

**XII** CBSE

**ORGANIC**  
**AMINES**  
**CHEMISTRY**

YOUR GATEWAY TO EXCELLENCE IN  
IIT-JEE, NEET AND CBSE EXAMS

**ORGANIC**  
**AMINES**  
**CHEMISTRY**

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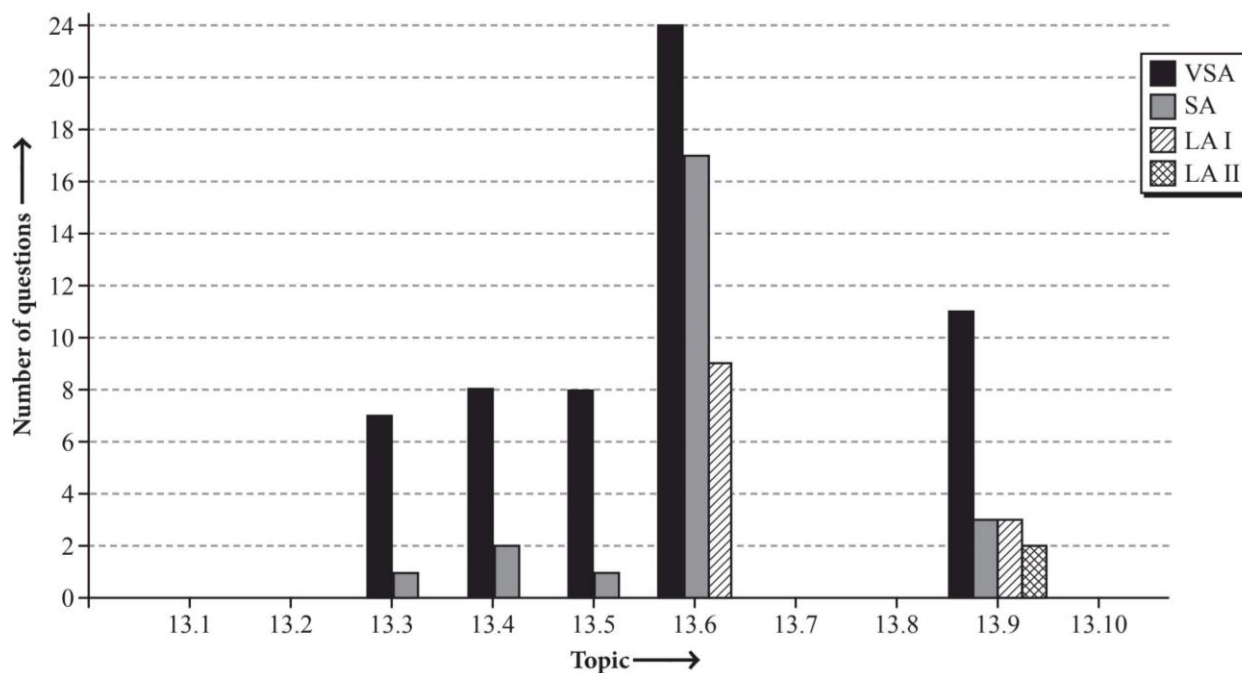


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ORGANIC  
**AMINES**  
**CHEMISTRY**

13.1 Structure of Amines	13.7 Method of Preparation of Diazonium Salts
13.2 Classification	13.8 Physical Properties
13.3 Nomenclature	13.9 Chemical Reactions
13.4 Preparation of Amines	13.10 Importance of Diazonium Salts in Synthesis of Aromatic Compounds
13.5 Physical Properties	
13.6 Chemical Reactions	

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



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

**QUICK RECAP**

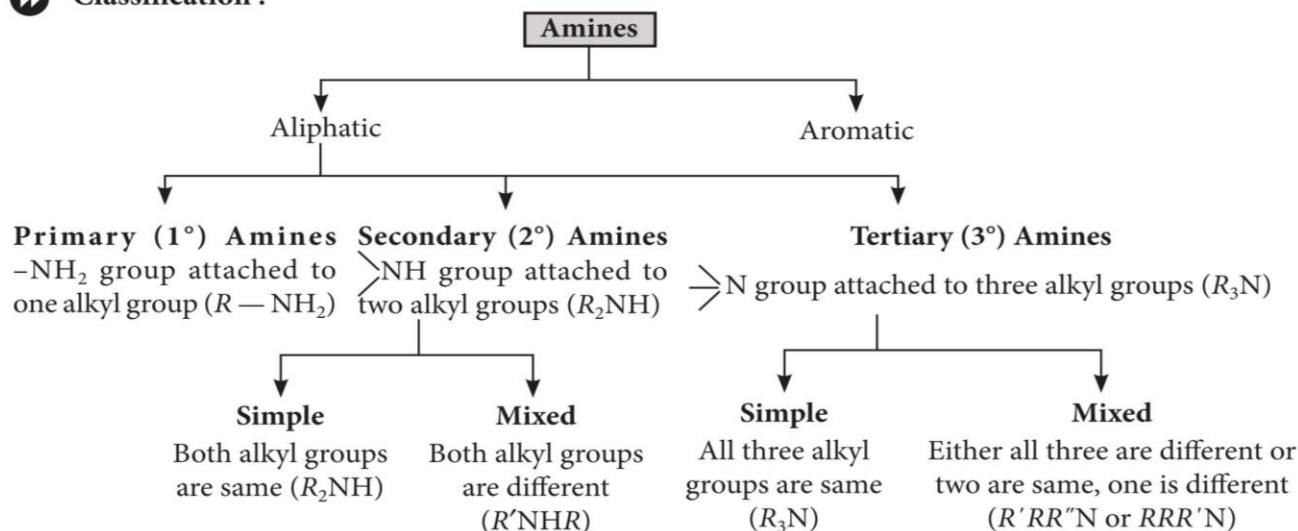
**AMINES**

- ▶▶ **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.

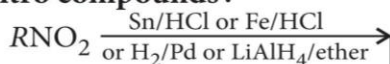
►► **Structure** : Nitrogen orbitals in amines are  $sp^3$ -hybridised and the geometry of amines is pyramidal. Due to the presence of unshared pair of electrons, the angle C—N—E, (where E is C or H) is less than  $109.5^\circ$ .

►► **Classification** :

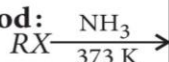


►► **Preparation** :

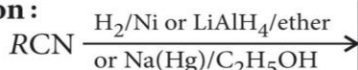
**Reduction of nitro compounds :**



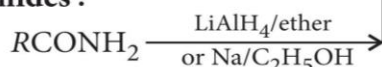
**Hofmann's ammonolysis method :**



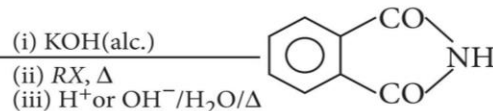
**Mendius reduction :**



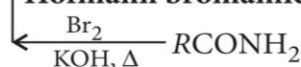
**Reduction of amides :**



**Gabriel phthalimide synthesis :**



**Hofmann bromamide degradation :**



► **Limitations of Gabriel phthalimide synthesis :**

- It is used for the preparation of only  $1^\circ$  amines. *tert*-Butylamine is a  $1^\circ$  amine, but cannot be prepared by this method. In this case, elimination takes place.
- Aromatic  $1^\circ$  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  $\text{>NH}_2$  and  $H_2O$  molecules.

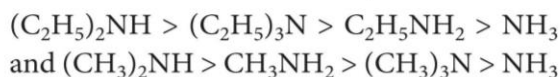
### ▶ Chemical properties :

#### ▶ Basic character of amines :

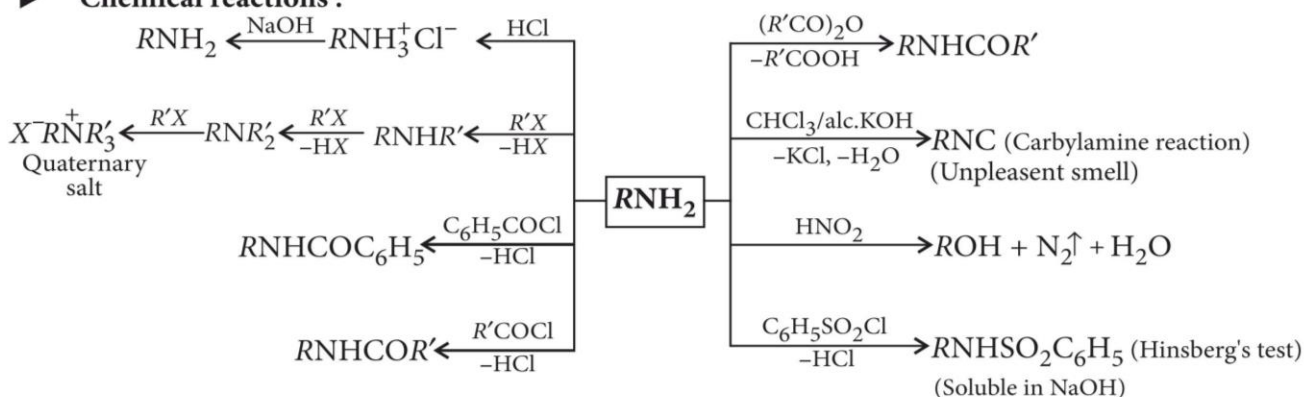
- Amines are basic in nature due to the presence of lone pair of electrons on nitrogen atom.
- Aliphatic amines are stronger bases than ammonia due to +I effect of alkyl groups present in amines.
- Aromatic amines are weaker bases than ammonia due to -I effect of aryl group.
- Beside inductive effect, 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  $3^\circ$  amine >  $2^\circ$  amine >  $1^\circ$  amine >  $\text{NH}_3$ .
- 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



#### ▶ Chemical reactions :



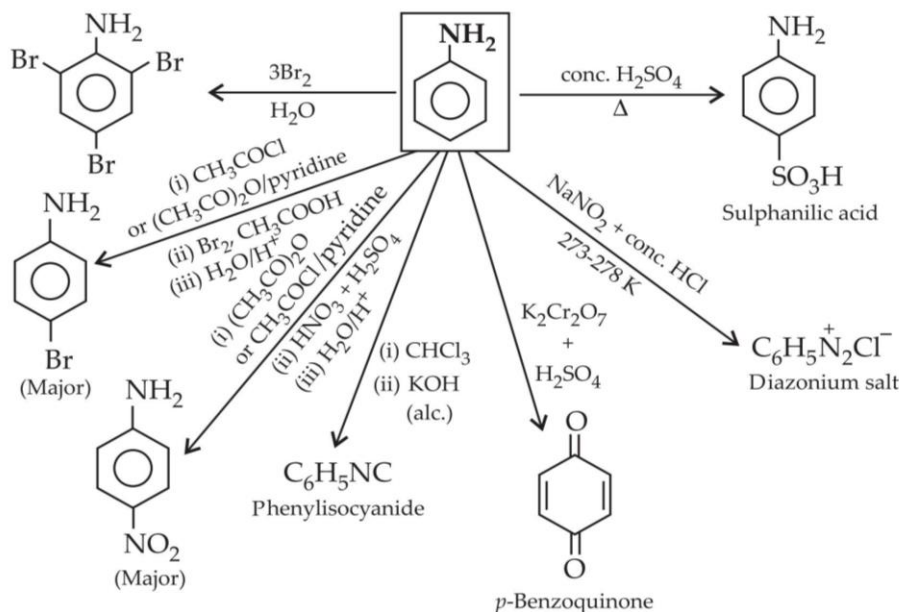
#### ▶ Identification of primary, secondary and tertiary amines :

	Test	Primary amine	Secondary amine	Tertiary amine
1.	Reaction with nitrous acid.	Gives alcohol with effervescence of $\text{N}_2$ 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 ( <i>Hinsberg's reagent</i> )	Gives <i>N</i> -alkylbenzene-sulphonamide which is soluble in alkali.	Gives <i>N,N</i> -dialkylbenzene sulphonamide which is insoluble in alkali.	No reaction
3.	<i>Carbylamine test</i> : Reaction with chloroform and alcoholic KOH	Forms carbylamine or isocyanide (RNC) with characteristic unpleasant odour.	No reaction	No reaction
4.	<i>Hofmann's mustard oil reaction</i> : Reaction with $\text{CS}_2$ and $\text{HgCl}_2$ .	Forms <i>N</i> -substituted isothiocyanate with characteristic unpleasant smell of mustard oil.	No reaction	No reaction

#### ▶ Electrophilic substitution reactions of arylamines :

Aniline undergoes electrophilic substitution reactions.  $-\text{NH}_2$  group is *ortho*-

and *para*-directing and a powerful activating group.



### DIAZONIUM SALTS

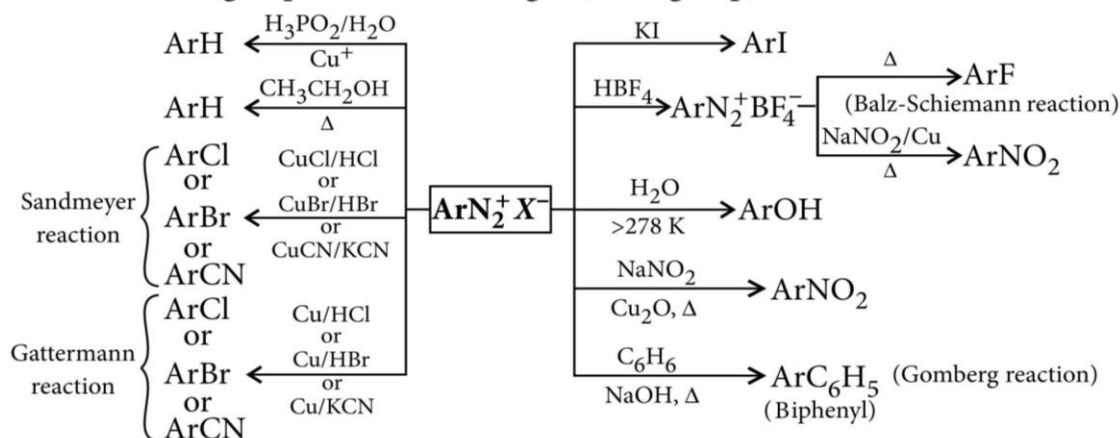
▶ **Arenediazonium salts** : They have the general formula  $\text{ArN}_2^+ \text{X}^-$ , Ar stands for the aryl ( $-\text{C}_6\text{H}_5$ ) group and  $\text{X}^-$  is  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{HSO}_4^-$ ,  $\text{BF}_4^-$ .

▶ **Nomenclature** : They are named by suffixing diazonium to the name of parent hydrocarbon followed by anion.

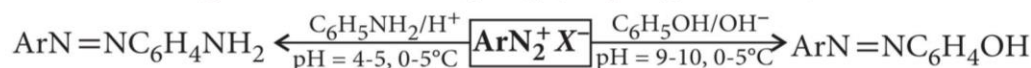
▶ **Preparation** : Benzenediazonium chloride is prepared by the reaction of aniline with nitrous acid (sodium nitrite and hydrochloric acid) at  $0-5^\circ\text{C}$ .

#### ▶ Chemical properties :

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



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

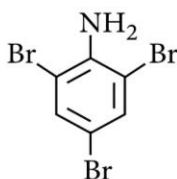


## Previous Years' CBSE Board Questions

### 13.3 Nomenclature

#### VSA (1 mark)

- Write IUPAC name of the following compound:  $(\text{CH}_3\text{CH}_2)_2\text{NCH}_3$  (Delhi 2017)
- Write the structure of 2, 4-dinitrochlorobenzene. (Delhi 2017)
- Write the IUPAC name of the following compound :  
 $\text{CH}_3\text{NHCH}(\text{CH}_3)_2$  (Delhi 2017)
- Write IUPAC name of the following compound:  
 $(\text{CH}_3)_2\text{N} - \text{CH}_2\text{CH}_3$  (Delhi 2017)
- Write the IUPAC name of the given compound:

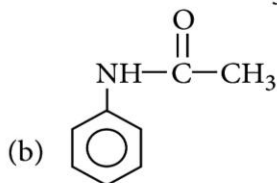
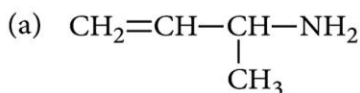


(Delhi 2016)

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

#### SA (2 marks)

- Give IUPAC names of the following compounds:



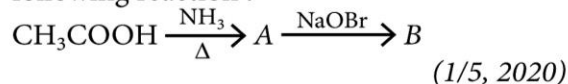
(Delhi 2012C)

### 13.4 Preparation of Amines

#### VSA (1 mark)

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

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



- Carry out the following conversion :  
Benzoic acid to aniline. (1/5, AI 2019)
- 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)
- State and illustrate the following :  
Gabriel synthesis (1/5, 2018, 1/2, AI 2013C, 1/3, Foreign 2011)
- How do you convert the following :  
Ethanenitrile to ethanamine (1/3, AI 2015)
- Write chemical equation for the following conversion :  
Benzyl chloride to 2-phenylethanamine.  
(1/3, Delhi 2012)
- Why cannot primary aromatic amines be prepared by Gabriel phthalimide synthesis? (1/2, AI 2011C)

#### SA (2 marks)

- How will you convert the following :  
(i) Nitrobenzene into aniline  
(ii) Ethanoic acid into methanamine  
(2/3, Delhi 2014)
- How are the following conversions carried out?  
(i)  $\text{CH}_3\text{CH}_2\text{Cl}$  to  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$   
(ii) Benzene to aniline (Delhi 2012C)

### 13.5 Physical Properties

#### VSA (1 mark)

- Out of  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_3\text{OH}$ , which has higher boiling point? (2020)
- Arrange the following compounds in decreasing order of their boiling points :  
Butanol, Butanamine, Butane (1/3, 2020)
- 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)

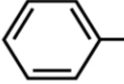
### SA (2 marks)

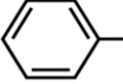
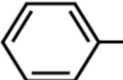
27. Arrange the following compounds as directed :
- In increasing order of solubility in water :  
 $(CH_3)_2NH$ ,  $CH_3NH_2$ ,  $C_6H_5NH_2$
  - In increasing order of boiling point :  
 $(C_2H_5)_2NH$ ,  $(C_2H_5)_3N$ ,  $C_2H_5NH_2$   
(2/3, 2020)

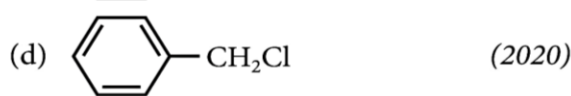
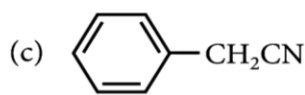
## 13.6 Chemical Reactions (Amines)

### 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

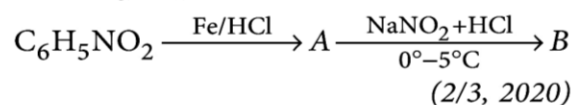
-   $CH_2OH$
-   $CH_2NC$



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 :



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)

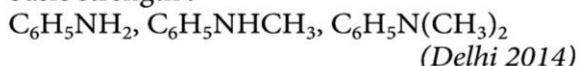
37. Give a simple chemical test to distinguish between the following pair of compounds :  
 $(CH_3)_2NH$  and  $(CH_3)_3N$  (1/5, Delhi 2015)

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)

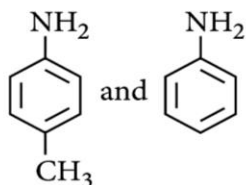
40. How will you convert the following :  
Aniline into *N*-phenylethanamide  
(Write the chemical equations involved.)  
(1/3, Delhi 2014)

41. Arrange the following in increasing order of basic strength :



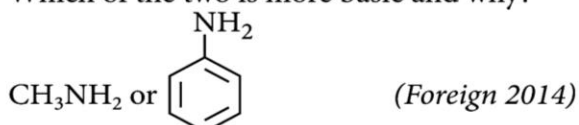
42. Which of the two is more basic and why?  
 $CH_3NH_2$  or  $NH_3$  (Foreign 2014)

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



(Foreign 2014)

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



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 :

- Aniline and ethanamine
  - Aniline and *N*-methylaniline
- (2/3, 2020)

53. Distinguish between the following :

- $CH_3CH_2NH_2$  and  $(CH_3CH_2)_2NH$
  - Aniline and  $CH_3NH_2$
- (2/5, 2020)

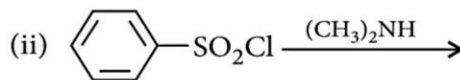
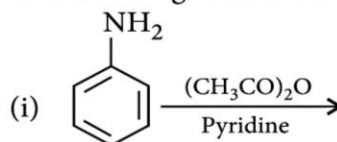
54. Give reasons :

- Although  $-NH_2$  group is *o/p* directing in electrophilic substitution reactions,

yet aniline, on nitration gives good yield of *m*-nitroaniline.

- $(CH_3)_2NH$  is more basic than  $(CH_3)_3N$  in an aqueous solution. (2/5, 2020)

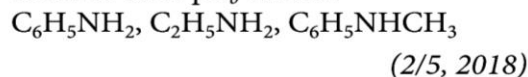
55. Write the structures of the main products of the following reactions :



(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 :



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)

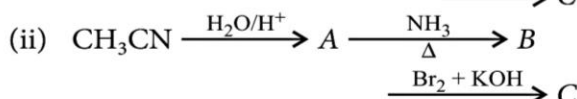
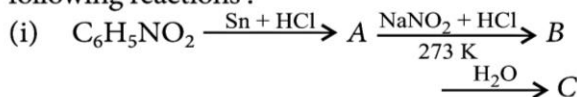
59. Illustrate the following reactions giving suitable example in each case :

(i) Ammonolysis

(ii) Acetylation of amines

(2/5, Foreign 2015)

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



(2/3, Delhi, AI 2014)

61. Account for the following :

(i) Aniline does not give Friedel-Crafts reaction.

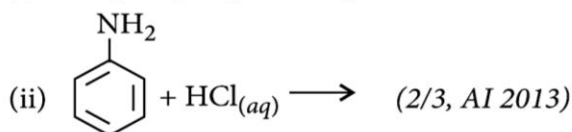
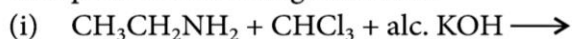
(ii)  $pK_b$  of methylamine is less than that of aniline. (2/3, Delhi 2014C)



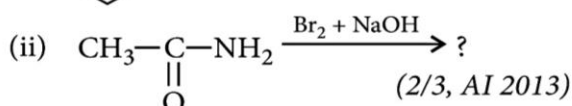
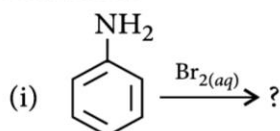
62. (i) Arrange the following compounds in an increasing order of basic strength :  
 $C_6H_5NH_2$ ,  $C_6H_5N(CH_3)_2$ ,  $(C_2H_5)_2NH$  and  $CH_3NH_2$
- (ii) Arrange the following compounds in a decreasing order of  $pK_b$  values :  
 $C_2H_5NH_2$ ,  $C_6H_5NHCH_3$ ,  $(C_2H_5)_2NH$  and  $C_6H_5NH_2$

(Delhi 2014C)

63. Complete the following reactions :



64. Write the main products of the following reactions :



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)

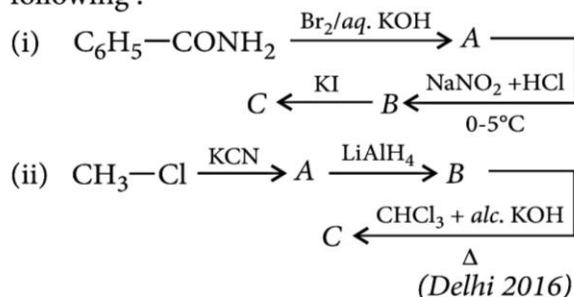
70. (a) Give one chemical test to distinguish between the compounds of the following pairs :

- (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 :



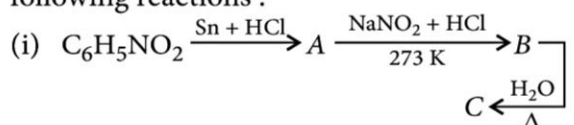
73. Write the structures of main products when aniline reacts with the following reagents :

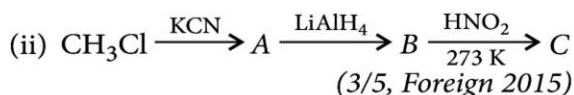
- (i)  $Br_2$  water (ii) HCl  
 (iii)  $(CH_3CO)_2O$ /pyridine (3/5, Delhi 2015)

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)

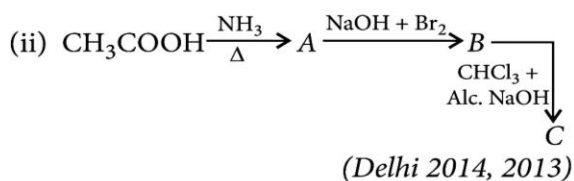
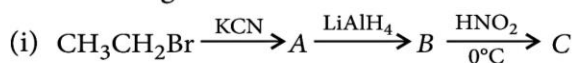
75. Write the structures of A, B and C in the following reactions :





76. An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br<sub>2</sub> and KOH forms a compound 'C' of molecular formula C<sub>6</sub>H<sub>7</sub>N. Write the structures and IUPAC names of compounds A, B and C. (Delhi 2015C)

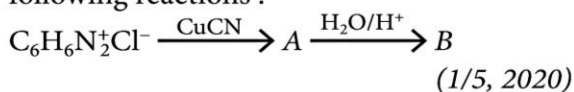
77. Give the structures of products A, B and C in the following reactions :



### 13.9 Chemical Reactions (Diazonium salts)

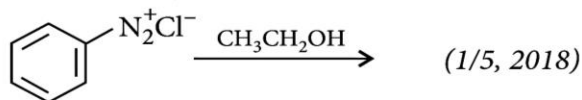
#### VSA (1 mark)

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



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 :



81. Complete the following reaction equation :  
C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>Cl + H<sub>3</sub>PO<sub>2</sub> + H<sub>2</sub>O →  
(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<sub>6</sub>H<sub>5</sub>N<sub>2</sub>Cl<sup>+</sup>Cl<sup>-</sup>  $\xrightarrow[\text{(Room temp.)}]{\text{H}_2\text{O}}$  \_\_\_\_\_ (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)

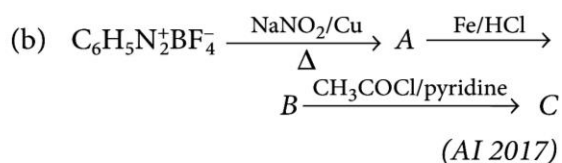
90. Write chemical equations for the following conversions :  
(i) Nitrobenzene to benzoic acid.  
(ii) Aniline to benzyl alcohol.  
(2/3, Delhi 2012)

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

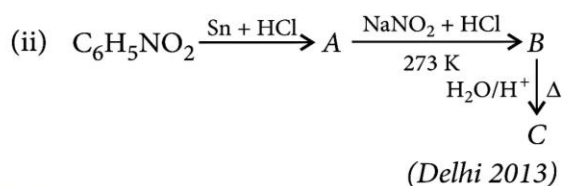
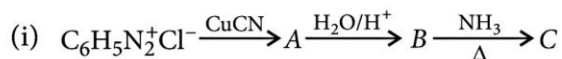
#### LAI (3 marks)

92. Write the structures of main products when benzene diazonium chloride reacts with the following reagents :  
(i) CuCN (ii) CH<sub>3</sub>CH<sub>2</sub>OH  
(iii) KI (Delhi 2019)

93. Write the structures of compounds A, B and C in the following reactions :  
(a) CH<sub>3</sub>—COOH  $\xrightarrow{\text{NH}_3/\Delta}$  A  $\xrightarrow{\text{Br}_2/\text{KOH}_{(aq)}}$  B  $\xrightarrow{\text{CHCl}_3 + \text{alc. KOH}}$  C

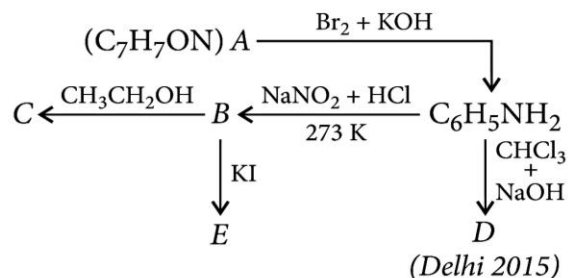


94. Give the structure of A, B and C in the following reactions :



**LA II (5 marks)**

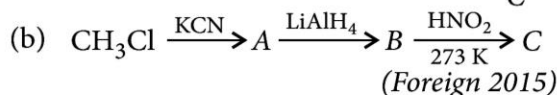
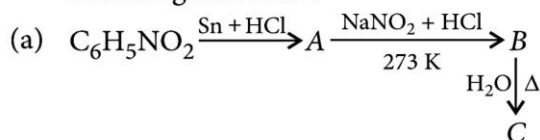
95. An aromatic compound 'A' of molecular formula  $\text{C}_7\text{H}_7\text{ON}$  undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions :



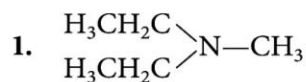
96. (i) Write the structures of main products when benzenediazonium chloride ( $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$ ) reacts with the following reagents :



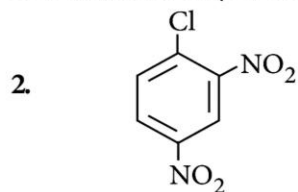
(ii) Write the structures of A, B and C in the following reactions :



**Detailed Solutions**

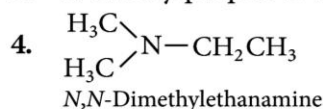


IUPAC name : N-Ethyl-N-methylethanamine



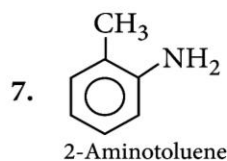
2, 4-Dinitrochlorobenzene

3. N-Methylpropan-2-amine (2° amine)



5. 2, 4, 6-Tribromoaniline

6.  $\text{CH}_3\text{CH}_2\text{NHCH}_3$

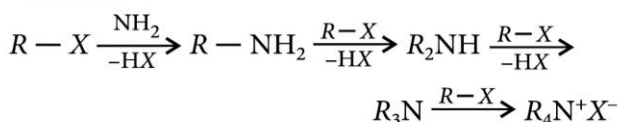


2-Aminotoluene

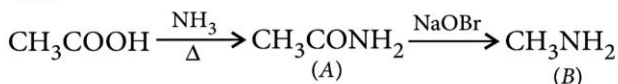
8. (a) But-3-en-2-amine

(b) N-Phenylethanamide

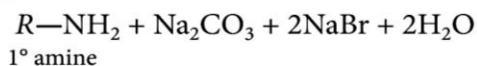
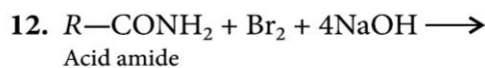
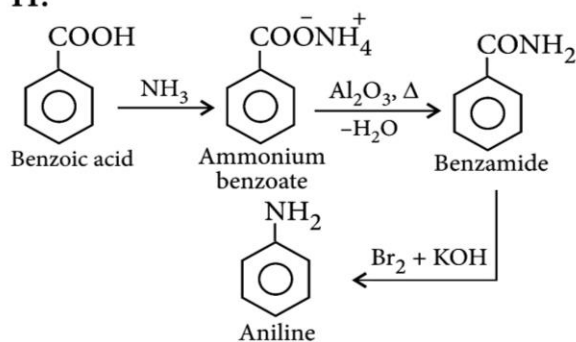
9. The ammonolysis of alkyl halides with ammonia is a nucleophilic substitution reaction in which ammonia acts as a nucleophile by donating the electron pair on nitrogen atom to form primary amine as the initial product. Now, the primary amine can act as a nucleophile and combine with alkyl halide (if 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.



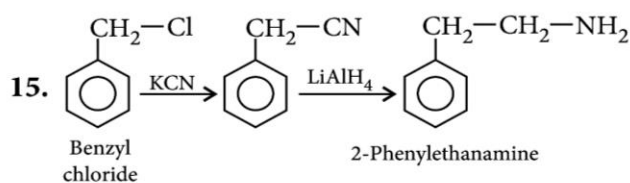
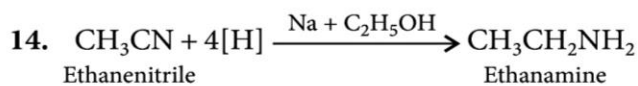
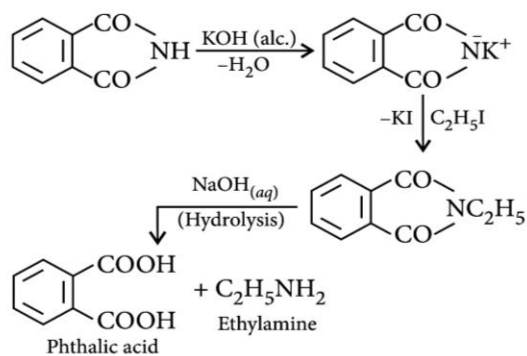
10.



11.

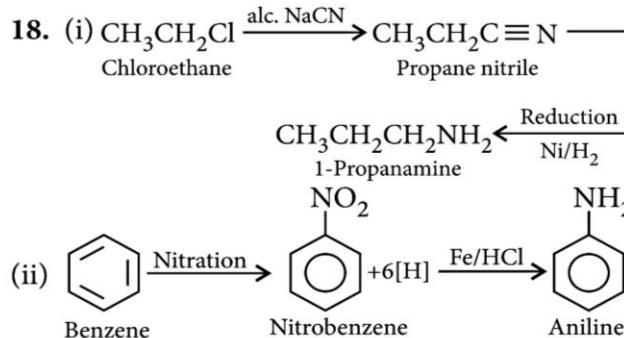
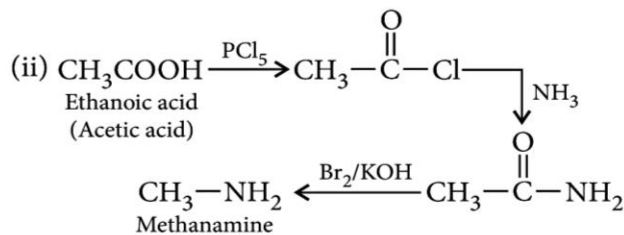
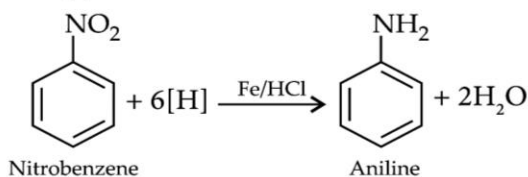


13. **Gabriel phthalimide synthesis** : In this reaction phthalimide is converted into its potassium salt by treating it with alcoholic potassium hydroxide. Then potassium phthalimide is heated with an alkyl halide to yield an *N*-alkylphthalimide which is hydrolysed to phthalic acid and primary amine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



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)



19.  $\text{CH}_3\text{OH}$  has higher boiling point than  $\text{CH}_3\text{NH}_2$ . 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 ( $\text{R}-\text{NH}_2$ ) have two hydrogen atoms on nitrogen which can undergo intermolecular hydrogen bonding whereas no such hydrogen bonding is present in tertiary amines ( $\text{R}_3\text{N}$ ). So, primary amines boil at a higher temperature than tertiary amines.

22. Refer to answer 21.

23. Increasing order of boiling points :

$(\text{CH}_3)_3\text{N} < \text{C}_2\text{H}_5\text{NH}_2 < \text{C}_2\text{H}_5\text{OH}$

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.  $\text{C}_6\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH} < \text{C}_2\text{H}_5\text{NH}_2$

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.

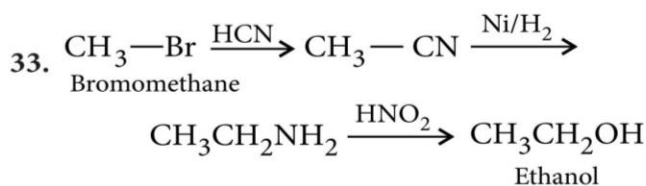
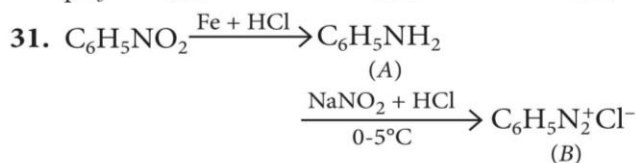
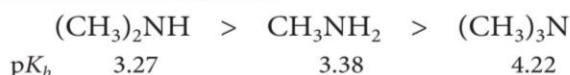
(ii) 1° amines have two, 2° amines have one while 3° amines have no hydrogen linked to nitrogen. The degree of association due to hydrogen bonding and hence the boiling point increase as  $(C_2H_5)_3N < (C_2H_5)_2NH < C_2H_5NH_2$

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.

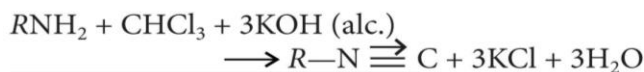
30. In case of small alkyl groups like  $-CH_3$  the order of basicity is secondary amine > primary amine > tertiary amine due to solvation effect and +I effect of  $-CH_3$  group.



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

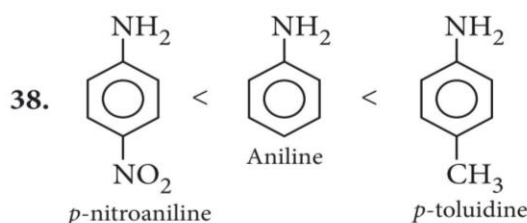


36. Carbylamine reaction is the reaction in which 1° amines produce a bad smelling compound when treated with chloroform in the presence of alkali.



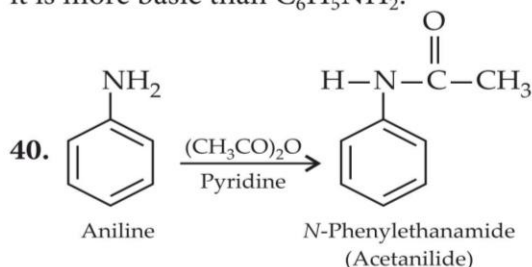
It is the test for primary amines.

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.



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  $C_6H_5NH_2$ .



41. Increasing order of basic strength in gaseous state is as follows :



As the number of  $-CH_3$  groups (+I effect) attached to nitrogen increases, its basicity will increase.

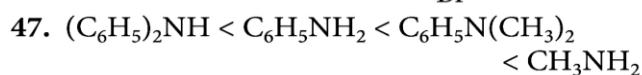
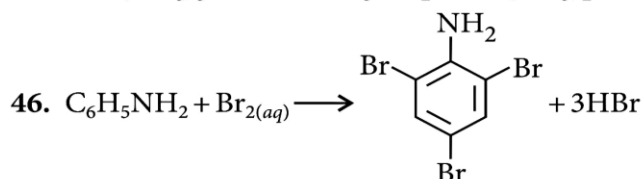
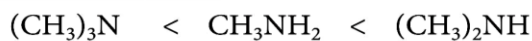
42. Methyl amine is more basic than ammonia because of the presence of electron donating methyl group (+I effect), which increases the electron density on nitrogen atom.

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

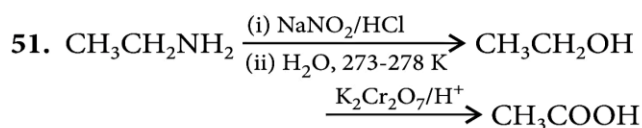
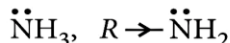
amine > tertiary amine due to solvation effect and +I effect of  $-\text{CH}_3$  group.



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  $-\text{C}_2\text{H}_5$  group increases electron density on the nitrogen atom. Therefore, aniline is a weaker base than ethylamine hence, its  $\text{pK}_b$  value is more than that for ethylamine.

49. Aniline being an aromatic primary amine on treatment with  $\text{HNO}_2[\text{NaNO}_2 + \text{HCl} (\text{dil.})]$  at 273–278 K followed by treatment with an alkaline solution of  $\beta$ -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.

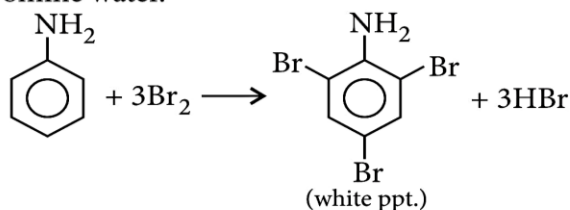


52. (i) Refer to answer 49.

(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  $\text{CHCl}_3$ , ethylamine gives foul smelling ethyl isocyanide. Diethylamine does not give this test.

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

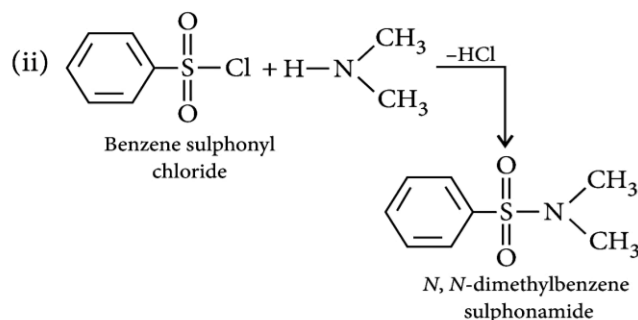


Methylamine does not react with bromine water.

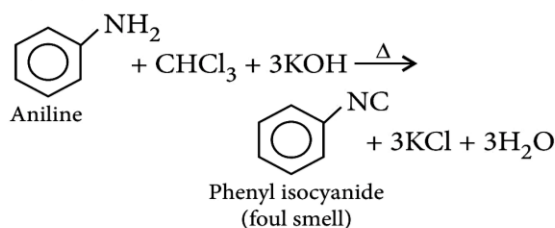
54. (i) Nitration is carried out with conc.  $\text{HNO}_3$  in the presence of conc.  $\text{H}_2\text{SO}_4$ . In the presence of these acids, the  $-\text{NH}_2$  group of aniline gets protonated and is converted into  $-\text{NH}_3^+$  group. This positively charged group acts as a strong electron 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.

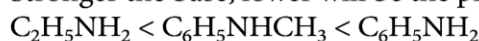
55. (i) Refer to answer 40.



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

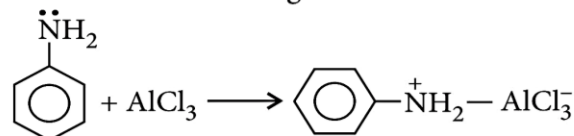


(b) Stronger the base, lower will be the  $\text{pK}_b$  value.

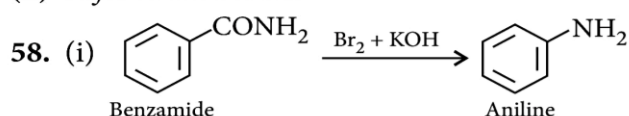


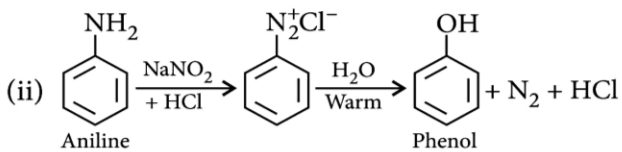
$\text{pK}_b$  3.29 4.63 9.38

57. (i) In Friedel — Crafts reaction,  $\text{AlCl}_3$  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.

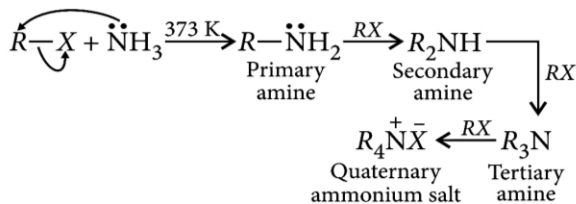


(ii) Refer to answer 34.

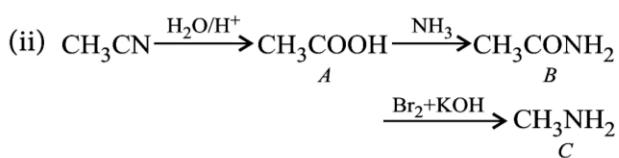
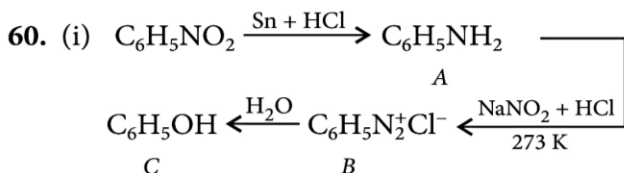
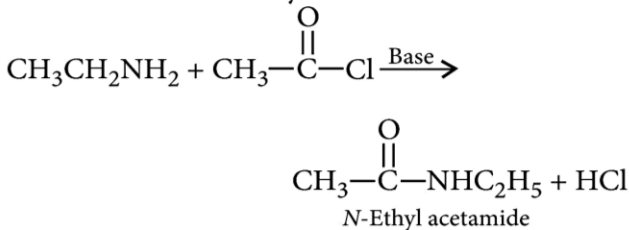




59. (i) **Ammonolysis** : Alkyl halides when treated with ethanolic solution of ammonia give a mixture of primary, secondary, tertiary amines and quaternary ammonium salt.



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

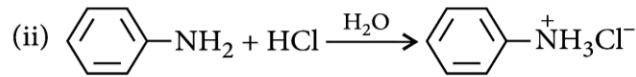
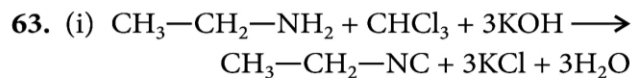
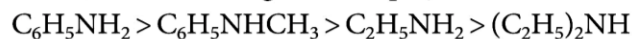


61. (i) Refer to answer 57(i).

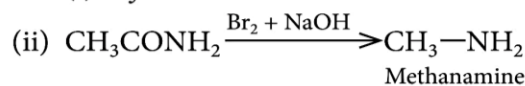
(ii) In aniline, the lone pair of electrons of N-atom are delocalised over the benzene ring. As a result, electron density on the nitrogen decreases. In contrast, in  $CH_3-NH_2$ , +I effect of  $-CH_3$  group increases the electron density on the N-atom. Therefore, aniline is a weaker base than methylamine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

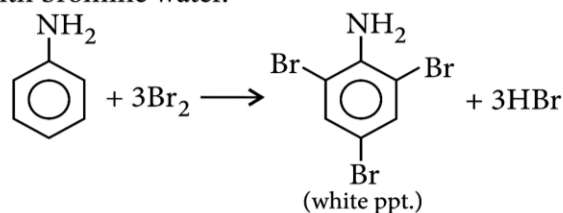
hence, the decreasing order of  $pK_b$  values :



64. (i) Refer to answer 46.



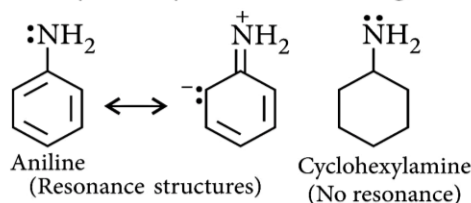
65. (i) Aniline gives white or brown precipitate with bromine water.



Ethylamine does not react with bromine water.

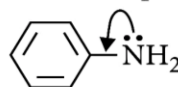
(ii) When heated with an alcoholic solution of KOH and  $CHCl_3$ , ethylamine gives foul smelling ethyl isocyanide. Dimethylamine does not give this test.

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  $-NH_2$  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.



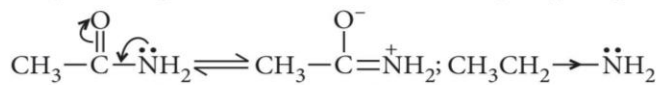
(ii) Refer to answer 9.

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.



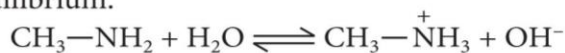
(ii) In  $CH_3CONH_2$ , the lone pair of electrons on nitrogen atom is involved in resonance with the

carbonyl group. So, the electron pair of nitrogen is not easily available for protonation. Hence,  $\text{CH}_3\text{CONH}_2$  is a weaker base than  $\text{CH}_3\text{CH}_2\text{NH}_2$ .



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

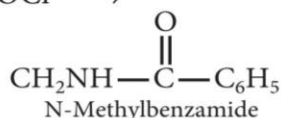
(ii) Methylamine forms hydroxide ions when dissolved in water due to the following acid - base equilibrium.



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



69. (a)  $\text{CH}_3\text{NH}_2 + \text{C}_6\text{H}_5\text{COCl} \longrightarrow$



(b) Stronger the base, lower will be its  $\text{p}K_b$  value. Hence increasing order of  $\text{p}K_b$  values is,  $(\text{C}_2\text{H}_5)_2\text{NH} < \text{C}_2\text{H}_5\text{NH}_2 < \text{NH}_3 < \text{C}_6\text{H}_5\text{NH}_2$

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.

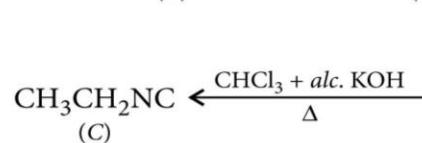
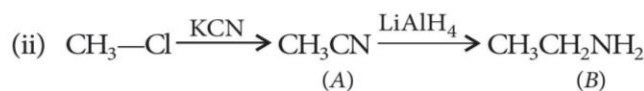
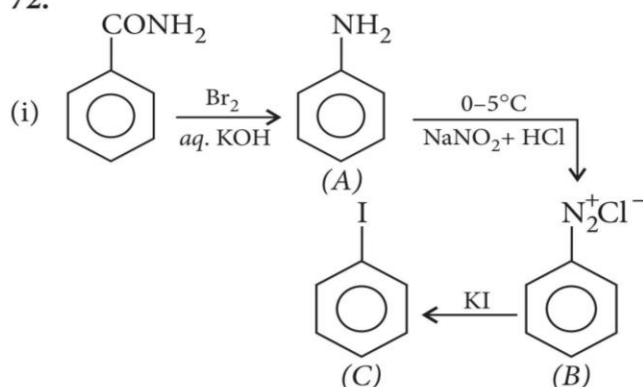
(b) Refer to answer 57 (i).

71. (i) After acetylation of aniline, acetanilide is formed in which due to the presence of  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$  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.

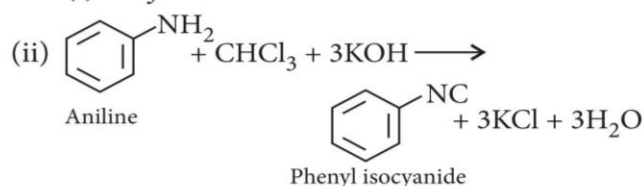


73. (i) Refer to answer 46.

(ii) Refer to answer 63(ii).

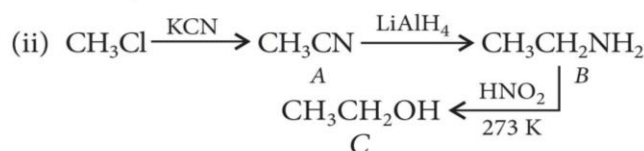
(iii) Refer to answer 40.

74. (i) Refer to answer 46.

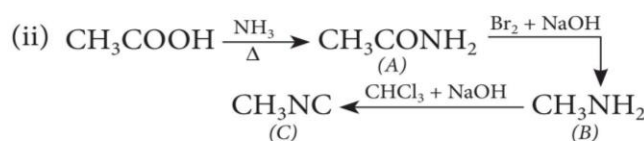
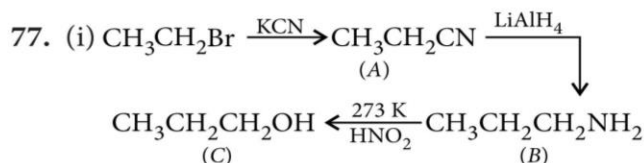
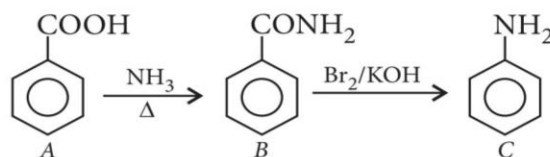


(iii) Refer to answer 63(ii).

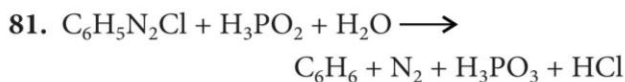
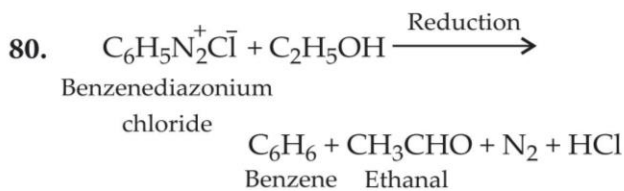
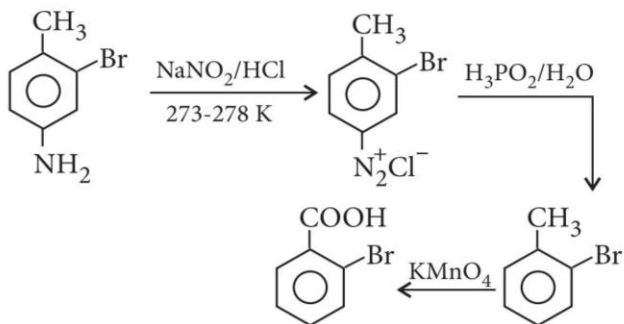
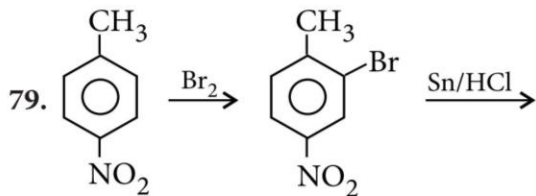
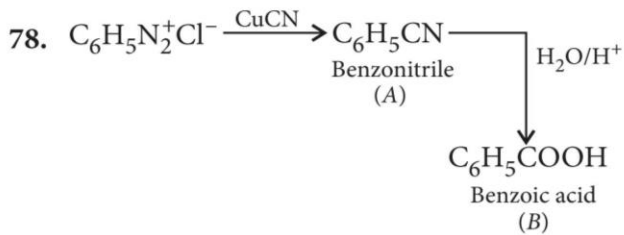
75. (i) Refer to answer 60(i).



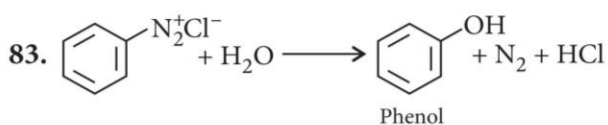
76. Formula of the compound 'C' indicates it is an amine. Since it is obtained by the reaction of  $\text{Br}_2$  and KOH with the compound 'B' so compound 'B' can be an amide. As 'B' is obtained from compound 'A' by reaction with ammonia followed by heating so, compound 'A' could be an aromatic acid. 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 :



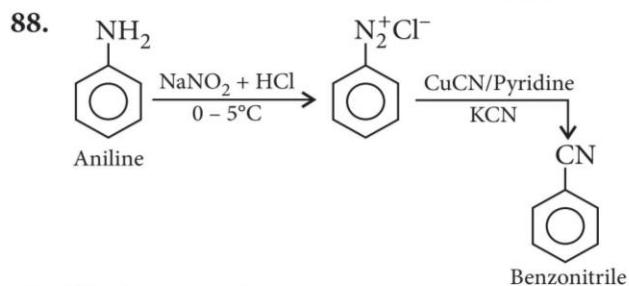
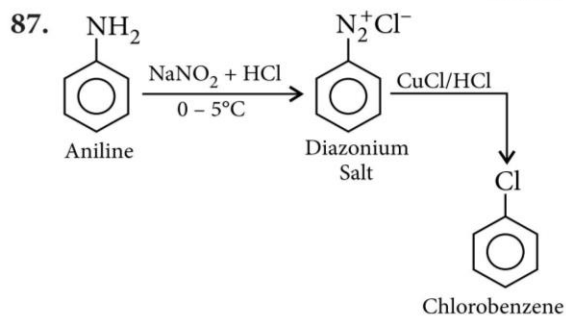
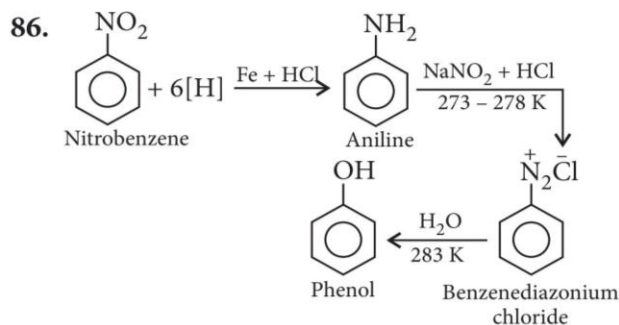
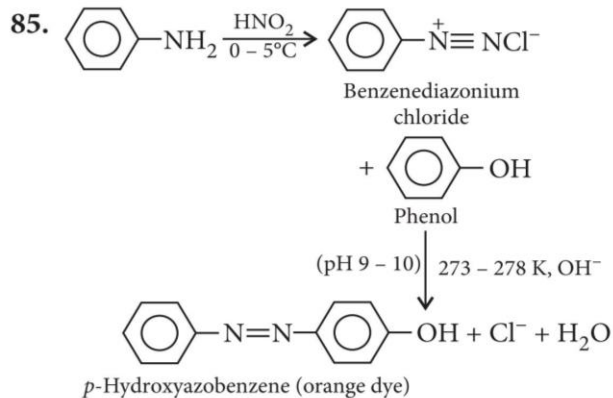
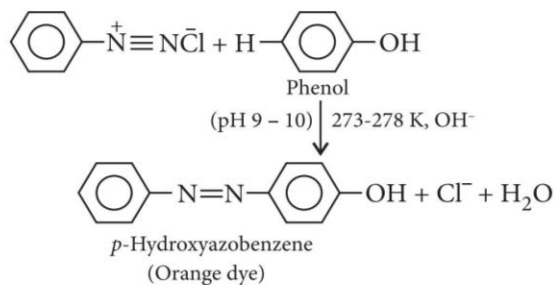




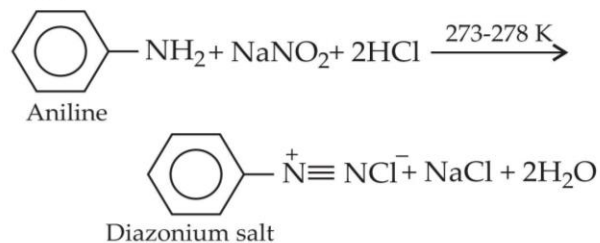
82. Diazotisation reaction.



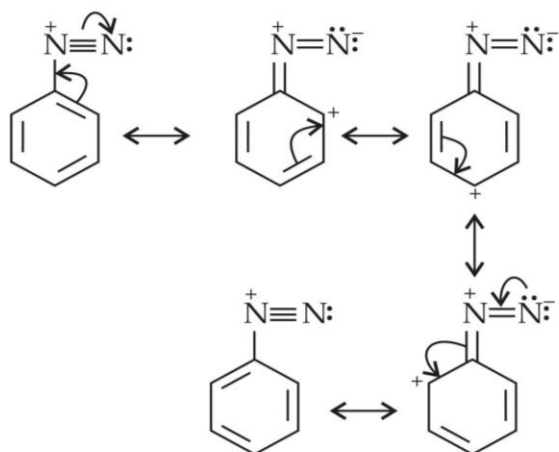
84. Diazonium salts react with aromatic amines in weakly acidic medium and phenols in weakly alkaline medium to form coloured compounds called azo dyes by coupling at *p*-position of amines or phenols.



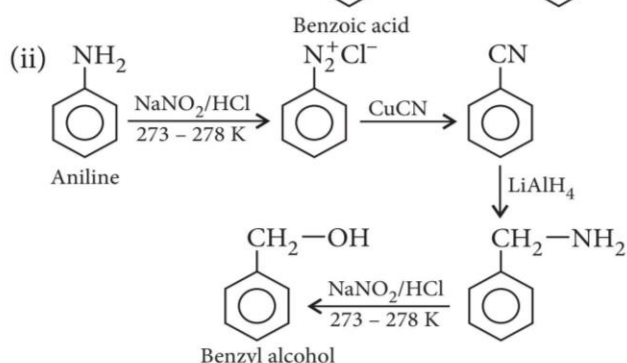
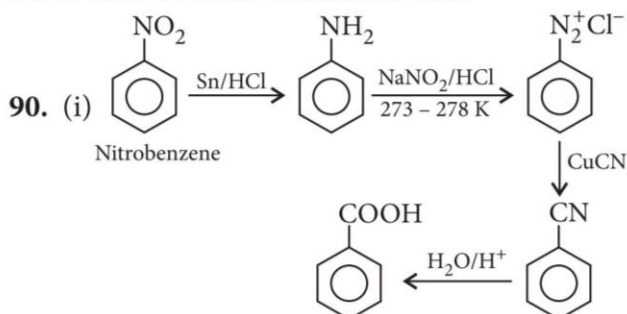
89. (a) Diazotisation :



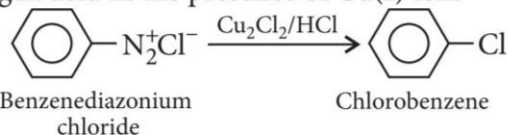
(b) Diazonium salts carry a nitrogen atom with a positive charge. This positive charge is well dispersed in aromatic diazonium salts through resonance as shown below :



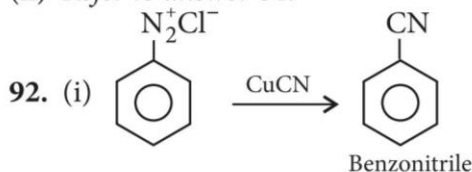
Such a charge delocalisation is not possible in aliphatic diazonium salts and hence they are less stable than aromatic diazonium salts.



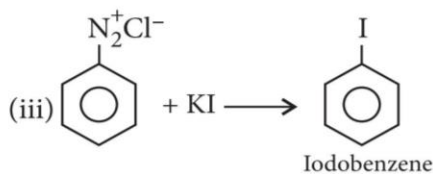
91. (i) **Sandmeyer reaction** : By this reaction nucleophiles like  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{CN}^-$  etc. can easily be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of  $\text{Cu(I)}$  ion.



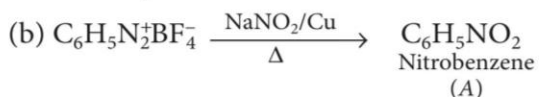
(ii) Refer to answer 84.



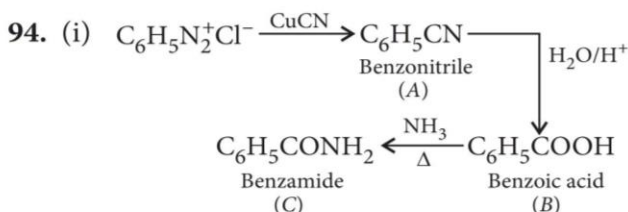
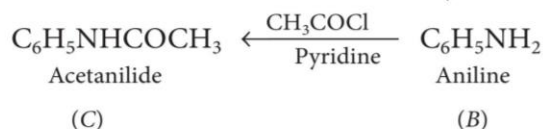
(ii) Refer to answer 80.



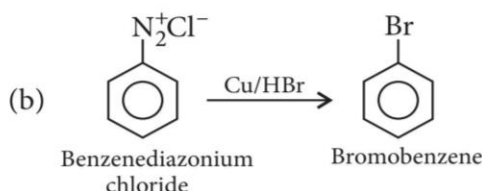
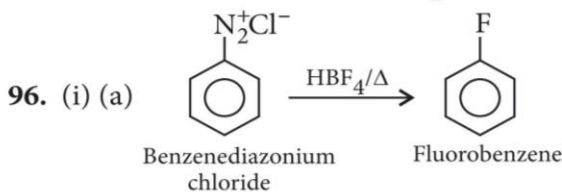
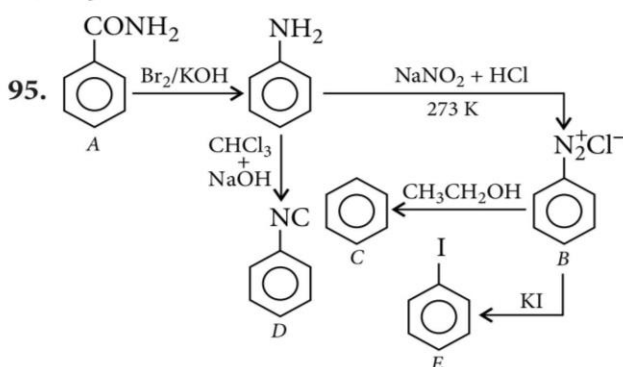
93. (a) Refer to answer 77 (ii).



Reduction  $\downarrow$   $\text{Fe/HCl}$



(ii) Refer to answer 60(i).



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

(b) Refer to answer 75(ii).

