27 Amines

1. The conversion of benzene diazonium chloride to bromobenzene can be accomplished by
(a) Reimer-Tiemann reaction
(b) Friedel-Crafts reaction
(c) Gattermann reaction
(d) Azo-Coupling reaction

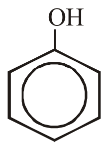
2. C_7H_9N has how many isomeric forms that contain a benzene ring? **Critical Thinking**
(a) 4 (b) 5 (c) 6 (d) 7

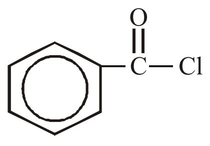
3. The amine that does not react with acetyl chloride is
(a) CH_3NH_2 (b) $(CH_3)_2NH$
(c) $(CH_3)_3N$ (d) None of these

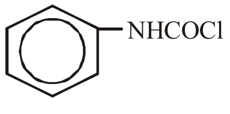
4. In the diazotisation of arylamines with sodium nitrite and hydrochloric acid, an excess of hydrochloric acid is used primarily to
(a) supress the concentration of free aniline available for coupling
(b) supress hydrolysis of phenol
(c) ensure a stoichiometric amount of nitrous acid
(d) neutralise the base liberated

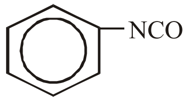
5. Nitrosoamines ($R_2N - N = O$) are insoluble in water. On heating with conc. H_2SO_4, they give secondary amines. The reaction is called
(a) Liebermann nitroso reaction
(b) Etard reaction
(c) Fries reaction
(d) Perkin reaction

6. Aniline reacts with phosgene and KOH to form

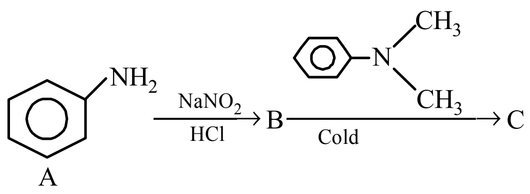
(a) 

(b) 

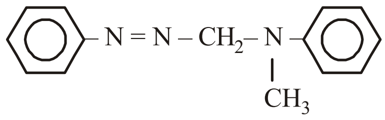
(c) 

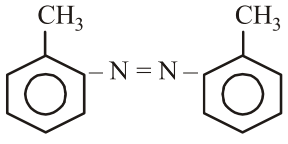
(d) 

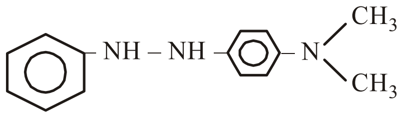
7. In a reaction of aniline a coloured product C was obtained.

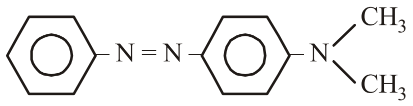


The structure of C would be :

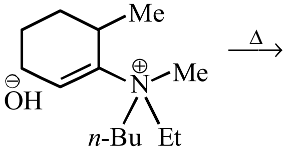
(a) 

(b) 

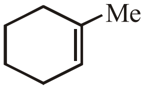
(c) 

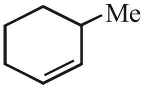
(d) 

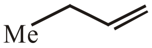
8. Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water during the reaction is continuously removed. The compound formed is generally known as **Critical Thinking**
(a) an amine (b) an imine
(c) an enamine (d) a Schiff's base

9. 

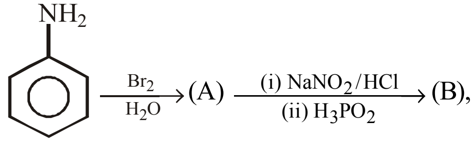
The alkene formed as a major product in the above elimination reaction is

(a) 

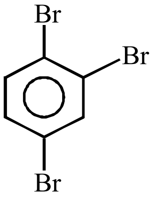
(b) 

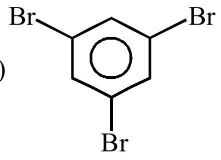
(c) 

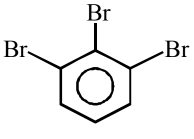
(d) $CH_2 = CH_2$

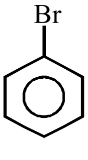
10. 

Product (B) in this reaction is:

(a) 

(b) 

(c) 

(d) 

11. *p*-Chloroaniline and anilinium hydrogen chloride can be distinguished by:

(a) Sandmeyer reaction
(b) Carbylamine reaction
(c) Hinsberg's reaction
(d) $AgNO_3$

12. Consider the following sequence of reactions :

$$\text{Compound}[A]\xrightarrow{\text{Reduction}}[B]\xrightarrow{HNO_2}CH_3CH_2OH$$

The compound [A] is

(a) CH_3CH_2CN (b) CH_3NO_2
(c) CH_3NC (d) CH_3CN

13. What will be the final product in the following reaction sequence?

$$CH_3CH_2CN\xrightarrow{H\ \ /H_2O}A\xrightarrow[\Delta]{NH_3}B\xrightarrow{NaOBr}C$$

(a) $CH_3CH_2CONH_2$ (b) CH_3CH_2COBr
(c) $CH_3CH_2NH_2$ (d) $CH_3CH_2CH_2NH_2$

14. $CH_3 - CH_2C \equiv N \xrightarrow{X} CH_3CH_2CHO.$

The compound X is

(a) $SnCl_2 / HCl / H_2O$, boil
(b) $H_2 / Pd - BaSO_4$
(c) $LiAlH_4$ / ether
(d) $NaBH_4$ / ether / H_3O^+

15. Tautomerism will be exhibited by

(a) $(CH_3)_3CNO$ (b) $(CH_3)_2NH$
(c) R_3CNO_2 (d) RCH_2NO_2

16. Hydrolysis of $CH_3CH_2NO_2$ with 85% H_2SO_4 gives

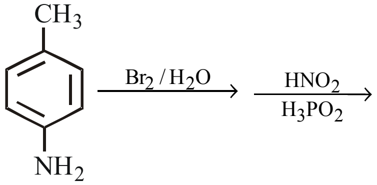
(a) CH_3CH_2OH (b) C_2H_6
(c) $CH_3CH\ \ NOH$ (d) CH_3COOH

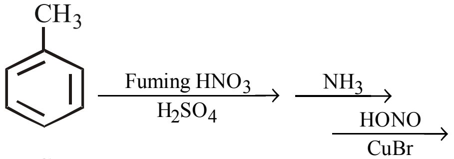
17. Towards electrophilic substitution, the most reactive will be

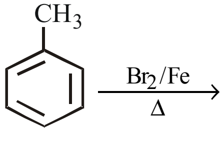
Critical Thinking

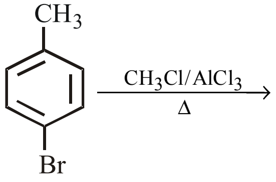
(a) Nitrobenzene
(b) Aniline
(c) Aniline hydrochloride
(d) N-Acetylaniline

18. 3, 5-dibromotoluene can be best synthesised by

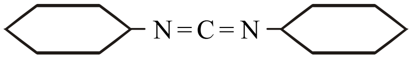
(a) 

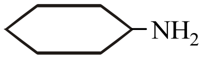
(b) 

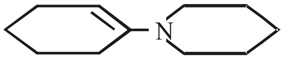
(c) 

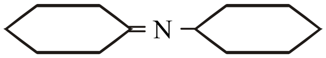
(d) 

19. Which of the following compounds is an enamine?

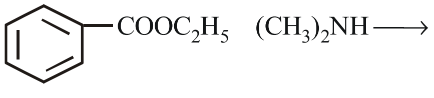
(a) 

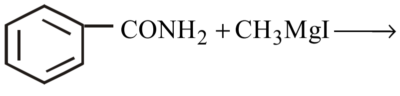
(b) 

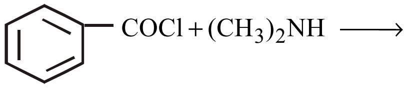
(c) 

(d) 

20. Which of the following reactions will not give N, N- dimethyl benzamide ?

(a) 

(b) 

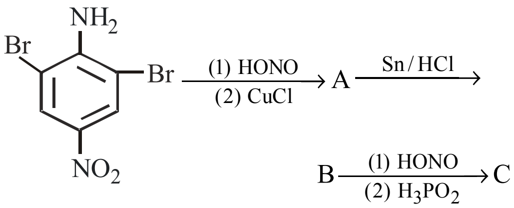
(c) 

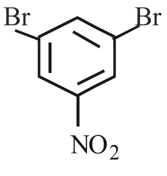
(d) 

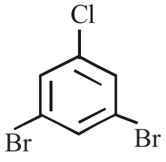
$(CH_3)_2NH \longrightarrow$

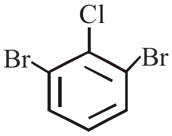
21. The product – (C) obtained in the following sequence of reactions is

Toughnut



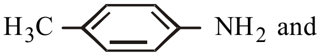
(a) 

(b) 

(c) 

(d) None of these

22. Which of the following reagents will be useful to distinguish between



and

?

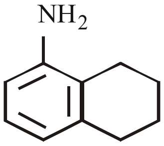
(a) Dilute HCl

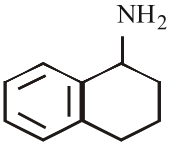
(b) $C_6H_5SO_2$ and OH^-/H_2O

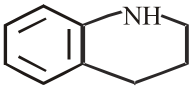
(c) HONO then β-naphthol

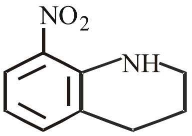
(d) $AgNO_3$ in H_2O

23. Which of the following is the strongest base ?

(a) 

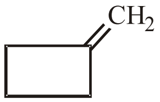
(b) 

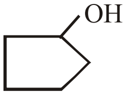
(c) 

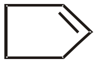
(c) 

24. The cyclobutyl methylamine with nitrous acid gives

Toughnut

(a) 

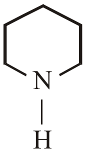
(b) 

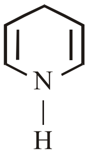
(c) 

(d) All of these

25. Which of the following amines will react with cyclohexanone to give enamine ?

(a) $(CH_3)_2NH$

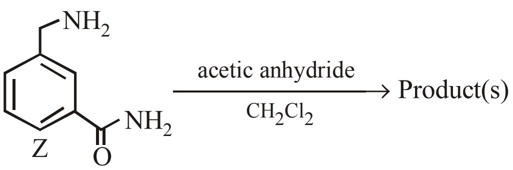
(b) 

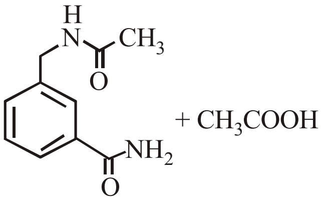
(c) 

(d) All of these

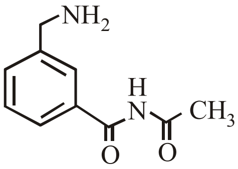
26. In the reaction shown below, the major product(s) formed is/are

Toughnut

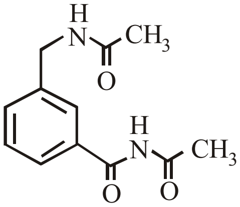


(a)


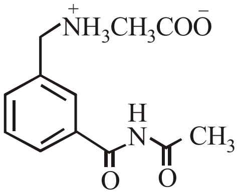
+ CH_3COOH

(b)


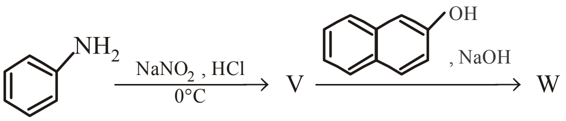
+ CH_3COOH

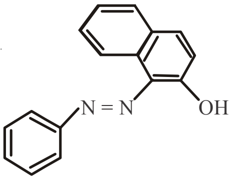
(c)


+ H_2O

(d)


27. In the following reactions, the major product W is



(a)


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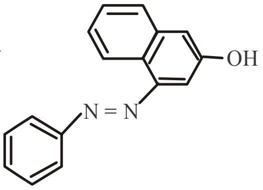

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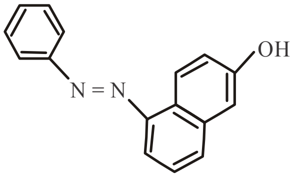

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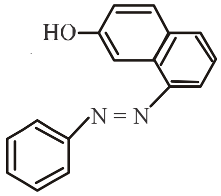
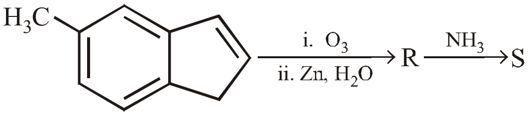
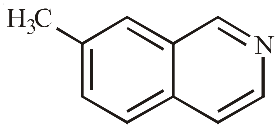


28. In the following reactions, the product S is



Tricky

(a)


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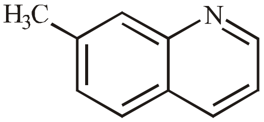

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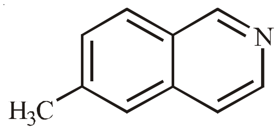

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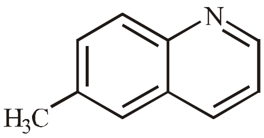


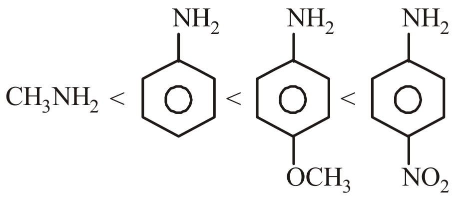
29. In the reaction,

$CH_3CN \quad 2H \longrightarrow X \xrightarrow{\text{Boiling } H_2O} Y$, the term Y is

(a) acetone (b) ethanamine
(c) acetaldehyde (d) dimethylamine

30. In the reaction $C_6H_5NH_2 \quad CS_2 \xrightarrow[\Delta]{HgCl_2}$ the product obtained is
(a) phenyl isocyanide
(b) phenyl cyanide
(c) *p*-amino benzene sulphonic acid
(d) phenyl isothiocyanate

31. Arrange the following amines in the order of increasing basicity.

(a)


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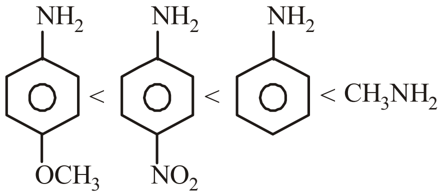
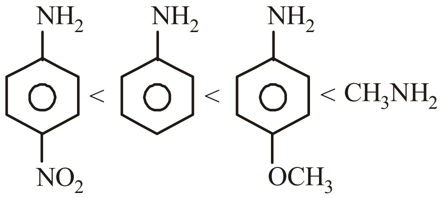


(c)


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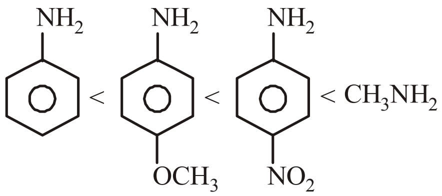


32. The final product formed when Methyl amine is treated with $NaNO_2$ and HCl is:
(a) Diazomethane (b) Methylalcohol
(c) Methylcyanide (d) Nitromethane

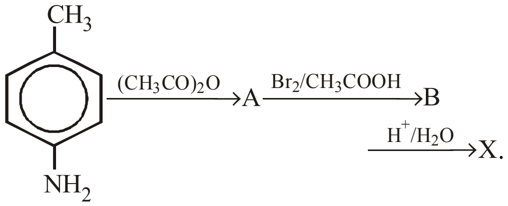
33. The order of basicity of amines in gaseous state is :
(a) $1° > 2° > 3° > NH_3$ (b) $3° > 2° > NH_3 > 1°$
(c) $3° > 2° > 1° > NH_3$ (d) $NH_3 > 1° > 2° > 3°$

34. Carbylamine forms from aliphatic or aromatic primary amine via which of the following intermediates ?
(a) Carbanion (b) Carbene
(c) Carbocation (d) Carbon radical

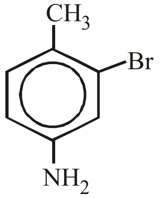
35. The most basic compound among the following is
(a) Acetanilide (b) Benzylamine
(c) *p*-Nitro aniline (d) Aniline

36. Which of the following compounds gives dye test?
(a) Aniline (b) Methylamine
(c) Diphenylamine (d) Ethylamine

37. Acetanilide on nitration followed by alkaline hydrolysis mainly gives
(a) *o*-Nitroacetanilide
(b) *p*-Nitroaniline
(c) *m*-Nitroaniline
(d) 2, 4, 6-Trinitroaniline

38.


What is X? Toughnut

(a)


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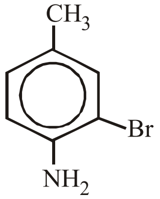

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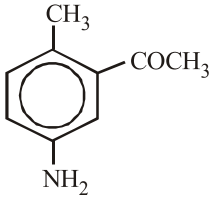

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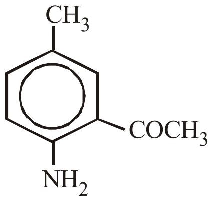
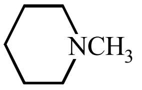


39. Which reaction sequence would be best to prepare 3-chloroanilne from benzene ?
(a) Chlorination, nitration, reduction
(b) Nitration, chlorination, reduction
(c) Nitration, reduction, chlorination
(d) Nitration, reduction, acetylation, chlorination, hydrolysis

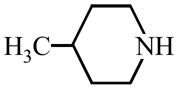
40. A compound 'A' when treated with HNO_3 (in presence of H_2SO_4) gives compound 'B', which is then reduced with Sn and HCl to aniline? The compound 'A' is
(a) toluene (b) benzene
(c) ethane (d) acetamide

41. An organic compound (A) on reduction gives compound (B). (B) on treatment with $CHCl_3$ and alcoholic KOH gives (C). (C) on catalytic reduction gives N-methylaniline. The compound A is
(a) Methylamine (b) Nitromethane
(c) Aniline (d) Nitrobenzene

42. Predict about the relative boiling point of the following two amines.

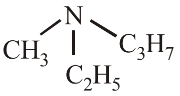

I

;


II

(a) Boiling point of I > II
(b) Boiling point of II > I
(c) Both should have equal boiling points
(d) It can't be predicted

43. Which statement is true regarding the following structure?



(a) It is a chiral molecule
(b) It exists in two resolvable optically active forms
(c) Both (a) and (b)
(d) Neither (a) nor (b)

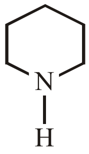
44. Which one of the following is not an oxidation product of a primary amine?
(a) A hydroxylamine
(b) A nitroso compound
(c) A nitro compound
(d) All of these

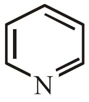
45. Identify Z in the following sequence of reactions–

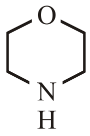
$$CH_3COONH_4 \xrightarrow{\Delta} X \xrightarrow{P_2O_5} Y \xrightarrow{H_2O/H} Z$$

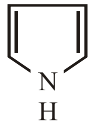
(a) $CH_3-CH_2-CO-NH_2$
(b) CH_3-CN
(c) $(CH_3CO)_2O$
(d) CH_3-COOH

46. The order of basicity of the compounds


(I)


(II)


(III)


(IV)

is

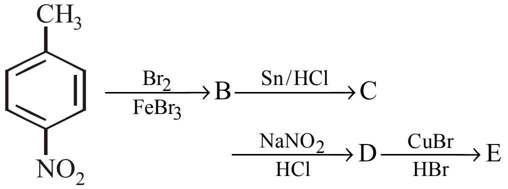
Toughnut

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

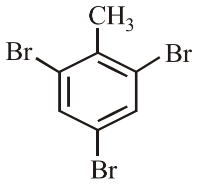
47. Complete reduction of benzene-diazonium chloride with Zn/HCl gives:
(a) Aniline (b) Phenylhydrazine
(c) Azobenzene (d) Hydrazobenzene

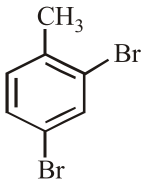
48. Conversion of benzene diazonium chloride to chlorobenzene is an example of which of the following reactions?
(a) Claisen (b) Friedel-craft
(c) Sandmeyer (d) Wurtz

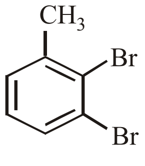
49. In a set of reactions *p*-nitrotoluene yielded a product E. **Toughnut**

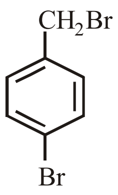


The product E would be:

(a)


(b)


(c)


(d)


50. Which of the following will produce isopropyl amine –

Tricky

(I) $(CH_3)_2CO \xrightarrow{NH_2OH} X \xrightarrow{LiAlH_4}$

(II) $CH_3-CH_2-CHO \xrightarrow[heat]{NH_3} X \xrightarrow{LiAlH_4}$

(III) $(CH_3)_2CH-OH + PCl_5 \longrightarrow X \xrightarrow{NH_3}$

(IV) $CH_3-CH_2-CH_2-NH_2 \xrightarrow{heat}$

(a) I, II (b) II, III

(c) I, III (d) IV only

51. Acetaldoxime reacts with P_2O_5 to give

(a) Methyl cyanide (b) Methyl cyanate

(c) Ethyl cyanide (d) None of these

52. Identify the prdouct C in the series

$$CH_3CN \xrightarrow{Na/C_2H_5OH} A \xrightarrow{HNO_2} B \xrightarrow{Cu/573K} C$$

(a) CH_3COOH (b) CH_3CH_2NHOH

(c) CH_3CONH_2 (d) CH_3CHO

53. An organic compound 'A' having molecular formula C_2H_3N on reduction gave another compound 'B'. Upon treatment with nitrous acid, 'B' gave ethyl alcohol. On warming with chloroform and alcoholic KOH, B formed an offensive smelling compound 'C'. The compound 'C' is

Critical Thinking

(a) $CH_3CH_2NH_2$ (b) $CH_3CH_2N^{\rightarrow}C$

(c) $CH_3C \equiv N$ (d) CH_2CH_2OH

54. Ethyl isocyanide on hydrolysis in acidic medium generates

(a) propanoic acid and ammonium salt

(b) ethanoic acid and ammonium salt

(c) methylamine salt and ethanoic acid

(d) ethylamine salt and methanoic acid

55. Primary nitro compounds react with nitrous acid to form nitrolic acids which dissolve in NaOH giving

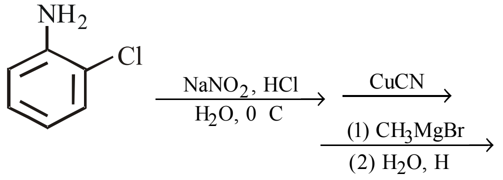
(a) yellow solution

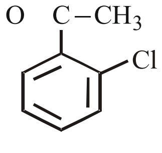
(b) blue solution

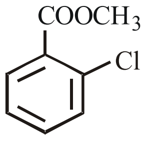
(c) colourless solution

(d) red solution

56. What is the product of the following series of reactions?



(a)


(b)


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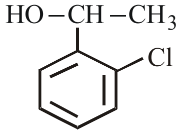

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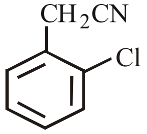
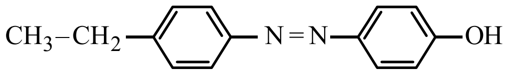
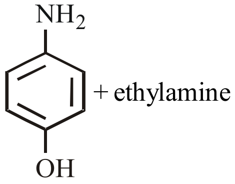


57. The starting reagents needed to make the azo compound shown below



(a)


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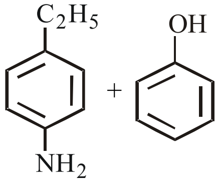

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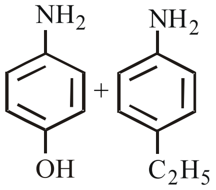

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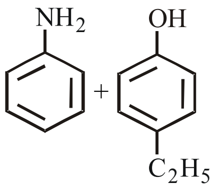

58. Which of the following does not give N–ethyl cyclopentylamine as major product ?

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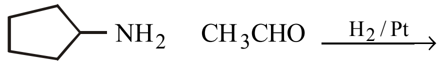
(a)


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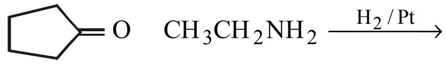

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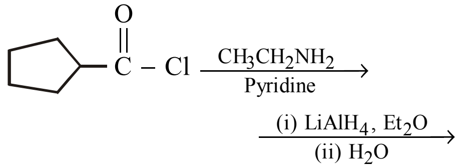

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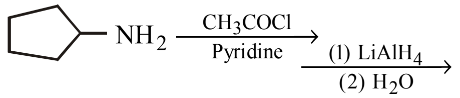


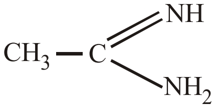
59. Match the compounds in List I with their nature from List II, as seen in aqueous medium

	List I		**List II**
I.	Acetamide	A.	Acidic
II.	Benzonitrile	B.	Basic
III.	Triethylamine	C.	Neutral
IV.	Phenol		

(a) I–C; II–C; III–B; IV–A
(b) I–B; II–C; III–C; IV–A
(c) I–C; II–B; III–B; IV–C
(d) I–A; II–A; III–C; IV–B

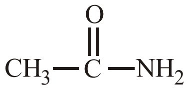
60. The correct order of basicities of the following compounds is

Critical Thinking


1

$CH_3-CH_2-NH_2$
2

$(CH_3)_2NH$
3


$CH_3-\overset{\overset{O}{\|}}{C}-NH_2$
4

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

61. In the following reaction, X is

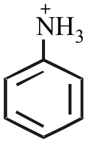
$$X \xrightarrow{\text{Bromination}} Y \xrightarrow{NaNO_2/HCl} Z \xrightarrow[C_2H_5OH]{\text{Boiling}} \text{Tribromobenzene}$$

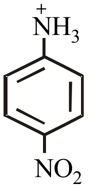
(a) benzoic acid
(b) salicylic acid
(c) phenol
(d) aniline

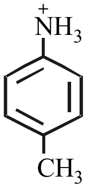
62. Aniline is reacted with bromine water and the resulting product is treated with an aqueous solution of sodium nitrite in presence of dilute HCl. The compound so formed is converted into tetrafluoroborate which is subsequently heated dry. The final product is

(a) *p*-Bromofluorobenzene
(b) *p*-Bromoaniline
(c) 2, 4, 6-Tribromofluorobenzene
(d) 1, 3, 5-Tribromobenzene

63. Arrange the following three compounds in order of decreasing acidity

(A)


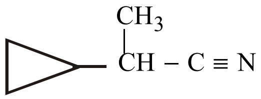
(B)


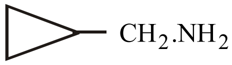
(C)


(a) B>A> C
(b) B>C>A
(c) C>B> A
(d) C>A>B

64. In the reaction

the products obtained are

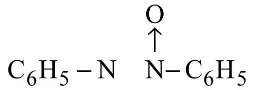
(a)


(b)


(c)

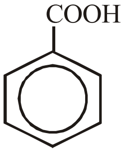

(d) None of these

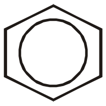
65. In the acidic reduction of nitrobenzene, which of the following is the intermediate?

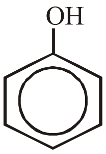
(a) $C_6H_5-N\quad O$
(b) $C_6H_5NH-NHC_6H_5$
(c) $C_6H_5-N\quad N-C_6H_5$
(d)

$C_6H_5-N\quad \overset{\overset{O}{\uparrow}}{N}-C_6H_5$

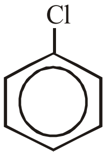
66. 'Z' in the following sequence of reactions is

$$C_6H_6 \xrightarrow[\Delta]{HNO_3/H_2SO_4} W \xrightarrow{Zn/HCl}$$
$$X \xrightarrow[HCl]{NaNO_2} Y \xrightarrow{H_2O/H_3PO_2} Z$$

(a) 

(b) 

(c) 

(d) 

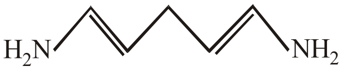
67. An organic compound (A) on reduction gives compound (B). (B) on treatment with $CHCl_3$ and alcoholic KOH gives (C). (C) on catalytic reduction gives N-methylaniline. The compound A is

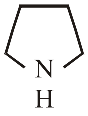
(a) Methylamine (b) Nitromethane

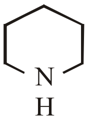
(c) Aniline (d) Nitrobenzene

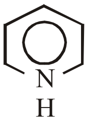
68. 

Z; Z is

(a) 

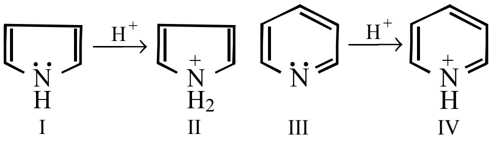
(b) 

(c) 

(d) 

69. Pyrrole and pyridine both are basic and form salts with acids?

Tricky



Which of the following statement is true regarding the aromatic character of the four species?

(a) All the four are aromatic

(b) I, III and IV are aromatic

(c) I, II and III are aromatic

(d) I and III are aromatic

70. Ethylene can be prepared in good yield by

(a) $CH_3CH_2N^+(CH_3)_3I^- \xrightarrow{heat} CH_2 = CH_2 + (CH_3)_3N + HI$

(b) $CH_3CH_2N^+(CH_3)_3OH^- \xrightarrow{heat} CH_2 = CH_2 + (CH_3)_3N + H_2O$

(c) Both (a) and (b)

(d) $CH_3CH_2NH_2 \xrightarrow{heat} CH_2 = CH_2 + NH_3$

71. Which of the following leads to carbon-carbon double bond?

(a) 1° Amine + RCHO →

(b) 2° Amine + R_2CO →

(c) 2° Amine + RCHO →

(d) Both (b) and (c)

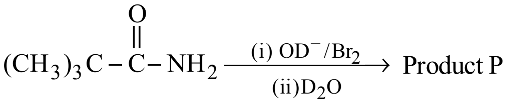
72. In Hofmann bromamide degradation, one of the important steps is the migration of

(a) an alkyl group without its electron pair to electron deficient N atom.

(b) an alkyl group with its electron pair to electron deficient O atom.

(c) an alkyl group with its electron pair to electron rich N atom.

(d) an alkyl group with its electron pair to electron deficient N atom.

73. 

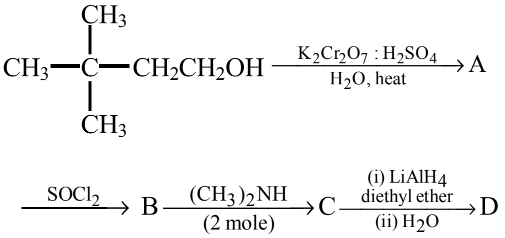
$$(CH_3)_3C-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[(ii)D_2O]{(i)\ OD^-/Br_2} \text{Product P}$$

is

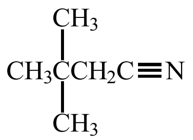
(a) $(CH_3)_3CNH_2$ (b) $(CH_3)_3CNHD$

(c) $(CH_3)_3CND_2$ (d) no reaction

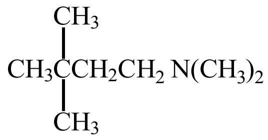
74. Identify product D in the following reaction sequence: **Tricky**



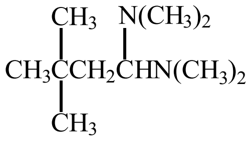
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2CH_2OH \xrightarrow[H_2O,\ heat]{K_2Cr_2O_7 : H_2SO_4} A \xrightarrow{SOCl_2} B \xrightarrow[(2\ mole)]{(CH_3)_2NH} C \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4\ \text{diethyl ether}} D$$

(a) 

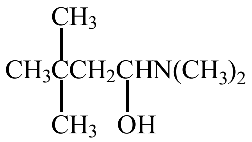
$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2C\equiv N$

(b) 

$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2\ N(CH_3)_2$

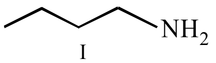
(c) 

$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\overset{N(CH_3)_2}{C}HN(CH_3)_2$

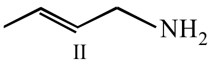
(d) 

$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\underset{OH}{C}HN(CH_3)_2$

75. The correct order of decreasing basic character of the three aliphatic primary amines is



I



II

III

(a) I > II > III (b) III > II > I

(c) I > II ≈ III (d) I = II ≡ III

76. Which of the following can undergo electrophilic substitution when treated with nitrous acid at 0°C?

(a) $C_6H_5NH_2$ (b) $C_6H_5NHCH_3$

(c) $C_6H_5N(CH_3)_2$ (d) None

77. When aniline reacts with oil of bitter almonds (C_6H_5CHO) condensation takes place and benzal derivative is formed. This is known as

(a) Million's base (b) Schiff's reagent

(c) Schiff's base (d) Benedict's reagent

78. The correct stability order of the following resonance structures is **Critical Thinking**

$H_2C = \overset{+}{N} = \overset{-}{N}$ (I)

$H_2\overset{+}{C} - N = \overset{-}{N}$ (II)

$H_2\overset{-}{C} - \overset{+}{N} \equiv N$ (III)

$H_2\overset{-}{C} - N = \overset{+}{N}$ (IV)

(a) (I) > (II) > (IV) > (III)

(b) (I) > (III) > (II) > (IV)

(c) (II) > (I) > (III) > (IV)

(d) (III) > (I) > (IV) > (II)

79. Introduction of a methyl group in ammonia markedly increases the basic strength of ammonia in aq. solution, introduction of the second methyl group increases only marginally the basic strength of methyl amine in water. This is due to

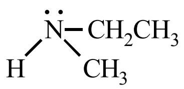
(a) different type of hybridisation in the two amines.

(b) protonated dimethyl amine is more solvated than methyl amine.

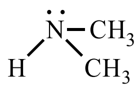
(c) protonated dimethyl amine is more solvated than the protonated methyl amine.

(d) protonated dimethyl amine is less stable than the protonated methyl amine.

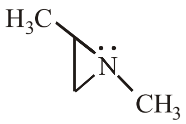
80. Which of the following amines can be resolved into two enantiomers? **Critical Thinking**



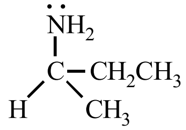
I



II



III



IV

(a) I, IV (b) I, II

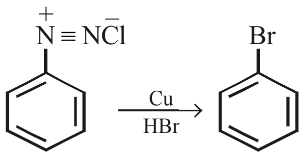
(c) I, III, IV (d) III, IV

Answer KEYs

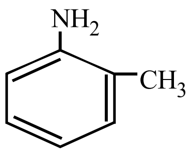
1	(c)	**9**	(d)	**17**	(b)	**25**	(d)	**33**	(c)	**41**	(d)	**49**	(b)	**57**	(b)	**65**	(a)	**73**	(c)
2	(b)	**10**	(b)	**18**	(a)	**26**	(a)	**34**	(b)	**42**	(b)	**50**	(c)	**58**	(c)	**66**	(b)	**74**	(b)
3	(c)	**11**	(d)	**19**	(c)	**27**	(a)	**35**	(b)	**43**	(a)	**51**	(a)	**59**	(a)	**67**	(d)	**75**	(a)
4	(a)	**12**	(d)	**20**	(b)	**28**	(a)	**36**	(a)	**44**	(d)	**52**	(d)	**60**	(b)	**68**	(c)	**76**	(c)
5	(a)	**13**	(c)	**21**	(c)	**29**	(c)	**37**	(b)	**45**	(d)	**53**	(b)	**61**	(d)	**69**	(b)	**77**	(c)
6	(d)	**14**	(a)	**22**	(c)	**30**	(d)	**38**	(b)	**46**	(b)	**54**	(d)	**62**	(c)	**70**	(b)	**78**	(b)
7	(d)	**15**	(d)	**23**	(b)	**31**	(c)	**39**	(b)	**47**	(a)	**55**	(d)	**63**	(a)	**71**	(d)	**79**	(d)
8	(c)	**16**	(d)	**24**	(d)	**32**	(b)	**40**	(b)	**48**	(c)	**56**	(a)	**64**	(a)	**72**	(d)	**80**	(d)

Hints & Solutions

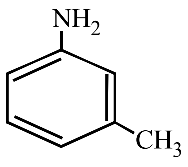
1. **(c)** Diazonium salts react with copper powder and hydrogen bromide to form bromobenzene. This reaction is known as **Gattermann reaction.**



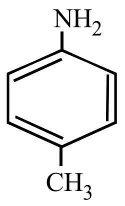
2. **(b)** C_7H_9N having one benzene ring may be represented as $C_6H_5CH_4N$, may be in the form of 1° and 2° amines in the following five isomeric forms.



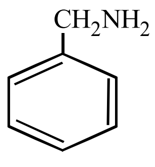
(I)



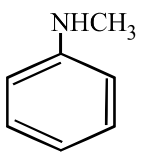
(II)



(III)



(IV)



(V)

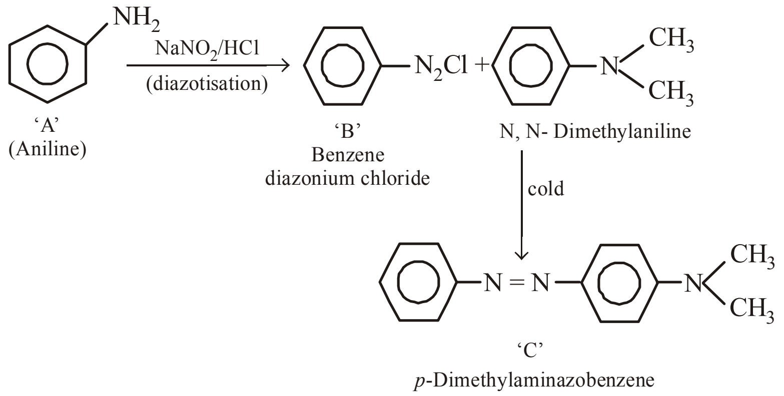
3. **(c)** The compounds containing active H-atoms (H atoms attached to N, O or S) react with CH_3COCl to form acetyl derivatives.

4. **(a)** Excess of HCl is used to convert free aniline to aniline hydrochloride otherwise free aniline would undergo coupling reaction with benzenediazonium chloride.

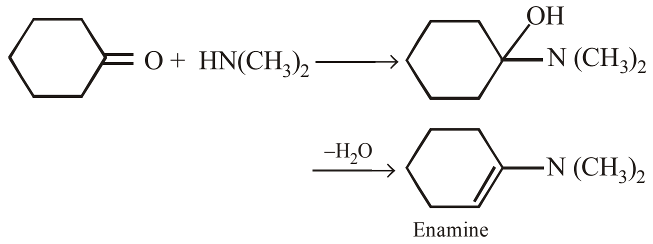
5. **(a)** $R_2NNO \quad H_2O \rightarrow R_2NH \quad HNO_2$

6. **(d)** $C_6H_5NH_2 \quad COCl_2 \quad KOH \rightarrow C_6H_5NH.COCl \quad HCl \xrightarrow{\Delta} C_6H_5NCO \quad HCl$

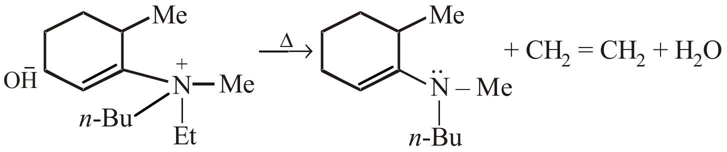
7. **(d)** The reaction can be completed as follows:



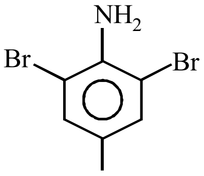
8. **(c)**



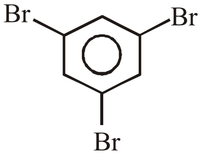
9. **(d)** **Hofmann's rule :** When theoretically more than one type of alkenes are possible, the alkene containing least alkylated double bond is formed. Hence



10. **(b)** (A)



(B)



11. **(d)** *p*-Chloroaniline and anilinium hydrogen chloride can be distinguished by $AgNO_3$. Anilinium hydrogen chloride will give white ppt of AgCl on reaction with $AgNO_3$, but *p*-chloronoaniline will not react with it because Cl is directly attached to benzene nucleus.

12. **(d)** $\underset{(A)}{CH_3CN} \xrightarrow{\text{Reduction}} \underset{(B)}{CH_3 - CH_2 - NH_2} \xrightarrow{\text{HONO}} CH_3CH_2OH$

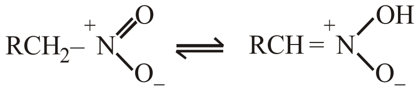
13. **(c)** $CH_3CH_2CN \xrightarrow{H\ /H_2O} \underset{(A)}{CH_3CH_2COOH} \xrightarrow[\Delta]{NH_3}$

$$\underset{(B)}{CH_3CH_2CONH_2} \xrightarrow[NaOBr]{\text{Hoffmann bromamide reaction}} \underset{(C)}{CH_3CH_2NH_2}$$

14. **(a)** It is Stephen's reaction.

$$CH_3CH_2C \equiv N \xrightarrow{SnCl_2/HCl} CH_3CH_2CH = NH.HCl \xrightarrow{H_2O} CH_3CH_2CHO + NH_4Cl$$

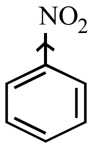
15. **(d)** Nitro compounds having α-hydrogen show tautomerism

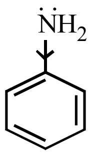


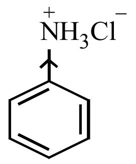
16. **(d)** 1° Nitroalkanes on hydrolysis with boiling 85% H_2SO_4 give acids.

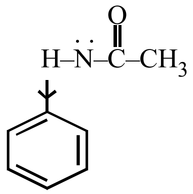
$$CH_3CH_2NO_2 \quad H_2O \quad H_2SO_4 \xrightarrow{heat} CH_3COOH \quad [NH_3OH] \quad HSO_4^-$$

17. **(b)**


Nitrobenzene

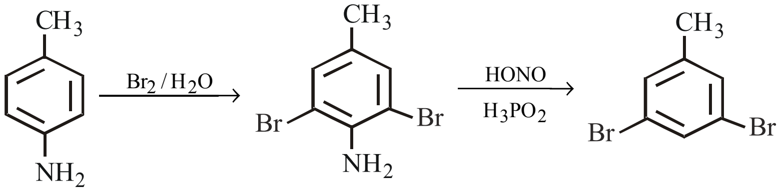

Aniline


Aniline hydrochloride


N- Acetylaniline

Nitrobenzene and aniline hydrochloride have electron- withdrawing (–NO_2 and – NH_3) groups, hence these will undergo electrophilic substitution with difficulty. Aniline and N– acetylaniline (acetanilide) have electron– releasing groups, however –$NHCOCH_3$ is less electron- releasing than – NH_2 due to delocalisation of lone pair of electron on N toward carbonyl group. Hence aniline (having – NH_2) will undergo electrophilic substitution most easily.

18. **(a)**



19. **(c)** Enamine (ene for carbon-carbon double bond and amine for amine group). $>C = C - N<$

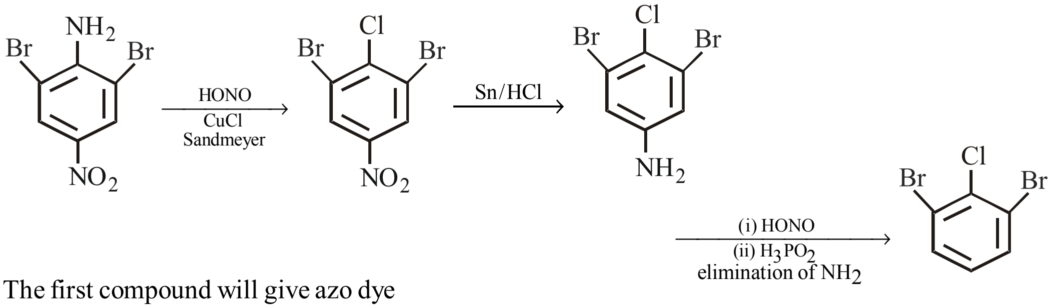
20. **(b)** (a) $C_6H_5COOC_2H_5 + (CH_3)_2NH \rightarrow C_6H_5CON(CH_3)_2 + C_2H_5OH$

(b) $C_6H_5CONH_2 + CH_3MgI \rightarrow C_6H_5CO\,NHMgI + CH_4$

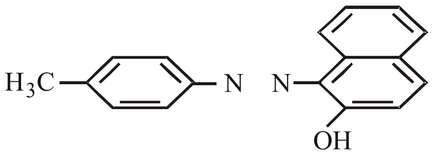
(c) $C_6H_5COCl + (CH_3)_2NH \rightarrow C_6H_5CON(CH_3)_2 + HCl$

(d) $C_6H_5CO.O.COC_6H_5 + (CH_3)_2NH \rightarrow C_6H_5CON(CH_3)_2 + C_6H_5COOH$

21. **(c)**

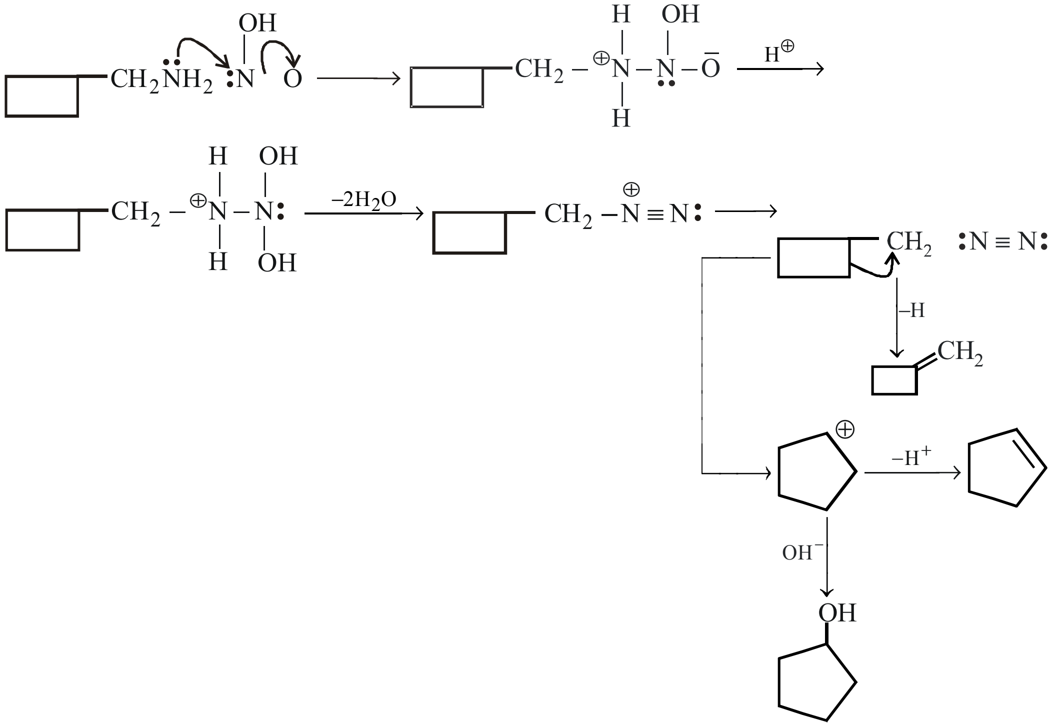


22. **(c)** The first compound will give azo dye

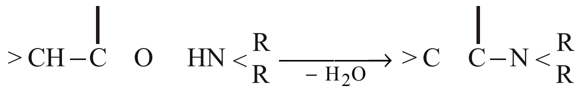


23. **(b)** Aliphatic amines are stronger base than aromatic amines. Further the order 2° > 1° > 3° > NH_3

24. **(d)**

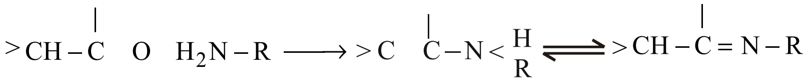


25. **(d)** Carbonyl compounds containing at least one α-hydrogen atom react with a secondary amine to give enamine



$$>CH-\overset{|}{C}\quad O\quad HN<^{R}_{R}\xrightarrow[-H_2O]{}>C\quad \overset{|}{C}-N<^{R}_{R}$$

Primary amines also form enamines

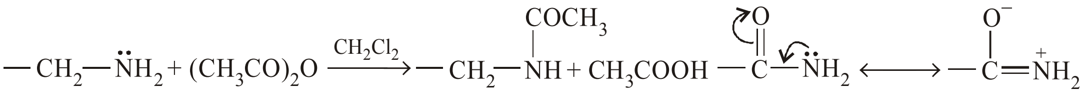


$$>CH-\overset{|}{C}\quad O\quad H_2N-R\longrightarrow>C\quad \overset{|}{C}-N<^{H}_{R}\rightleftharpoons>CH-\overset{|}{C}=N-R$$

enamine imine

In second case enamine – amine tautomerism is possible and equilibrium lies completely on the imine side.

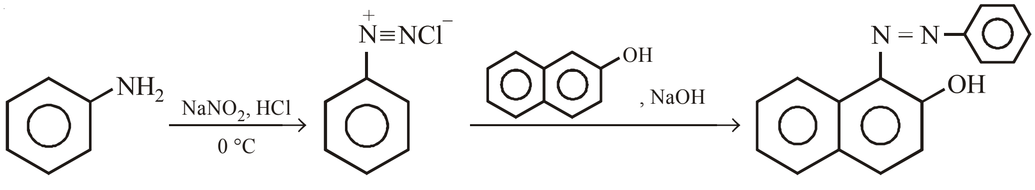
26. **(a)** — $\ddot{N}H_2$ group is acetylated by acetic anhydride in methylene chloride (solvent).



$$-CH_2-\ddot{N}H_2 + (CH_3CO)_2O \xrightarrow{CH_2Cl_2} -CH_2-\overset{\overset{\displaystyle COCH_3}{|}}{N}H + CH_3COOH \quad -\overset{\overset{\displaystyle O}{\|}}{C}-\ddot{N}H_2 \longleftrightarrow -\overset{\overset{\displaystyle O^-}{|}}{C}=\overset{+}{N}H_2$$

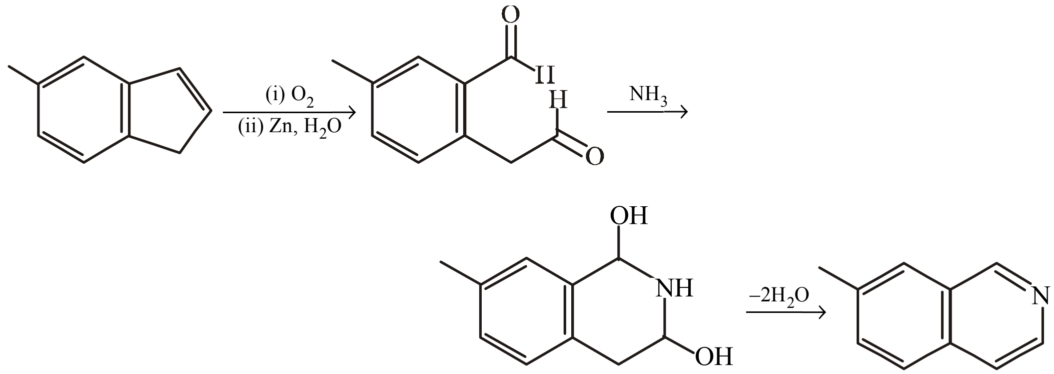
Note that —$CONH_2$ group does not undergo acetylation because here lone pair of electrons is delocalised.

27. **(a)**



(V) (W)

28. **(a)**



29. **(c)** $CH_3CN \quad 2H \rightarrow CH_3CH \quad NH \xrightarrow{H_2O,\text{boil}} CH_3CHO$

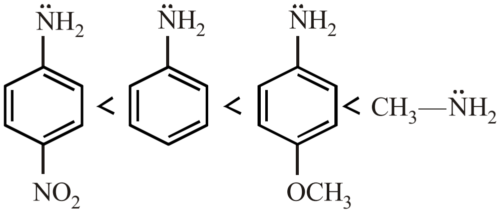
X Y

Note that cyanides are reduced only by 2H atoms, so reduction stops at aldimine stage which on hydrolysis with water gives aldehyde; it is an example of Stephen's reaction.

30. **(d)** $C_6H_5NH_2 \quad CS_2 \rightarrow C_6H_5NH.CS.SH \xrightarrow{HgCl_2} C_6H_5N = C = S + HgS + 2HCl$

The reaction is called mustard oil reaction.

31. **(c)** Aliphatic amines are more basic than aromatic amines thus methylamine is most basic. Electron donating groups increase the basicity whereas electron withdrawing groups decrease the basicity of the aromatic amines. Thus *p*-methoxyaniline is more basic then aniline which is further more basic then *p*-nitroaniline.



32. **(b)** $CH_3NH_2 + HNO_2 \longrightarrow CH_3OH \quad N_2 \quad H_2O$

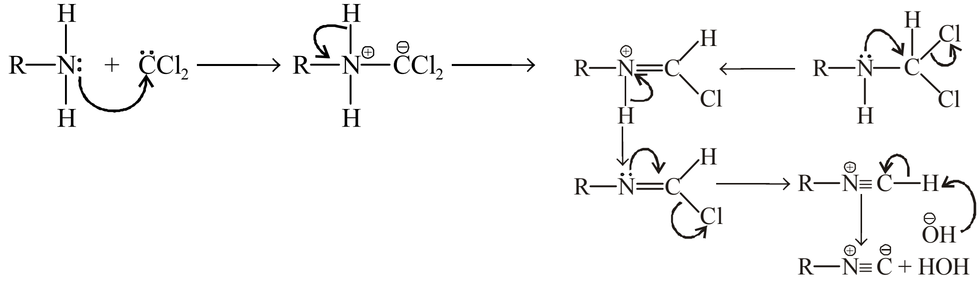
33. **(c)** The correct order of relative basicity of amines in the gas phase is 3° > 2° > 1° > NH_3

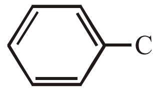
The alkyl group releases electron and thus, tends to disperse the positive charge of the alkyl ammonium ion and therefore stabilises it. Since, NH_4^+ (from NH_3) has no such alkyl group, it is not stabilised to such an extent as alkylammonium ion.

34. **(b)** $RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$

Mechanism

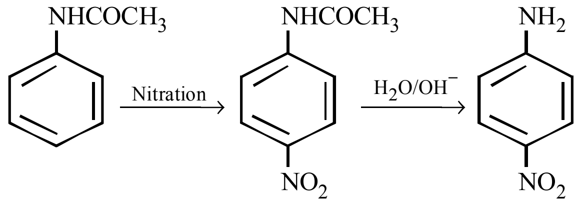
$$CHCl_3 \xrightarrow[\alpha-\text{ elimination}]{OH^-/\Delta} \underset{\text{Dichlorocarbene}}{\ddot{C}Cl_2}$$



35. **(b)**  $CH_2–NH_2$ compound is most basic due to presence of localized lone pair of electron on nitrogen atom while other compounds have delocalized lone pair of electron.

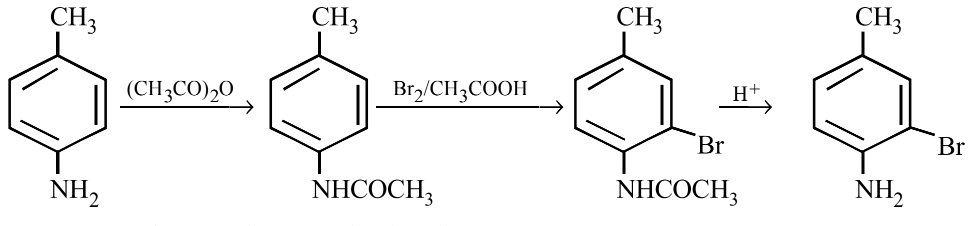
36. **(a)** Only 1° aromatic amines undergo coupling reactions to form a dye

37. **(b)**



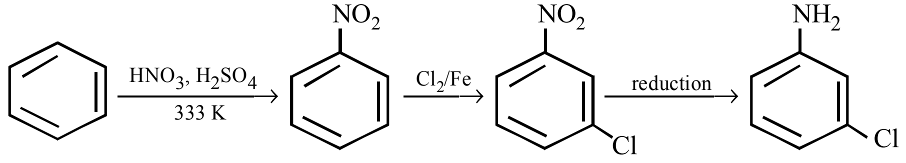
p-Nitroaniline

38. **(b)**



(–$NHCOCH_3$ is more electron-releasing than –CH_3 group)

39. **(b)**



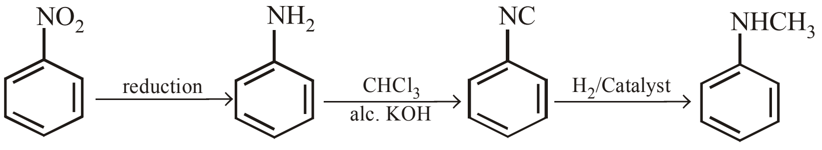
(a) When chlorination is done earlier than nitration, chlorobenzene formed at first step would introduce $-NO_2$ group in ortho-position, not in *m*-position.

(b) Again if $-NO_2$ group is reduced earlier than the chlorination step, $-NH_2$ group formed on reduction will again introduce $-Cl$ in *o*-position.

40. **(b)** $A \xrightarrow{HNO_3/H_2SO_4} B \xrightarrow{Sn/HCl} C_6H_5NH_2$

This indicates that B is $C_6H_5NO_2$ and hence A is C_6H_6

41. **(d)**

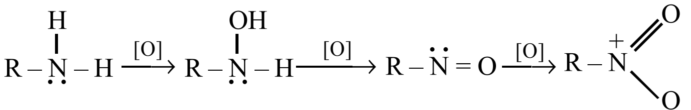


(A) (B) (C) N-Methylaniline

42. **(b)** In II, intermolecular H-bonding between similar molecules is possible, while this is not so in I.

43. **(a)** In amines, N is sp^3 hybridised and thus has pyramidal shape. In the given structure, since the three alkyl groups are different, and the fourth corner of the pyramid is occupied by lone pair of electrons, the molecule is chiral. However, the two enantiomers of the amine are not resolvable because of their rapid interconversion through a transition state having planar structure (sp^2 hybridised nitrogen)

44. **(d)** All of the three are oxidation products of a 1° amine.



$$R-\overset{H}{\underset{\cdot\cdot}{N}}-H \xrightarrow{[O]} R-\overset{OH}{\underset{\cdot\cdot}{N}}-H \xrightarrow{[O]} R-\overset{\cdot\cdot}{N}=O \xrightarrow{[O]} R-\overset{+}{N}\begin{smallmatrix}\nearrow O \\ \searrow O^-\end{smallmatrix}$$

1° Amine Hydroxylamine Nitroso Nitro

45. **(d)** $CH_3COONH_4 \xrightarrow{\Delta} \underset{(X)}{CH_3CONH_2} \xrightarrow{\Delta/P_2O_5} \underset{(Y)}{CH_3CN} \xrightarrow{H_3O^{\oplus}} \underset{(Z)}{CH_3COOH}$

46. **(b)** The order of basicity is I > III > II > IV.

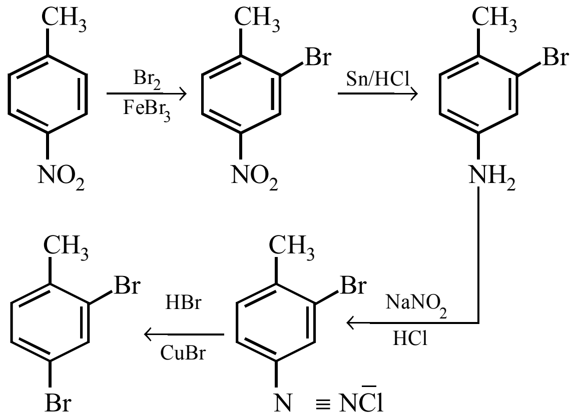
The lone pair of electrons on N is more readily available for protonation in I and III then in II. III contains an oxygen atom which has – I effect due to which it is less basic than I. In compound IV lone pair of e^-s on N–atom is contributed towards the aromatic sextet formation and hence is not at all available for protonation. Hence option (b) is correct.

47. **(a)** On reduction with Zn and HCl, $C_6H_5N_2Cl$ forms aniline as the main product.

48. **(c)** $\underset{\text{Benzene diazoniumchloride}}{C_6H_5N_2Cl} \xrightarrow[\text{or Cu HCl}]{CuCl/HCl} \underset{\text{Chloro benzene}}{C_6H_5Cl} \quad N_2$

The above reaction is known as Sandmayer's reaction.

49. **(b)**



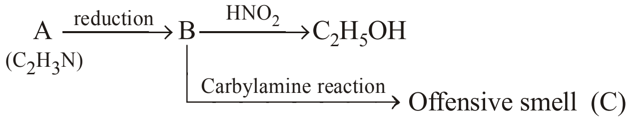
50. **(c)** $(CH_3)_2CO \xrightarrow{NH_2OH} (CH_3)_2CH = N - OH \xrightarrow{LiAlH_4} (CH_3)_2CHNH_2$

$(CH_3)_2CHOH \xrightarrow{PCl_5} (CH_3)_2CHCl \xrightarrow{NH_3} (CH_3)_2CHNH_2$

51. **(a)** $CH_3CH \quad NOH \xrightarrow{P_2O_5} CH_3CN \quad H_2O$

52. **(d)** $CH_3CN \xrightarrow{Na/C_2H_5OH} \underset{(A)}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{(B)}{CH_3CH_2OH} \xrightarrow[573\ K]{Cu} \underset{(C)}{CH_3CHO}$

53. **(b)**



$\underset{(C_2H_3N)}{A} \xrightarrow{reduction} B \xrightarrow{HNO_2} C_2H_5OH$

$B \xrightarrow{\text{Carbylamine reaction}} \text{Offensive smell (C)}$

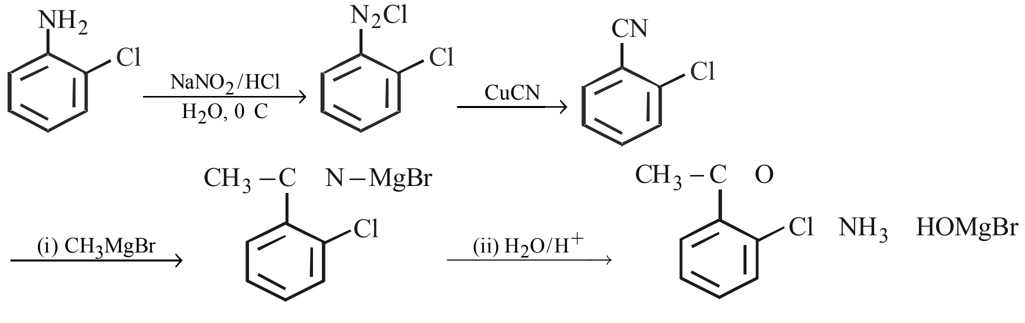
Given reactions indicate that B has 1° NH_2 group, and thus A, C_2H_3N, should be $CH_3C \equiv N$. Hence C should be CH_3CH_2NC

$\underset{A}{CH_3C \equiv N} \xrightarrow{reduction} \underset{B}{CH_3CH_2NH_2} \xrightarrow[KOH]{CHCl_3} \underset{C}{CH_3CH_2N \overset{\rightarrow}{\ } C}$

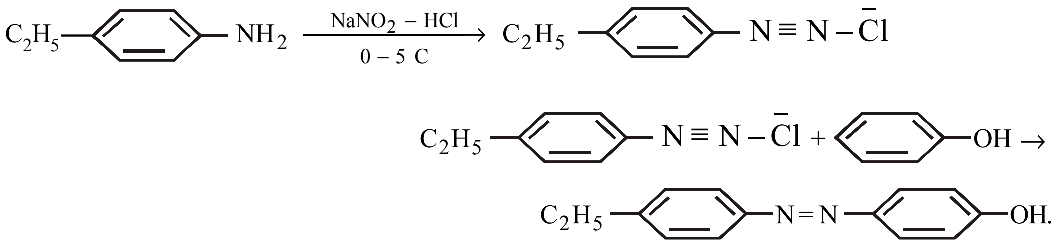
54. **(d)** $CH_3CH_2N_{\rightarrow}C + H_2O \xrightarrow{H} CH_3CH_2NH_2 \quad HCOOH$

55. **(d)** Red solution

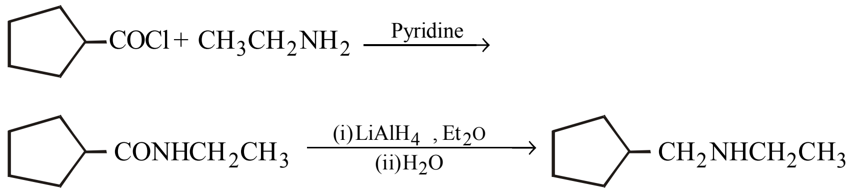
56. **(a)**



57. (b)

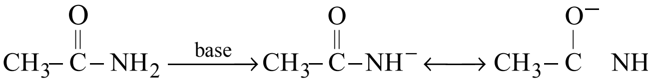


58. (c)



N-ethyl cyclopentyl methyl amine

59. (a) Acetamide is basic due to the presence of lone pair of electrons of N; it is also acidic because its conjugate base shows resonance.

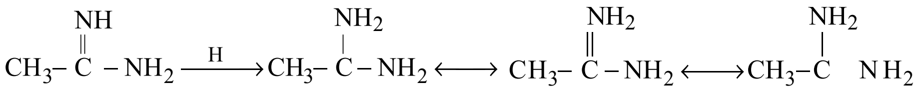


$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{base} CH_3-\overset{\overset{O}{\|}}{C}-NH^- \longleftrightarrow CH_3-\overset{\overset{O^-}{|}}{C}\quad NH$$

(more stable due to –ve charge on O)

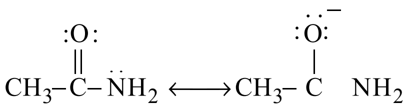
Benzonitrile ($C_6H_5C\equiv N$) acts as an electrophile (Lewis acid) due to electron deficiency of C of CN as well as nucleophile (Lewis base) in nature due to presence of lone pair electrons on N; hence it is neutral Triethylamine and phenol are basic and acidic in nature respectively.

60. (b) Guanidine is most basic because its conjugate acid is stabilized by two equivalent resonance structures,.



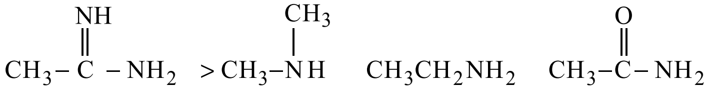
$$CH_3-\overset{\overset{NH}{\|}}{C}-NH_2 \xrightarrow{H} CH_3-\overset{\overset{NH_2}{|}}{C}-NH_2 \longleftrightarrow CH_3-\overset{\overset{NH_2}{\|}}{C}-NH_2 \longleftrightarrow CH_3-\overset{\overset{NH_2}{|}}{C}\quad NH_2$$

Further 2° amines are more basic than 1°, while amides are least basic due to delocalisation of the lone pair of electrons on N



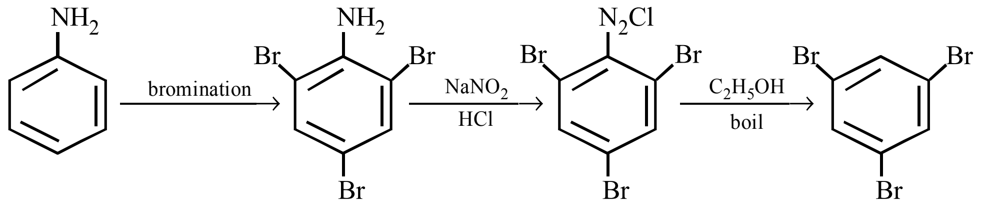
$$CH_3-\overset{\overset{:O:}{\|}}{C}-\ddot{N}H_2 \longleftrightarrow CH_3-\overset{\overset{:\ddot{O}:^-}{|}}{C}\quad NH_2$$

Thus the correct order of basicities is



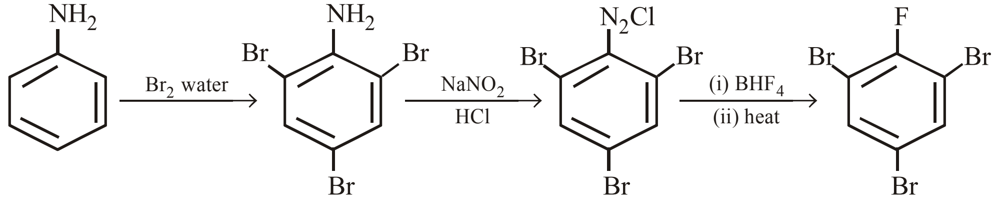
$$CH_3-\overset{\overset{NH}{\|}}{C}-NH_2 > CH_3-\overset{\overset{CH_3}{|}}{N}H \quad CH_3CH_2NH_2 \quad CH_3-\overset{\overset{O}{\|}}{C}-NH_2$$

61. **(d)** Proceed backward ; tribromobenzene is produced by boiling compound Z with C_2H_5OH ; Z in turn is obtained by diazotisation of Y, so Y and Z should have $-NH_2$ and $-N_2Cl$ groups respectively, in addition to three Br atoms. Hence X should be $C_6H_5NH_2$



X Y Z

62. **(c)**



63. **(a)** The electrons withdrawing groups decrease the basic character and increase the acid character by inductive effect and resonance.

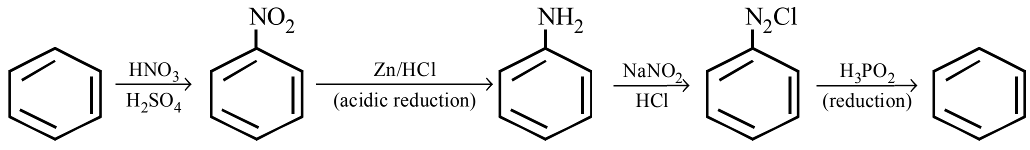
64. **(a)** Nitriles having α-hydrogen atom form alkyl derivatives with RBr in presence of $NaNH_2 / NH_3$.

65. **(a)** Nitrobenzene is reduced in the following manner through various intermediates to form aniline as the final product.

$$C_6H_5NO_2 \xrightarrow{2[H]} C_6H_5NO \xrightarrow{2[H]} C_6H_5NHOH \xrightarrow{2[H]} C_6H_5NH_2$$

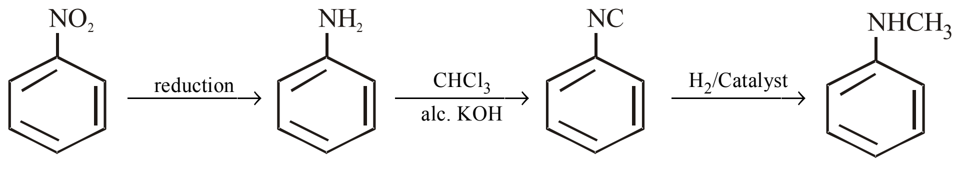
nitrobenzene nitrosobenzene phenylhydroxylamine aniline

66. **(b)**



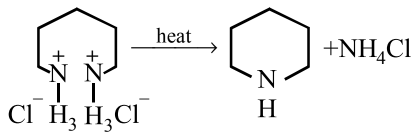
W X Y Z

67. **(d)**

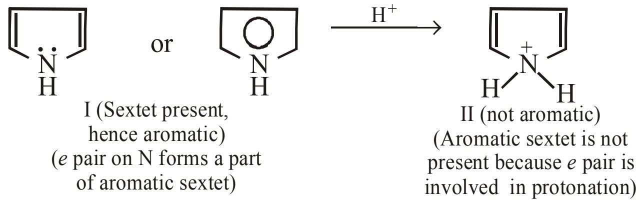


(A) (B) (C) N-Methylaniline

68. **(c)**

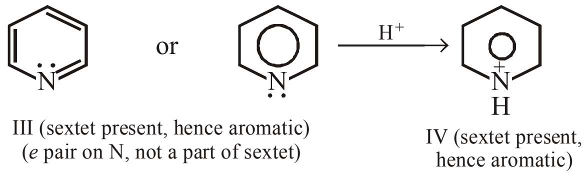


69. **(b)**



I (Sextet present, hence aromatic) (*e* pair on N forms a part of aromatic sextet)

II (not aromatic) (Aromatic sextet is not present because *e* pair is involved in protonation)

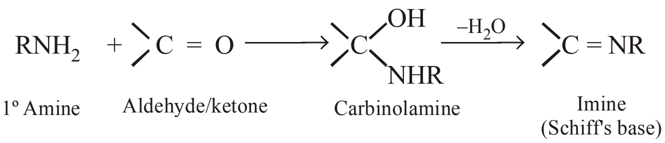


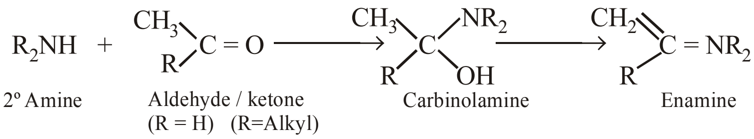
III (sextet present, hence aromatic) (*e* pair on N, not a part of sextet)

IV (sextet present, hence aromatic)

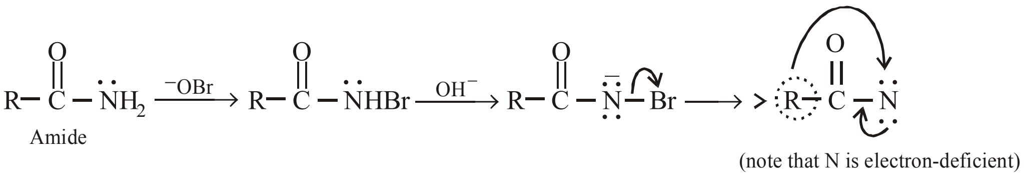
70. **(b)** This is an example of Hofmann elimination which generally takes place by E2 mechanism and the latter requires a strong base (recall that OH^- is a strong base than I^-). The NH_2^-, being a strong base, can't be eliminiated easily.

71. **(d)**





72. **(d)** For this one should remember that Hofmann's degradation involves migration to electron deficient nitrogen atom, hence the alkyl group will migrate with its bonding pair of electrons.

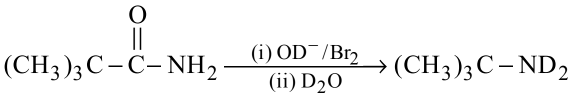


(note that N is electron-deficient)

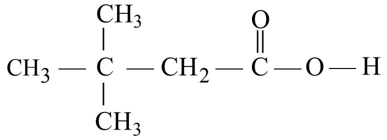
$$\longrightarrow O{=}C{=}\ddot{N}R \xrightarrow{H_2O} RNH_2 + CO_3^{2-}$$

Alkyl isocyanate　　Amine

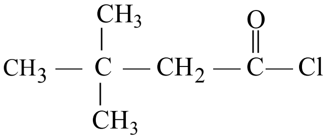
73. **(c)** Remember that in Hofmann rearrangement, the two original H atoms of the $-CONH_2$ group are removed by base (OH^-) and new H's are derived from H_2O.



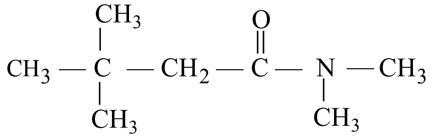
$$(CH_3)_3C-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[\text{(ii) } D_2O]{\text{(i) } OD^-/Br_2} (CH_3)_3C-ND_2$$

74. **(b)** (A) 

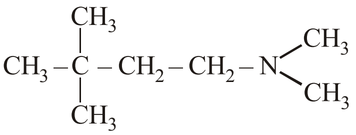
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-O-H$$

(B) 

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-Cl$$

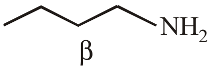
(C) 

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{N}-CH_3$$

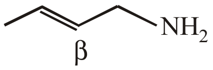
(D) 

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_2-N\begin{matrix}CH_3\\CH_3\end{matrix}$$

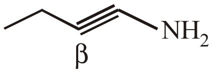
75. **(a)** Note the point of difference in the given compounds which here lies at β-carbon. In I, II, III, the β-carbon atoms are *sp*^{3}, *sp*^{2} and *sp* hybridised respectively which in turn cause the difference in their *s*-character. We know that more is the *s* character of an atom, greater will be its electron-withdrawing nature. Thus *sp* (50% *s* character) hybridised carbon is most electron-withdrawing, while *sp*^{3} (25% *s*-character) is least electron-withdrawing. Further, we know that presence of an electron-withdrawing group decreases basicity of an amine. Thus



I. (β – *sp*^{3} hybridised)

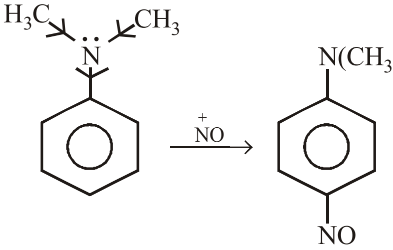


II. (β – *sp*^{2})



III. (β – C *sp*^{2})

76. **(c)** Nitrosonium ion, N O from HONO is a weak electrophile, hence it can attack only on highly activated benzene nucleus, provided proper position, *p*- or *o*- is free.



77. **(c)** Benzaldehyde reacts with primary aromatic amine to form schiff's base

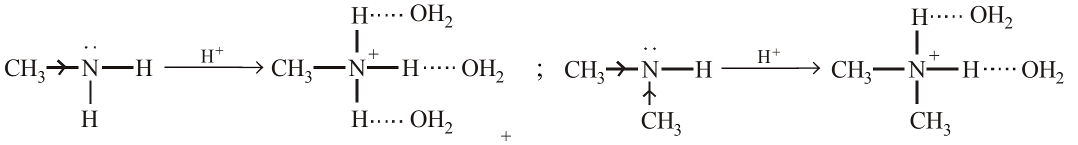
$$C_6H_5CH \quad O \quad C_6H_5NH_2 \longrightarrow C_6H_5CH \quad NC_6H_5$$

Benzaldehyde Aniline Benzylidene aniline

78. **(b)**

$H_2C \quad N^+ \quad N^-$	$H_2C^- - N \equiv N$	$> H_2C^+ - N \quad N^-$	$H_2C^- - N \quad N$
I	III	II	IV
Octet complete, 6 covalent bond, –ve charge on N	Octet complete, 6 covalent bond, –ve charge on C	Octet incomplete, 5 covalent bond, –ve charge on N	Octet incomplete, 5 covalent bond, –ve charge on C

79. **(d)** The basic character of an amine in water is determined by (i) electron availability on the N atom and (ii) the extent of stabilization of the cation (protonated amine) due to solvation by hydrogen bonding



Methyl amine; Protonated methyl amine, $CH_3\overset{+}{N}H_3$ (Highly stabilized); Dimethyl amine; Protonated dimethyl amine (Lesser stabilized than $CH_3\overset{+}{N}H_3$)

80. **(d)** Most of the simple amines those having smaller alkyl (groups) can't be resolved , although they may contain three different alkyl groups.