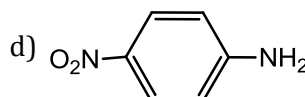
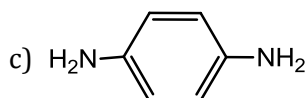
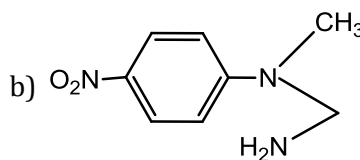
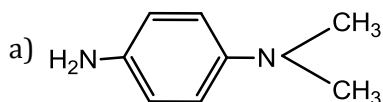
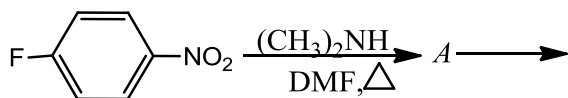
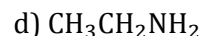
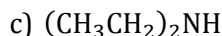
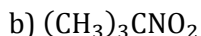
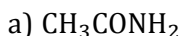


## Single Correct Answer Type

1.

2. Which of the following cannot react with  $\text{HNO}_2$ ?

3. Primary, secondary, tertiary amines can be separated by the following except:

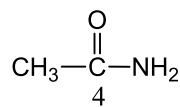
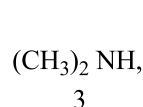
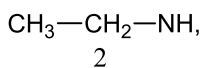
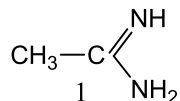
a) Fractional distillation

b) Fractional method using diethyl oxalate

c) Hinsberg's method using  $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ 

d) Selective crystallisation

4. The correct order of basicities of the following compound is:

a)  $(2) > (1) > (3) > (4)$ b)  $(1) > (3) > (2) > (4)$ c)  $(3) > (1) > (2) > (4)$ d)  $(1) > (2) > (3) > (4)$ 

5. Stephen's reduction converts nitriles into:

a) Aldehydes

b) Ketones

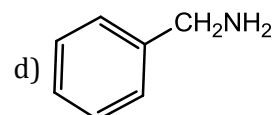
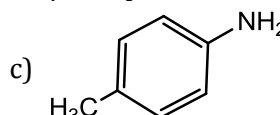
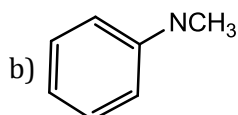
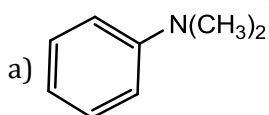
c) Amines

d) Carboxylic acids

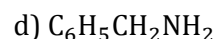
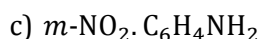
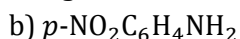
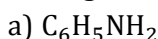
6. Which of the following will yield phenylhydrazine hydrochloride?

a) Benzene and hydrazine

b) Hydrazine and HCl

c) Benzenediazonium chloride and  $\text{SnCl}_2/\text{HCl}$ d) Nitrobenzene and  $\text{SnCl}_2/\text{HCl}$ 7. Amongst the compound given, the one that would form a brilliant coloured dye on treatment with  $\text{NaNO}_2$  in dil. HCl followed by addition to an alkaline solution of  $\beta$ -naphthol is

8. Among the following, the strongest base is:



9. Mendius reaction involves the:

a) Reduction of aldehydes to give alcohols

b) Reduction of nitriles with sodium and ethanol

c) Oxidation of nitriles

d) Hydrolysis of cyanides

10. In order to distinguish between  $\text{C}_2\text{H}_5\text{NH}_2$  and  $\text{C}_6\text{H}_5\text{NH}_2$ , which of the following reagents is useful?

a) Hinsberg reagent

b)  $p$ -Naphthol

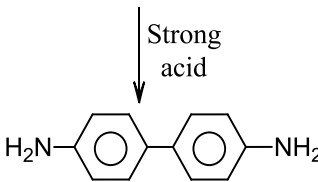
c) Benzene diazonium chloride

d) None of the above

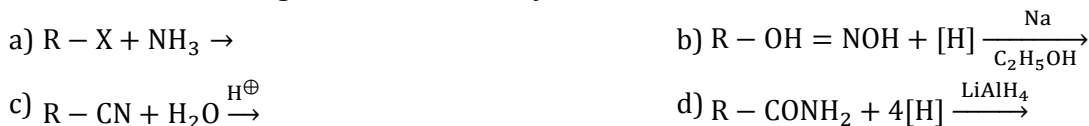
11. Primary and secondary amines are distinguished by:

- a) Br<sub>2</sub>/KOH                      b) HClO                      c) HNO<sub>2</sub>                      d) NH<sub>3</sub>
12. The following reaction constitutes:  

$$\text{RNH}_2 + \text{S} = \text{C} = \text{S} \xrightarrow[\text{H}_2\text{S}]{\text{HgCl}_2} \text{R} - \text{N} = \text{C} = \text{S} + \text{H}_2\text{S}$$
 Alkyl isothiocyanate
- a) Mustard oil reaction      b) Test for 3° amine      c) Test for 2° amine      d) Test for CS<sub>2</sub>
13. Nitrobenzene on electrolytic reduction gives:  
 a) Azobenzene                      b) Hydrazobenzene                      c) Aminophenol                      d) Aniline
14. When propane is subjected to the treatment with fuming nitric acid at 673 K, which of the following will not be formed?  
 a) 1-Nitropropane                      b) 2-Nitropropane                      c) Nitromethane                      d) Nitrohexane
15. Which of the following is the weakest base?  
 a) (CH<sub>3</sub>)<sub>2</sub>NH                      b) (CH<sub>3</sub>)<sub>3</sub>N                      c) C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>                      d) C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub>
16. Nitrobenzene is subjected to reduction with zinc dust and ammonium chloride. The main product formed will be:  
 a) Benzenamine                      b) Aniline                      c) N-Phenylhydroxylamine                      d) None of these
17. Nitrogen is likely to be evolved when NaNO<sub>2</sub> in dilute HCl is reacted with:  
 a) CH<sub>3</sub>NHCH<sub>2</sub>CH<sub>3</sub>                      b) (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N                      c) C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>                      d) H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>
18. The electrolytic reduction of nitrobenzene in strongly acidic medium produces:  
 a) Phenol                      b) *p*-Aminophenol                      c) Hydroazobenzene                      d) Azobenzene
19. The conjugate base of (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub><sup>⊕</sup> is:  
 a) (CH<sub>3</sub>)<sub>3</sub>N                      b) (CH<sub>3</sub>)<sub>2</sub>NH                      c) (CH<sub>3</sub>)<sub>2</sub>N<sup>⊖</sup>                      d) (CH<sub>3</sub>)<sub>2</sub>N<sup>⊕</sup>
20. A compound (X) has the molecular formula C<sub>7</sub>H<sub>7</sub>NO. On treatment with Br<sub>2</sub> and KOH, (X) gives an amine (Y); (Y) gives carbylamine test. (Y) upon diazotisation and coupling with phenol gives an azodye (Z). (X) is:  
 a) PhCONH<sub>2</sub>                      b) PhCONHCOCH<sub>3</sub>                      c) PhNO<sub>2</sub>                      d) PhCOONH<sub>4</sub>
21. Which of the following amines will form stable diazonium salt at 273-283 K?  
 a) C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>                      b) C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>                      c) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NH<sub>2</sub>                      d) CH<sub>3</sub>NH<sub>2</sub>
22. Diazo coupling is useful to prepare some:  
 a) Pesticides                      b) Dyes                      c) Proteins                      d) Vitamins
23. Which of the following produces one mononitro and three isomeric dinitro derivatives?  
 a) *p*-Xylene                      b) Ethyl benzene                      c) *o*-Xylene                      d) *m*-Xylene
24. The following reaction is:  

$$\text{Ph}-\text{NH}-\text{NH}-\text{Ph}$$

 a) Benzidine rearrangement                      b) Pinacol-Pinacolone rearrangement  
 c) Fries rearrangement                      d) Benzil-benzilic acid arrangement
25. The compound which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosoamine is:  
 a) Methylamine                      b) Ethylamine                      c) Diethylamine                      d) Triethylamine
26. Which of the following are not functional isomers of each other?  
 a) CH<sub>3</sub>CH<sub>2</sub>NO<sub>2</sub> and CH<sub>3</sub>CH<sub>2</sub>ON = O                      b) C<sub>2</sub>H<sub>5</sub>CHO and CH<sub>3</sub>COCH<sub>3</sub>  
 c) CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> and CH<sub>3</sub>NHCH<sub>3</sub>                      d) C<sub>3</sub>H<sub>7</sub>NH<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>CHNH<sub>2</sub>
27. Indicate which nitrogen compound amongst the following would undergo Hofmann reaction (i.e., reaction with Br<sub>2</sub> and strong KOH) to furnish the primary amine (R – NH<sub>2</sub>)  
 a) RCONHCH<sub>3</sub>                      b) RCOONH<sub>4</sub>                      c) RCONH<sub>2</sub>                      d) R – CO – NHOH

28. The product of the reaction of alcoholic silver nitrite with ethyl bromide is:  
 a) Ethane                      b) Ethene                      c) Nitroethane                      d) Ethyl alcohol
29. Hinsberg's reagent is:  
 a)  $C_6H_5COCl$                       b)  $CH_3COCl$                       c)  $C_6H_5CH_2Cl$                       d)  $C_6H_5SO_2Cl$
30. The product formed by the treatment of ethanol and ethane nitrile in the presence of sulphuric acid is:  
 a) Ethyl acetate                      b) Diethyl ether                      c) Ethyl methyl ketone                      d) Butanal
31. Which of the following statements is correct?  
 a) Methyl amine is slightly acidic                      b) Methyl amine is less basic than ammonia  
 c) Methyl amine is less basic than dimethyl amine                      d) Methyl amine is less basic than aniline
32. The compound 1-(N-ethyl-N-methyl)-propanamine forms non-superimposable mirror images. But this compound does not show optical activity because of the:  
 a) Absence of a chiral N atom                      b) Presence of chiral N atom  
 c) Presence of lone pair on N atom                      d) Rapid flipping of one form into the other
33. Tertiary nitro compounds cannot show tautomerism because:  
 a) They are very stable  
 b) They isomerise to give secondary nitro compounds  
 c) They do not have labile hydrogen atom  
 d) They are highly reactive
34. (A) is subjected to reduction with Zn-Hg/HCl and the product formed is N-methylmethanamine. (A) can be:  
 a) Ethane nitrile                      b) Nitroethane                      c) Carbylaminoethane                      d) Carbylaminomethane
35. Which of the following reactions does not yield an amine?



36. Which  $C_6H_5N_2Cl$  is reduced with  $Na_2SnO_2$ , the product is:

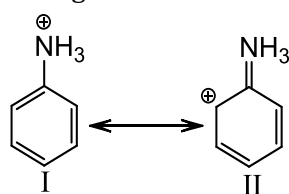


37. Nitromethane is subjected to treatment with chlorine in the presence of sodium hydroxide, the main product is:  
 a) Monochloronitromethane                      b) Trichloromethane  
 c) Chloropicrin                      d) None of the above
38. Which of the following is the weakest base?  
 a)  $NH_3$                       b)  $C_6H_5NH_2$                       c)  $C_6H_5CH_2NH_2$                       d)  $CH_3NH_2$
39. Which of the following groups will facilitate the electrophilic attack on benzene ring?  
 a)  $-NO_2$                       b)  $-CHO$                       c)  $-Cl$                       d)  $-SO_3H$

40. Pick up the correct statement:

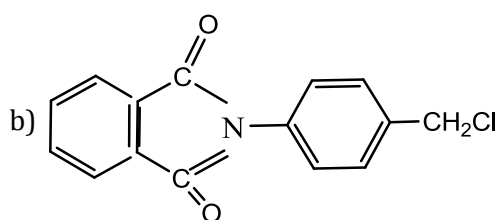
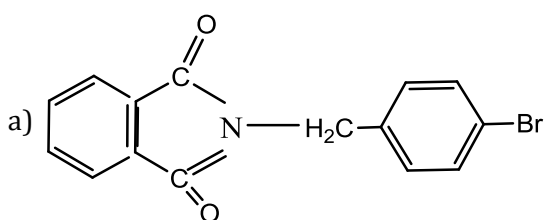
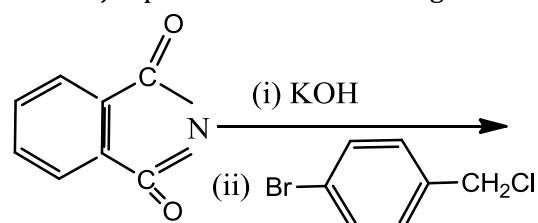
- a) The boiling points of alkyl halides are more than those of the corresponding alkenes  
 b) In water, the solubility of  $CH_3OH > C_2H_5OH > C_6H_5OH$   
 c)  $C_6H_5NH_2$  is a weaker base than  $NH_3$   
 d) All the above statements are correct

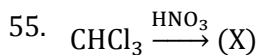
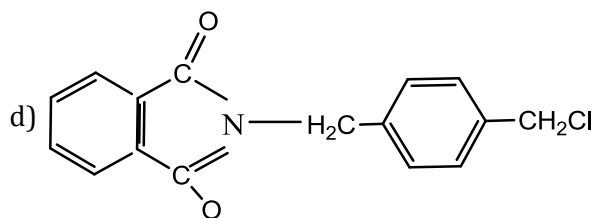
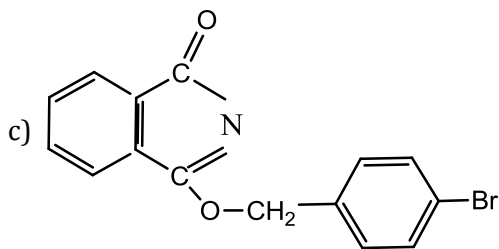
41. Examine the following two structures for the anilinium ion and choose the correct statement from the ones given below:



- a) (II) is not an acceptable canonical structure because carbonium ions are less stable than ammonium ions

- b) (II) is not an acceptable, canonical structure because it is non-aromatic  
 c) (II) is not an acceptable canonical structure because nitrogen has 10 valence electrons  
 d) (II) is an acceptable canonical structure
42. Which of the following reagents on treatment with benzenamine in basic medium produces phenyl isocyanide?  
 a)  $\text{CCl}_4$                                       b) Trichloromethane                      c) Methylene dichloride                      d) Hexachloroethane
43. A compound (X) has the molecular formula  $\text{C}_3\text{H}_7\text{NO}$ . With  $\text{Br}_2$  and  $\text{KOH}$ , (X) gives (Y). (Y) responds to mustard oil reaction. (Y) upon treatment with  $\text{HNO}_2$  evolves  $\text{N}_2$  and gives an alcohol (Z) which gives iodoform test. (X) is likely to be:  
 a)  $\text{C}_2\text{H}_5\text{CONH}_2$                               b)  $\text{CH}_3\text{CONH}_2$                               c)  $\text{CH}_3\text{COONH}_4$                               d)  $\text{C}_2\text{H}_5\text{CNO}$
44. An amine on treatment with  $\text{HNO}_2$  evolved  $\text{N}_2$ . The amine on exhaustive methylation with  $\text{CH}_3\text{I}$  formed a quaternary salt containing 59.07% iodine. The amine is likely to be:  
 a)  $\text{CH}_3\text{NH}_2$                                       b)  $(\text{CH}_3)_2\text{NH}$                                       c)  $\text{C}_2\text{H}_5\text{NH}_2$                                       d)  $(\text{CH}_3)_3\text{N}$
45. Which of the following nitro compounds will show tautomerism?  
 a)  $\text{C}_6\text{H}_5\text{NO}_2$                                       b)  $(\text{CH}_3)_3\text{CNO}_2$                                       c)  $\text{CH}_3\text{CH}_2\text{NO}_2$                                       d) None of the above
46. The reaction of primary amine with chloroform and ethanoic solution of  $\text{KOH}$  is called:  
 a) Hofmann reaction                                      b) Reimer-Tiemann reaction  
 c) Carbylamine reaction                                      d) Kolbe reaction
47. A primary nitroalkane is treated with nitrous acid, which of the following will be the main product?  
 a) Pseudonitriol                                      b) Nitrolic acid                                      c) A primary amine                                      d) Primary alcohol
48.  $1^\circ$ ,  $2^\circ$ , and  $3^\circ$  amines can be best distinguished by:  
 a)  $\text{HNO}_2$  treatment                                      b) Exhaustive alkylation                                      c) Mustard oil reaction                                      d) Carbylamine reaction
49. A nitrogenous substance (X) is treated with  $\text{HNO}_2$  and the product so formed is further treated with  $\text{NaOH}$  solution, which produces blue colouration. Which of the following can (X) be?  
 a)  $\text{CH}_3\text{CH}_2\text{NH}_2$                                       b)  $\text{CH}_3\text{CH}_2\text{NO}_2$                                       c)  $\text{CH}_3\text{CH}_2\text{ONO}$                                       d)  $(\text{CH}_3)_2\text{CHNO}_2$
50. Which of the following substances on treatment with  $\text{P}_2\text{O}_5$  gives ethanenitrile?  
 a) Propanamide                                      b) Ethanamide                                      c) Ethanoic acid                                      d) *N*-Methylethyl amine
51. Methyl cyanide on treatment with methyl magnesium bromide followed by of subsequent hydrolysis gives:  
 a) Propanone                                      b) Ethanone                                      c) Ethanal                                      d) Propanal
52. When  $\text{PhNO}_2$  is reduced in alkaline medium, the product is:  
 a)  $\text{Ph}-\overset{\text{O}}{\parallel}{\text{N}}=\text{N}-\text{N}-\text{Ph}$  (Azoxy-benzene)                                      b)  $\text{Ph}-\text{N}=\text{N}-\text{Ph}$  (Azobenzene)  
 c)  $\text{Ph}-\text{NH}-\text{NH}-\text{Ph}$  (Hydrazobenzene)                                      d) All
53. Which of the following represents the poisonous gas which caused the tragedy in Bhopal in 1984?  
 a)  $\text{CH}_3\text{C}=\text{N}=\text{S}$                                       b)  $\text{CH}_3-\text{N}=\text{C}=\text{O}$                                       c)  $\text{CH}_3-\text{N}=\text{C}=\text{S}$                                       d)  $\text{CH}_3-\text{O}-\text{N}=\text{C}$
54. The major product of the following reaction is

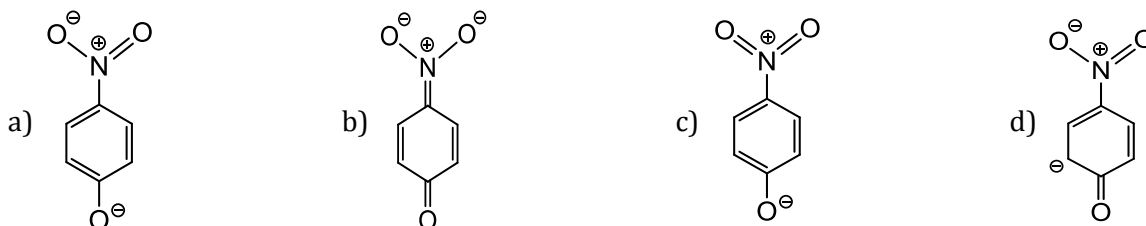




In the above sequence, (X) is:

- a) Nitrochloromethane    b) Chloropicrin    c) Ethanenitrile    d) None of the above

56. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is:



57. Azoxybenzene can be obtained by the treatment of nitrobenzene with:

- a)  $\text{O}_2$     b)  $\text{H}_2/\text{Pt}$     c)  $\text{Na}_3\text{AsO}_3/\text{NaOH}$     d)  $\text{Zn}/\text{NaOH}$

58. Carbylamine test is performed in alc. KOH by heating a mixture of:

- a) Chloroform and silver powder  
b) Trihalogenated methane and a primary amine  
c) An alkyl halide and a primary amine  
d) An alkyl cyanide and a primary amine

59. Which of the following is not an ambident nucleophile?

- a)  $\text{NO}_2^-$     b)  $\text{OH}^-$     c)  $\text{CSN}^-$     d)  $\text{CN}^-$

60. An organic compound with the formula  $\text{C}_3\text{H}_5\text{N}$  on hydrolysis forms an acid which reduces Fehling's solution. The compound can be:

- a) Ethanenitrile    b) Isocyanethane    c) Ethoxyethane    d) Propanenitrile

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

- a)  $\text{PCl}_5$     b) Soda lime    c)  $\text{NaOH} + \text{Br}_2$     d) Hot conc.  $\text{H}_2\text{SO}_4$

62.  $\text{CH}_3\text{NH}_2 + \text{CHCl}_3 + \text{KOH} \rightarrow$  nitrogen containing compound +  $\text{KCl} + \text{H}_2\text{O}$ . Nitrogen containing compound is

- a)  $\text{CH}_3 - \text{C} \equiv \text{N}$     b)  $\text{CH}_3 - \text{NH} - \text{CH}_3$     c)  $\text{CH}_3 - \text{N}^+ \equiv \text{C}^-$     d)  $\text{CH}_3 - \text{N}^+ \equiv \text{C}$

63. Gabriel synthesis is used for the preparation of:

- a)  $1^\circ$  amine    b)  $2^\circ$  amine    c)  $3^\circ$  amine    d) All can be prepared

64. Which of the following is formed when  $\text{RNH}_2$  reacts with  $\text{RCHO}$ ?

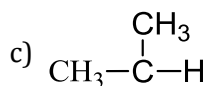
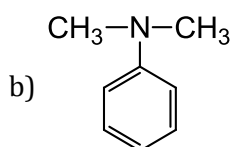
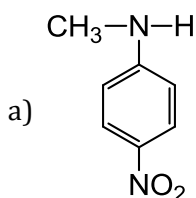
- a) Hemiacetals    b) Acetals    c) Ketals    d) Imines

65. Ethanamine is treated with nitrous acid at ordinary temperature; the products will be:

- a) Ethanol only    b) Ethanol, acetic acid,  $\text{N}_2$ , and  $\text{H}_2\text{O}$   
c) Acetic acid, ethane, and  $\text{H}_2\text{O}$     d) Ethanol, ethene,  $\text{N}_2$ , and  $\text{H}_2\text{O}$

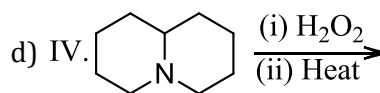
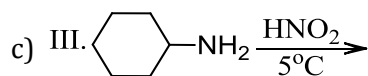
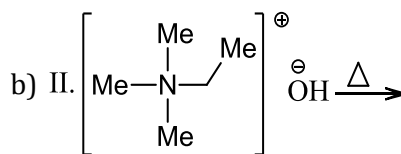
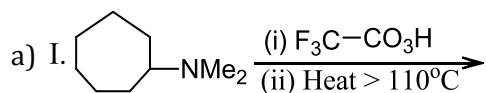
### Multiple Correct Answers Type

66. Which of the following amines will show positive Liebermann's nitroso test?



d) None of these

67. Which of the following are Cope reactions?



68. (A)  $\xrightarrow[\text{[H]}]{\text{Reduction}}$  primary amine

The compound (A) may be

- a) Alkyl isocyanide      b) Alkyl cyanide      c) Acidamide      d) 1° nitroalkane

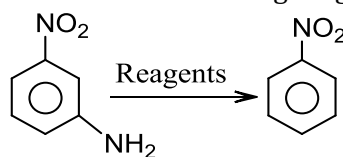
69. When nitrobenzene is treated with Br<sub>2</sub> in the presence of FeBr<sub>3</sub>, the major product formed is *m*-bromonitro-benzene. Statements which are related to obtaining the *m*-isomer are:

- a) The electron density on *meta*-carbon is more than that on *ortho*- and *para*-positions  
 b) The intermediate carbonium ion formed after initial attack of Br<sup>⊕</sup> at the *meta*-position is least destabilised  
 c) Loss of aromaticity when Br<sup>⊕</sup> attacks at the *ortho*- and *para*-positions and not at *meta*-positions  
 d) Easier loss of H<sup>⊕</sup> to regain aromaticity from the *meta*-position than from the *ortho*- and *para*-positions

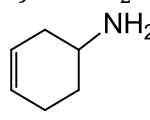
70. Which of the following statements are correct?

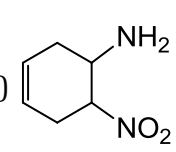
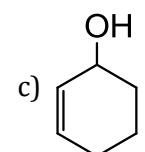
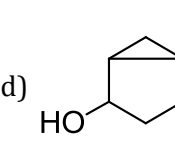
- a) Ethanenitrile on partial hydrolysis gives acetamide  
 b) Ethanenitrile on complete hydrolysis gives acetic acid and NH<sub>3</sub>  
 c) Cyanides are hydrolysed with aqueous mineral acids or alkali  
 d) Isocyanides are hydrolysed with dilute acids and not by alkali

71. Which of the following reagents are correct for the given reaction



- a) i. NaNO<sub>2</sub> + HCl, 0 – °C ii. H<sub>3</sub>PO<sub>2</sub>      b) i. KNO<sub>2</sub> + HBr, 0 – 5°C, ii. Na<sub>2</sub>SnO<sub>2</sub>  
 c) i. HNO<sub>2</sub> ii. C<sub>2</sub>H<sub>5</sub>OH and heat      d) i. KNO<sub>2</sub> + HCl ii. H<sub>2</sub>O (steam)

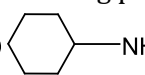
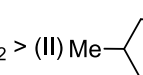
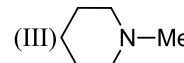
72.  on reaction with HNO<sub>2</sub> forms

- a)       b)       c)       d) 

73. Which of the following statements are correct?

- a) The extent of H-bonding is greater in 1° than 2° and 3° amines  
 b) The boiling points of isometric amines are in the order: 1° > 2° > 3°

The boiling points of

- c) (I)  > (II)  > (III) 

- d) The boiling points of (I) C<sub>4</sub>H<sub>9</sub>NH<sub>2</sub> > (II) Me<sub>2</sub>N – Et > (III) (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH

74. Which of the following statements are correct?

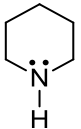
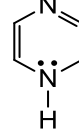
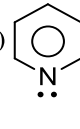
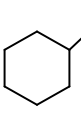
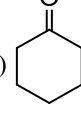
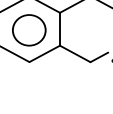
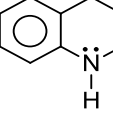
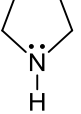
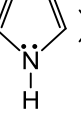
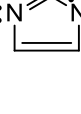
- a) Aryldiazonium ions are more stable than alkyldiazonium ions  
 b) Electron release from the *ortho*- and *para*-positions of the ring stabilises the aryldiazonium ion  
 c) The increased stability of aryldiazonium ions due to the great difficulty of forming Ar<sup>⊕</sup> as compared to R<sup>⊕</sup>

d) Alkyldiazium is more stable than aryldiazonium ion

75. Which of the following statements are correct?

- a)  $\text{CH}_3\text{N}^{\oplus}\equiv\text{C}^{\ominus}$  on partial hydrolysis gives *N*-methyl methanamide
- b)  $\text{CH}_3\text{N}^{\oplus}\equiv\text{C}^{\ominus}$  on complete hydrolysis gives  $\text{CH}_3\text{NH}_2$  and  $\text{HCOOH}$
- c) In an isocyanide, first an electrophile and then a nucleophile add at the same C atom bearing negative charge
- d) In an isocyanide, first a nucleophile and then an electrophile add at the same C atom bearing negative charge

76. Which of the following are the correct orders of basic character?

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





77. Which of the following statements are correct?

- a) In gas phase, the basic character of amine is  $3^\circ > 2^\circ > 1^\circ$ . Due to the +I effect of (R-), the availability of LP  $\bar{e}$ 's on N increases
- b) In aqueous medium, the basic character of amines is  $\text{Me}_2\text{NH} > \text{Me}_3\text{N} > \text{MeNH}_2 > \text{NH}_3$
- c) In aqueous medium, the addition of protons increases crowding and thus strains setup, which being the highest in  $3^\circ$  amine decreases its basic character
- d) In aqueous medium, the ammonium ions in solution are stabilised not only by alkyl groups but also by H-bond donation to the solvent

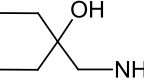
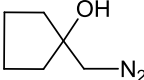
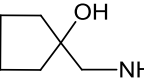
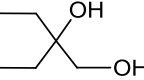
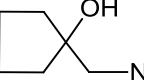
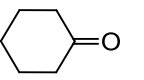
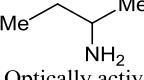
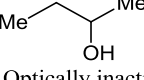
78. A positive carbylamine test is given by:

- a) *N,N*-Dimethyl aniline
- b) 2, 4-Dimethyl aniline
- c) *N*-Methyl-*o*-methyl aniline
- d) *p*-Methyl benzylamine




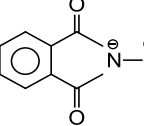


79. Choose the incorrect reaction

- a)  $\text{Ph}-\underset{\text{CH}_3}{\text{CH}}-\text{OH} \xrightarrow{\text{NaCN, H}^+} \text{Ph}-\underset{\text{CH}_3}{\text{CH}}-\text{NH}_2 \xrightarrow{\text{H}_2\text{O, H}^+ / \text{Br}_2/\text{KOH}}$
- b)  $\text{Ph}-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{Cl} \xrightarrow{\text{NH}_3} \text{Ph}-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{NH}_2$
- c)   $\xrightarrow{\text{Fe, Cl}_2} \text{NH}_3 \rightarrow$  
- d)   $\xrightarrow{\text{Conc HNO}_3 / \text{H}_2\text{SO}_4} \text{LiAlH}_4 \rightarrow$  

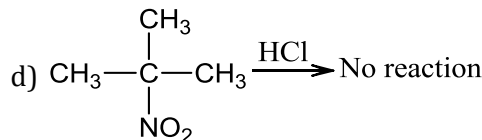
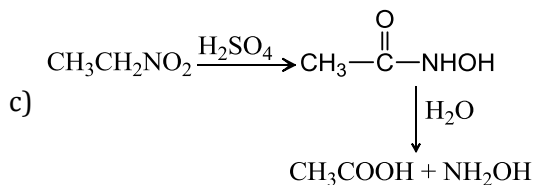
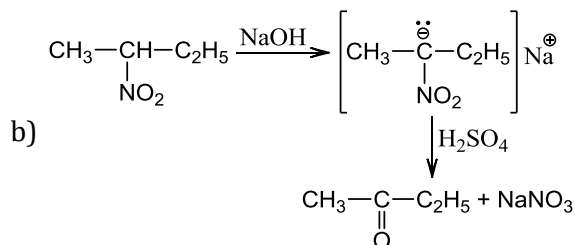
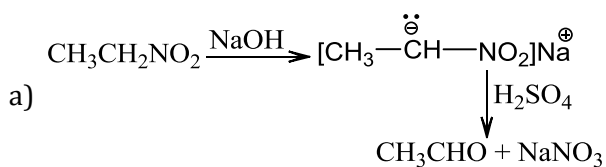
80. Which of the following reactions are correct?

- a)   $\xrightarrow{\text{NaNO}_2 + \text{HCl}}$  
- b)   $\xrightarrow{\text{NaNO}_2 + \text{HCl}}$  
- c)   $\xrightarrow{\text{NaNO}_2 + \text{HCl}}$  
- d)  (Optically active)  $\xrightarrow{\text{NaNO}_2 + \text{HCl}}$   (Optically inactive)

81. Which of the following are correct reactions?

- a)   $\xrightarrow{\text{NH}_3} \text{C}=\text{NH} \xrightarrow{\text{NaCNBH}_3} \text{NH}_2$
- b)   $\xrightarrow{\text{NH}_3} \text{NH}_2$
- c)   $\xrightarrow{\text{NaN}_3} \text{N}_3 \xrightarrow{\text{LAH}} \text{NH}_2$
- d)  +   $\xrightarrow{\text{OH}^-/\text{H}_2\text{O}}$  

82. Which of the following reactions are correct?



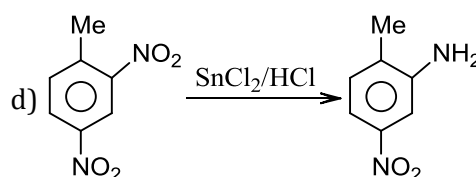
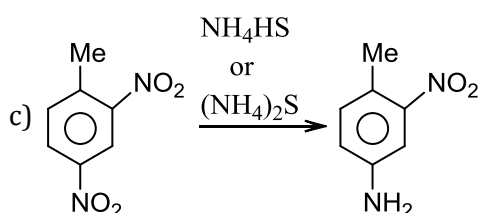
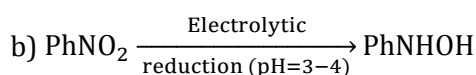
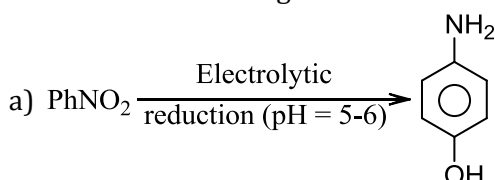
83. Mixture of 1°, 2° and 3° amines can be separated by

- a) Hinsberg's method  
 b) Fractional distillation  
 c) Hofmann's method  
 d) Victor Meyer's method

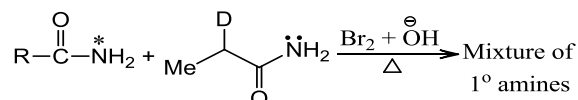
84. By which of the following reactions can MIC (methyl isocyanate) be obtained?

- a)  $\text{CH}_3-\overset{\oplus}{\text{N}}\equiv\overset{\ominus}{\text{C}} + \text{HgO} \rightarrow$   
 b)  $\text{CH}_3-\overset{\oplus}{\text{N}}\equiv\overset{\ominus}{\text{C}} + \text{O}_3 \rightarrow$   
 c)  $\text{CH}_3-\overset{\oplus}{\text{N}}\equiv\overset{\ominus}{\text{C}} + \text{S} \rightarrow$   
 d)  $\text{CH}_3-\overset{\oplus}{\text{N}}\equiv\overset{\ominus}{\text{C}} + \text{DMSO} \rightarrow$

85. Which of the following reactions are wrong?



86. Which statements are correct about the reaction?



- a) A mixture of two amines is formed, which suggests that rearrangement is intramolecular  
 b) If R is chiral, it migrates with retention of configuration

c) A mixture of four different amines is formed, which suggests that a free acyl nitrene  $\left[ \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\cdot}{\text{N}} \right]$  intermediate is formed

d) A mixture of two different amines and a free acyl nitrene intermediate is formed

87. Which statements are correct about MIC (methyl isocyanate, Me - N = C = O)

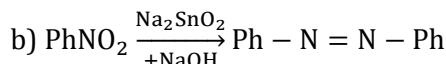
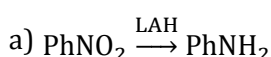
a) MIC is prepared by the reaction of MeNH<sub>2</sub> and COCl<sub>2</sub> (phosgene)

b) Hydrolysis of MIC gives  $\left( \text{Me}-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} \right)$  as the intermediate, which gives MeNH<sub>2</sub> and CO<sub>2</sub> on further hydrolysis

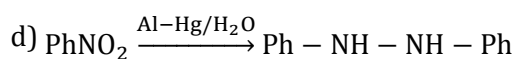
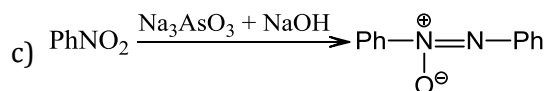
c) MIC is used to prepare insecticide, carbarly under the commercial name Sevin

d)  $\left( \text{N}=\text{C} \right)$  bond takes part when 1-naphthol is reacted with MIC because N is more basic and nucleophilic

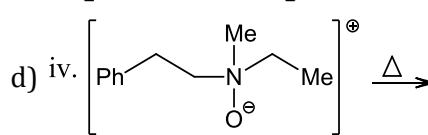
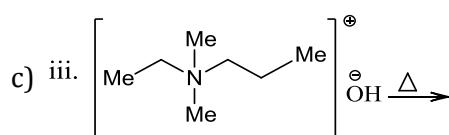
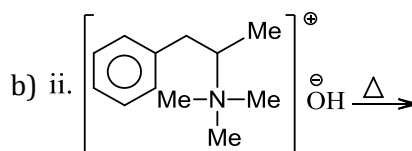
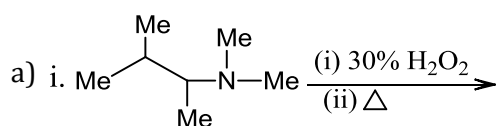
88. Which of the following reactions is/are correct?







89. *p*-Chloroaniline and anilinium hydrochloride can be distinguished by:  
 a) Sandmeyer reaction    b)  $\text{NaHCO}_3$     c)  $\text{AgNO}_3$     d) Carbylamine test
90. Which statements are correct?  
 a) Phenol and aniline give coupling reaction with diazonium salt  
 b) Phenol couples with diazonium salt in mild basic condition ( $\text{pH} = 8 - 10$ )  
 c) Aniline couples with diazonium salt in mild acidic condition ( $\text{pH} = 4 - 6$ )  
 d) Both phenol and aniline couple with diazonium salt in neutral condition ( $\text{pH} = 7$ )
91. Which of the following statements are correct?  
 a)  $\alpha$ -Amino acids on heating give piperazine (cyclic diamide)  
 b)  $\beta$ -Amino acids on heating give  $\alpha, \beta$ -unsaturated acids  
 c)  $\gamma$ -Amino acids on heating give lactam (five-membered cyclic ester)  
 d)  $\delta$ -Amino acids on heating give lactam (six-membered cyclic ester)
92. Which of the following statements are correct?  
 a)  $1^\circ, 2^\circ$  and  $3^\circ$  nitro compounds can be distinguished by  $\text{HNO}_2$   
 b)  $1^\circ$  nitro compound with  $\text{HNO}_2$  gives nitrolic acid, which gives blood-red colour with base  
 c)  $2^\circ$  nitro compound with  $\text{HNO}_2$  gives pseudo nitrole, which gives blue colour with base  
 d)  $3^\circ$  nitro compound does not react with  $\text{HNO}_2$
93. Which of the following would give Hofmann alkene?



### Assertion - Reasoning Type

This section contain(s) 0 questions numbered 94 to 93. Each question contains STATEMENT 1(Assertion) and STATEMENT 2(Reason). Each question has the 4 choices (a), (b), (c) and (d) out of which **ONLY ONE** is correct.

- a) Statement 1 is True, Statement 2 is True; Statement 2 **is** correct explanation for Statement 1  
 b) Statement 1 is True, Statement 2 is True; Statement 2 **is not** correct explanation for Statement 1  
 c) Statement 1 is True, Statement 2 is False  
 d) Statement 1 is False, Statement 2 is True

94

**Statement 1:** Stable diazonium salt is formed when primary amines reacts with nitrous acid

**Statement 2:**  $\text{Cl}^-$  is the leaving group

95

**Statement 1:** Aniline hydrogen sulphate on heating forms a mixture of *o*- and *p*-amino-sulphonic acid

**Statement 2:** The sulphonic acid is  $\bar{e}$  withdrawing

96

**Statement 1:** In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents

**Statement 2:** The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on nitrogen is no longer available for resonance

97

**Statement 1:** Tertiary amine is less basic than secondary amine in aqueous solution

**Statement 2:** Over crowding due to  $I^+$  effect of three alkyl groups increases strain

98

**Statement 1:** Pyridine is more basic than piperidine

**Statement 2:** N atom is  $sp^2$ -hybridised in both

99

**Statement 1:** Hofmann degradation and Curtius degradation methods are used to prepare  $1^\circ$  amines

**Statement 2:** Both involve intermolecular alkyl shift

100

**Statement 1:** Carbylamine reaction takes place between  $1^\circ$  amine and  $\text{CHBrCl}$  in basic medium

**Statement 2:** The reaction takes place by the formation of bromidocarbene ( $:\text{CBrI}$ ) as intermediate

101

**Statement 1:**  $\text{PhN}_2^+\text{Br}^-$  couples with *N,N*-dimethylaniline (I) but not with 2,6-dimethyl-*N,N*-dimethylaniline (II)

**Statement 2:** Due to steric inhibition of resonance, the *p*-position of (II) is not sufficiently activated for the coupling reaction

102

**Statement 1:** Gabriel phthalimide reaction is used for the preparation of  $\text{C}_2\text{H}_5\text{NH}_2$  and *p*-nitro aniline

**Statement 2:**  $\text{S}_\text{N}2$  reaction takes place with  $1^\circ$  RX and  $1^\circ$  ArX containing  $\bar{e}$ -withdrawing group at *o*- and *p*-positions

103

**Statement 1:**  $\text{PhN}_2^+\text{Br}^-$  on reaction with nitrobenzene in the presence of NaOH gives *p*-nitro biphenyl

**Statement 2:** The reaction takes place by free radical mechanism

104

**Statement 1:**  $\text{PhN}_2^+\text{Br}^-$  on reaction with NaOH gives benzene diazohydroxide

**Statement 2:**  $\text{OH}^-$  is a strong nucleophile, attacks the terminal N atom, and forms a covalent bond

105

**Statement 1:**  $\text{PhN}_2^+\text{Br}^-$  is more acidic than  $\text{NH}_4\text{Br}$

- Statement 2:**  $\text{PhNH}_3^+$  (anilinium ion) is resonance stabilised
- 106
- Statement 1:** In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents
- Statement 2:** The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance
- 107
- Statement 1:** Coupling of  $\text{PhNH}_2^+$  with aniline is faster than with phenol
- Statement 2:** Aniline is more  $\bar{e}$  donating than phenol
- 108
- Statement 1:** Hofmann bromamide reaction takes place between an amide and  $\text{Br}_2$  in basic medium
- Statement 2:** The reaction proceeds by the formation of  $(\text{R}-\ddot{\text{N}}:)$  nitrene intermediate
- 109
- Statement 1:** Carbylamines reaction involves chemical reaction between  $1^\circ$  amine and chloroform in basic medium
- Statement 2:** In carbylamines reaction,  $-\text{NH}_2$  group changes into  $-\text{NC}$  group

### Matrix-Match Type

This section contain(s) 0 question(s). Each question contains Statements given in 2 columns which have to be matched. Statements (A, B, C, D) in **columns I** have to be matched with Statements (p, q, r, s) in **columns II**.

110.

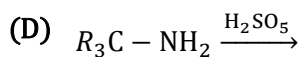
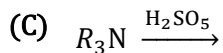
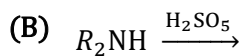
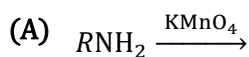
Column-I	Column- II
(A) $\phi\text{NO}_2 \xrightarrow{\text{Zn}/\text{NH}_4\text{Cl}}$	(1) $\phi - \text{N} = \text{N} - \phi$
(B) $\phi\text{NO}_2 \xrightarrow[\text{NaOH}]{\text{Zn}/\text{alc.}}$	(2) $\phi - \text{NH} - \text{NH} - \phi$
(C) $\phi\text{NO}_2 \xrightarrow{\text{LAH}}$	(3) $\phi\text{NHOH}$
(D) $\phi\text{NO}_2 \xrightarrow{\text{Na}_3\text{AsO}_3/\text{NaOH}}$	(4) $\begin{array}{c} \text{O} \\ \uparrow \\ \phi - \text{N} = \text{N} - \phi \end{array}$

**CODES :**

	A	B	C	D
a)	1	2	3	4
b)	2	3	1	4
c)	2	3	1	4
d)	2	4	3	1

111. Match the list

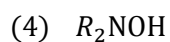
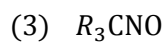
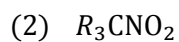
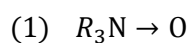
Column-I



CODES :

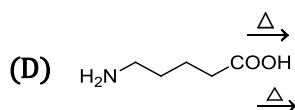
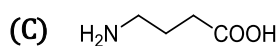
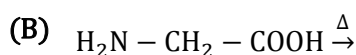
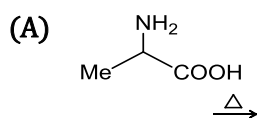
	A	B	C	D
a)	3	1	4	2
b)	2	3	4	1
c)	3	2	1	4
d)	1	2	3	4

Column- II



112.

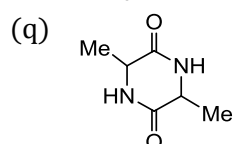
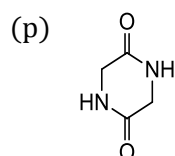
Column-I



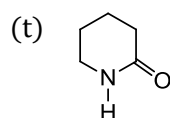
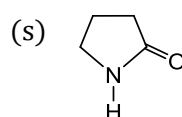
CODES :

	A	B	C	D
a)	P,q	r	s	t
b)	q,s	t	s,t	r
c)	r,s	t	p	s
d)	q,r	p	s	t

Column- II

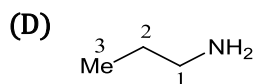
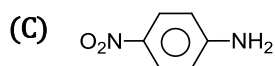
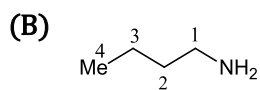


(r) Three stereoisomers



113.

**Column-I**



**Column- II**

(p) Gabrielphthalimide synthesis

(q) Ritter reaction

(r) Hofmann bromamide reaction of butanamide

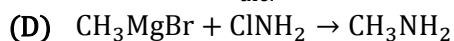
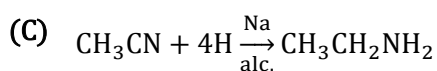
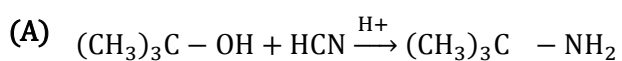
(s) Reduction of butanamide of with LAH

**CODES :**

	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>
<b>a)</b>	P,s	p	p,r	q
<b>b)</b>	q	p,s	p	p,r
<b>c)</b>	p	p,r	q	p,s
<b>d)</b>	p,r	q	p,s	p

114. Match the following

**Column-I**



**Column- II**

(1) Grignard

(2) Mendius

(3) Hofmann bromamide

(4) Ritter

**CODES :**

	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>
<b>a)</b>	1	2	3	4
<b>b)</b>	4	3	2	1
<b>c)</b>	2	3	4	1
<b>d)</b>	4	2	3	1

115. Match the following

**Column-I**

(A) Aniline

(B) TNT

(C) Sulphanilamide

**Column- II**

(1) Sulpha drug

(2) Solvent in Friedel-Craft

(3) Explosive

(D) Nitrobenzene

(4) Used in azo dyes

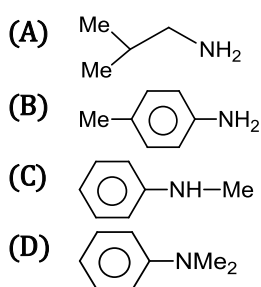
**CODES :**

	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>
<b>a)</b>	1	2	3	4
<b>b)</b>	4	3	2	1
<b>c)</b>	2	3	4	1
<b>d)</b>	4	3	1	2

116.

**Column-I**

**Column- II**



(p) Lieberman's nitroso reaction

(q) Evolution of  $N_2$  with  $HNO_2$

(r) Dye test

(s) Green colour with  $HNO_2$

(t) Carbylamine test

**CODES :**

	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>
<b>a)</b>	Q,t	r,t	p	s
<b>b)</b>	r	t	p,s	q,t
<b>c)</b>	t	p,s	q,t	r
<b>d)</b>	p,s	q,t	r	t

117. Aromatic diazonium group can be replaced by various groups/atoms. In this context, match list I with list II and select the correct answer using the codes given below the lists

**Column-I**

**Column- II**

(A)  $H_3PO_2$

(1) Hydrogen

(B) Sandmeyer reaction

(2) Hydroxyl group

(C) Boiling with water

(3) Aryl group

(D) Gomberg reaction

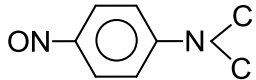
(4) Chlorine

**CODES :**

	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>
<b>a)</b>	4	3	2	1

- b) 1 4 2 3  
 c) 1 2 3 4  
 d) 2 3 4 1

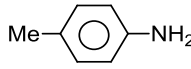
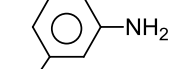
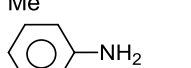

118.

	Column-I		Column-II
(A)	$RNH_2 \xrightarrow{NaNO_2+HCl}$	(1)	$R_2NNO$
(B)	$\phi NH_2 \xrightarrow{NaNO_2+HCl}$	(2)	$ROH + N_2$
(C)	$\phi N(CH_3)_2 \xrightarrow{NaNO_2+HCl}$	(3)	$\phi NNCl$
(D)	$R_2NH \xrightarrow{NaNO_2+HCl}$	(4)	

CODES :

	A	B	C	D
a)	2	3	4	1
b)	1	3	4	2
c)	2	4	3	1
d)	1	2	3	4

119.

	Column-I		Column-II
(A)		(p)	4.69
(B)		(q)	5.12
(C)		(r)	4.58
(D)		(s)	4.39

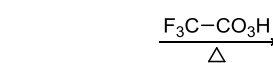
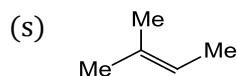
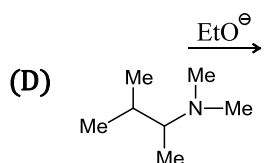
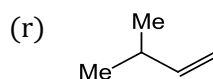
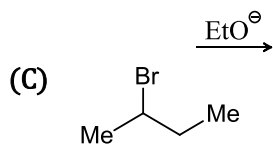
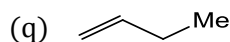
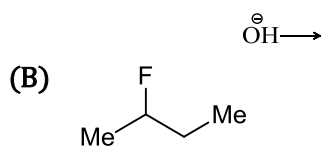
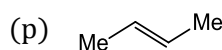
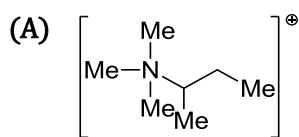
CODES :

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

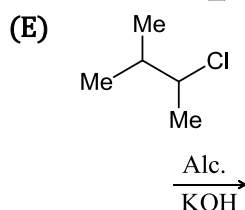
120.

Column-I

Column-II



(t)



CODES :

	A	B	C	D	E
a)	p	r	s	q	q
b)	r	s	p	q	q
c)	q	q	p	r	q
d)	q	p	r	s	q

Linked Comprehension Type

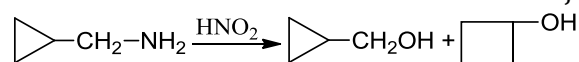
This section contain(s) 19 paragraph(s) and based upon each paragraph, multiple choice questions have to be answered. Each question has atleast 4 choices (a), (b), (c) and (d) out of which **ONLY ONE** is correct.

Paragraph for Question Nos. 121 to -121

Nitrous acid reacts with all classes of amines. The products obtained from there reactions depend on whether the amine is primary, secondary or tertiary and whether the amine is aliphatic or aromatic.

Aliphatic primary amines reacts with nitrous acid ( $\text{NaNO}_2 + \text{HCl}$ ) to form alcohol as major product. In addition to alcohol, alkene and alkyl halides are also formed as minor product.

Certain cyclic primary amines can undergo either ring expansion or ring contraction reactions on treatment with nitrous acid. The reaction is called Demjanor ring expansion or contraction



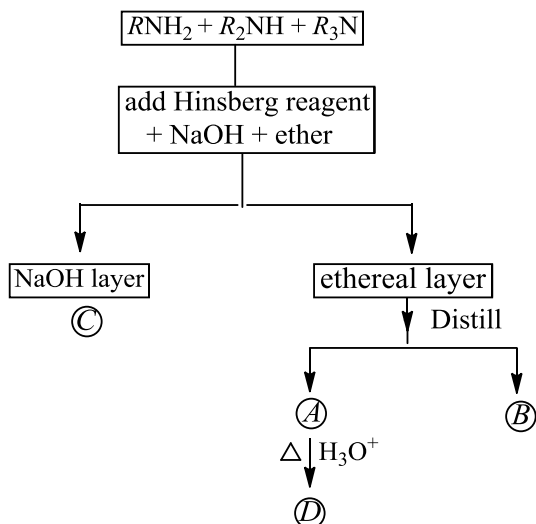
Answer the following question



121. What will be the major product when 2-amino propane is treated with nitrous acid?  
 a) 1-propanol                      b) 2-propanol                      c) Propene                      d) Cyclopropane

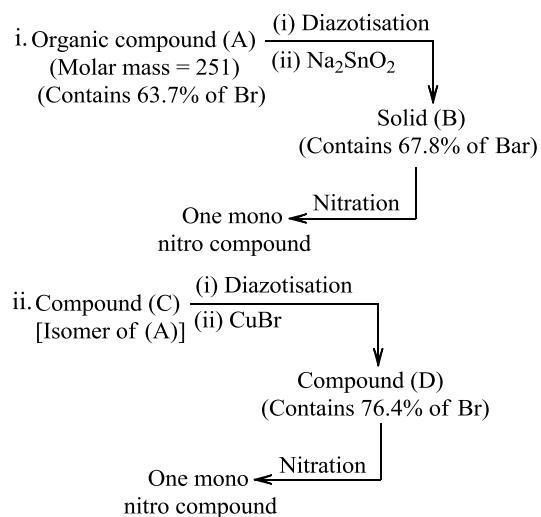
**Paragraph for Question Nos. 122 to - 122**

When alkyl halide and ammonia react, there is always formation of 1°, 2° and 3° amines even under controlled conditions. Given outline describes the technique to separate the mixture. Go through it and properties of the amines to answer the questions at the end

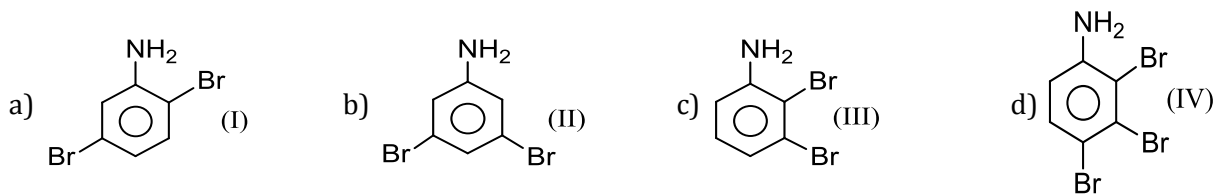


122. NaOH layer (C) contains
- a) Sodium salt of 1° amine N-alkyl benzene sulphonamide
  - b) Sodium salt of 2° amine N, N-dialkyl benzene sulphonamide
  - c) Both (a) and (b)
  - d) None of the above

**Paragraph for Question Nos. 123 to - 123**



123. Compound (A) is:



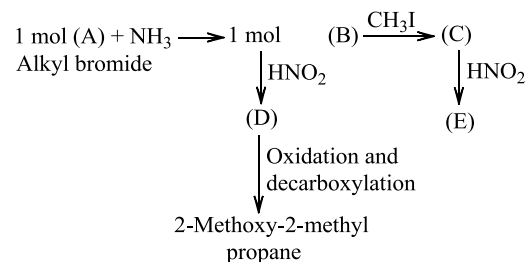
**Paragraph for Question Nos. 124 to - 124**

An amino acid reacts with 10 ml 0.05 M NaOH and the final solution has pH=2.30. When 20 ml of the same base is added in the resulting solution, the pH becomes 9.7. Identify the amino acid and calculate the isoelectric point of the amino acid. This amino acid is prepared by the reaction of compound (X) with  $\text{NH}_3$  and further hydrolysis with HCN. Compound (X) is less C atom containing compound that gives positive iodoform test and positive Fehling's solution test

124. Amino acid is:



**Paragraph for Question Nos. 125 to - 125**



125. Compound (A) is:



**Paragraph for Question Nos. 126 to - 126**

[A], [B], [C], [E], [F], and [G] are amines, each of which forms a hydrochloride containing 32.42% chlorine. [A], [B], [C] and [D] evolve  $\text{N}_2$  on reaction with  $\text{HNO}_2$ , but [E], [F], and [G] do not

126. Which of the following are  $1^\circ$  amines?

- a) (A), (B), (C), (D)      b) (E), (F), (G)      c) All      d) None

**Paragraph for Question Nos. 127 to - 127**

A substance (X) contains 41.37% C, 6.89% H. 0.0116 gm of (X) gave  $\text{NH}_3$ , which was absorbed in 50 ml of N/10  $\text{H}_2\text{SO}_4$ . The excess of acid required 30 ml of N/10 NaOH for neutralisation. (X) on treatment with  $\text{HNO}_2$  gave succinic acid. (X) on heating lost  $\text{NH}_3$  to give (A). (A) reacts with  $\text{Br}_2$  and NaOH to give (B) containing 41.02% C, 5.88% H, and 11.96% N. (B) on further treatment with  $\text{Br}_2$  and NaOH gives (C) (3-amino propanoic acid). (C) reacts with  $\text{HNO}_2$  to give  $\beta$ -hydroxy-propanoic acid

127. Percentage of N in (X) is:

a) 34.38%

b) 24.38%

c) 14.38%

d) 44.48%

**: ANSWER KEY :**

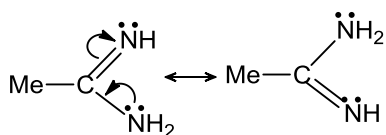
1)	a	2)	b	3)	d	4)	b
5)	a	6)	c	7)	c	8)	d
9)	b	10)	b	11)	c	12)	a
13)	d	14)	d	15)	c	16)	c
17)	d	18)	b	19)	b	20)	a
21)	c	22)	b	23)	a	24)	a
25)	c	26)	d	27)	c	28)	c
29)	d	30)	a	31)	c	32)	d
33)	c	34)	d	35)	c	36)	b
37)	c	38)	b	39)	c	40)	d
41)	c	42)	b	43)	a	44)	c
45)	c	46)	c	47)	b	48)	a
49)	d	50)	b	51)	a	52)	d
53)	b	54)	a	55)	b	56)	c
57)	c	58)	b	59)	b	60)	b
61)	c	62)	b	63)	a	64)	d
65)	d	1)	a,c	2)	a,d	3)	
	b,c,d	4)	a,d				
5)	a,b,c,d	6)	a,b,c	7)	b,c,d	8)	
	a,b,c						
9)	a,b,c	10)	a,b,c	11)	a,b,c	12)	
	a,c,d						
13)	b,d	14)	b,c,d	15)	c,d	16)	
	a,b,c						
17)	a,b,c,d	18)	a,b,c	19)	a,c,d	20)	
	a,b						
21)	a,b	22)	a,b,c,d	23)	b,c	24)	c
25)	a,b,c	26)	a,b,c,d	27)	a,b,c,d	28)	
	a,c						
1)	d	2)	b	3)	d	4)	a
5)	d	6)	a	7)	c	8)	a
9)	a	10)	a	11)	a	12)	c
13)	d	14)	a	15)	c	16)	a
1)	c	2)	a	3)	d	4)	b
5)	b	6)	d	7)	a	8)	b
9)	a	10)	a	11)	c	1)	b
	2)	a	3)	a	4)	b	
5)	a	6)	a	7)	b		

## : HINTS AND SOLUTIONS :

2 (b)  
3° nitro compound does not react with HNO<sub>2</sub>

3 (d)  
Statement is self explanatory

4 (b)  
(1) > (3) > (2) > (4)  
1.



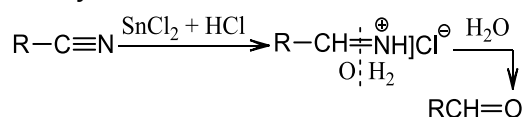
More basic due to the presence of two LP  $\bar{e}$ 's on each N

2. EtNH<sub>2</sub>. Due to +I effect of (Et) group, but +I effect of two Me group is greater than +I effect of (Et) group. Hence, (3) is more basic than (2)

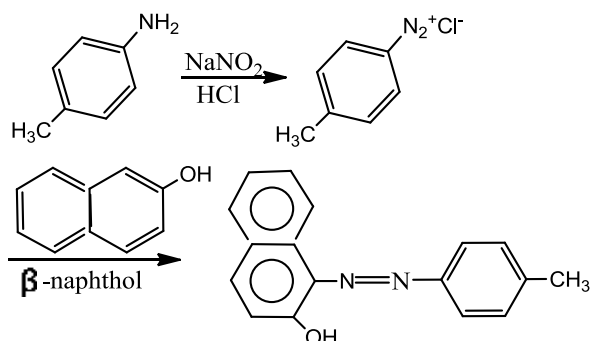
3. (CH<sub>3</sub>)<sub>2</sub>NH. Due to (+I) effect of two Me groups

4. (Amides are resonance stabilised; so they are the weakest bases. Amides behave as amphoteric.)

5 (a)  
Stephen's reduction is partial reduction of RCN to aldehydes



7 (c)  
As we know, benzenediazonium salt forms brilliant coloured dye with  $\beta$ -naphthol, the compound under consideration must be *p*-toluidine (c) as it is a primary aromatic amine. Primary aromatic amine, on treatment with NaNO<sub>2</sub> in dil. HCl forms the corresponding diazonium chloride salt.



8 (d)  
(d) is an aliphatic amine; so it is stronger base than aromatic amine. Moreover, EWG

[(−NO<sub>2</sub>) at *o*, *m*, or *p*] decreases the basic character. The basicity order is:

(d) > (a) > (c) > (b)

9 (b)  
 $\text{R}-\text{C}\equiv\text{N} \xrightarrow[\text{Na+EtOH}]{\text{Mendius reduction}} \text{RCH}_2\text{NH}_2$

10 (b)  
1° aromatic amine on diazotisation followed by coupling with  $\beta$ -naphthol gives azo dye test

11 (c)  
HNO<sub>2</sub> is used to distinguish between 1°, 2°, and 3° amines

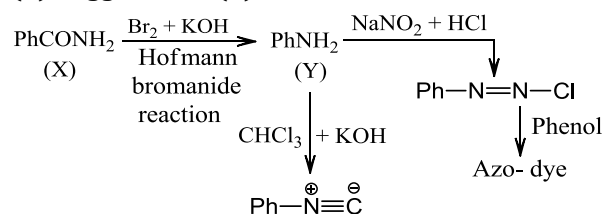
13 (d)  
 $\text{PhNO}_2 \xrightarrow[\text{Weakly acidic medium}]{\text{Electrolytic reduction}} \text{PhNH}_2$

15 (c)  
Basic order: (CH<sub>3</sub>)<sub>2</sub>NH > (CH<sub>3</sub>)<sub>3</sub>N > C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub> > C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>

16 (c)  
 $\text{PhNO}_2 \xrightarrow{\text{Zn+NH}_4\text{Cl}} \text{PhNHOH}$   
*N*-Phenyl hydroxylamine

17 (d)  
Only in 1° aliphatic amines

20 (a)  
Reaction of (X) with Br<sub>2</sub> + KOH suggests that (X) is an amide. Carbylamine test coupling reaction of (Y) suggest that (Y) is 1° aromatic amine



21 (c)  
Stable diazonium salts are formed by 1° aromatic amine (PhNH<sub>2</sub>)

22 (b)  
Azo dyes

25 (c)  
2° amines react with HNO<sub>2</sub> at low temperature to give oily nitrosamine  
 $\text{Et}_2\text{NH} + \text{HNO}_2 \longrightarrow \text{Et}_2\text{N}-\text{N}=\text{O} + \text{H}_2\text{O}$   
*N*-Nitroso-*N*-ethyl ethanamine

26 (d)  
1° amine to different 1° amines are not functional isomers but (1° and 2°), (1° and 3°), and (2° and

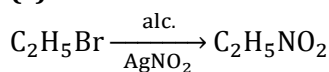
3°) of same molecular formula are functional isomers.

Therefore, (a), (b), and (c) are functional isomers

27 (c)

Amides give Hofmann bromamide reaction

28 (c)

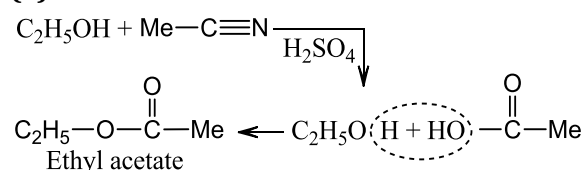


Nitroethane

29 (d)

Benzenesulphonyl chloride ( $\text{PhSO}_2\text{Cl}$ ) is called Hinsberg's reagent

30 (a)



$\text{Me}-\text{C}\equiv\text{N}$  is hydrolysed to acid which reacts with alcohol to give ester

31 (c)

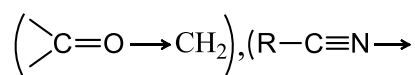
Dimethyl amine ( $\text{Me}_2\text{NH}$ ) is more basic than  $\text{MeNH}_2$ , due to (+I) effect of two (Me) groups

33 (c)

Nitroalkane containing  $\alpha$ -H atoms, i.e., 1° and 2° nitro alkanes show tautomerism

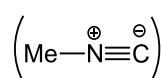
34 (d)

Reduction with Zn-Hg/HCl is Clemmensen reduction which converts



$(\text{R}-\text{C}\equiv\text{N} \rightarrow \text{RCH}_2\text{NH}_2)$ , and

$(\text{R}-\overset{\oplus}{\text{N}}\equiv\overset{\ominus}{\text{C}} \rightarrow \text{RNHCH}_3)$ . Carbylamino methane is



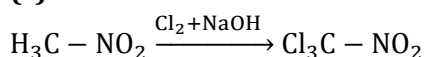
35 (c)

RCN on hydrolysis gives RCOOH and  $\text{NH}_3$

36 (b)

Diazo group can be replaced by (H) on reduction with  $\text{Na}_2\text{SnO}_2$  or  $\text{H}_3\text{PO}_2$  or warm with  $\text{C}_2\text{H}_5\text{OH}$

37 (c)



Chloropicrin (tear gas)

38 (b)

Aromatic amines are weaker than aliphatic amines and  $\text{NH}_3$

39 (c)

SE reaction is favoured by EDG

( $-\text{NO}_2$ ), ( $-\text{CHO}$ ), and ( $\text{SO}_3\text{H}$ ) are EWG. Cl is  $\bar{e}$  donating by (+R) effect and deactivating by (-I)

40 (d)

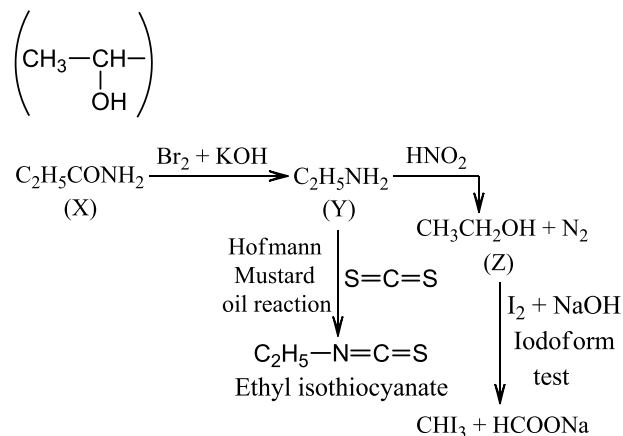
All statements are correct and self explanatory

41 (c)

(II) is not acceptable canonical structure because N has 10 valence  $\bar{e}$ 's

43 (a)

Reaction of (X) with  $\text{Br}_2 + \text{KOH}$  suggests that (X) is an amine. Evolution of  $\text{N}_2$  and formation of alcohol suggest that (Y) is a 1° aliphatic amine. Iodoform test of (Z) suggests that it is an alcohol of the type

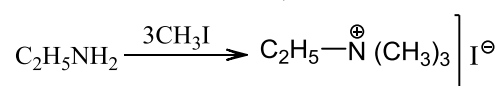
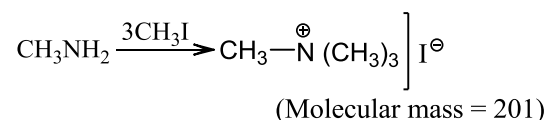


44 (c)

Evolution of  $\text{N}_2$  with  $\text{HNO}_2$  suggests that 1° amine [either (a) or (c)]

59.07 gm of (I) is present in 100 gm of compound  
127 gm of I (1 mol) is present in  $\frac{100 \times 127}{59.07} = 215$

Molecular mass = 215

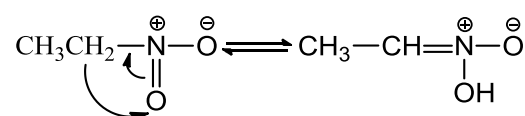


(Molecular mass = 215)

Hence, the amine is  $\text{C}_2\text{H}_5\text{NH}_2$  (c)

45 (c)

(c) has an  $\alpha$ -H atom and hence shows tautomerism

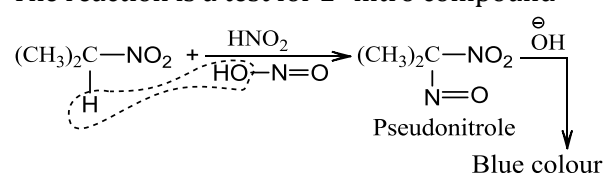


46 (c)

Carbylamine reaction

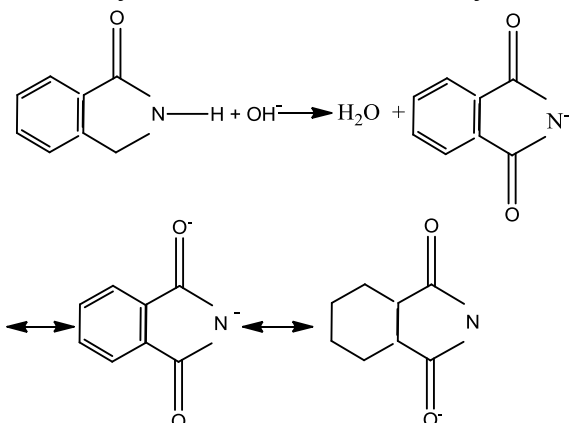
49 (d)

The reaction is a test for 2° nitro compound

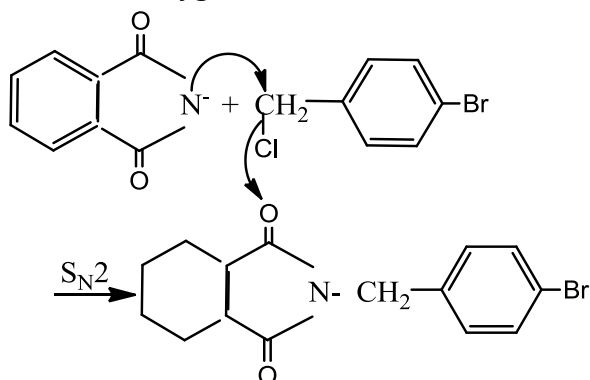


54 (a)

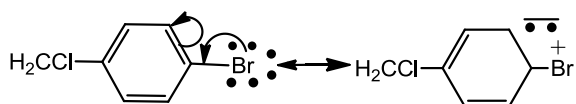
It is the first step of Gabriel's phthalimide synthesis. The hydrogen bonded to nitrogen is sufficiently acidic due to two  $\alpha$ -carbonyls.



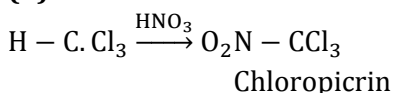
The conjugate base forms above act as nucleophile in the subsequent step of reaction. As shown above, the nucleophile exist in three resonating form, one may think of oxygen being the donor atom in the nucleophilic attack. However, nitrogen act as donor as it is better donor than oxygen.



Bromine is not substituted in the above reaction as it is in resonance with benzene ring giving partial double bond character to C - Br bond, hence difficult to break.



55 (b)

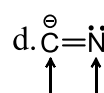
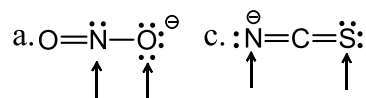


56 (c)

(c) is an unlikely structure because N atoms form five bonds and contain positive charge

59 (b)

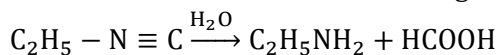
(b) is not an ambident nucleophile, but others are



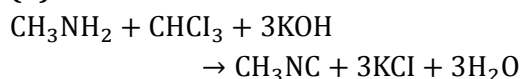
(↑) indicates nucleophilic centres.

60 (b)

Isocyanides on hydrolysis give 1° amine and HCOOH. Formic acid reduces Fehling's solution



62 (b)



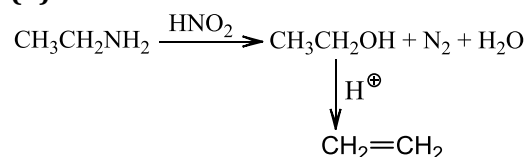
$\text{CH}_3\text{NC}$  or  $\text{CH}_3 - \text{N}^+ \equiv \text{C}^-$  methyl isocyanide or methyl carbylamine.

This reaction is an example of carbylamine reaction and it is used for the distinction of *p*-amines from *s*- and *t*-amines or identification of *p*-amino group.

63 (a)

1° amine or 1° aromatic amine containing EWG at *o*- and *p*-positions

65 (d)



Under acidic conditions, alcohol is dehydrated to alkene

66 (a,c)

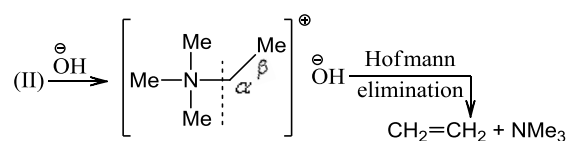
3° amines because of the absence of H-atoms, attached directly to N-atom, will not show positive Liebermann's nitroso test. Thus,  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$  being a 3° amine, does not show positive Liebermann's nitroso test

67 (a,d)

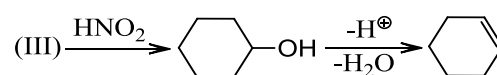
a.



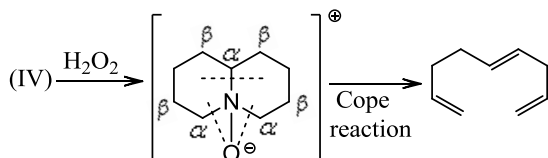
b.



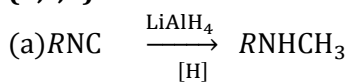
c. It is neither Cope nor Hofmann elimination reaction



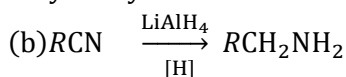
d.



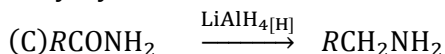
68 (b,c,d)



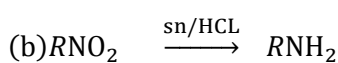
Alkyl isocyanide      2° amine



Alkyl cyanide      1° amine



Acid amide      1° amine



1° nitroalkane      1° amine

Thus, (A) can be alkyl cyanide or acid amide or 1° nitroalkane

71 (a,b,c)

Diazonium ion can be replaced by H by (a)  $H_3PO_2$  or (B)  $Na_2SnO_2$  or (c)  $C_2H_5OH$  and heat

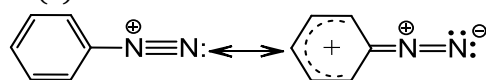
73 (a,b,c)

(d) The order of boiling points is:  $1^\circ > 2^\circ > 3^\circ$  (I > III > II)

1° amine forms more H-bonding with 2 H than 2° amine (1 H) and than 3° amine

74 (a,b,c)

(a, b, c) are correct and (b, c) are the explanations of (a)



76 (a,b,c)

1. (I) No delocalisation of LP  $\bar{e}$ 's on N and  $sp^3$

(II) Delocalisation of LP  $\bar{e}$ 's of one N atom, but no delocalisation of LP  $\bar{e}$ 's on second N

(III) No delocalisation of LP  $\bar{e}$ 's of N, but  $sp^2$

2. (I) No delocalisation of LP  $\bar{e}$ 's of N

(II) Delocalisation of LP  $\bar{e}$ 's of N by (C = O) group

3. (I) No delocalisation of LP  $\bar{e}$ 's of N

(II) Delocalisation of LP  $\bar{e}$ 's with the benzene ring

4. The order is (I) > (III) > (II)

(I) No delocalisation and  $sp^3$

(III) Delocalisation of LP  $\bar{e}$ 's of one N but no delocalisation of second N atom

LP  $\bar{e}$ 's and  $sp^2$

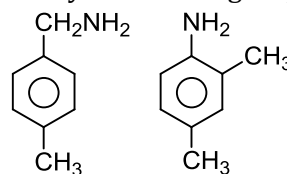
(II) Delocalisation of LP  $\bar{e}$ 's of N and  $sp^2$

77 (a,c,d)

b. The order is:  $Me_2NH > MeNH_2 > Me_3N > NH_3$  ( $2^\circ > 1^\circ > 3^\circ > NH_3$ ). Statements (a), (c), and (d) are correct

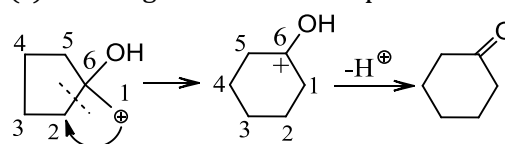
78 (b,d)

Carbylamine test is given by primary amines. Therefore, 2,4-dimethyl amine and *p*-methyl benzylamine will give positive carbylamine test



80 (c,d)

(c) The ring extension takes place



(d) It becomes optically inactive due to the formation of racemic mixture

81 (a,b,c)

(d) is incorrect, since Gabriel method is used to prepare 1° aliphatic amines

a. Reductive amination gives better yield

b. Although 2° alkyl bromide, elimination of HBr may take place; however it can be prepared by this method

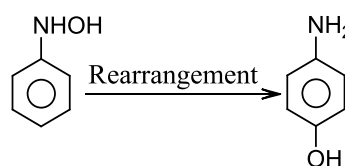
c. Azide method is also feasible since  $N_3^-$  is a good nucleophile

83 (a,b,c)

Hinsberg's method, fraction distillation and Hofmann's method all are used to separate a mixture of 1°, 2° and 3° amines while Victor Meyer's method is used to separate a mixture of 1°, 2° and 3° alcohols, instead of amines

85 (a,b)

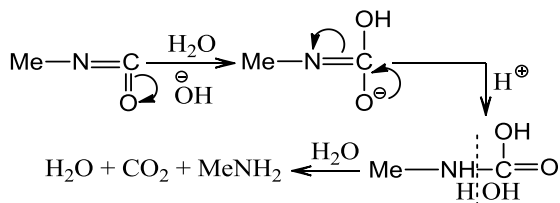
1.  $PhNH_2$



87 (a,b,c,d)

Note: In  $CH_2 = C = O$ ,  $R - C \equiv N$ ,  $R - N = C = O$ , and  $R - N = C = S$ , NA reaction occurs





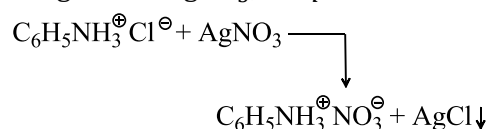
88 (b,c)

a. Ph - N = N - Ph (Azobenzene)

d. PhNHOH (Phenyl hydroxyl amine)

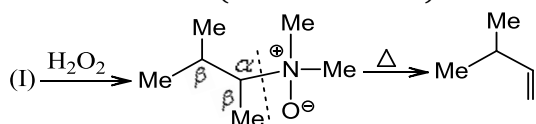
89 (c)

Anilinium hydrochloride gives a white precipitate of AgCl with AgNO<sub>3</sub>, but *p*-chloroaniline does not

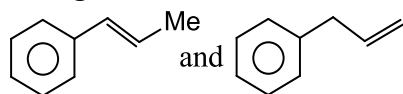


93 (a,c)

a. The oxidation of 3° amine to amine oxide followed by Cope reaction on heating gives Hofmann alkene (less substituted)



b. (II) will not give Hoffmann alkene. Benzylic H atom is more acidic due to (-I) effect of Ph. (II) would give



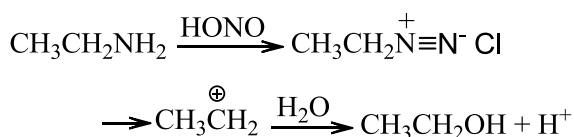
(Stability of benzyl C<sup>+</sup> Hofmann alkene)

c. (III) will give Hofmann alkene CH<sub>2</sub> = CH<sub>2</sub>

d. (IV) will not give Hofmann alkene (Cope reaction). Same explanation as in (b) above

94 (d)

When primary amines (aliphatic) react with HNO<sub>2</sub>, unstable diazonium salt is obtained which readily dissociate to give a carbocation, N<sub>2</sub> and Cl<sup>-</sup> (the leaving group). The carbocation upon hydrolysis gives alcohol



95 (b)

Correct explanation:

Aniline hydrogen sulphate on heating decomposes to aniline and H<sub>2</sub>SO<sub>4</sub>. Sulphonation of aniline with H<sub>2</sub>SO<sub>4</sub> takes place (SE reaction) at *o*- and *p*-positions, since (-NH<sub>2</sub>) group is *o*- and *p*-

directing

96 (d)

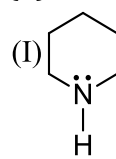
In strongly acidic medium, aniline is protonated, so LP e<sup>-</sup>'s are not available to produce mesomeric or electromeric effect; thus, aniline becomes less reactive towards SE reactions

Statement I is incorrect, but Statement II is correct

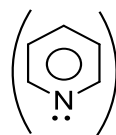
97 (a)

Alkyl group is +I showing group. In general, it increases the electron density over nitrogen, thus increase the availability of lone pair for donation. But in case of tertiary amines, in aqueous solution, the over crowding of three bulkier alkyl group result in increased strain, which decreases the availability of lone pairs for donation and thus result in decreased basicity. Hence, in aqueous solution, 3° amines are less basic as compared to 2° amine

98 (d)



(piperidine) is more basic than pyridine



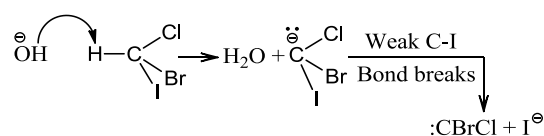
(II). Although there is no delocalisation of LP e<sup>-</sup>'s of N atom in both, but N is sp<sup>3</sup>-hybridised in (I) and sp<sup>2</sup>-hybridised in (II). So (I) is more basic than (II)

99 (a)

Hofmann bromamide degradation and Curtius degradation both involve the intramolecular alkyl shift and, thus result in the formation of 1° amines

100 (c)

The reaction takes place by the formation of (:CBrCl)



101 (a)

Both (A) and (R) are true and (R) is the correct

explanation of (A)

103 (a)

It is an example of Gomberg reaction which takes place by free radical mechanism.

104 (a)

Both (A) and (R) are true and (R) is the correct explanation of (A)

105 (c)

NH<sub>3</sub> is a stronger base than aniline; therefore, the conjugate acid of aniline (i.e., Ph N<sup>⊕</sup>H<sub>3</sub>) is more acidic than the conjugate acid of NH<sub>3</sub> (i.e., N<sup>⊕</sup>H<sub>4</sub> ion)

106 (d)

Since aniline gets protonated in strongly acidic medium, the lone pair of electrons are not available to produce mesomeric or electrometric effect. Thus, aniline becomes less reactive

108 (c)

The intermediate is acyl nitrene  $\left( \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\ddot{\text{N}}: \right)$

109 (a)

When primary amine is treated with chloroform and alkali, a very bad smelling compound, called isocyanide or carbylamine is obtained. On the basis of the name of the product, the reaction is called carbylamines reaction



1° amine chloroform alkali isocyanide

or carbylamine

112 (d)

(a→q,r) α-Amino acid on heating gives piperazine and the product exhibits three stereo-isomers (*cis* and *trans*) and *cis* is optically active

(b→p) It is also α-amino acid. It also gives piperazine on heating but this type does not give any stereoisomers since it does not have any alkyl group

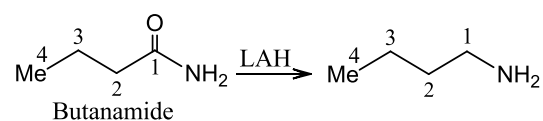
(c→s) It is γ-amino. So on heating it gives five-membered lactum

(d→t) It is δ-amino acid. So on heating it gives six-membered lactum

113 (b)

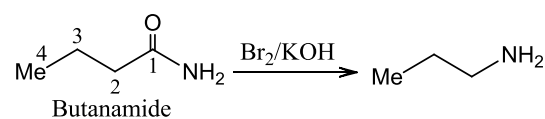
(a→q) 1° amine containing 3° alkyl group can only be prepared by Ritter reaction

(b→p,s) 1° aliphatic amine can be synthesised by Gabriel method and by reduction of amide with LAH



(c→p) 1° aromatic amine containing EWG at *o*- and *p*-positions can be synthesised by Gabriel method

(d→p,r) 1° aliphatic amine can be synthesised by Gabriel method and by Hofmann bromamide reaction of butanamide



116 (a)

(a→q,t) 1° aliphatic amine with HNO<sub>2</sub> gives alcohol and N<sub>2</sub> and also gives carbylamine test

(b→r,t) 1° aromatic amine gives dye test and also gives carbylamine test

(c→p) 2° aromatic gives N-nitroso compound with HNO<sub>2</sub>, which gives Liebermann's nitroso reaction

(d→s) 3° aromatic gives *p*-nitroso compound which is green in colour

119 (a)

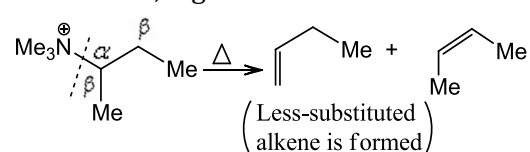
Since pK<sub>a</sub> values are given, for base the pK<sub>a</sub> values are required. Lower the pK<sub>a</sub> value, stronger is the base, or higher the pK<sub>a</sub> value (pK<sub>b</sub> = 14 - pK<sub>a</sub>) stronger is the base  
*p*-Toluidine > *m*-Toluidine > Aniline > *o*-Toluidine

pK<sub>a</sub> = 5.12            4.69            4.58            4.39

pK<sub>b</sub> = 8.88            9.31            9.42            9.61

120 (c)

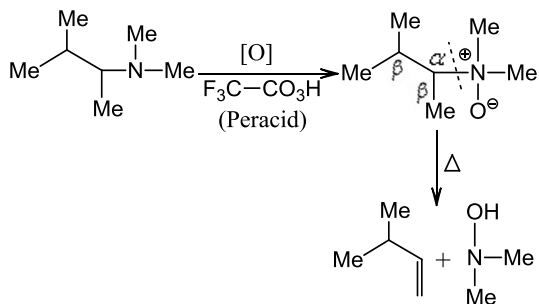
(a→q) It is an example of Hofmann exhaustive elimination, it gives less-substituted alkene



(b→q) Elimination of RF, with bulky or non-bulky base gives less-substituted alkene

(c→p) Elimination of RX (except RF) with non-bulky base gives Saytzeff alkene (more substituted) but with bulky base gives Hofmann alkene (less substituted)

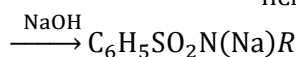
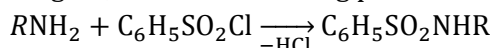
(d→r) It is an example of Cope reaction. It gives less-substituted alkene



(e→s) Same explanation as in (a) above

122 (a)

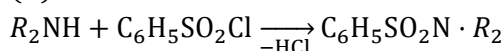
The mixture of amines when reacts with Hinsberg reagent, form the following products



Soluble in NaOH

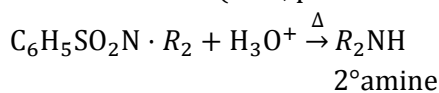
(present in NaOH layer)

(C)



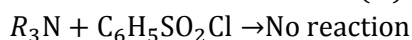
Insoluble in NaOH

(thus, present in ethereal layer)



2° amine

(D)



(thus, present in ethereal layer)

Hence,

A = N,N-dialkyl benzene sulphonamide

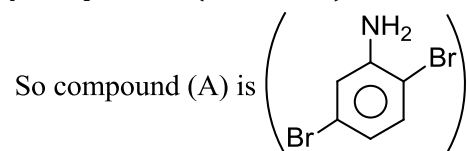
B =  $R_3N$

C = sodium salt of 1° amine (N-alkyl benzene sulphonamide)

D = 2° amine ( $R_2NH$ )

123 (a)

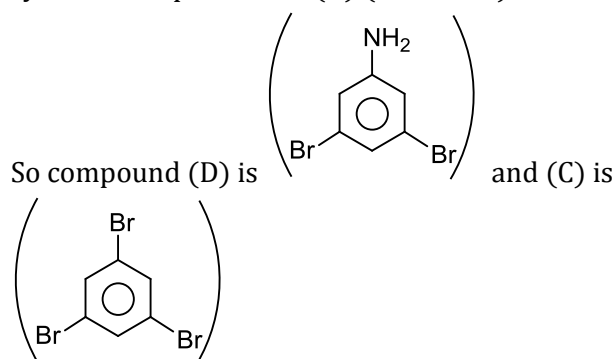
In compound (A), the ( $-NH_2$ ) group is removed and from the percentage of Br in (A), it is suggested that two (Br) groups are present in (A). The formation of one mono-nitro derivative from (B) suggests that two (Br) groups are present at *para*-position (OMP=231)



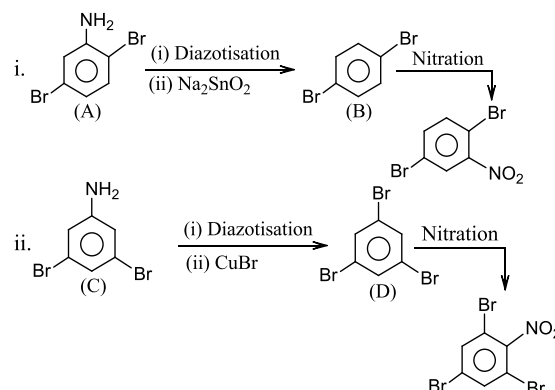
In compound (C), the ( $-NH_2$ ) group is removed and one more (Br) group is introduced in (C); this suggests that compound (D) contains three (Br) groups, which is confirmed from the percentage of Br in (D).

The formation of one mono-nitro derivative from

(D) suggests that three Br groups are present at symmetrical position in (D) (AUS=231)



Reactions:



Calculation of number of Br in (A), (B), and (D)

In (A): 100 gm of compound contains = 63.7 gm of Br

251 gm of compound contains =  $\frac{63.7 \times 251}{100}$  gm of

Br =  $\frac{63.7 \times 251}{100 \times 80}$  mol of Br = 1.99  $\approx$  2 mol Br

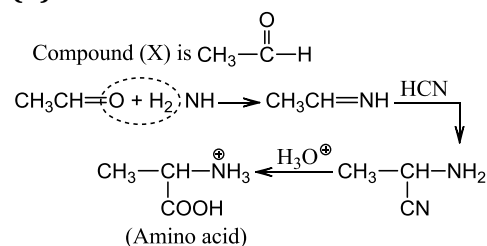
In (B): Molar mass of (B) ( $C_6H_4Br_2$ ) = 236 gm

Moles of Br in (B) =  $\frac{67.80 \times 236}{100 \times 80} \approx 2$  mol Br

In (D): Molar mass of (D) ( $C_6H_3Br_3$ ) = 315 gm

Moles of Br in (D) =  $\frac{76.4 \times 315}{100 \times 80} = 3$  mol Br

124 (b)



When partial neutralisation of alanine occurs,

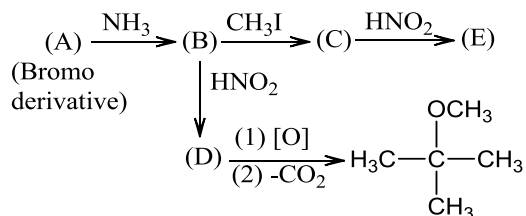
Then,  $pH = pK_a + \log \left[ \frac{[salt]}{[acid]} \right]$

[salt] = [acid]

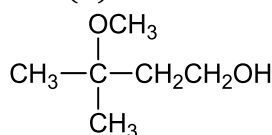
$pH_1 = pK_{a1}$  and  $pH_2 = pK_{a2}$

$\therefore pH = \frac{pK_{a1} + pK_{a2}}{2} = \frac{9.7 + 2.3}{2} = \frac{12.0}{2} = 6.0$

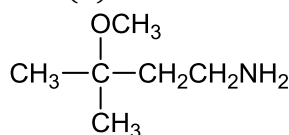
125 (a)



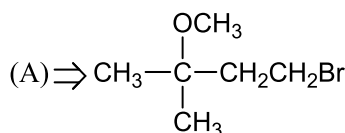
i. 2-Methoxy-2-methyl propane is obtained by the oxidation of (D) followed by decarboxylation, and thus (D) is



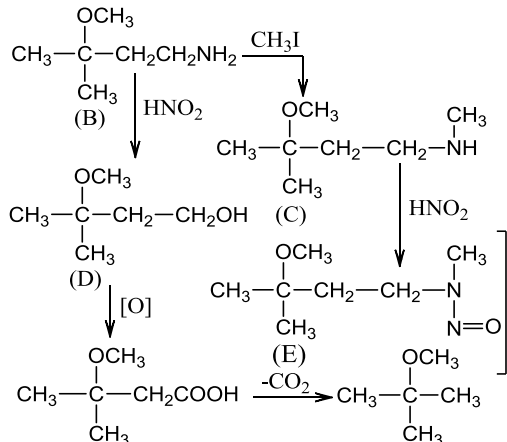
ii. (D) is formed by the action of  $\text{HNO}_2$  on (B), thus (B) is



iii. (B) is formed by the action of  $\text{NH}_3$  over (A), a bromoderivative



Reactions:



### 126 (a)

Let the formula of amines be  $\text{RNH}_2$  and that of the

hydrochloride be  $\overset{\oplus}{\text{R}}\overset{\ominus}{\text{NH}_3}\text{Cl}$  Let the weight of  $\overset{\oplus}{\text{R}}\overset{\ominus}{\text{NH}_3}\text{Cl}$  be  $x$  gm

$\therefore x$  gm of  $\overset{\oplus}{\text{R}}\overset{\ominus}{\text{NH}_3}\text{Cl}$  contains  $\Rightarrow 35$  gm of Cl

100 gm of  $\overset{\oplus}{\text{R}}\overset{\ominus}{\text{NH}_3}\text{Cl} \Rightarrow \frac{35.5}{x} \times 100 = 32.42$

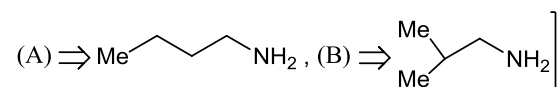
$\therefore x = 109.5 \quad \therefore \overset{\oplus}{\text{R}}\overset{\ominus}{\text{NH}_3}\text{Cl}$

Let the weight of R =  $y$

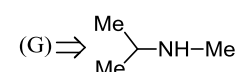
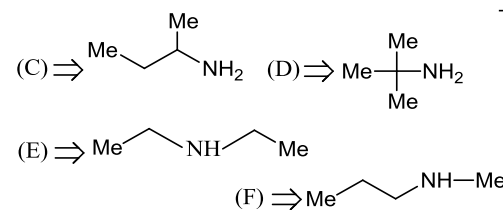
$\therefore y + 17 + 35.5 = 109.5$

$y = 57$ ; R can be  $\text{C}_4\text{H}_9$

Formula is  $\text{C}_4\text{H}_9\overset{\oplus}{\text{NH}_3}\overset{\ominus}{\text{Cl}}$



(A), (B), (C), and (D) are  $1^\circ$  aliphatic amines and they give alcohol and  $\text{N}_2$ , on treatment with  $\text{NaNNO}_2/\text{acid}$ , and also form hydrochloride



(E), (F), and (G) are  $2^\circ$  aliphatic amines and they do not give  $\text{N}_2$  gas but form hydrochloride salt

### 127 (b)

Percentage of N = ?

$$\text{Total acid} = 50 \times \frac{1}{10} = 5 \text{ mEq}$$

$$\text{Excess acid} = 30 \times \frac{1}{10} = 3 \text{ mEq}$$

$$\text{Acid used} = 5 - 3 = 2 \text{ mEq}$$

$$\text{Percentage of N} = \frac{1.4 \times \text{mEq. of acid used}}{\text{Weight of compound}}$$

$$= \frac{1.4 \times 2}{0.116} = 24.38\%$$

$$\text{C} = 41.37\% \quad \text{H} = 6.89\% \quad \text{N} = 24.38\%$$

$$\text{O} = 100 - (41.37 + 6.89 + 24.38) = 27.36$$

$$\text{Formula} = \text{C}_4\text{H}_8\text{O}_2\text{N}_2; \text{ degree of unsaturation} = 2^\circ$$

