

# AMINES

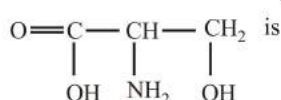
## FACT/DEFINITION TYPE QUESTIONS

- A secondary amine is
  - a compound with two carbon atoms and an  $-NH_2$  group.
  - a compound containing two  $-NH_2$  groups.
  - a compound in which hydrogens of  $NH_3$  have been replaced by two alkyl groups.
  - a compound with an  $-NH_2$  group on carbon atom in number two position.

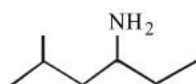
- The general formula of quaternary ammonium compound is
  - $R-NH_2$
  - $R_3N$
  - $R_4N^+X^-$
  - $NH_4X$

- The total number of electrons around the nitrogen atom in amines are
  - 8
  - 7
  - 4
  - 3

- The IUPAC name of the compound having formula,



- 3-amino-hydroxy propine acid
  - 2-amino-propan-3-oic acid
  - amino hydroxy propanoic acid
  - 2-amino-3-hydroxy propanoic acid
- The number of primary amines of formula  $C_4H_{11}N$  is :
    - 1
    - 3
    - 4
    - 2
  - What is the IUPAC name of the following compound ?



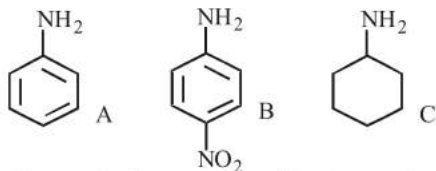
- 2-methyl-4-hexanamine
- 5-methyl-3-hexanamine
- 2-methyl-4-amino hexane
- 5-methyl-3-amino hexane

- The correct IUPAC name for  $CH_2=CHCH_2NHCH_3$  is
  - Allylmethylamine
  - 2-amino-4-pentene
  - 4-aminopent-1-ene
  - N-methylprop-2-en-1-amine
- Amines play an important role in the survival of life. Naturally they are found in
  - proteins
  - vitamins
  - alkaloids
  - All of these
- Intermediates formed during reaction of  $RCONH_2$  with  $Br_2$  and  $KOH$  are
  - $RCONHBr$  and  $RNCO$
  - $RNHCOBr$  and  $RNCO$
  - $RNHBr$  and  $RCONHBr$
  - $RCONBr_2$
- Which of the following reactions will not give a primary amine?
  - $CH_3CONH_2 \xrightarrow{Br_2/KOH}$
  - $CH_3CN \xrightarrow{LiAlH_4}$
  - $CH_3NC \xrightarrow{LiAlH_4}$
  - $CH_3CONH_2 \xrightarrow{LiAlH_4}$
- Propionamide on Hofmann degradation gives –
  - methyl amine
  - ethyl amine
  - propyl amine
  - ethyl cyanide
- Secondary amines could be prepared by
  - reduction of nitriles
  - Hofmann bromamide reaction
  - reduction of amides
  - reduction of isonitriles
- Gabriel's phthalimide synthesis is used for the preparation of
  - Primary aromatic amines
  - Secondary amines
  - Primary aliphatic amines
  - Tertiary amines
- Ethyl amine can be obtained by the
  - Action of  $NH_3$  on ethyl iodide.
  - Action of  $NH_3$  on ethyl alcohol.
  - Both (a) and (b)
  - Neither (a) nor (b)

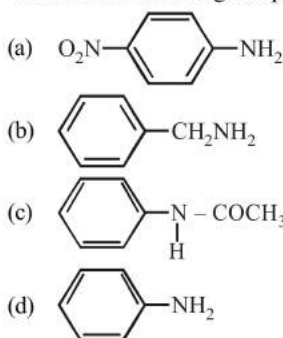
15. Treatment of ammonia with excess of ethyl iodide will yield  
 (a) diethylamine  
 (b) ethylamine  
 (c) triethylamine  
 (d) tetraethylammonium iodide
16. For alkylation of ammonia which of the following is not used?  
 (a)  $\text{CH}_3\text{-X}$  (b)  $\text{CH}_3\text{-CH}_2\text{-X}$   
 (c)  $(\text{CH}_3)_2\text{CH-X}$  (d)  $(\text{CH}_3)_3\text{C-X}$
17. Which of the following amines can be prepared by Gabriel method?  
 (i)  $\text{CH}_3\text{CH}_2\text{NH}_2$  (ii)  $(\text{CH}_3)_2\text{CHNH}_2$   
 (iii)  $(\text{CH}_3)_3\text{CNH}_2$  (iv)  $\text{C}_6\text{H}_5\text{NH}_2$   
 (a) (i) and (iii) (b) (ii) and (iv)  
 (c) (i), (ii) and (iii) (d) (i) and (ii)
18. Amongst the given set of reactants, the most appropriate for preparing 2° amine is \_\_\_\_\_.  
 (a)  $2^\circ\text{R-Br} + \text{NH}_3$   
 (b)  $2^\circ\text{R-Br} + \text{NaCN}$  followed by  $\text{H}_2/\text{Pt}$   
 (c)  $1^\circ\text{R-NH}_2 + \text{RCHO}$  followed by  $\text{H}_2/\text{Pt}$   
 (d)  $1^\circ\text{R-Br}$  (2 mol) + Potassium phthalimide followed by  $\text{H}_3\text{O}^+/\text{heat}$
19. The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is \_\_\_\_\_.  
 (a) excess  $\text{H}_2$   
 (b)  $\text{Br}_2$  in aqueous  $\text{NaOH}$   
 (c)  $\text{Br}_2$  in the presence of red phosphorus  
 (d)  $\text{LiAlH}_4$  in ether
20. Which of the following methods of preparation of amines will give same number of carbon atoms in the chain of amines as in the reactant?  
 (a) Reaction of nitrite with  $\text{LiAlH}_4$ .  
 (b) Reaction of amide with  $\text{LiAlH}_4$  followed by treatment with water.  
 (c) Heating alkylhalide with potassium salt of phthalimide followed by hydrolysis.  
 (d) Treatment of amide with bromine in aqueous solution of sodium hydroxide.
21. The reduction of nitro compounds is most preferred in the presence of  
 (a)  $\text{Pd}/\text{H}_2$  in ethanol (b)  $\text{Sn} + \text{HCl}$   
 (c) finely divided  $\text{Ni}$  (d) iron scrap and  $\text{HCl}$ .
22. An alkyl or benzyl halide on reaction with an ethanolic solution of ammonia undergoes  
 (a) electrophilic substitution reaction  
 (b) nucleophilic substitution reaction.  
 (c) free radical mechanism.  
 (d) nucleophilic addition reaction.
23. In the ammonolysis of alkyl halides the halogen atom is replaced by an amino ( $-\text{NH}_2$ ) group which of the following represent the correct order of reactivity of halides with amines.  
 (a)  $\text{RBr} > \text{RI} > \text{RCl}$  (b)  $\text{RI} > \text{RCl} > \text{RBr}$   
 (c)  $\text{RI} > \text{RBr} > \text{RCl}$  (d)  $\text{RCl} > \text{RBr} > \text{RI}$
24. Which of the following will give primary amine only?  
 (i) ammonia + propylchloride  
 (ii) potassium phthalimide + ethylchloride  
 (iii) potassium phthalimide + chlorobenzene  
 (a) (i) and (ii) (b) (i) and (iii)  
 (c) (ii) and (iii) (d) (i), (ii) and (iii)
25. Amines have  
 (a) Garlic odour (b) Fishy odour  
 (c) Jasmine odour (d) Bitter almonds odour
26. Aniline is less soluble in water than ethyl amine due to  
 (a) resonance stabilization of benzene ring  
 (b) resonance stabilization of anilium ion  
 (c) more hydrophobic nature of  $\text{C}_6\text{H}_5$  group than  $\text{C}_2\text{H}_5$  group  
 (d) more hydrophobic nature of  $\text{C}_6\text{H}_5$  group than  $\text{C}_2\text{H}_5$  group
27. Which of the following should be most volatile?  
 (I)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  (II)  $(\text{CH}_3)_3\text{N}$   
 (III)  $\begin{matrix} \text{CH}_3\text{CH}_2 \\ \diagdown \quad \diagup \\ \text{NH} \\ \diagup \quad \diagdown \\ \text{CH}_3 \end{matrix}$  (IV)  $\text{CH}_3\text{CH}_2\text{CH}_3$   
 (a) II (b) IV  
 (c) I (d) III
28. Amines behave as  
 (a) Lewis acids (b) Lewis bases  
 (c) protic acids (d) amphoteric compounds
29. The basic character of amines is due to  
 (a) presence of nitrogen atom  
 (b) lone pair of electrons on nitrogen atom  
 (c) tetrahedral structure  
 (d) high electronegativity of nitrogen
30. Aliphatic amines are.....basic than  $\text{NH}_3$  but aromatic amines are.....basic than  $\text{NH}_3$ .  
 (a) more, less (b) less, more  
 (c) both (a) and (b) (d) None of these
31. Substitution of one alkyl group by replacing hydrogen of primary amines  
 (a) increases the base strength  
 (b) decreases the base strength  
 (c) remains the same  
 (d) None of the above
32. Which of the following is not characteristic of amines?  
 (a) They smell like ammonia  
 (b) They are inflammable in air  
 (c) They show the property of hydrogen bonding  
 (d) They are amphoteric in nature
33. The correct order of basicity in amines  
 (i)  $\text{C}_2\text{H}_5\text{NH}_2$  (ii)  $\text{CH}_3\text{NH}_2$   
 (iii)  $(\text{CH}_3)_2\text{NH}$  (iv)  $(\text{CH}_3)_3\text{N}$   
 (a) (i) < (iv) < (ii) < (iii) (b) (iv) < (ii) < (iii) < (i)  
 (c) (i) < (ii) < (iii) < (iv) (d) (ii) < (iii) < (iv) < (i)
34. The conjugate base of  $(\text{CH}_3)_2\text{NH}_2^+$  is  
 (a)  $(\text{CH}_3)_2\text{NH}$  (b)  $(\text{CH}_3)_2\text{N}^+$   
 (c)  $(\text{CH}_3)_3\text{N}^+$  (d)  $(\text{CH}_3)_2\text{N}^-$



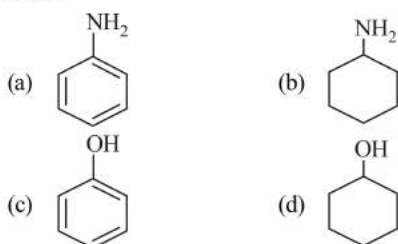
35. High basicity of  $\text{Me}_2\text{NH}$  relative to  $\text{Me}_3\text{N}$  is attributed to:  
 (a) effect of solvent (b) inductive effect of Me  
 (c) shape of  $\text{Me}_2\text{NH}$  (d) shape of  $\text{Me}_3\text{N}$
36. The correct order of basicity of the following compounds



- (a)  $B > A > C$  (b)  $A > B > C$   
 (c)  $C > A > B$  (d)  $C > B > A$
37. Which of the following statement is correct ?  
 (a) Ammonia is more basic than methylamine.  
 (b) Methylamine is more basic than ammonia.  
 (c) Dimethylamine is less basic than methylamine.  
 (d) Dimethylamine is less basic than trimethylamine.
38. Which of the following compounds is most basic?



39. Which of the following compounds is the weakest Brønsted base?



40. The correct decreasing order of basic strength of the following species is \_\_\_\_\_  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{OH}^-$ ,  $\text{NH}_2^-$   
 (a)  $\text{NH}_2^- > \text{OH}^- > \text{NH}_3 > \text{H}_2\text{O}$   
 (b)  $\text{OH}^- > \text{NH}_2^- > \text{H}_2\text{O} > \text{NH}_3$   
 (c)  $\text{NH}_3 > \text{H}_2\text{O} > \text{NH}_2^- > \text{OH}^-$   
 (d)  $\text{H}_2\text{O} > \text{NH}_3 > \text{OH}^- > \text{NH}_2^-$

41. Which of the following factors affect the basic strength of amine?  
 (i) Inductive effect  
 (ii) Steric hindrance  
 (iii) Solvation effect  
 (iv) Solubility in organic solvents.  
 (a) (i) and (iv) (b) (i), (ii) and (iii)  
 (c) (ii) and (iii) (d) (ii) and (iv)

42. Which statement is not true among the following?

- (a) Amines are bases  
 (b) They turn red litmus blue  
 (c) Trimethyl amine is less basic than dimethyl amine  
 (d) Amines yield alcohols on aqueous hydrolysis.

43. Aniline is used

- (a) in crimping of wool (b) in dyeing industry  
 (c) in making of glue (d) in fast drying varnish

44. Which of the following statements about primary amines is 'False' ?

- (a) Alkyl amines are stronger bases than aryl amines  
 (b) Alkyl amines react with nitrous acid to produce alcohols  
 (c) Aryl amines react with nitrous acid to produce phenols  
 (d) Alkyl amines are stronger bases than ammonia

45. Mark the correct statement

- (a) Methylamine is slightly acidic  
 (b) Methylamine is less basic than ammonia  
 (c) Methylamine is a stronger base than ammonia  
 (d) Methylamine forms salts with alkalis.

46. For carbylamine reaction, we need hot alcoholic KOH and

- (a) any primary amine and chloroform  
 (b) chloroform and silver powder  
 (c) a primary amine and an alkyl halide  
 (d) a monoalkylamine and trichloromethane.

47. The compound obtained by heating a mixture of a primary amine and chloroform with ethanolic potassium hydroxide (KOH) is

- (a) an alkyl cyanide (b) a nitro compound  
 (c) an alkyl isocyanide (d) an amide

48.  $\text{R}-\text{NH}_2 + \text{CH}_3\text{COCl} \xrightarrow{\text{excess}} \text{A}$

The product (A) will be –

- (a)  $\text{RNHCOCH}_3$  (b)  $\text{RN}(\text{COCH}_3)_2$   
 (c)  $\text{RN}^+(\text{COCH}_3)_3\text{Cl}^-$  (d)  $\text{R}-\text{CONH}_2$
49. Carbylamine reaction is used for the detection of  
 (a) aliphatic  $2^\circ$  amines (b) aliphatic  $1^\circ$  amines  
 (c) aromatic  $1^\circ$  amines (d) Both (b) and (c)

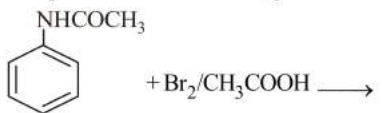
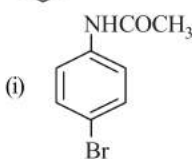
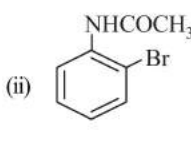
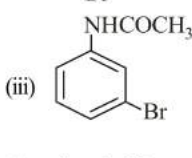
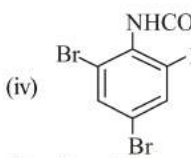
50. In the reaction,



- (a)  $\text{NH}_3$  (b)  $\text{N}_2$   
 (c)  $\text{O}_2$  (d)  $\text{CO}_2$
51. An organic amino compound reacts with aqueous nitrous acid at low temperature to produce an oily nitrosoamine. The compound is

- (a)  $\text{CH}_3\text{NH}_2$  (b)  $\text{CH}_3\text{CH}_2\text{NH}_2$   
 (c)  $\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3$  (d)  $(\text{CH}_3\text{CH}_2)_3\text{N}$
52. Ethylamine reacts with  $\text{HNO}_2$  giving :

- (a)  $\text{C}_2\text{H}_5\text{OH}$  (b)  $\text{C}_2\text{H}_5\text{NO}_2$   
 (c)  $\text{NH}_3$  (d)  $\text{C}_2\text{H}_6$

53. Primary amines can be distinguished from secondary and tertiary amines by reacting with
- Chloroform and alcoholic KOH
  - Methyl iodide
  - Chloroform alone
  - Zinc dust
54. Which of the following is not correct ?
- Ethyl amine and aniline both have  $-NH_2$  group
  - Ethyl amine and aniline dissolve in HCl
  - KOH to amine and aniline both react with  $CHCl_3$  and Ethyl amine unpleasent smelling compound
  - Ethyl amine and aniline both react with  $HNO_2$  in cold to give hydroxy compounds
55. Hinsberg reagent is
- $C_6H_5SO_3H$
  - $C_6H_5NO$
  - $C_6H_5SO_2Cl$
  - $C_6H_5N_2Cl$
56. Reaction of aniline with benzaldehyde is
- substitution
  - addition
  - condensation
  - polymerization
57. The amine that does not react with acetyl chloride is
- $CH_3NH_2$
  - $(CH_3)_2NH$
  - $(CH_3)_3N$
  - None of these
58. Which of the following compounds cannot be identified by carbylamine test?
- $CH_3CH_2NH_2$
  - $CHCl_3$
  - $C_6H_5NH_2$
  - $C_6H_5-NH-C_6H_5$
59.  $(CH_3)_2CHNH_2$  is reacted with excess acetic anhydride, the compound formed is
- $(CH_3)_2CHNCOCH_3$
  - $(CH_3)_2CN(COCH_3)_2$
  - $(CH_3)_2CHOH$
  - $(CH_3)_2CN(COOCH_3)_2$
60. In order to distinguish between  $C_2H_5-NH_2$  and  $C_6H_5-NH_2$ , which of the following reagent is useful
- Hinsberg's reagent
  - $HNO_2$
  - $CHCl_3 + KOH$
  - NaOH
61. All three amines  $1^\circ, 2^\circ, 3^\circ$  react with
- $H_2O$
  - $R-X$
  - HCl
  - $(CH_3CO)_2O$
- 1, 2
  - 4 only
  - 1, 2, 4
  - 1, 2, 3
62.  $-NH_2$  group in aniline is
- only *o*-directing
  - only *p*-directing
  - only *m*-directing
  - o*- and *p*-directing
63. Strong activating effect of  $-NH_2$  group is reduced by using
- $CH_3COCl$
  - $CH_3Cl$
  - $CH_3ONa$
  - $CH_3-CHO$
64. When bromination of aniline is carried out by protecting  $-NH_2$ . The product is
- o*-bromoaniline
  - 2, 4, 6 tribromoaniline
  - p*-bromoaniline
  - mixture of *o*- and *p*-bromoaniline
65. Hinsberg's method to separate amines is based on the use of
- benzene sulphonyl chloride
  - benzene sulphonic acid
  - ethyl oxalate
  - acetyl chloride
66. The reaction,  $C_6H_5NH_2 + ClCOC_6H_5 \longrightarrow C_6H_5NHCOC_6H_5$  is called:
- Friedel-crafts reaction
  - Claisen condensation
  - Benzoilation or Schotten Baumann reaction
  - None of these
67. Which of the following statements is not correct regarding aniline?
- It is less basic than ethylamine
  - It can be steam-distilled
  - It reacts with sodium to give hydrogen
  - It is soluble in water
68. Benzylamine may be alkylated as shown in the following equation:
- $$C_6H_5CH_2NH_2 + R - X \longrightarrow C_6H_5CH_2NHR$$
- Which of the following alkylhalides is best suited for this reaction through  $S_N1$  mechanism?
- $CH_3Br$
  - $C_6H_5Br$
  - $C_6H_5CH_2Br$
  - $C_2H_5Br$
69. The product of the following reaction is \_\_\_\_\_.
- 
- The reaction shows N-acetylbenzamide (a benzene ring with an  $NHCOCH_3$  group) reacting with  $Br_2/CH_3COOH$ . The product is one of the following four structures:
- 
  - 
  - 
  - 
- (i) and (iii)
  - (i) and (ii)
  - (iii) and (iv)
  - (i), (ii) and (iii)
70. Aniline and other arylamines are usually colourless but get coloured on storage due to \_\_\_\_\_.
- hydrolysis
  - dehydration
  - reduction
  - atmospheric oxidation
71. The acylation reaction of amines is carried out in presence of pyridine because
- pyridine is stronger base than amine.
  - pyridine is weaker base than amine.
  - pyridine removes HCl formed and shifts the equilibrium to the right hand side.
  - pyridine removes HCl formed and shifts the equilibrium to the left hand side.
- (i) and (iii)
  - (ii) and (iv)
  - (ii) and (iii)
  - (i) and (iv)



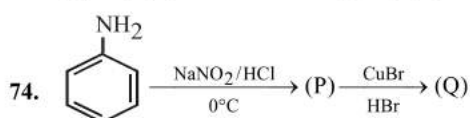
72. *N*-ethyl benzene sulphonyl amide is strongly acidic and soluble in alkali due to presence of

- strong electron donating sulphonyl group.
- strong electron withdrawing sulphonyl group.
- weak electron donating sulphonyl group.
- weak electron withdrawing sulphonyl group.

73. Arrange the following in increasing order of their basic strength?

*p*-nitroaniline(1); *m*-nitroaniline (2); 2,6-trimethylaniline(3); 3-methylaniline(4).

- 1, 3, 2, 4
- 2, 3, 4, 1
- 3, 1, 2, 4
- 1, 2, 4, 3



The compound Q is –

- bromobenzene
- chlorobenzene
- benzyl bromide
- benzyl chloride

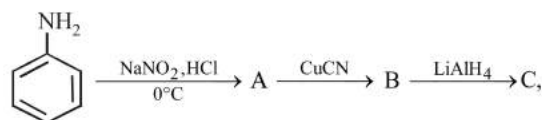
75. Diazonium salt is obtained when aniline reacts with :

- cold NaOH
- NaNO<sub>2</sub> and HCl (0–5°C)
- SnCl<sub>2</sub> at 10°C
- N<sub>2</sub>O at (0–5°C)

76. Azo dye is prepared by the coupling of phenol and

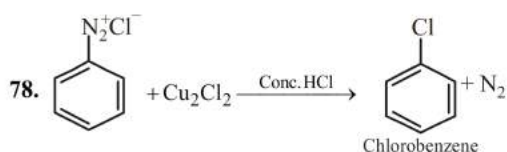
- diazonium chloride
- o*-nitroaniline
- benzoic acid
- chlorobenzene

77. In the reaction sequence



the product 'C' is:

- benzonitrile
- benzaldehyde
- benzoic acid
- benzylamine



Above reaction is known as:

- Strecker's reaction
- Sandmeyer's reaction
- Wohl-Ziegler reaction
- Stephen's reaction

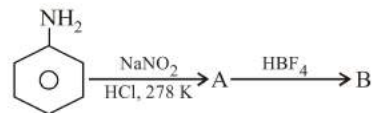
79. Which of the following reagents will convert *p*-methylbenzenediazonium chloride into *p*-cresol?

- Cu powder
- H<sub>2</sub>O
- H<sub>3</sub>PO<sub>2</sub>
- C<sub>6</sub>H<sub>5</sub>OH

80. When phenol and benzene diazonium chloride are coupled, the main product is :

- aniline
- p*-hydroxyazobenzene
- azobenzene
- chlorobenzene

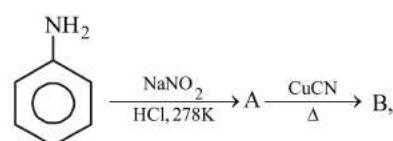
81. In the chemical reactions,



the compounds 'A' and 'B' respectively are

- nitrobenzene and fluorobenzene
- phenol and benzene
- benzene diazonium chloride and fluorobenzene
- nitrobenzene and chlorobenzene

82. In the chemical reactions :



the compounds A and B respectively are :

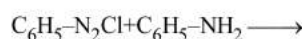
- benzene diazonium chloride and benzonitrile
- nitrobenzene and chlorobenzene
- phenol and bromobenzene
- fluorobenzene and phenol

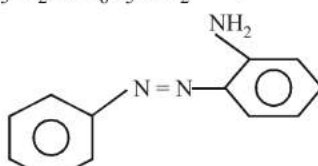
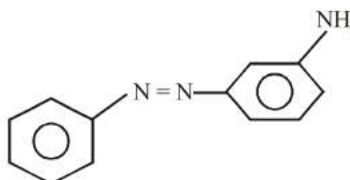
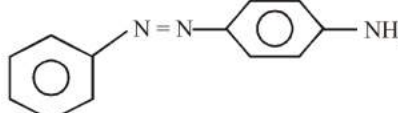
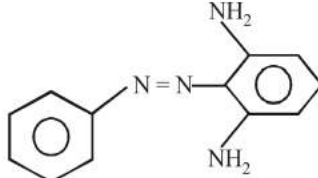
83. Replacement of –N<sub>2</sub><sup>+</sup>Cl<sup>–</sup> from benzene diazonium chloride

by iodine can be done by using

- HI
- NaOI
- PI<sub>3</sub>
- KI

84. Product of the following reaction is



- 
- 
- 
- 

85. Which of the following are intermediates in Sandmeyer reaction ?

- (i)  $C_6H_5N^+ \equiv NCl^-$       (ii)  $C_6H_5N^+ \equiv N$   
 (iii)  $\dot{C}_6H_5$       (iv)  $C_6H_5Cl$   
 (a) (ii) and (iii)      (b) (i) and (iv)  
 (c) (ii) and (iv)      (d) (i) and (ii)

86. In the diazotization of arylamines with sodium nitrite and hydrochloric acid, an excess of hydrochloric acid is used primarily to

- (a) Suppress the concentration of free aniline available for coupling  
 (b) Suppress hydrolysis of phenol  
 (c) Ensure a stoichiometric amount of nitrous acid  
 (d) Neutralise the base liberated

87. Which of the following reagent can be used to convert benzenediazonium chloride into benzene?

- (a)  $CH_3OH$       (b)  $H_3PO_2$   
 (c)  $Br_2-H_2O$       (d)  $LiAlH_4$

88. When benzenediazonium chloride in hydrochloric acid reacts with cuprous chloride, then chlorobenzene is formed. The reaction is called

- (a) Gattermann reaction      (b) Perkin reaction  
 (c) Etard reaction      (d) Sandmeyer reaction

89. The reaction  $ArN_2^+Cl^- \xrightarrow{Cu/HCl} ArCl + N_2 + CuCl$  is named as \_\_\_\_\_.

- (a) Sandmeyer reaction      (b) Gatterman reaction  
 (c) Claisen reaction      (d) Carbylamine reaction

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

- (a) Aniline      (b) Phenol  
 (c) Anisole      (d) Nitrobenzene

91. Which of the following cannot be prepared by Sandmeyer's reaction?

- (i) Chlorobenzene      (ii) Bromobenzene  
 (iii) Iodobenzene      (iv) Fluorobenzene  
 (a) (i) and (ii)      (b) (ii) and (iii)  
 (c) (iii) and (iv)      (d) (i) and (iv)

92. The reagents that can be used to convert benzenediazonium chloride to benzene are \_\_\_\_\_.

- (i)  $SnCl_2/HCl$       (ii)  $CH_3CH_2OH$   
 (iii)  $H_3PO_2$       (iv)  $LiAlH_4$   
 (a) (i) and (ii)      (b) (ii) and (iii)  
 (c) (iii) and (iv)      (d) (i) and (iii)

### STATEMENT TYPE QUESTIONS

93. Read the following statements and choose the correct option.

- (i) Nitrogen atom in amines is  $sp^3$ -hybridised.  
 (ii) The geometry of amines is pyramidal.

(iii) The angle C-N-C or C-N-H is slightly more than  $109.5^\circ$ .

- (a) (i), (ii) and (iii)      (b) (i) and (ii)  
 (c) (i) and (iii)      (d) (ii) and (iii)

94. Which of the following statements are correct ?

- (i) Lower aliphatic amines are soluble in water.  
 (ii) Solubility increases with decrease in molar mass of amines.  
 (iii) Higher amines are insoluble in water.  
 (iv) Amines are soluble in organic solvents.

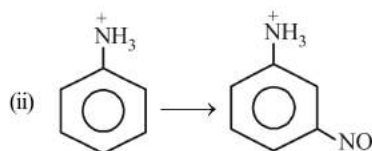
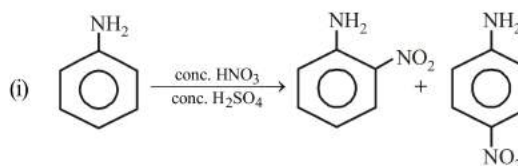
- (a) (i), (ii) and (iii)      (b) (i), (iii) and (iv)  
 (c) (ii), (iii) and (iv)      (d) (i) and (iv)

95. Which of the following statements are correct ?

- (i) Primary amines show more intermolecular association than secondary amines.  
 (ii) Tertiary amines do not show intermolecular association.  
 (iii) Boiling points of isomeric alkenes follow the order  $3^\circ > 2^\circ > 1^\circ$

- (a) (i) and (iii)      (b) (i) and (ii)  
 (c) (i), (ii) and (iii)      (d) (ii) and (iii)

96. Which of the following is/are correct regarding nitration of aniline with conc.  $HNO_3$  and conc.  $H_2SO_4$  ?



(iii) The substitution can be explained on the basis of inductive effect (-I)

(iv) The substitution can be influenced by +M and +E effects.

- (a) (i), (ii) and (iii)      (b) (ii) and (iii)  
 (c) (ii) and (iv)      (d) (i) and (iii)

97. Which of the following statements are correct ?

- (i) In Sandmeyer reaction nucleophiles like  $Cl^-$ ,  $Br^-$  and  $CN^-$  are introduced in benzene ring in the presence of  $Cu^+$  ion  
 (ii) In Gattermann reaction nucleophiles are introduced in benzene ring in the presence of copper powder and HCl.  
 (iii) The yield in Gattermann reaction is found to be better than Sandmeyer reaction.

- (a) (i) and (ii)      (b) (i), (ii) and (iii)  
 (c) (ii) and (iii)      (d) (i) and (iii)



## MATCHING TYPE QUESTIONS

98. Match the columns

Column-I	Column-II
(A) Gabriel phthalimide reaction	(p) $C_6H_5CH_2NH_2$
(B) Reduction with $LiAlH_4$	(q) $C_6H_5NH_2$
(C) Reaction with alc. $KOH + CHCl_3$	(r) $C_6H_5CN$
(D) $1^\circ$ Amide with $Br_2 + KOH$	(s) $CH_3CH_2NH_2$

(a) A – (p, s); B – (p, s); C – (p, q, s); D – (p, q, s)  
 (b) A – (s); B – (p); C – (q); D – (p, q)  
 (c) A – (p, s); B – (r); C – (q); D – (s)  
 (d) A – (p, q); B – (p); C – (p, q); D – (s)

99. Match the columns

Column-I	Column-II
(A) Ammonolysis	(p) Amine with lesser number of carbon atoms
(B) Gabriel phthalimide synthesis	(q) Detection test for primary amines.
(C) Hoffmann bromamide reaction	(r) Reaction of Phthalimide with $KOH$ and $R-X$
(D) Carbylamine reaction	(s) Reaction of alkylhalides with $NH_3$

(a) A – (s), B – (r), C – (p), D – (q)  
 (b) A – (r), B – (p), C – (r), D – (s)  
 (c) A – (q), B – (r), C – (s), D – (p)  
 (d) A – (s), B – (p), C – (q), D – (r)

100. Match the columns

Column-I	Column-II
(A) Benzene sulphonyl chloride	(p) Zwitter ion
(B) Sulphanilic acid	(q) Hinsberg reagent
(C) Alkyl diazonium salts	(r) Dyes
(D) Aryl diazonium salts	(s) Conversion to alcohols

(a) A – (s), B – (q), C – (r), D – (p)  
 (b) A – (q), B – (p), C – (s), D – (r)  
 (c) A – (r), B – (s), C – (p), D – (q)  
 (d) A – (s), B – (p), C – (r), D – (q)

101. Match the columns

Column-I	Column-II
(A) $ArN_2^+Cl^- \longrightarrow ArOH$	(p) $HBF_4 / NaNO_2$
(B) $ArN_2^+Cl^- \longrightarrow ArNO_2$	(q) $H_2O$
(C) $ArN_2^+Cl^- \longrightarrow ArH$	(r) $HBF_4$
(D) $ArN_2^+Cl^- \longrightarrow ArF$	(s) $CH_3CH_2OH$

- (a) A – (q), B – (p), C – (s), D – (r)  
 (b) A – (s), B – (p), C – (q), D – (r)  
 (c) A – (q), B – (s), C – (p), D – (r)  
 (d) A – (q), B – (s), C – (r), D – (p)

## ASSERTION-REASON TYPE QUESTIONS

**Directions :** Each of these questions contain two statements, Assertion and Reason. Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below.

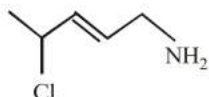
- (a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.  
 (b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion  
 (c) Assertion is correct, reason is incorrect  
 (d) Assertion is incorrect, reason is correct.
- 102. Assertion :** Aromatic  $1^\circ$  amines can be prepared by Gabriel phthalimide synthesis.  
**Reason :** Aryl halides undergo nucleophilic substitution with anion formed by phthalimide.
- 103. Assertion :** Only a small amount of  $HCl$  is required in the reduction of nitro compounds with  $HCl$  scrap and  $HCl$  in the presence of steam.  
**Reason :**  $FeCl_2$  formed gets hydrolysed to release  $HCl$  during the reaction.
- 104. Assertion :** Amines are basic in nature.  
**Reason :** Amines have lone pair of electrons on nitrogen atom.
- 105. Assertion :** Acetanilide is less basic than aniline.  
**Reason :** Acetylation of aniline results in decrease of electron density on nitrogen.
- 106. Assertion :** Nitration of aniline can be conveniently done by protecting the amino group by acetylation.  
**Reason :** Acetylation increases the electron-density in the benzene ring.
- 107. Assertion :** Aniline does not undergo Friedel-Crafts reaction.  
**Reason :**  $-NH_2$  group of aniline reacts with  $AlCl_3$  (Lewis acid) to give acid-base reaction.
- 108. Assertion :** Acylation of amines gives a monosubstituted product whereas alkylation of amines gives polysubstituted product.  
**Reason :** Acyl group sterically hinders the approach of further acyl groups
- 109. Assertion :** Nitrating mixture used for carrying out nitration of benzene consists of conc.  $HNO_3 +$  conc.  $H_2SO_4$ .  
**Reason :** In presence of  $H_2SO_4$ ,  $HNO_3$  acts as a base and produces  $NO_2^+$  ions.

### CRITICAL THINKING TYPE QUESTIONS

110. The IUPAC name of diethyl isopropyl amine is

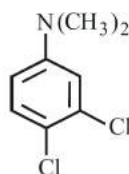
- N, N-diethylpropan-2-amine
- N, N-diethylpropan-1-amine
- N, N-diethylisopropylamine
- N, N-diethylaminopropane

111. IUPAC name of the following compound is



- 2-chloro pentanamine
- 4-chloro pentan-1-amine
- 4-chloro pent-2-en-1-amine
- 2-chloro pent-3-en-5-amine

112. Which of the following is the correct IUPAC name of the compound ?



- 1, 2-dichloro-4-(N, N-dimethyl) aniline
- Dimethyl - (3, 4-dichlorophenyl) amine
- 3, 4-dichloro - N, N-dimethyl aniline
- N, N-dimethylamino - 3, 4-dichlorobenzene

113. Acetamide is treated with the following reagents separately. Which one of these would yield methylamine?

- NaOH - Br<sub>2</sub>
- Sodalime
- Hot conc. H<sub>2</sub>SO<sub>4</sub>
- PCl<sub>5</sub>

114. Amine that cannot be prepared by Gabriel phthalimide synthesis is

- aniline
- benzylamine
- methylamine
- iso*-butylamine

115. A primary amine is formed by an amide on treatment with bromine and alkali. The primary amine has

- 1 carbon atom less than amide
- 1 carbon atom more than amide
- 1 hydrogen atom less than amide
- 1 hydrogen atom more than amide

116. High basicity of Me<sub>2</sub>NH relative to Me<sub>3</sub>N is attributed to:

- effect of solvent
- inductive effect of Me
- shape of Me<sub>2</sub>NH
- shape of Me<sub>3</sub>N

117. Which one of the following is the strongest base in aqueous solution ?

- Methylamine
- Trimethylamine
- Aniline
- Dimethylamine

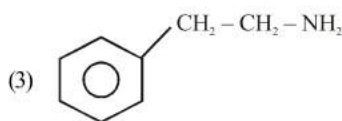
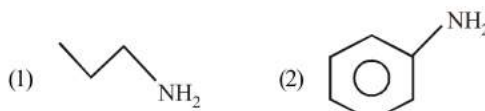
118. What is the decreasing order of basicity of primary, secondary and tertiary ethylamines and NH<sub>3</sub> ?

- NH<sub>3</sub> > C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> > (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH > (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N
- (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N > (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH > C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> > NH<sub>3</sub>
- (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH > C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> > (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N > NH<sub>3</sub>
- (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH > C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> > (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NH > NH<sub>3</sub>

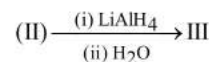
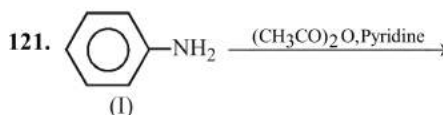
119. The correct order of the increasing basicity of methyl amine, ammonia and aniline is

- methyl amine < aniline < ammonia
- aniline < ammonia < methyl amine
- aniline < methyl amine < ammonia
- ammonia < aniline < methyl amine

120. Arrange the following amines in the decreasing order of their basicity



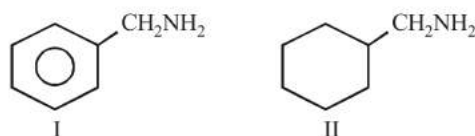
- 1 > 3 > 2
- 3 > 2 > 1
- 1 > 2 > 3
- 2 > 1 > 3



The basicity order of I, II and III is –

- III > I > II
- I > II > III
- III > II > I
- II > III > I

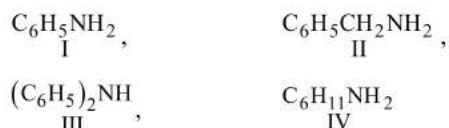
122. Which of the statement is true regarding the basicity of the following two primary amines ?



- Both are equally basic because both are 1° amines
- I > II because it is an aromatic amine
- II > I because it is an aliphatic amine
- I < II because of difference in the nature of β-carbon



123. The correct order of decreasing basic character is

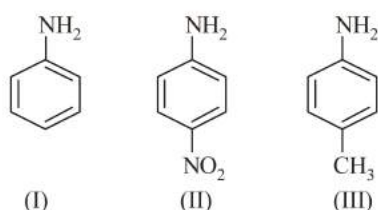


- (a) II > I > III > IV (b) IV > II > I > III  
 (c) IV > III > II > I (d) IV > II > III > I

124. Aniline when treated with conc.  $\text{HNO}_3$  gives

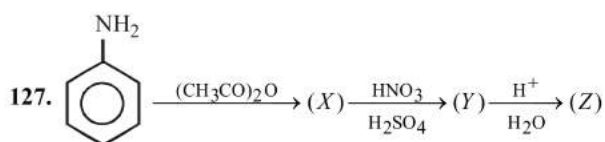
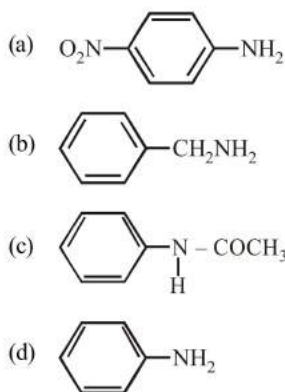
- (a) *p*-Phenylenediamine (b) *m*-Nitroaniline  
 (c) *p*-Benzoquinone (d) Nitrobenzene

125. The correct increasing order of basic strength for the following compounds is \_\_\_\_\_.

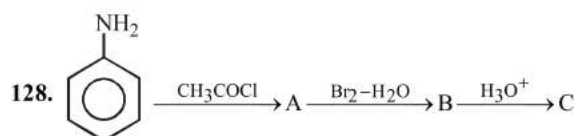
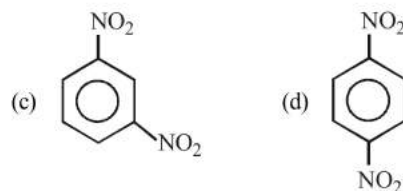
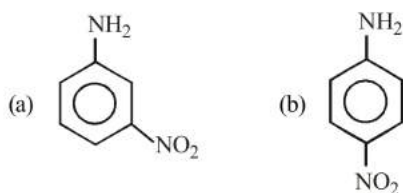


- (a) II < III < I (b) III < I < II  
 (c) III < II < I (d) II < I < III

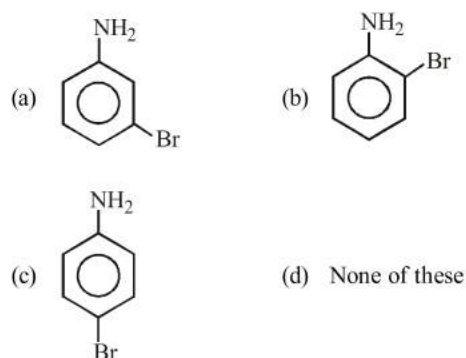
126. Which of the following compounds is most basic?



Product Z of the reaction



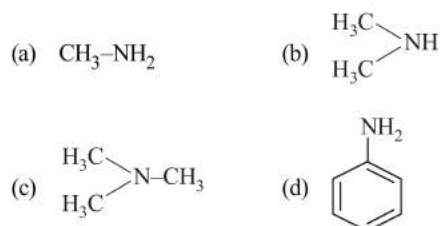
C (major product) is –



129. Towards electrophilic substitution, the most reactive will be

- (a) Nitrobenzene  
 (b) Aniline  
 (c) Aniline hydrochloride  
 (d) N-Acetylaniline

130. The most reactive amine towards dilute hydrochloric acid is \_\_\_\_\_.



131. Nitration of nitrobenzene is carried out than obtained product is reduced with  $\text{Fe}/\text{HCl}$ , product so formed on reaction with  $\text{HNO}_2$  and than with  $\text{H}_2\text{O}$ , forms

- (a) 1,3-dihydroxybenzene  
 (b) 3-nitrophenol  
 (c) 2-nitrophenol  
 (d) 1,2-dihydroxybenzene

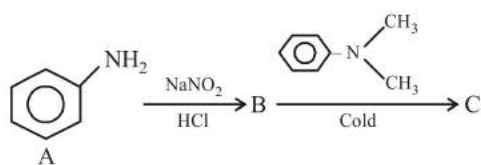


132. A compound of molecular formulae  $C_3H_6N$  shows following characteristics

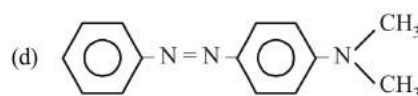
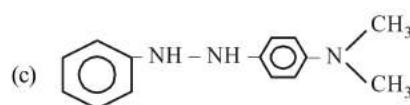
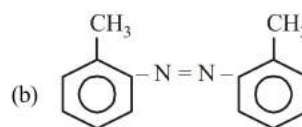
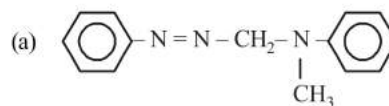
- (i) Get dissolved in acidic medium.
- (ii) Does not react with benzoylchloride
- (iii) Does not give carbylamine test
- (iv) Does not evolve nitrogen gas on reacting with  $HNO_2$  than structure of the compound is

- (a) trimethylamine            (b) isopropylamine
- (c) propylamine            (d) None of these

133. In a reaction of aniline a coloured product C was obtained.



The structure of C would be :

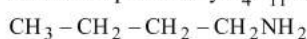




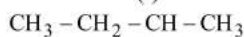
## HINTS AND SOLUTIONS

### FACT/DEFINITION TYPE QUESTIONS

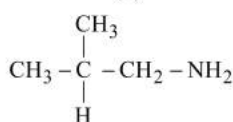
1. (c)  $\text{RNH}_2$        $\text{R}_2\text{NH}$        $\text{R}_3\text{N}$   
 Primary amine      Secondary amine      Tertiary amine
2. (c)      3. (a)      4. (d)
5. (c)  $1^\circ$  amines have  $-\text{NH}_2$  group in their structure. 4 primary amines are possible by  $\text{C}_4\text{H}_{11}\text{N}$ .



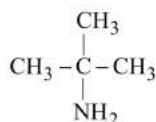
(i)



(ii)

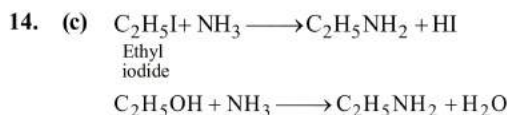
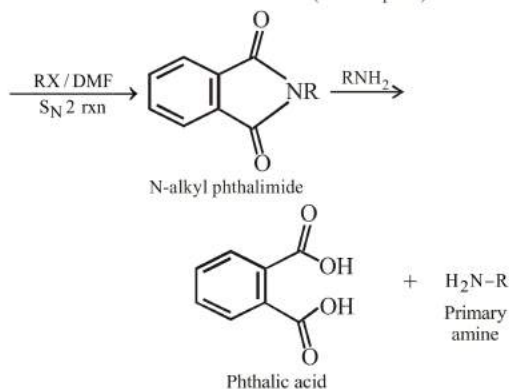
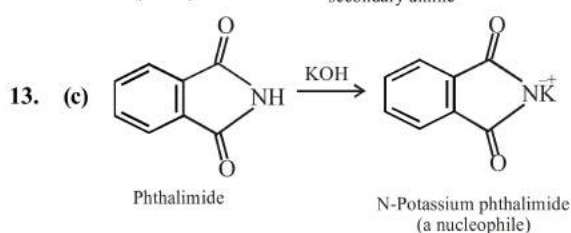
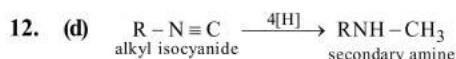
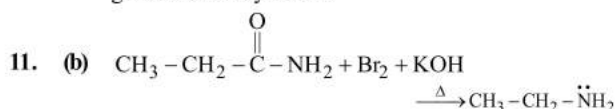


(iii)



(iv)


6. (b) The amound contains longest chain of 6C atoms and amino group. Hence it is an alkanamine.
7. (d)      8. (d)      9. (a)
10. (c)  $\text{CH}_3\text{NC}$  (methyl isocyanide) on reduction with  $\text{LiAlH}_4$  gives secondary amine



15. (d)      16. (d)
17. (d) For the preparation of  $\text{Me}_3\text{CNH}_2$ , the required alkyl halide is  $\text{Me}_3\text{CX}$  which will react with potassium phthalimide, a strong base, to form alkene rather than substituted product. For preparing  $\text{C}_6\text{H}_5\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{Cl}$  will be the starting halide in which Cl is non-reactive.

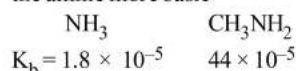
18. (c)      19. (d)      20. (c)
21. (d) Reduction with iron scrap and hydrochloric acid is preferred because  $\text{FeCl}_2$  formed gets hydrolysed to release hydrochloric acid during the reaction. Thus, only a small amount of hydrochloric acid is required to initiate the reaction.
22. (b)      23. (c)      24. (a)
25. (b) Amines possess fishy smell.
26. (c)      27. (b)      28. (b)
29. (b) Basic of amines arises due to presence of lone pair of  $e^-$ s on the N-atom, which can be shared with an electron deficient species.

30. (a)
31. (a) Secondary amine is more basic than primary amine.
32. (d) Amines are basic in nature
33. (b)  $(\text{CH}_3)_3\text{N} < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH} < \text{C}_2\text{H}_5\text{NH}_2$
34. (a)
35. (a) Secondary amines are more basic than tertiary amines due to stabilisation of  $2^\circ$  amine by hydrogen bonding with solvent molecule.
36. (c) Aliphatic amines are more basic than aromatic amines. Resonance decreases the basic character due to delocalisation of shared pair of electrons on nitrogen within benzene nucleus
37. (b) Basic character of amines is  $2^\circ > 1^\circ > 3^\circ > \text{NH}_3$

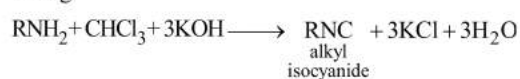
38. (b)  compound is most basic due to localized lone pair of electron on nitrogen atom while other compounds have delocalized lone pair of electron.

39. (c)      40. (a)      41. (b)
42. (d) Amines give alcohols only on reaction with  $\text{HNO}_2$  and not on hydrolysis.
43. (b) Aniline gives dyes on coupling reaction with phenols and *p*-amines.
44. (c) Aryl amines do not produce phenol on treatment with nitrous acid

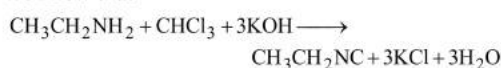
45. (c) Methyl amine is a stronger base than ammonia due to +I effect. The alkyl groups which are electron releasing groups increase the electron density around the nitrogen thereby increasing the availability of the lone pair of electrons to proton or Lewis acid and making the amine more basic



46. (a) Any primary amine means both aliphatic as well as aromatic but monoalkylamines means only 1° aliphatic amines. Therefore, option (a) is correct while (d) is wrong.



47. (c) We know that

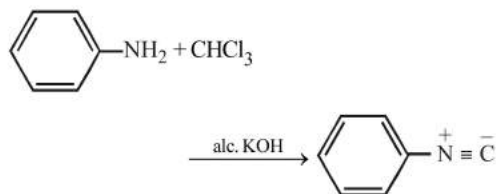


In this reaction, bad smelling compound ethyl isocyanide ( $\text{CH}_3\text{CH}_2\text{NC}$ ) is produced. This equation is known as **carbylamine reaction**.

48. (a) Acylation occurs in one step only because lone pair of nitrogen is delocalized with acyl group.



49. (d)  $\text{R}-\text{NH}_2 + \text{CHCl}_3 \xrightarrow{\text{alc. KOH}} \text{R}-\overset{\oplus}{\text{N}} \equiv \overset{\ominus}{\text{C}}$



50. (b)  $\text{RNH}_2 \xrightarrow{\text{HNO}_2} \text{ROH} + \text{H}_2\text{O} + \text{N}_2 \uparrow$   
(A) (B) (C)

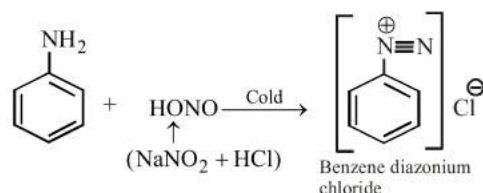
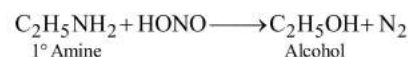
51. (c) Since the organic amino compound on reaction with nitrous acid at low temperature produces an oily nitrosoamine so the organic amino compound is a secondary aliphatic amine.

52. (a)  $\text{C}_2\text{H}_5\text{NH}_2 + \text{HNO}_2 \xrightarrow{273-278\text{K}}$   
Ethyl amine      Nitrous acid
- $$\text{C}_2\text{H}_5\text{OH} + \text{N}_2 + \text{H}_2\text{O}$$
- Ethanol

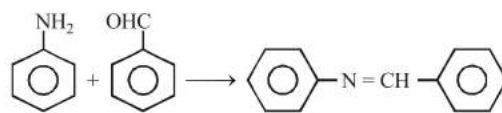
**Note:** This reaction is used as a test for aliphatic amines since no other class of amines liberates  $\text{N}_2$  gas on treatment with  $\text{HNO}_2$ .

53. (a) 1° amines (aliphatic and aromatic) react with  $\text{CHCl}_3/\text{KOH}$  to yield isocyanide (foul smelling) This is known as carbylamine test which is not given by 2° and 3° amines.

54. (d) Nitrous acid reacts differently with aliphatic and aromatic amines in cold.



55. (c)



56. (c)
57. (c) The compounds containing active H-atoms (H atoms attached to N, O or S) react with  $\text{CH}_3\text{COCl}$  to form acetyl derivatives.

58. (d)      59. (b)      60. (b)      61. (d)      62. (d)

63. (a)      64. (d)

65. (a) Hinsberg's method is based on the use of benzene sulphonyl chloride.

66. (c) The inclusion of  $\text{C}_6\text{H}_5\text{CO}$  gp. in a molecule is called benzoylation

67. (d) Aniline is insoluble in water, because its  $-\text{NH}_2$  group can't form H-bond with water due to bulky phenyl group.

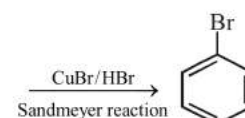
68. (c)      69. (b)      70. (d)

71. (a) Pyridine is a stronger base than the amine, pyridine removes HCl formed in acylation reaction of amines and shifts the equilibrium to the right hand side.

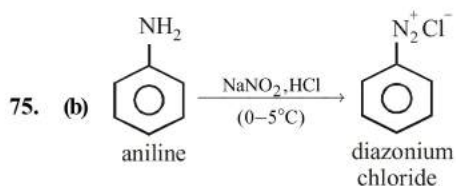
72. (b) The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

73. (d) In case of substituted aniline, electron releasing groups like  $-\text{OCH}_3$ ,  $-\text{CH}_3$  increase basic strength whereas electron withdrawing groups like  $-\text{NO}_2$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{COOH}$ ,  $-\text{X}$  decrease it.

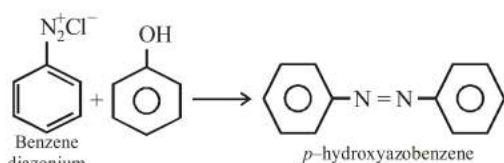
74. (a)  $\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow[0^\circ\text{C}]{\text{NaNO}_2/\text{HCl}} \left[ \text{C}_6\text{H}_5\overset{\oplus}{\text{N}} \equiv \overset{\ominus}{\text{N}} \text{Cl} \right]$   
Diazotisation



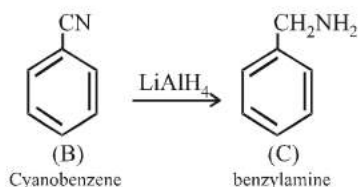
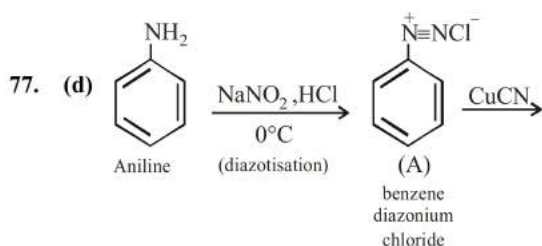




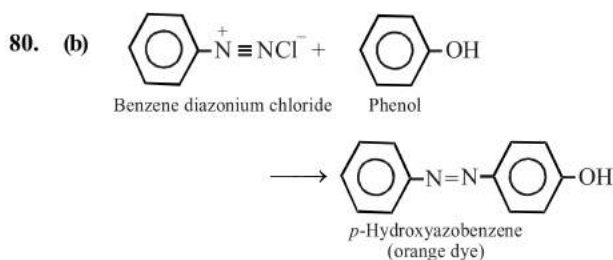
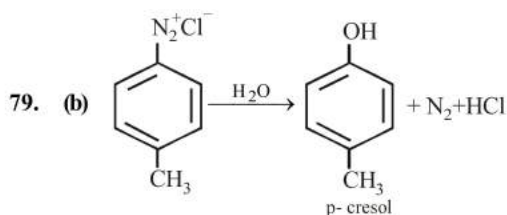
76. (a) Azo dye is prepared by diazo coupling reaction of phenol with diazonium salt.



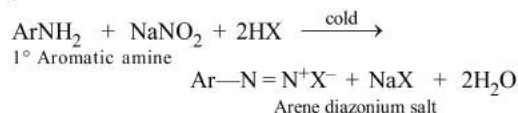
(-N=N-) group is called azo-group.



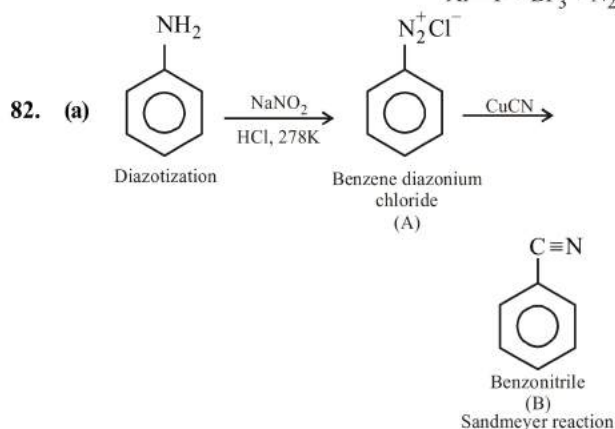
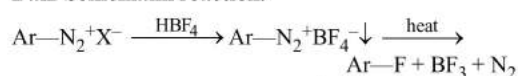
78. (b) The given reaction is known as Sandmeyer's reaction.



81. (c) Primary aromatic amines react with nitrous acid to yield arene diazonium salts.



The diazonium group can be replaced by fluorine by treating the diazonium salt with fluoroboric acid (HBF<sub>4</sub>). The precipitated diazonium fluoroborate is isolated, dried and heated until decomposition occurs to yield the aryl fluoride. This reaction is known as **Balz-Schiemann reaction**.



83. (d) 84. (c) 85. (a)  
 86. (a) Excess of HCl is used to convert free aniline to aniline hydrochloride otherwise free aniline would undergo coupling reaction with benzenediazonium chloride.  
 87. (b) 88. (d) 89. (b) 90. (d) 91. (b)  
 92. (b)

### STATEMENT TYPE QUESTIONS

93. (b) The fourth orbital of nitrogen in all amines contains an unshared pair of electrons. 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°.
94. (b) Lower aliphatic amines are soluble in water solubility decreases with increase in molar mass of amines. Higher amines are essentially insoluble in water.
95. (b) Primary and secondary amines are engaged in intermolecular association due to hydrogen bonding between nitrogen of one and hydrogen of another molecule. This intermolecular association is more in primary amines than in secondary amines as there are two hydrogen atoms available for hydrogen bond formation in it. Tertiary amines do not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation. Therefore, the order of boiling points of isomeric amines is as follows :  
 Primary > Secondary > Tertiary

96. (b)

97. (a) The yield in Sandmeyer reaction is found to be better than Gattermann reaction.

### MATCHING TYPE QUESTIONS

98. (a) 99. (a) 100. (b) 101. (c)

### ASSERTION-REASON TYPE QUESTIONS

102. (a) 103. (d)

104. (a) Amines are basic due to the presence of a lone pair of electrons on nitrogen atom. The lone pair can be easily donated.

105. (d)

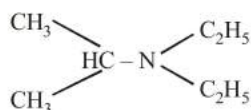
106. (c) Acetylation decreases the electron-density in the benzene ring thereby preventing oxidation.

107. (a) 108. (c)

109. (a)  $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{HSO}_4^- + \text{NO}_2^+ + \text{H}_3\text{O}^+$

### CRITICAL THINKING TYPE QUESTIONS

110. (a)



N, N- diethyl propan - 2-amine

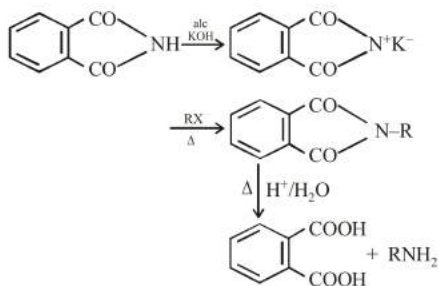
111. (c)

112. (c) The compound is derivative of aniline. The positions of groups are shown by numbering the nuclear C-atoms.

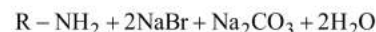
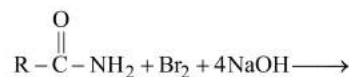
113. (a)  $\text{CH}_3\text{CONH}_2 \xrightarrow[\text{Br}_2]{\text{NaOH}} \text{CH}_3\text{NH}_2$

(Hofmann bromamide reaction)

114. (a) Aniline cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with potassium phthalimide under ordinary conditions to give N-phenyl phthalimide (i.e., cleavage of C-X bond in haloarenes is quite difficult).



115. (a) The reaction is Hoffmann bromamide reaction



R-NH<sub>2</sub> contains one carbon less than  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$

116. (a) Secondary amines are more basic than tertiary amines due to stabilisation of 2° amine by hydrogen bonding with solvent molecule.

117. (d) Aromatic amines are less basic than aliphatic amines. Among aliphatic amines the order of basicity is 2° > 1° > 3°. The electron density is decreased in 3° amine due to crowding of alkyl group over N atom which makes the approach and bonding by a proton relatively difficult. Therefore the basicity decreases. Further Phenyl group show -I effect, thus decreases the electron density on nitrogen atom and hence the basicity.

∴ dimethylamine (2° aliphatic amine) is strongest base among given choices.

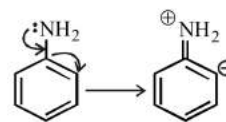
∴ The correct order of basic strength is  
Dimethylamine > Methyl amine > Trimethyl amine > Aniline.

118. (d) All aliphatic amines are stronger bases than NH<sub>3</sub> and among different ethylamines order of basicity is 2° > 1° > 3°. Thus, the correct order is (d) i.e.,



This anomalous behaviour of tertiary ethyl amine is due to steric factors i.e., crowding of alkyl groups cover nitrogen atom from all sides and thus makes the approach and bonding by a lewis acid relatively difficult which results the maximum steric strain in tertiary amines. The electrons are there but the path is blocked resulting the reduction in its basicity.

119. (b) In aniline the lone pair on N is involved in delocalization with benzene ring and is not available for protonation. Methyl amine is a stronger base than ammonia because +I effect of methyl group increases electron density on N making it more basic than NH<sub>3</sub>.

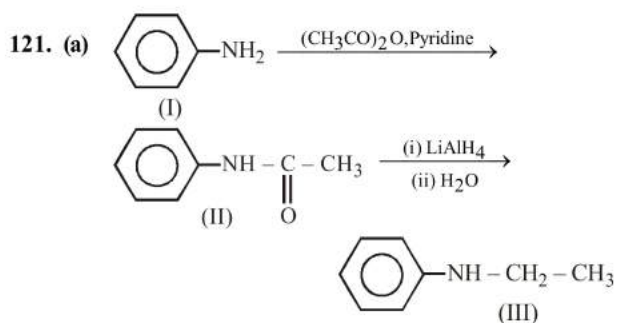


Cannot be protonated. least basic

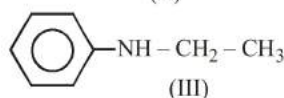
$\text{CH}_3 \rightarrow \text{NH}_2$   
+I Effect increases basicity.

120. (a)



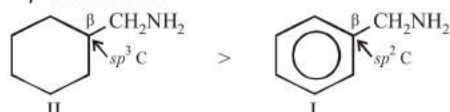


Product (II) is and (III) is

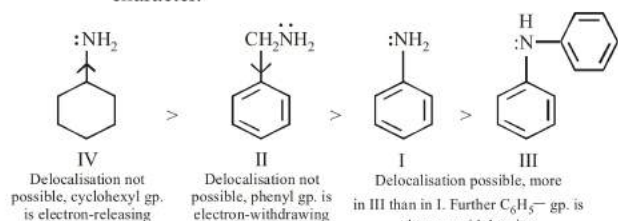


$\therefore \text{III} > \text{I} > \text{II}$ , As + I effect increases the basic strength and - R, - I effect shown by - COCH<sub>3</sub> reduces the basic strength.

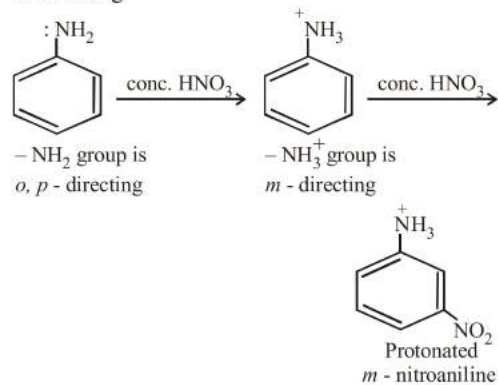
122. (d) Here again the two amines differ in the nature of  $\beta$ -carbon atom



123. (b) Greater the delocalisation of electron pair on N, lesser is its availability for protonation leading to lesser basic character.

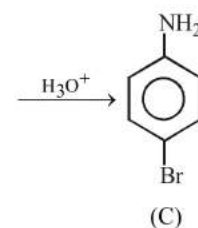
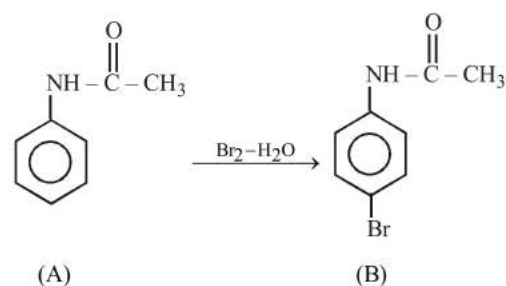
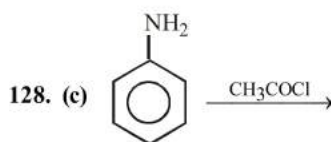
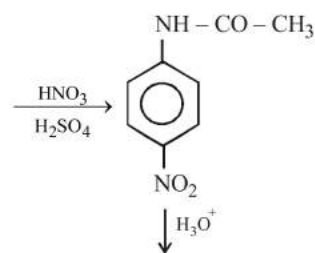
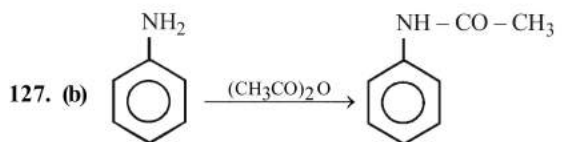


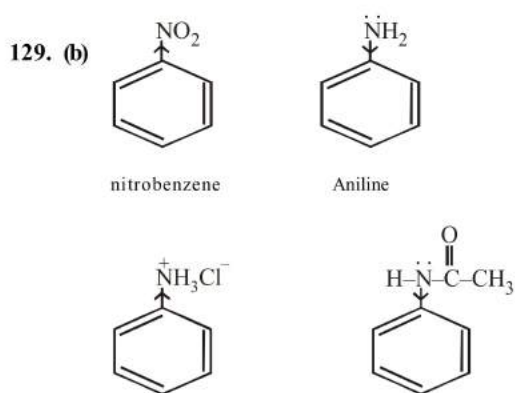
124. (b) Although - NH<sub>2</sub> group is *o,p*-directing but in presence of conc. HNO<sub>3</sub> it undergoes protonation to form  $\text{-NH}_3^+$  which, being electron-deficient, becomes *m*-directing.



125. (d)

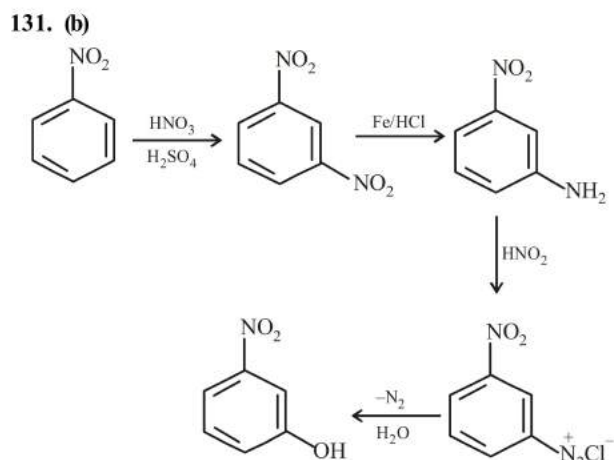
126. (b) compound is most basic due to localized lone pair of electron on nitrogen atom while other compounds have delocalized lone pair of electron.





Nitrobenzene and aniline hydrochloride have electron-withdrawing ( $-\text{NO}_2$  and  $-\text{NH}_3^+$ ) groups, hence these will undergo electrophilic substitution with difficulty. Aniline and N- acetylaniline (acetanilide) have electron-releasing groups, however  $-\text{NHCOCH}_3$  is less electron-releasing than  $-\text{NH}_2$  due to delocalisation of lone pair of electron on N toward carbonyl group. Hence aniline (having  $-\text{NH}_2$ ) will undergo electrophilic substitution most easily.

130. (b)



132. (a) It is a tertiary amine hence shows above observations.

133. (d) The reaction can be completed as follows:

