Unit

13

AMINES

I. Multiple Choice Questions (Type-I)

1. Which of the following is a 3° amine?

(i) 1-methylcyclohexylamine

(ii) Triethylamine

(iii) *tert*-butylamine

(iv) N-methylaniline

2. The correct IUPAC name for $CH_2{=}CHCH_2NHCH_3$ is

(i) Allylmethylamine

(ii) 2-amino-4-pentene

(iii) 4-aminopent-1-ene

(iv) N-methylprop-2-en-1-amine

3. Amongst the following, the strongest base in aqueous medium is _____.

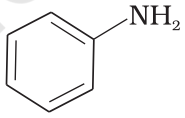
(i) CH_3NH_2

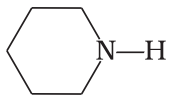
(ii) $NCCH_2NH_2$

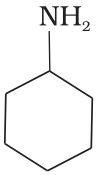
(iii) $(CH_3)_2NH$

(iv) $C_6H_5NHCH_3$

4. Which of the following is the weakest Brönsted base?

(i) 

(ii) 

(iii) 

(iv) CH_3NH_2

5. Benzylamine may be alkylated as shown in the following equation :

$$C_6H_5CH_2NH_2 + R—X \longrightarrow C_6H_5CH_2NHR$$

Which of the following alkylhalides is best suited for this reaction through S_N1 mechanism?

(i) CH_3Br

(ii) C_6H_5Br

(iii) $C_6H_5CH_2Br$

(iv) C_2H_5 Br

6. Which of the following reagents would **not** be a good choice for reducing an aryl nitro compound to an amine?

(i) H_2 (excess)/Pt

(ii) $LiAlH_4$ in ether

(iii) Fe and HCl

(iv) Sn and HCl

7. In order to prepare a 1° amine from an alkyl halide with simultaneous addition of one CH_2 group in the carbon chain, the reagent used as source of nitrogen is _____.

(i) Sodium amide, $NaNH_2$

(ii) Sodium azide, NaN_3

(iii) Potassium cyanide, KCN

(iv) Potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

8. The source of nitrogen in Gabriel synthesis of amines is _____.

(i) Sodium azide, NaN_3

(ii) Sodium nitrite, $NaNO_2$

(iii) Potassium cyanide, KCN

(iv) Potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

9. Amongst the given set of reactants, the most appropriate for preparing 2° amine is _____.

(i) 2° R—Br + NH_3

(ii) 2° R—Br + NaCN followed by H_2/Pt

(iii) 1° R—NH_2 + RCHO followed by H_2/Pt

(iv) 1° R—Br (2 mol) + potassium phthalimide followed by H_3O^+/heat

10. The best reagent for converting 2–phenylpropanamide into 2-phenylpropanamine is _____.

(i) excess H_2

(ii) Br_2 in aqueous NaOH

(iii) iodine in the presence of red phosphorus

(iv) $LiAlH_4$ in ether

11. The best reagent for converting, 2-phenylpropanamide into 1- phenylethanamine is ____.

(i) excess H_2/Pt

(ii) NaOH/Br_2

(iii) $NaBH_4$/methanol

(iv) $LiAlH_4$/ether

12. Hoffmann Bromamide Degradation reaction is shown by _____.

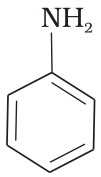
(i) $ArNH_2$

(ii) $ArCONH_2$

(iii) $ArNO_2$

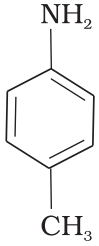
(iv) $ArCH_2NH_2$

13. The correct increasing order of basic strength for the following compounds is _____.



(I)

(II)



(III)

(i) II < III < I

(ii) III < I < II

(iii) III < II < I

(iv) II < I < III

14. Methylamine reacts with HNO_2 to form _____.

(i) CH_3—O—N═O

(ii) CH_3—O—CH_3

(iii) CH_3OH

(iv) CH_3CHO

15. The gas evolved when methylamine reacts with nitrous acid is _____.

(i) NH_3

(ii) N_2

(iii) H_2

(iv) C_2H_6

16. In the nitration of benzene using a mixture of conc. H_2SO_4 and conc. HNO_3, the species which initiates the reaction is _____.

(i) NO_2

(ii) NO^+

(iii) NO_2^+

(iv) NO_2^-

17. Reduction of aromatic nitro compounds using Fe and HCl gives _____.

(i) aromatic oxime

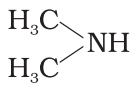
(ii) aromatic hydrocarbon

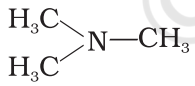
(iii) aromatic primary amine

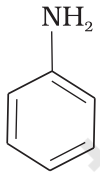
(iv) aromatic amide

18. The most reactive amine towards dilute hydrochloric acid is _____.

(i) $CH_3—NH_2$

(ii) 

(iii) 

(iv) 

19. Acid anhydrides on reaction with primary amines give _____.

(i) amide

(ii) imide

(iii) secondary amine

(iv) imine

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

(i) Sandmeyer reaction

(ii) Gatterman reaction

(iii) Claisen reaction

(iv) Carbylamine reaction

21. Best method for preparing primary amines from alkyl halides without changing the number of carbon atoms in the chain is

(i) Hoffmann Bromamide reaction

(ii) Gabriel phthalimide synthesis

(iii) Sandmeyer reaction

(iv) Reaction with NH_3

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

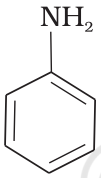
(i) Aniline

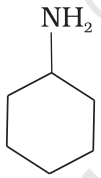
(ii) Phenol

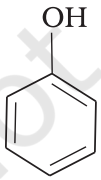
(iii) Anisole

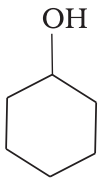
(iv) Nitrobenzene

23. Which of the following compounds is the weakest Brönsted base?

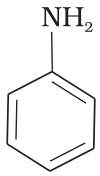
(i) 

(ii) 

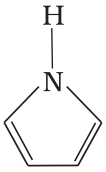
(iii) 

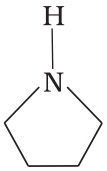
(iv) 

24. Among the following amines, the strongest Brönsted base is _____.

(i) 

(ii) NH_3

(iii) 

(iv) 

25. The correct decreasing order of basic strength of the following species is _____.

H_2O, NH_3, OH^-, NH_2^-

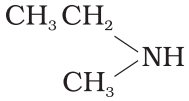
(i) $NH_2^- > OH^- > NH_3 > H_2O$

(ii) $OH^- > NH_2^- > H_2O > NH_3$

(iii) $NH_3 > H_2O > NH_2^- > OH^-$

(iv) $H_2O > NH_3 > OH^- > NH_2^-$

26. Which of the following should be most volatile?

(I) $CH_3CH_2CH_2NH_2$ (II) $(CH_3)_3N$ (III)  (IV) $CH_3CH_2CH_3$

(i) II

(ii) IV

(iii) I

(iv) III

27. Which of the following methods of preparation of amines will give same number of carbon atoms in the chain of amines as in the reactant?

(i) Reaction of nitrite with $LiAlH_4$.

(ii) Reaction of amide with $LiAlH_4$ followed by treatment with water.

(iii) Heating alkylhalide with potassium salt of phthalimide followed by hydrolysis.

(iv) Treatment of amide with bromine in aqueous solution of sodium hydroxide.

II. Multiple Choice Questions (Type-II)

Note : In the following questions two or more options may be correct.

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

(i) Chlorobenzene

(ii) Bromobenzene

(iii) Iodobenzene

(iv) Fluorobenzene

29. Reduction of nitrobenzene by which of the following reagent gives aniline?

(i) Sn/HCl

(ii) Fe/HCl

(iii) H_2-Pd

(iv) Sn/NH_4OH

30. Which of the following species are involved in the carbylamine test?

(i) R—NC

(ii) $CHCl_3$

(iii) $COCl_2$

(iv) $NaNO_2$ + HCl

31. The reagents that can be used to convert benzenediazonium chloride to benzene are _____.

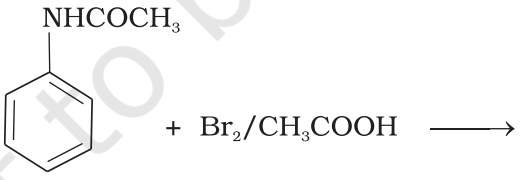
(i) $SnCl_2$/HCl

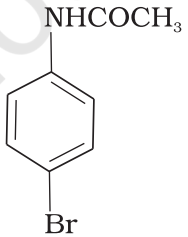
(ii) CH_3CH_2OH

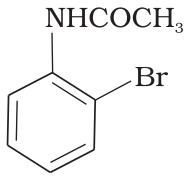
(iii) H_3PO_2

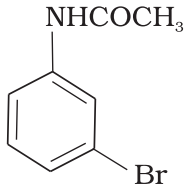
(iv) $LiAlH_4$

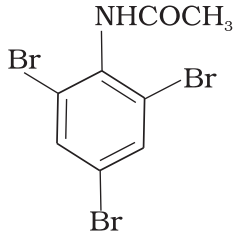
32. The product of the following reaction is _____.



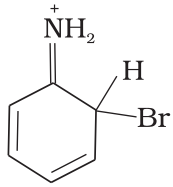
(i) 

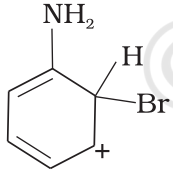
(ii) 

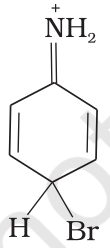
(iii) 

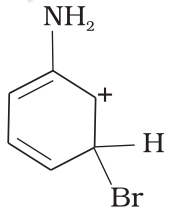
(iv) 

33. Arenium ion involved in the bromination of aniline is _____.

(i) 

(ii) 

(iii) 

(iv) 

34. Which of the following amines can be prepared by Gabriel synthesis.

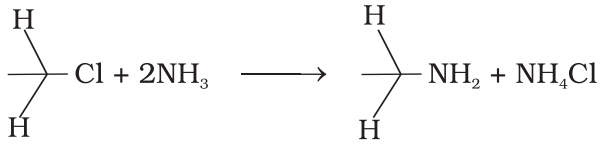
(i) Isobutyl amine

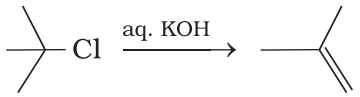
(ii) 2-Phenylethylamine

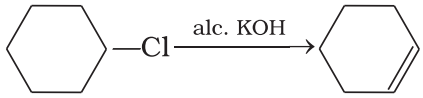
(iii) N-methylbenzylamine

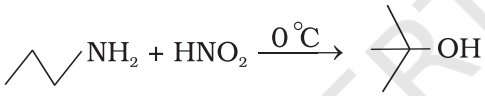
(iv) Aniline

35. Which of the following reactions are correct?

(i) 

(ii) 

(iii) 

(iv) 

36. Under which of the following reaction conditions, aniline gives *p*-nitro derivative as the major product?

(i) Acetyl chloride/pyridine followed by reaction with conc. H_2SO_4 + conc. HNO_3.

(ii) Acetic anyhdride/pyridine followed by conc. H_2SO_4 + conc. HNO_3.

(iii) Dil. HCl followed by reaction with conc. H_2SO_4 + conc. HNO_3.

(iv) Reaction with conc. HNO_3 + conc.H_2SO_4.

37. Which of the following reactions belong to electrophilic aromatic substitution?

(i) Bromination of acetanilide

(ii) Coupling reaction of aryldiazonium salts

(iii) Diazotisation of aniline

(iv) Acylation of aniline

III. Short Answer Type

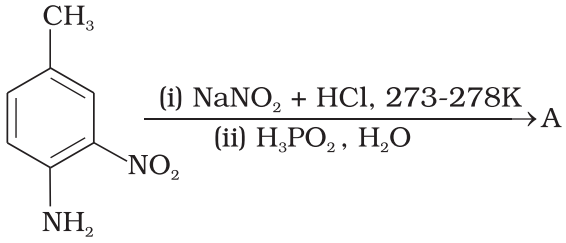
38. What is the role of HNO_3 in the nitrating mixture used for nitration of benzene?

39. Why is NH_2 group of aniline acetylated before carrying out nitration?

40. What is the product when $C_6H_5CH_2NH_2$ reacts with HNO_2?

41. What is the best reagent to convert nitrile to primary amine?

42. Give the structure of 'A' in the following reaction.



43. What is Hinsberg reagent?

44. Why is benzene diazonium chloride not stored and is used immediately after its preparation?

45. Why does acetylation of —NH_2 group of aniline reduce its activating effect?

46. Explain why $MeNH_2$ is stronger base than MeOH?

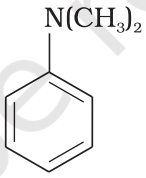
47. What is the role of pyridine in the acylation reaction of amines?

48. Under what reaction conditions (acidic/basic), the coupling reaction of aryldiazonium chloride with aniline is carried out?

49. Predict the product of reaction of aniline with bromine in non-polar solvent such as CS_2.

50. Arrange the following compounds in increasing order of dipole moment.
$CH_3CH_2CH_3$, $CH_3CH_2NH_2$, CH_3CH_2OH

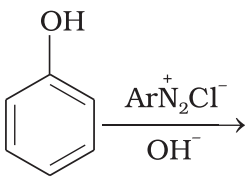
51. What is the structure and IUPAC name of the compound, allyl amine?

52. Write down the IUPAC name of 

53. A compound Z with molecular formula C_3H_9N reacts with $C_6H_5SO_2Cl$ to give a solid, insoluble in alkali. Identify Z.

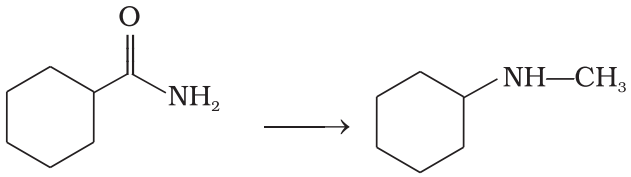
54. A primary amine, RNH_2 can be reacted with CH_3—X to get secondary amine, R—$NHCH_3$ but the only disadvantage is that 3° amine and quaternary ammonium salts are also obtained as side products. Can you suggest a method where RNH_2 forms only 2° amine?

55. Complete the following reaction.

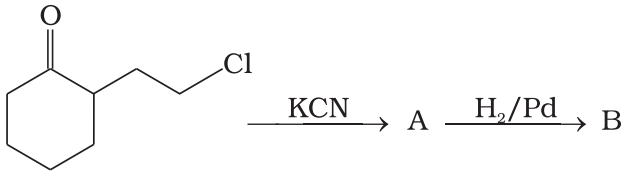


56. Why is aniline soluble in aqueous HCl?

57. Suggest a route by which the following conversion can be accomplished.



58. Identify A and B in the following reaction.



59. How will you carry out the following conversions?

(i) toluene ⟶ *p*-toluidine

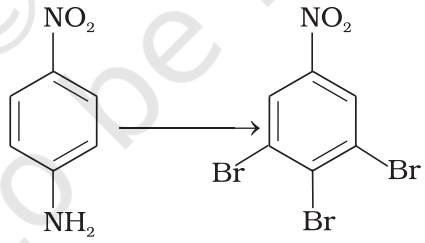
(ii) *p*-toluidine diazonium chloride ⟶ *p*-toluic acid

60. Write following conversions:

(i) nitrobenzene ⟶ acetanilide (ii) acetanilide ⟶ *p*-nitroaniline

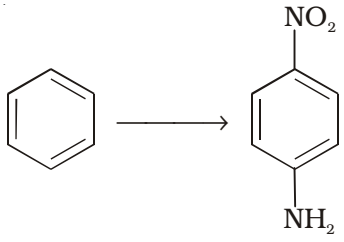
61. A solution contains 1 g mol. each of p-toluene diazonium chloride and *p*-nitrophenyl diazonium chloride. To this 1 g mol. of alkaline solution of phenol is added. Predict the major product. Explain your answer.

62. How will you bring out the following conversion?

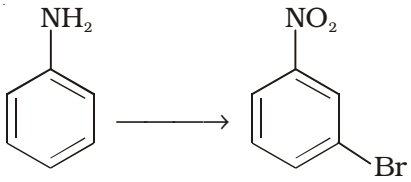


p-Nitroaniline 3,4,5-Tribromonitrobenzene

63. How will you carry out the following conversion?

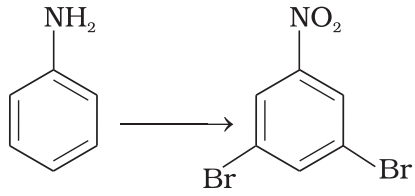


64. How will you carry out the following conversion?

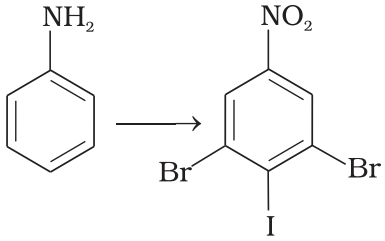


65. How will you carry out the following conversions?

(i)



(ii)



IV. Matching Type

Note : Match the items of Column I and Column II in the following questions.

66. Match the reactions given in Column I with the statements given in Column II.

	Column I		**Column II**
(i)	Ammonolysis	(a)	Amine with lesser number of carbon atoms
(ii)	Gabriel phthalimide synthesis	(b)	Detection test for primary amines.
(iii)	Hoffmann Bromamide reaction	(c)	Reaction of phthalimide with KOH and R—X
(iv)	Carbylamine reaction	(d)	Reaction of alkylhalides with NH_3

67. Match the compounds given in Column I with the items given in Column II.

	Column I		**Column II**
(i)	Benzene sulphonyl chloride	(a)	Zwitter ion
(ii)	Sulphanilic acid	(b)	Hinsberg reagent
(iii)	Alkyl diazonium salts	(c)	Dyes
(iv)	Aryl diazonium salts	(d)	Conversion to alcohols

V. Assertion and Reason Type

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(i) Both assertion and reason are wrong.

(ii) Both assertion and reason are correct statements but reason is not correct explanation of assertion.

(iii) Assertion is correct statement but reason is wrong statement.

(iv) Both assertion and reason are correct statements and reason is correct explanation of assertion.

(v) Assertion is wrong statement but reason is correct statement.

68. **Assertion** : Acylation of amines gives a monosubstituted product whereas alkylation of amines gives polysubstituted product.

Reason : Acyl group sterically hinders the approach of further acyl groups.

69. **Assertion** : Hoffmann's bromamide reaction is given by primary amines.

Reason : Primary amines are more basic than secondary amines.

70. **Assertion** : N-Ethylbenzene sulphonamide is soluble in alkali.

Reason : Hydrogen attached to nitrogen in sulphonamide is strongly acidic.

71. **Assertion** : N, N-Diethylbenzene sulphonamide is insoluble in alkali.

Reason : Sulphonyl group attached to nitrogen atom is strong electron withdrawing group.

72. **Assertion** : Only a small amount of HCl is required in the reduction of nitro compounds with iron scrap and HCl in the presence of steam.

Reason : $FeCl_2$ formed gets hydrolysed to release HCl during the reaction.

73. **Assertion** : Aromatic 1° amines can be prepared by Gabriel Phthalimide Synthesis.

Reason : Aryl halides undergo nucleophilic substitution with anion formed by phthalimide.

74. **Assertion** : Acetanilide is less basic than aniline.

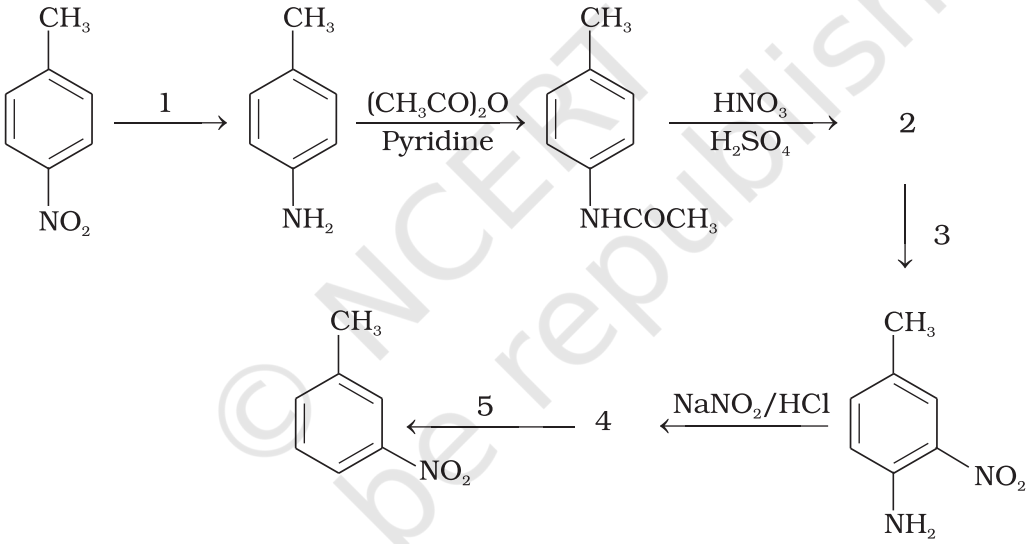
Reason : Acetylation of aniline results in decrease of electron density on nitrogen.

VI. Long Answer Type

75. A hydrocarbon 'A', (C_4H_8) on reaction with HCl gives a compound 'B', (C_4H_9Cl), which on reaction with 1 mol of NH_3 gives compound 'C', ($C_4H_{11}N$). On reacting with $NaNO_2$ and HCl followed by treatment with water, compound 'C' yields an optically active alcohol, 'D'. Ozonolysis of 'A' gives 2 mols of acetaldehyde. Identify compounds 'A' to 'D'. Explain the reactions involved.

76. A colourless substance 'A' (C_6H_7N) is sparingly soluble in water and gives a water soluble compound 'B' on treating with mineral acid. On reacting with $CHCl_3$ and alcoholic potash 'A' produces an obnoxious smell due to the formation of compound 'C'. Reaction of 'A' with benzenesulphonyl chloride gives compound 'D' which is soluble in alkali. With $NaNO_2$ and HCl, 'A' forms compound 'E' which reacts with phenol in alkaline medium to give an orange dye 'F'. Identify compounds 'A' to 'F'.

77. Predict the reagent or the product in the following reaction sequence.



ANSWERS

I. Multiple Choice Questions (Type-I)

1. (ii)	2. (iv)	3. (iii)	4. (i)	5. (iii)	6. (ii)
7. (iii)	8. (iv)	9. (iii)	10. (iv)	11. (ii)	12. (ii)
13. (iv)	14. (iii)	15. (ii)	16. (iii)	17. (iii)	18. (ii)
19. (i)	20. (ii)	21. (ii)	22. (iv)	23. (iii)	24. (iv)
25. (i)	26. (ii)	27. (iii)			

II. Multiple Choice Questions (Type-II)

28. (iii), (iv)	29. (i), (ii), (iii)	30. (i), (ii)	31. (ii), (iii)
32. (i), (ii)	33. (i), (ii), (iii)	34. (i), (ii)	35. (i), (iii)
36. (i), (ii)	37. (i), (ii)		

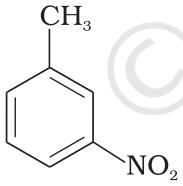
III. Short Answer Type

38. HNO_3 acts as a base in the nitrating mixture and provides the electrophile, NO_2^+ .

39. See NCERT textbook for Class XII.

40. $C_6H_5CH_2OH$

41. Reduction of nitriles with sodium/alcohol or $LiAlH_4$ gives primary amine.

42. 

43. Benzene sulphonylchloride.

44. Benzene diazonium chloride is very unstable.

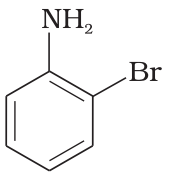
45. See NCERT textbook for Class XII.

46. Nitrogen is less electronegative than oxygen therefore lone pair of electrons on nitrogen is readily available for donation. Hence, $MeNH_2$ is more basic than MeOH.

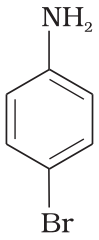
47. Pyridine and other bases are used to remove the side product i.e. HCl from the reaction mixture.

48. Reaction is done in mild basic conditions.

49. A mixture of 2-bromoaniline and 4-bromoaniline is formed.



(2-Bromoaniline)



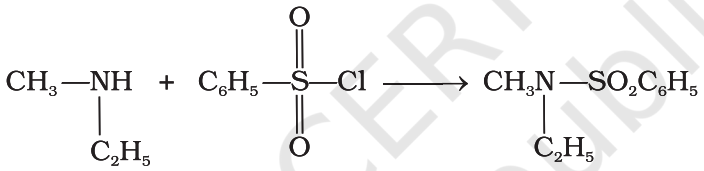
(4-Bromoaniline)

50. $CH_3CH_2CH_3 < CH_3CH_2NH_2 < CH_3CH_2OH$

51. $CH_2{=}CH{-}CH_2{-}NH_2$, prop-2-en-1-amine

52. N, N-Dimethylbenzenamine

53. Z is an aliphatic amine which gives a solid insoluble in base. This implies that reaction with $C_6H_5SO_2Cl$ must give a product without any replaceable hydrogen attached to nitrogen. In other words, the amine must be a secondary amine. i.e. Z is ethylmethylamine.

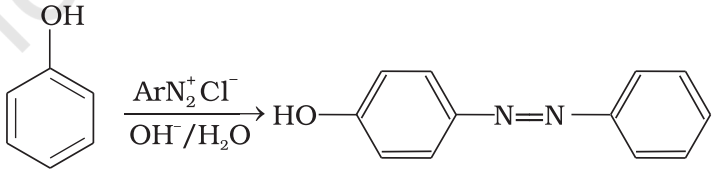


N-Ethyl-N-methyl benzene sulphonamide

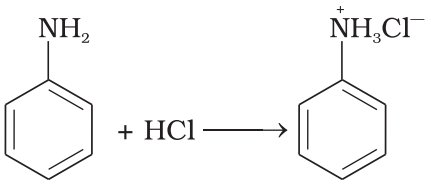
54. $RNH_2 \xrightarrow{KOH/CHCl_3} RNC \xrightarrow{H_2/Pd} RNHCH_3$

Carbylamine reaction is shown by 1° amine only which results in the replacement of two hydrogen atoms attached to nitrogen atom of NH_2 group by one carbon atom. On catalytic reduction the isocyanide will give a secondary amine with one methyl group.

55. The reaction exhibits azo-coupling of phenols. In mild alkaline conditions phenol moiety participates in the azo-coupling and para position of phenol is occupied.



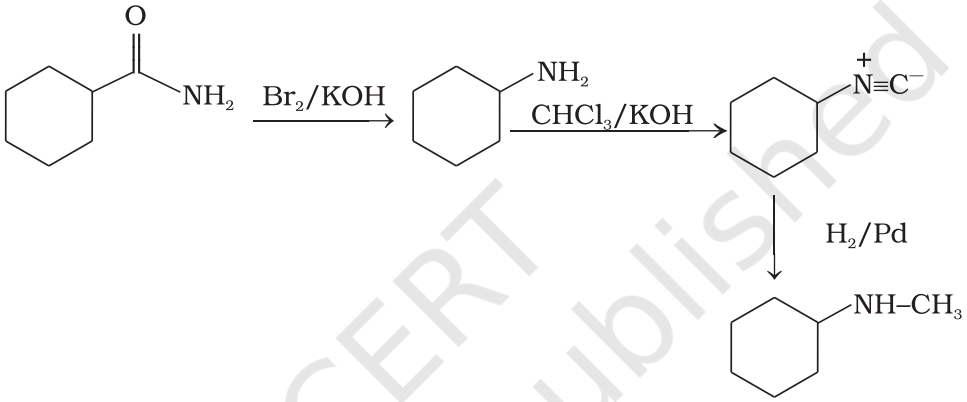
56. Aniline forms the salt anilinium chloride which is water soluble.



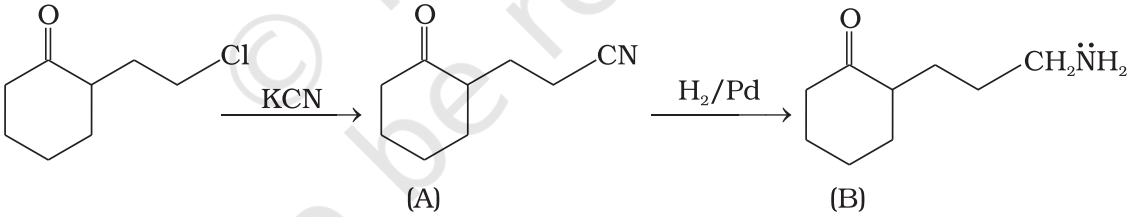
(A) Aniline (Colourless liquid, sparingly soluble in water)

(B) Anilinium chloride (Water soluble salt)

57.

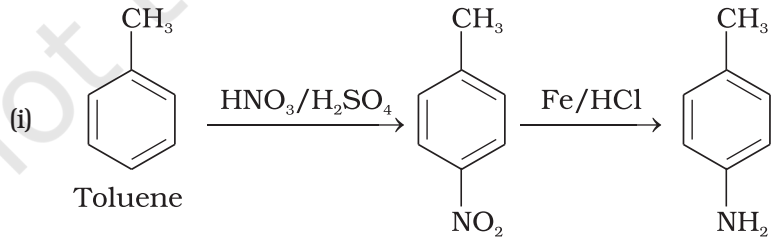


58.



(A) (B)

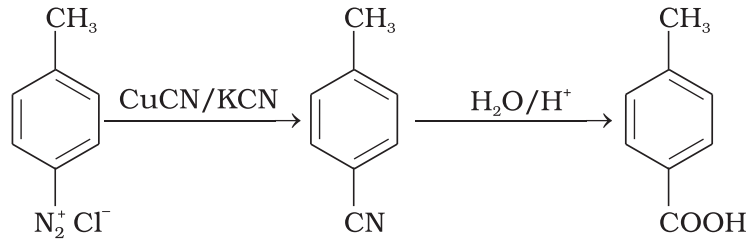
59.



Toluene

p-Toluidine

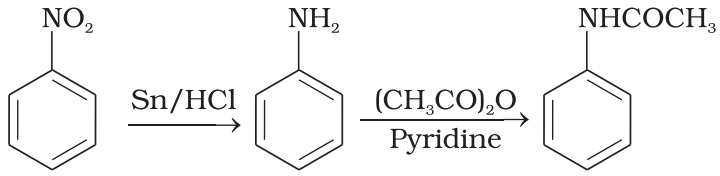
(ii)



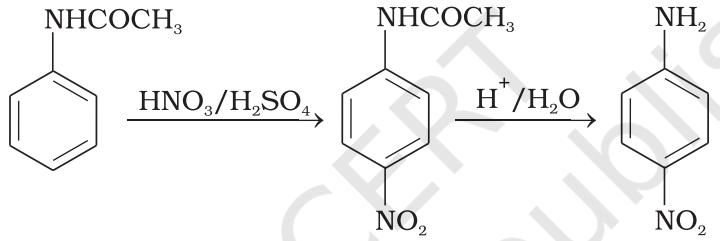
p-Toluic acid

60.

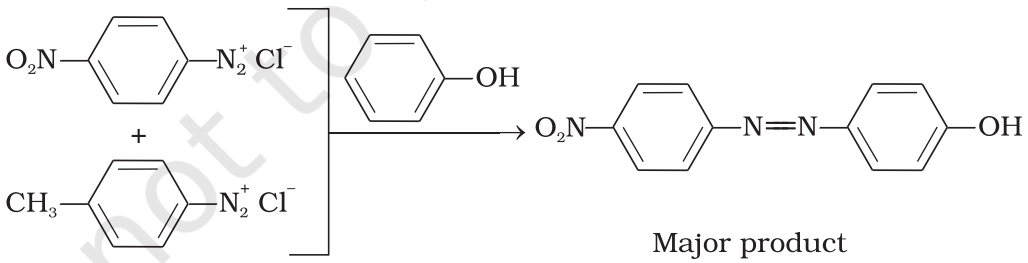
(i)



(ii)

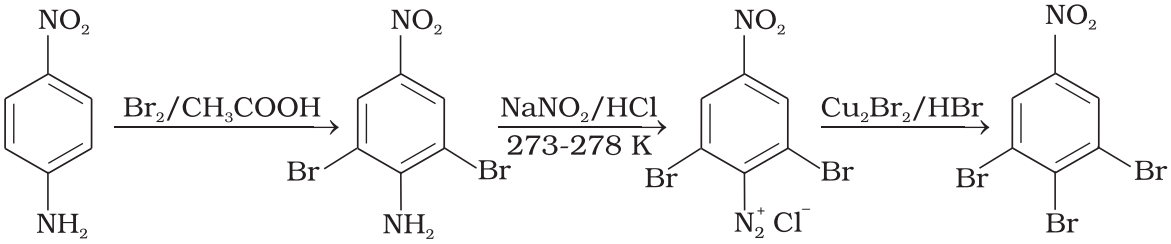


61. This reaction is an example of electrophilic aromatic substitution. In alkaline medium, phenol generates phenoxide ion which is more electron rich than phenol and hence more reactive for electrophilic attack. The electrophile in this reaction is aryldiazonium cation. Stronger the electrophile faster is the reaction. *p*-Nitrophenyldiazonium cation is a stronger electrophile than *p*-toluene diazonium cation. Therefore, it couples preferentially with phenol.

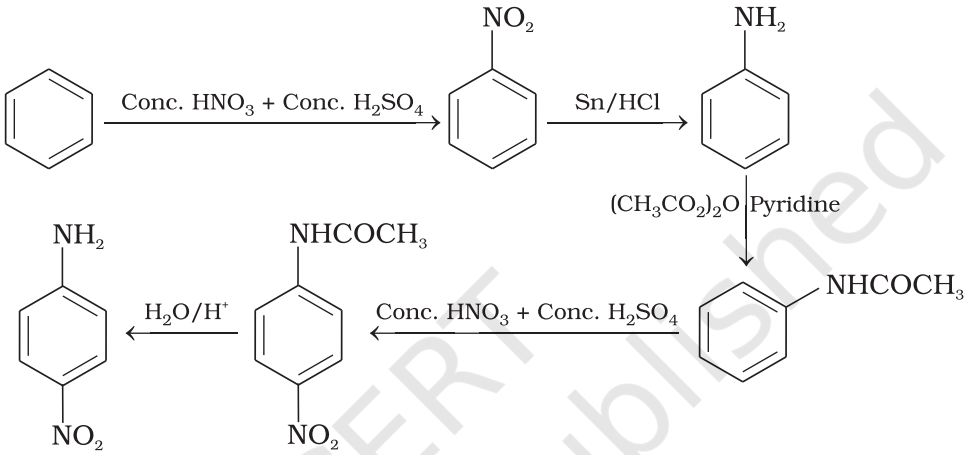


Major product

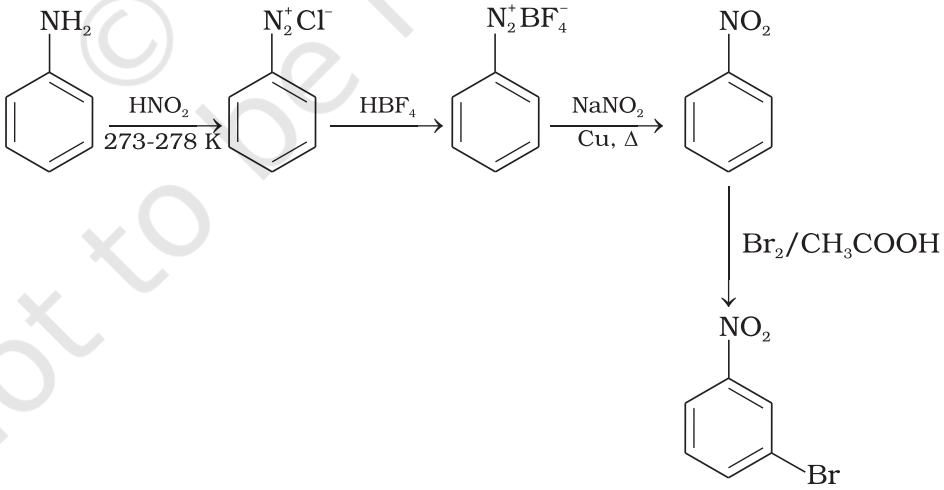
62.



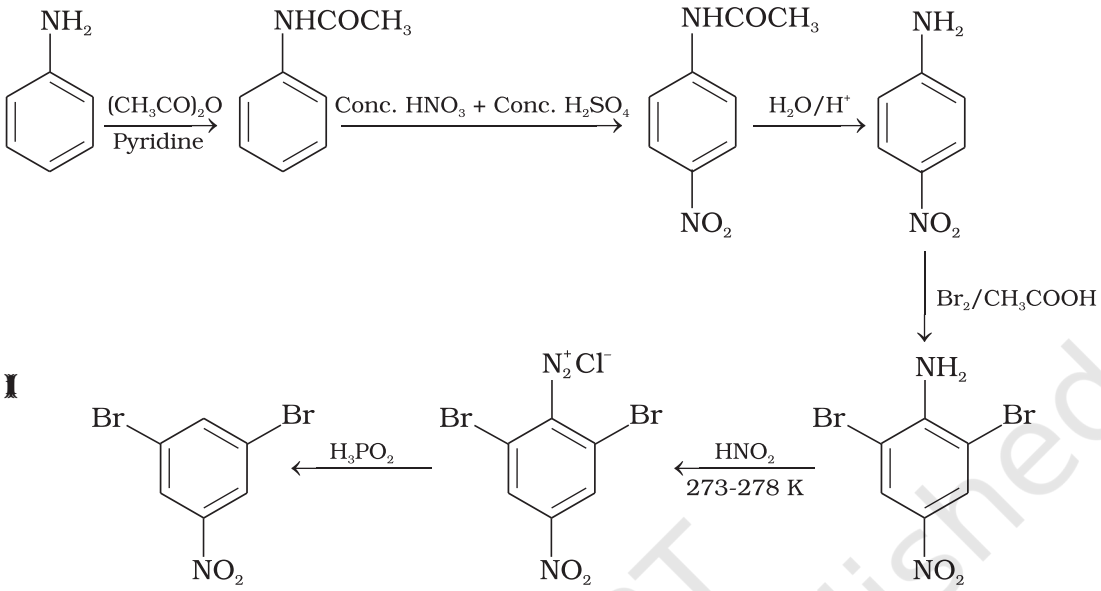
63.



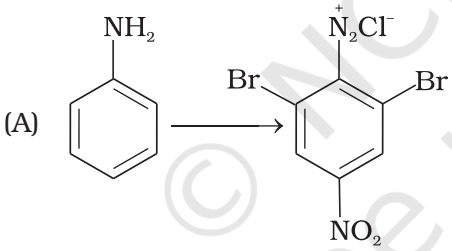
64.

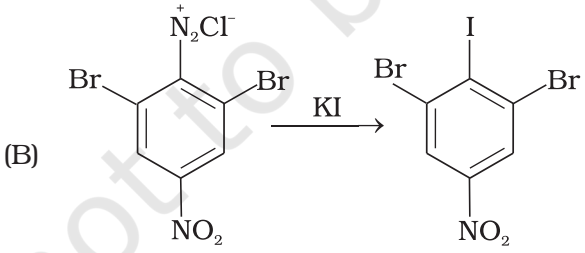


65. (i)



(ii) Conversion (A) given below is same as in part (i) given above after that reaction (B) can be carried out.





IV. Matching Type

66. (i) → (d) (ii) → (c) (iii) → (a) (iv) → (b)
67. (i) → (b) (ii) → (a) (iii) → (d) (iv) → (c)

V. Assertion and Reason Type

68. (iii) 69. (iii) 70. (iv) 71. (ii) 72. (iv) 73. (i) 74. (iv)

VI. Long Answer Type

75. (A) $\xrightarrow{\text{Ozonolysis}}$ $2CH_3CHO$

$C_4H_8 \xrightarrow{HCl} C_4H_9Cl$
(A) (B)

Addition of HCl has occurred on 'A'. This implies 'A' is an alkene.

$C_4H_9Cl \xrightarrow{NH_3} C_4H_{11}N$
(B) (C)

Cl in compound 'B' is substituted by NH_2 to give 'C'.

(C) $\xrightarrow[H_2O]{NaNO_2/HCl}$ (D)

'C' gives a diazonium salt with $NaNO_2/HCl$ that liberates N_2 to give optically active alcohol. This means that 'C' is an aliphatic amine. Number of carbon atoms in amine is same as in compound 'A'.

Since products of ozonolysis of compound 'A' are $CH_3-CH=O$ and $O=CH-CH_3$. The compound 'A' is $CH_3-CH=CH-CH_3$

On the basis of structure of 'A' reactions can be explained as follows :

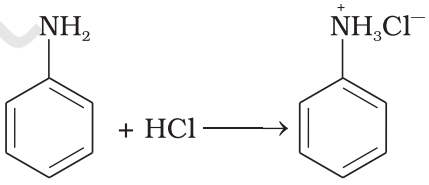
$$CH_3-CH=CH-CH_3 \xrightarrow{HCl} CH_3CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$$
(A) (B)

$$CH_3-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3 \xrightarrow{NH_3} CH_3-CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_3$$
(B) (C)

$$CH_3-CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_3 \xrightarrow[H_2O]{NaNO_2/HCl} CH_3-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_2CH_3}{\overset{|}{C}}}}-H$$
(Optically active)

(C) (D)

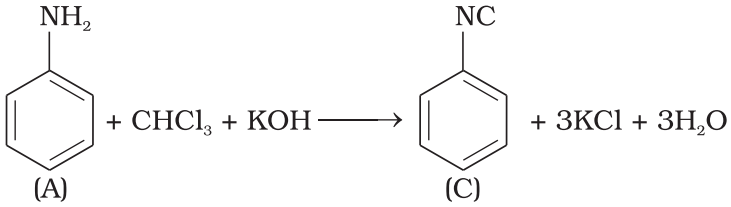
76.



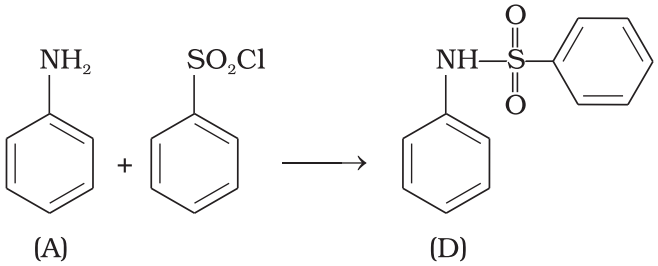
(A) (B)

Aniline (Colourless liquid, sparingly soluble in water)

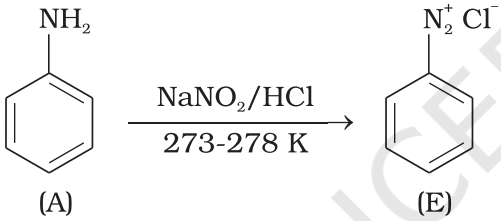
Anilinium chloride (Water soluble salt)

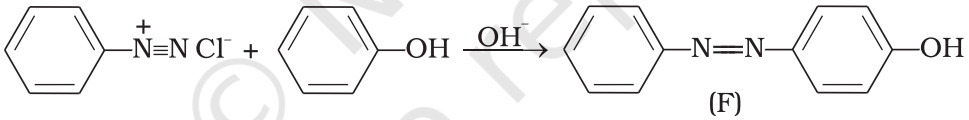


Benzene isonitrile

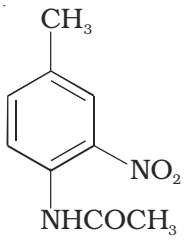


N-Phenylbenzenesulphonamide
(soluble in alkali)

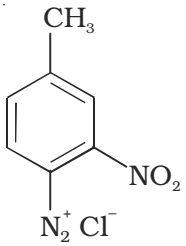




(F)
Orange dye

77. 1. Sn-HCl 2. 

3. H_2O/H^+

4. 

5. H_3PO_2/H_2O