

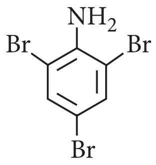
$$ArN{=}NC_6H_4NH_2 \xleftarrow[pH = 4\text{-}5,\ 0\text{-}5°C]{C_6H_5NH_2/H^+} \boxed{ArN_2^+X^-} \xrightarrow[pH = 9\text{-}10,\ 0\text{-}5°C]{C_6H_5OH/OH^-} ArN{=}NC_6H_4OH$$

Previous Years' CBSE Board Questions

13.3 Nomenclature

VSA (1 mark)

1. Write the IUPAC name of the given compound:



(Delhi 2016)

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

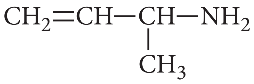
3. Write the structure of 2-aminotoluene. *(AI 2013)*

4. Give the IUPAC name of $H_2N-CH_2-CH_2-CH=CH_2$. *(Delhi 2010)*

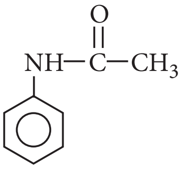
5. Write the structure for *N*, *N*-ethylmethylamine. *(1/3, Delhi 2010C)*

SA I (2 marks)

6. Give IUPAC names of the following compounds:

(a) 

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

(b) 

(Delhi 2012C)

13.4 Preparation of Amines

VSA (1 mark)

7. Write the chemical equation involved in the following reaction :
Hofmann bromamide degradation reaction *(1/2, AI 2016, 2012, Delhi 2008C)*

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

9. State and illustrate the following :
Gabriel synthesis *(1/2, AI 2013C)*

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

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

12. Write the chemical reaction to illustrate the following :
Ammonolysis *(1/2, Delhi 2009C)*

SA I (2 marks)

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

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

15. Illustrate the following reactions giving a chemical equation in each case :
    (i) Gabriel phthalimide synthesis
    (ii) Hofmann's bromamide reaction.
    (2/3, Foreign 2011, AI 2008)

16. How would you achieve the following conversions :
    (i) Nitrobenzene to aniline.
    (ii) An alkyl halide to a quaternary ammonium salt.
    Write the chemical equation with reaction conditions in each case. *(2/3, Delhi 2007)*

13.5 Physical Properties

VSA (1 mark)

17. Give reasons for the following :
Primary amines have higher boiling point than tertiary amines. *(1/3, AI 2016, Delhi 2008C)*

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

19. Account for the following :
Primary amines ($R—NH_2$) have higher boiling point than tertiary amines (R_3N). *(1/3, AI 2014)*

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

21. Account for the following :
Ethylamine is soluble in water whereas aniline is not. *(1/3, Delhi 2014C, Delhi 2009C)*

22. Account for the following :
Nitro compounds have higher boiling points than the hydrocarbons having almost the same molecular mass. *(1/3, AI 2007)*

SA I **(2 marks)**

23. State reasons for the following :
(i) Ethylamine is soluble in water whereas aniline is not soluble in water.
(ii) Primary amines have higher boiling points than tertiary amines. *(2/3, AI 2011)*

13.6 Chemical Reactions (Amines)

VSA **(1 mark)**

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

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

26. 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)*

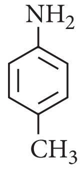
27. How will you convert the following :
Aniline into *N*-phenylethanamide
(Write the chemical equations involved.) *(1/3, Delhi 2014)*

28. Arrange the following in increasing order of basic strength :
$C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$ *(Delhi 2014)*

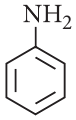
29. Arrange the following in increasing order of basic strength :
$C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5N(CH_3)_2$ *(Delhi 2014)*

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

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

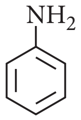


and



(Foreign 2014)

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

CH_3NH_2 or 

(Foreign 2014)

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

34. 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 *(Delhi 2012, AI 2009)*

35. Describe the following giving the relevant chemical equation :
Carbylamine reaction *(1/2, AI 2012, Delhi 2008C)*

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

37. 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)*

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

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

40. Why is an alkylamine more basic than ammonia? *(Foreign 2011, Delhi 2009)*

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

42. Assign reason for the following :
The pK_b of aniline is higher than that of methylamine. *(1/2, Delhi 2009C)*

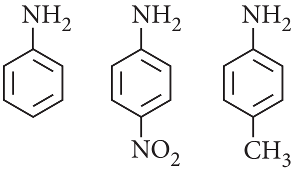
43. Why do amines act as nucleophiles? *(AI 2007)*

44. Account for the following :
Amines are basic substances while amides are neutral. *(1/3, AI 2007)*

SA I (2 marks)

45. 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)*

46. Arrange the following in increasing order of their basic strength :
(i) $C_6H_5—NH_2$, $C_6H_5—CH_2—NH_2$, $C_6H_5—NH—CH_3$
(ii)



(AI 2015)

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

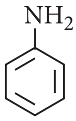
48. Illustrate the following reactions giving suitable example in each case :
(i) Ammonolysis
(ii) Acetylation of amines *(2/5, Foreign 2015)*

49. Give the structures of *A*, *B* and *C* in the following reactions :
(i) $C_6H_5NO_2 \xrightarrow{Sn + HCl} A \xrightarrow[273\ K]{NaNO_2 + HCl} B \xrightarrow{H_2O} C$
(ii) $CH_3CN \xrightarrow{H_2O/H^+} A \xrightarrow[\Delta]{NH_3} B \xrightarrow{Br_2 + KOH} C$
(2/3, Delhi, AI 2014)

50. 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)*

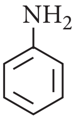
51. (i) Arrange the following compounds in an increasing order of basic strength :
$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2
(ii) Arrange the following compounds in a decreasing order of pK_b values :
$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$ *(Delhi 2014C)*

52. Complete the following reactions :
(i) $CH_3CH_2NH_2 + CHCl_3 + \text{alc. KOH} \longrightarrow$
(ii)



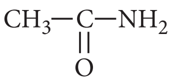
$+ HCl_{(aq)} \longrightarrow$ *(2/3, AI 2013)*

53. 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)

54. Give chemical tests to distinguish between the following pairs of compounds :
(i) Aniline and ethylamine
(ii) Ethylamine and dimethylamine
(Delhi 2013C)

55. 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)*

56. 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)*

57. 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)

58. Give the chemical tests to distinguish between the following pairs of compounds :
(i) Ethylamine and aniline
(ii) Aniline and benzylamine *(AI 2010)*

59. Give the chemical tests to distinguish between the following pairs of compounds :
(i) Methylamine and dimethylamine
(ii) Aniline and *N*-methylaniline *(AI 2010)*

60. Write one chemical reaction each to illustrate the following :
(i) Carbylamine reaction
(ii) Acetylation reaction *(2/3, Delhi 2010C)*

61. Account for the following :
(i) pK_b of aniline is more than that of methylamine.
(ii) Aniline does not undergo Friedel-Crafts reaction. *(AI 2010C)*

62. Describe a chemical test each to distinguish between the following :
(i) Ethylamine and aniline
(ii) Methylamine and dimethylamine *(AI 2010C, 2009C)*

63. Assign reason for the following :
(i) Amines are less acidic than alcohols of comparable molecular masses.
(ii) Aliphatic amines are stronger bases than aromatic amines. *(AI 2009C)*

64. (i) Arrange the following in an increasing order of basic strength in water :
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3.
(ii) Arrange the following in increasing order or basic strength in gas phase :
$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and CH_3NH_2. *(AI 2008)*

65. Account for the following :
(i) Aniline does not undergo Friedel-Crafts reaction.
(ii) Aliphatic amines are stronger bases than aromatic amines. *(AI 2008C)*

66. Give one chemical test each to distinguish between the following pairs of compounds :
(i) Ethylamine and aniline
(ii) Aniline and *N*-methylaniline *(AI 2008C)*

SA II (3 marks)

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

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

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

(Delhi 2016)

68. 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)*

69. 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)*

70. 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)

71. 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)*

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

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

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

(Delhi 2014)

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

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

(ii) $$\begin{tikzcd} CH_3COOH \arrow[r, "NH_3", "\Delta"'] & A \arrow[r, "NaOH + Br_2"] & B \arrow[d, "CHCl_3 + \\ Alc.\ NaOH"'] \\ & & C \end{tikzcd}$$

(Delhi 2013)

74. Account for the following observations :
(i) pK_b for aniline is more than that for methylamine.
(ii) Methylamine solution in water reacts with ferric chloride solution to give a precipitate of ferric hydroxide.
(iii) Aniline does not undergo Friedel-Crafts reaction. *(Delhi, AI 2008)*

13.9 Chemical Reactions (Diazonium salts)

VSA (1 mark)

75. Complete the following reaction equation :
$C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow \ldots$
(Delhi 2015C, AI 2013, 2012)

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

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

78. State and illustrate the following :
Coupling reaction *(1/2, AI 2013C, Foreign 2011)*

79. How is the following conversion carried out :
Aniline to *p*-hydroxyazobenzene.
(1/2, Delhi 2012C)

80. How will you bring about the following conversion :
Nitrobenzene to phenol *(1/2, Delhi 2011C)*

81. How will you bring about the following conversion :
Aniline to chlorobenzene
Write the chemical equation involved.
(1/2, Delhi 2011C)

82. How will you bring about the following conversion :
Aniline to benzonitrile. *(Delhi 2011C)*

83. Write a chemical reaction in which the iodide ion replaces the diazonium group in a diazonium salt. *(Delhi 2008)*

84. How would you achieve the following conversion :
Aniline to benzonitrile.
Write the chemical equation with reaction conditions in each case. *(Delhi 2007)*

SA I (2 marks)

85. Write chemical equations for the following conversions :
(i) Nitrobenzene to benzoic acid.
(ii) Aniline to benzyl alcohol. *(2/3, Delhi 2012)*

86. Illustrate the following with an example of reaction in each case :
(i) Sandmeyer's reaction
(ii) Coupling reaction.
(AI 2012C, Delhi 2011C)

SA II (3 marks)

87. 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 (5 marks)

88. 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 :

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

(Delhi 2015)

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

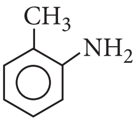
(Foreign 2015)

Detailed Solutions

1. 2, 4, 6-Tribromoaniline

2. $CH_3CH_2NHCH_3$ (*N*-methylethanamine)

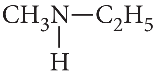
3.



2-Aminotoluene

4. But-3-en-1-amine

5.



$CH_3\underset{\displaystyle H}{\underset{|}{N}}—C_2H_5$ (*N*, *N*-ethylmethylamine)

6. (a) But-3-en-2-amine

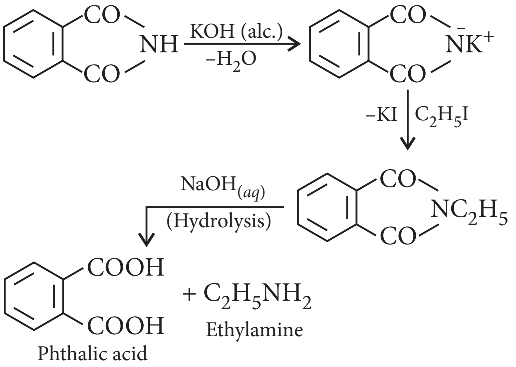
(b) *N*-phenylethanamide

7. $\underset{\text{Acid amide}}{R—CONH_2} + Br_2 + 4NaOH \longrightarrow$

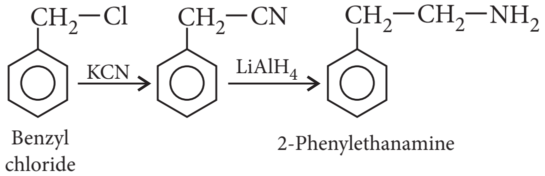
$$\underset{1^\circ\text{ amine}}{R—NH_2} + Na_2CO_3 + 2\,NaBr + 2H_2O$$

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

9. 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.

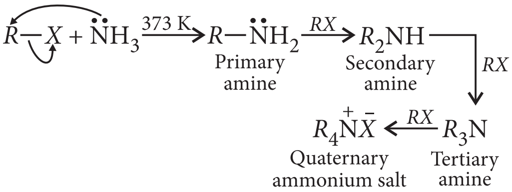


10.

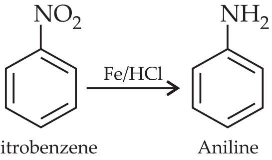


11. Aromatic amines cannot be prepared by Gabriel phthalimide synthesis because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

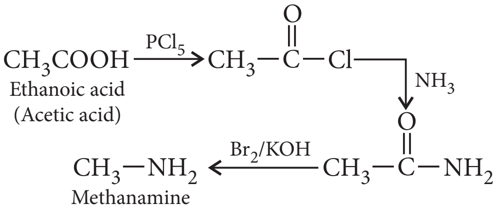
12. Alkyl halides when treated with ethanolic solution of ammonia give a mixture of primary, secondary, tertiary amines and quaternary ammonium salt.



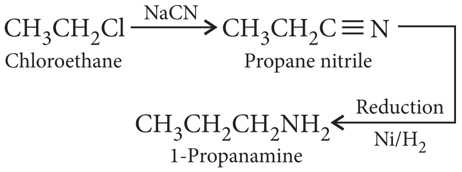
13. (i)



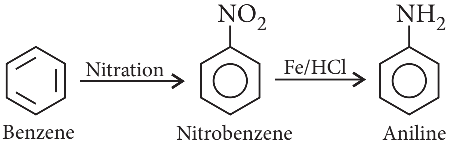
(ii)



14. (i)



(ii)



15. (i) *Refer to answer 9.*

(ii) *Refer to answer 7.*

16. (i) *Refer to answer 13(i).*

(ii) *Refer to answer 12.*

17. 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.

18. 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 amines because oxygen is more electronegative than nitrogen.

19. *Refer to answer 17.*

20. *Refer to answer 17.*

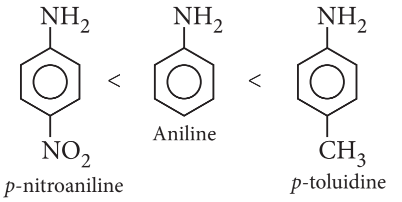
21. Ethylamine is soluble in water due to formation of intermolecular hydrogen bonds with water molecules. However, in aniline due to large hydrophobic aryl group the extent of hydrogen bonding decreases considerably and hence aniline is insoluble in water.

22. The nitro compounds are highly polar molecules. Due to this polarity they have strong intermolecular dipole - dipole interactions which causes them to have higher boiling points in comparison to the hydrocarbons having almost same molecular mass.

23. (i) *Refer to answer 21.*
(ii) *Refer to answer 17.*

24. 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.

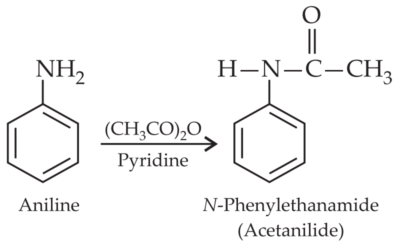
25.



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.

26. $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$
1° amines are more soluble in water than 2° amines. Aniline due to large hydrophobic benzene ring is least soluble.

27.



28. $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$
$C_6H_5NH_2$ 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 $C_6H_5NH_2$.

29. 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 its basicity will increases.

30. 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.

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

32. 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.

33. 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.

	$(CH_3)_2NH$	>	CH_3NH_2	>	$(CH_3)_3N$
pK_b	3.27		3.38		4.22

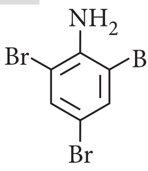
34. $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

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

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

It is the test for primary amines.

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



+ 3HBr

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

38. 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 methylamine, $+I$-effect of CH_3 group increases electron density on the nitrogen atom. Therefore, aniline is a weaker base than methylamine hence, its pK_b value is more than that for methylamine.

39. 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.

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

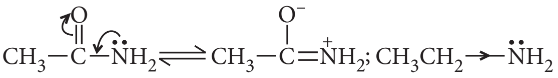
$$\ddot{N}H_3,\quad R \rightarrowtail \ddot{N}H_2$$

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

42. 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.

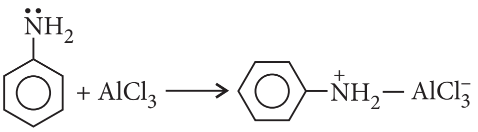
43. Because the electron pair of nitrogen can coordinate with the electron deficient electrophiles.

44. 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 $CH_3CH_2NH_2$.



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

45. (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.

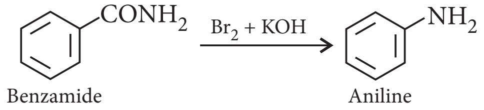


(ii) In aqueous solution 2° amine is more basic than 3° amine due to the combination of inductive effect, solvation effect and steric reasons.

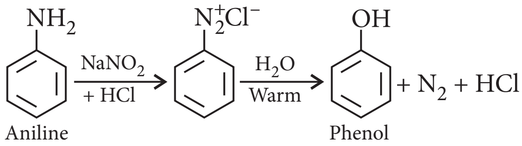
46. (i) *Refer to answer 28.*

(ii) *Refer to answer 25.*

47. (i)

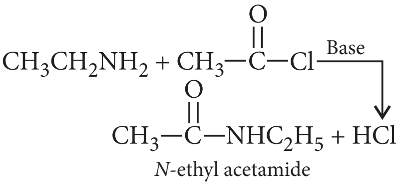


(ii)



48. (i) *Refer to answer 12.*

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



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

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

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

50. (i) *Refer to answer 45(i).*

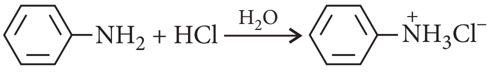
(ii) *Refer to answer 42.*

51. (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 : $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

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

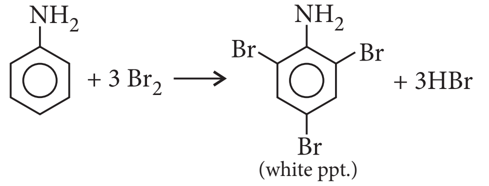
(ii)



53. (i) *Refer to answer 36.*

(ii) $\underset{\text{Methanamine}}{CH_3\text{—}NH_2}$

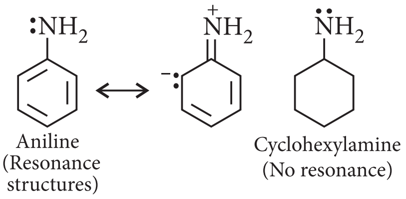
54. (i) Aniline gives white or brown precipitate with bromine water.



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.

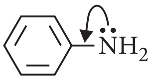
55. (i) Aniline is weaker base than cyclohexylamine because of resonance. Due to electromeric effect, the lone pair on nitrogen is attracted by benzene ring. Hence, donor tendency of $\text{—}\ddot{N}H_2$ group decreases. There is no resonance in cyclohexylamine. Electron repelling nature of cyclohexyl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



(ii) 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.

$$R-X \xrightarrow[-HX]{NH_3} R-NH_2 \xrightarrow[-HX]{R-X} R_2NH \xrightarrow[-HX]{R-X} R_3N \xrightarrow{R-X} R_4N^+X^-$$

56. (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) *Refer to answer 44.*

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

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

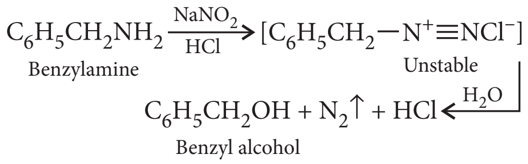
$$CH_3\text{—}NH_2 + H_2O \rightleftharpoons CH_3\text{—}\overset{+}{N}H_3 + OH^-$$

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

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

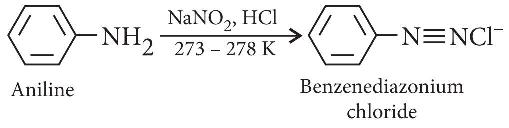
58. (i) *Refer to answer 54 (i).*

(ii) **Aniline and benzylamine :** Benzylamine reacts with nitrous acid to form a diazonium salt which is unstable at low temperature and decomposes with evolution of N_2 gas.



$$\underset{\text{Benzylamine}}{C_6H_5CH_2NH_2} \xrightarrow[HCl]{NaNO_2} \underset{\text{Unstable}}{[C_6H_5CH_2\text{—}N^+{\equiv}NCl^-]}$$
$$\xrightarrow{H_2O} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + N_2\uparrow + HCl$$

Aniline reacts with HNO_2 to form benzene diazonium chloride which is stable at 273 - 278 K and hence does not evolve N_2 gas. It forms orange dye with 2-naphthol.



59. (i) Methyl amine gives carbylamine test, *i.e.,* on treatment with alc. KOH and chloroform, followed by heating it gives offensive odour of methyl isocyanide. Dimethyl amine does not give this test.

(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.

60. (i) *Refer to answer 35.*

(ii) *Refer to answer 48(ii).*

61. (i) *Refer to answer 42(ii).*

(ii) *Refer to answer 45(i).*

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

(ii) *Refer to answer 59(i).*

63. (i) Loss of proton from amines gives RNH^- ion whereas loss of proton from alcohol forms alkoxide ion. Since, O is more electronegative than N therefore, RO^- can accommodate the negative charge more easily than RN^-H. Further, O—H bond is more polar than N—H bond. Hence, amines are less acidic than alcohols.

(ii) In aromatic amines, the lone pair of electrons present on nitrogen takes part in resonance and hence, not available for donation. However, in aliphatic amines, the lone pair is available for donation. That's why aliphatic amines are more basic than aromatic amines.

64. (i) The increasing order of basic strength in water of the given amines and ammonia follows the following order :

$C_6H_5NH_2 < NH_3 < (C_2H_5)_3N < (C_2H_5)_2NH$

(ii) The increasing order of basic strength in gas phase of the given amines follows the order :

$CH_3NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH < (C_2H_5)_3N$

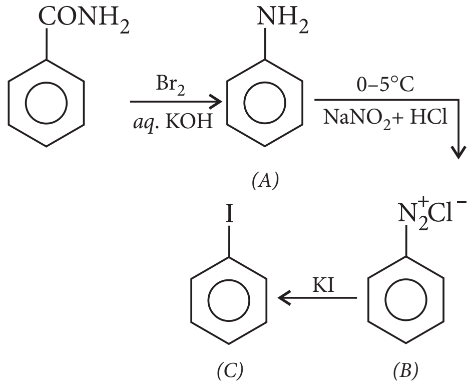
65. (i) *Refer to answer 45(i).*

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

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

(ii) *Refer to answer 59(ii).*

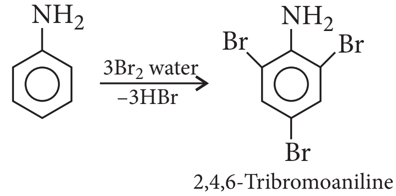
67. (i)



(ii)

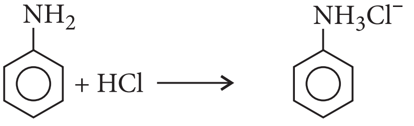
$$\begin{tikzcd}
CH_3{-}Cl \arrow[r, "KCN"] & \underset{(A)}{CH_3CN} \arrow[r, "LiAlH_4"] & \underset{(B)}{CH_3CH_2NH_2} \arrow[d, dash] \\
\underset{(C)}{CH_3CH_2NC} & & {} \arrow[ll, "CHCl_3 + alc.\ KOH", "\Delta"']
\end{tikzcd}$$

68. (i)



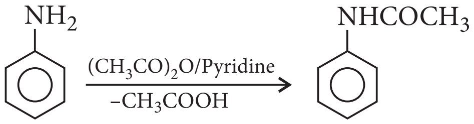
2,4,6-Tribromoaniline

(ii)



Anilinium chloride

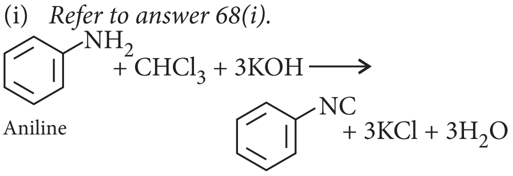
(iii)



Acetanilide

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

(ii)



Aniline

Phenyl isocyanide

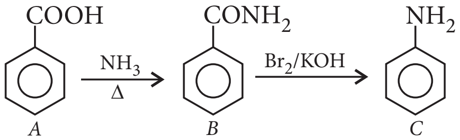
(iii) *Refer to answer 68(ii).*

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

(ii)

$$\begin{tikzcd}
CH_3Cl \arrow[r, "KCN"] & \underset{A}{CH_3CN} \arrow[r, "LiAlH_4"] & \underset{B}{CH_3CH_2NH_2} \arrow[d, dash] \\
& \underset{C}{CH_3CH_2OH} & {} \arrow[l, "HNO_2", "273\ K"']
\end{tikzcd}$$

71. Formula of the compound '*C*' indicates it to be 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 :



72. (i)

$$\begin{tikzcd}
CH_3Br \arrow[r, "KCN"] & \underset{(A)}{CH_3CN} \arrow[r, "LiAlH_4"] & \underset{(B)}{CH_3CH_2NH_2} \arrow[d, "273\ K"', "HNO_2"] \\
& & \underset{(C)}{CH_3CH_2OH}
\end{tikzcd}$$

(ii)
$$\begin{tikzcd} CH_3COOH \arrow[r, "NH_3", "\Delta"'] & \underset{(A)}{CH_3CONH_2} \arrow[d, "Br_2 + KOH"] \\ \underset{(C)}{CH_3NC} & \underset{(B)}{CH_3NH_2} \arrow[l, "CHCl_3 + NaOH"'] \end{tikzcd}$$

73. (i) $A = CH_3CH_2CN$
$B = CH_3CH_2CH_2NH_2$
$C = CH_3CH_2CH_2OH$

(ii) *Refer to answer 72(ii).*

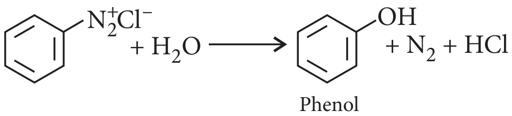
74. (i) *Refer to answer 42.*

(ii) *Refer to answer 57(ii).*

(iii) *Refer to answer 45(i).*

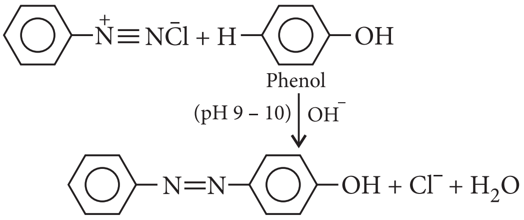
75. $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow C_6H_6 + N_2 + H_3PO_3 + HCl$

76. Diazotisation reaction.

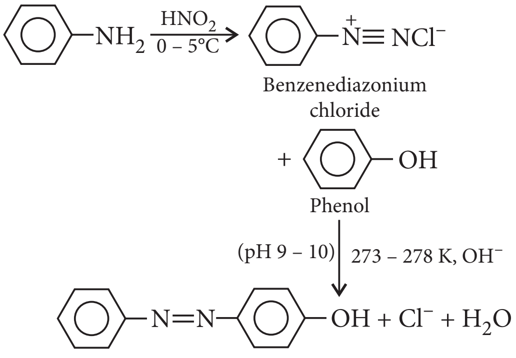
77.


Phenol

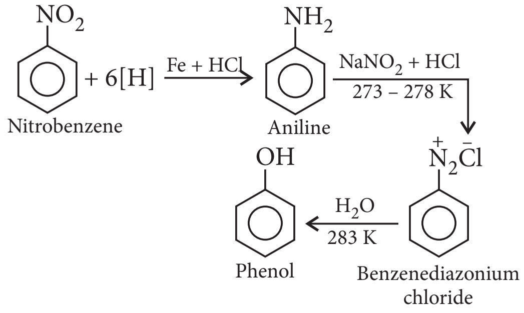
78. Diazonium salts react with aromatic amines in weakly acidic medium and phenols in weakly alkaline medium to form coloured compounds called azo dyes by coupling at *p*-position of amines or phenols.

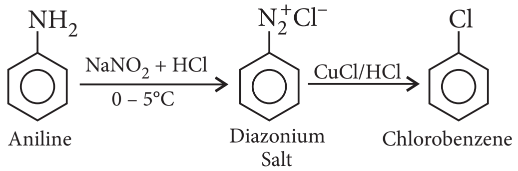


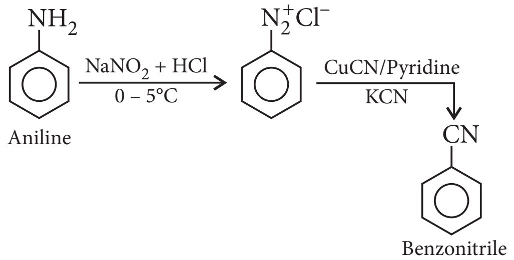
p-Hydroxyazobenzene
(Orange dye)

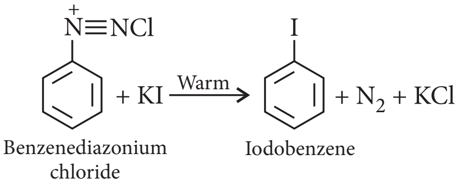
79.


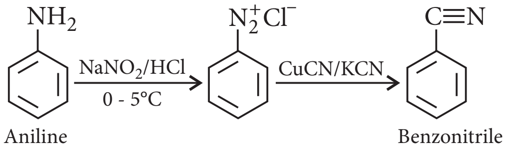
p-Hydroxyazobenzene (orange dye)

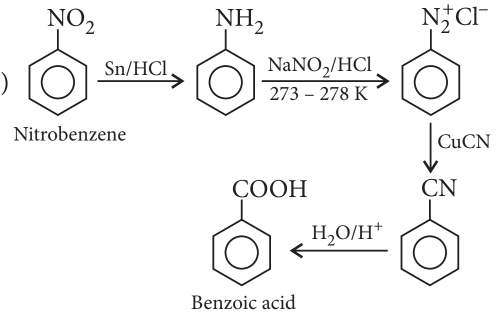
80.


81.


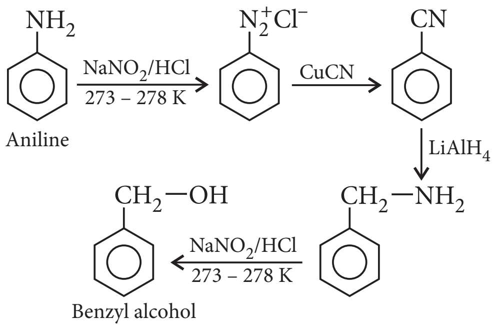
82.


83.


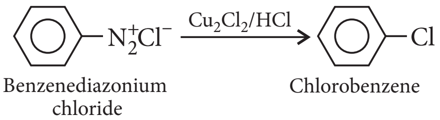
84.


85. (i)


(ii)



86. (i) **Sandmeyer reaction :** By this reaction nulceophiles 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.

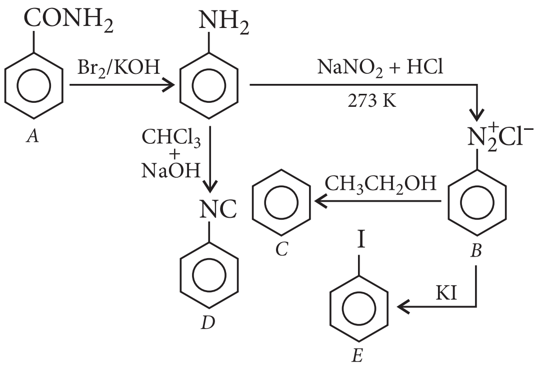


(ii) *Refer to answer 78.*

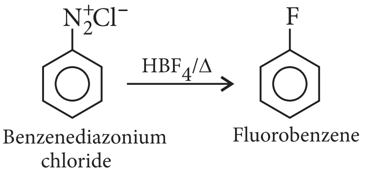
87. (i)
$$C_6H_5N_2^+Cl^- \xrightarrow{CuCN} \underset{\substack{\text{Benzonitrile}\\(A)}}{C_6H_5CN} \xrightarrow{H_2O/H^+} \underset{\substack{\text{Benzoic acid}\\(B)}}{C_6H_5COOH} \xrightarrow[\Delta]{NH_3} \underset{\substack{\text{Benzamide}\\(C)}}{C_6H_5CONH_2}$$

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

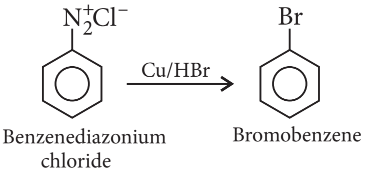
88.



89. (i) (a)



(b)



(ii) (a) *Refer to answer 49(i).*

(b) *Refer to answer 70(ii).*