

# 13

## Amines

### Previous Years' Examination Questions

Practice the Real Questions

#### 1 Mark Questions

1. Arrange the following in increasing order of their basic strength in aqueous solution :  
 $\text{CH}_3\text{NH}_2$ ,  $(\text{CH}_3)_3\text{N}$ ,  $(\text{CH}_3)_2\text{NH}$  [Delhi 2013]
2. Write the structure of prop-2-en-1-amine.  
[All India 2013]
3. Write the structure of N-methylethanamine.  
[All India 2013]
4. Write the structure of 2-aminotoluene.  
[All India 2013]
5. Arrange the following compound in an increasing order of basic strengths in their aqueous solutions  
 $\text{NH}_3$ ,  $\text{CH}_3\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$ ,  $(\text{CH}_3)_3\text{N}$   
[Delhi 2012, All India, Foreign 2009]
6. Arrange the following compounds in an increasing order of their solubility in water.  
 $\text{C}_6\text{H}_5\text{NH}_2$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$ ,  $\text{C}_2\text{H}_5\text{NH}_2$   
[All India 2011C; 2008; Delhi 2011]
7. Write one reaction that can be used as a test for primary amines. [Foreign 2011]
8. Rearrange the following in an increasing order of their basic strength.  
 $\text{C}_6\text{H}_5\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$  and  $\text{CH}_3\text{NH}_2$  [All India 2011; Foreign 2009]
9. Give a chemical test to distinguish between ethylamine and aniline.  
[All India 2011, 2010, 2009C]
10. Give IUPAC name of  
 $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$ .  
[Delhi 2010]
11. Give a chemical test to distinguish between aniline and N-methylaniline.  
[All India 2010; Delhi 2006]
12. Why electrophilic substitution takes place more readily in aromatic amines than benzene? [Delhi 2010C]
13. Write a chemical equation to illustrate the ammonolysis reaction. [Delhi 2009C]
14. Rearrange in increasing order of their basic strength.  
Aniline, p-nitroaniline and p-toluidine.  
[Foreign 2008]

15. Write a chemical reaction in which iodide ion displaces diazonium group from a diazonium salt. [All India 2008]
16. Account methylamine in water reacts with ferric chloride to give a precipitate of ferric hydroxide. [All India 2008]
17. Write commercial use of N, N-dimethyl aniline. [Foreign 2007]
18. Why do amines react as nucleophiles? [All India 2007]
19. Write the chemical equations for the following chemical reactions. A primary amine is prepared from a primary alkyl halide. [Foreign 2007]
20. Write IUPAC name of  $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CONHCH}_3$ . [Delhi 2006]
21. Why aqueous ethylamine turns red litmus blue? [Delhi 2006]
22. Give a chemical test to distinguish a primary and a secondary amine. [All India 2006]
23. What happens when aniline is treated with bromine? [All India 2006]
24. Like ammonia, amines are good nucleophiles, why? [Delhi 2006C]
25. Why is an aqueous solution of amines basic in nature? [Delhi 2006C]

## 2 Marks Questions

26. Describe the following giving the relevant chemical equation in each case.  
 (i) Carbylamine reaction  
 (ii) Hofmann's bromamide reaction [All India 2012; Delhi 2012]
27. Complete the following reaction equations,  
 (i)  $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{H}_3\text{PO}_2 + \text{H}_2\text{O} \longrightarrow$   
 (ii)  $\text{C}_6\text{H}_5\text{NH}_2 + \text{Br}_2 (\text{aq}) \longrightarrow$  [All India 2012]
28. How will you convert  
 (i) nitrobenzene to aniline?  
 (ii) aniline to iodobenzene? [Delhi 2011]
29. Illustrate the following with an example of reaction in each case. [Delhi 2011C]  
 (i) Sandmeyer's reaction  
 (ii) Coupling reaction
30. Convert [Delhi 2011C]  
 (i) nitrobenzene to phenol  
 (ii) aniline to chlorobenzene
31. Account for the following  
 (i) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.  
 (ii) Amines are more basic than alcohols of comparable molecular masses. [All india 2011 C]
32. How will you convert  
 (i) aniline to benzonitrile?  
 (ii) ethanamine to ethanoic acid? [Delhi 2011C]
33. How will you bring about the following conversions?  
 (i) Methylamine into iodomethane  
 (ii) Chlorobenzene into *p*-chloroaniline. [Delhi 2011C]
34. (i) Why aniline does not undergo Friedel-Craft's reaction? [Delhi 2008C]  
 (ii) Why can primary aromatic amines be not prepared by Gabriel phthalimide synthesis? [All India 2011C]
35. Write equations for  
 (i) Gabriel phthalimide reaction  
 (ii) Hofmann's bromamide reaction [Foreign 2011]
36. Give a chemical test to distinguish between  
 (i) methylamine and dimethylamine  
 (ii) aniline and N-methyl amine [Delhi 2010, 2008; Foreign 2009]
37. Identify A and B in each of the following processes  
 (i)  $\text{CH}_3\text{CH}_2\text{Cl} \xrightarrow{\text{NaCN}} \text{A} \xrightarrow[\text{NH}_2]{\text{Reduction}} \text{B}$   
 (ii)  $\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow{\text{NaNO}_2/\text{HCl}} \text{A} \xrightarrow[\text{OH}^-]{\text{C}_6\text{H}_5\text{NH}_2} \text{B}$  [All India 2010]

## Amines

38. Write one chemical reaction each to illustrate the following:

(i) Acetylation

(ii) Gabriel phthalimide synthesis

[Delhi 2010C]

39. Assign reason for

(i) amines are less acidic than alcohols of comparable molecular masses.

(ii) aliphatic amines are stronger bases than aromatic amines. [All India 2009C]

40. How are the following conversions carried?

(i) Aniline to nitrobenzene.

(ii) Ethanamine to N-ethylethanamide.

[Foreign 2009]

41. Arrange the following substances.

$C_6H_5NH_2$ ,  $(C_2H_5)_2NH$ ,  $(C_2H_5)_3N$ ,  $C_2H_5NH_2$

(i) In an increasing order of basic strength in water.

(ii) In a decreasing order of basic strength in gas phase. [Foreign 2008]

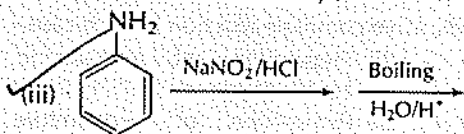
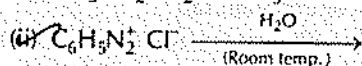
42. State the reactions and reaction conditions for the following conversions.

(i) Benzene diazonium chloride to nitrobenzene.

(ii) Aniline to benzene diazonium chloride [Foreign 2008]

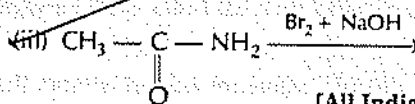
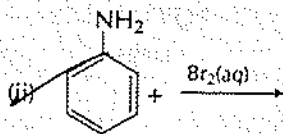
## 3 Marks Questions

43. Complete the following reactions



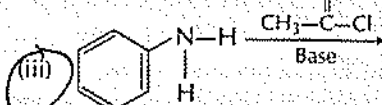
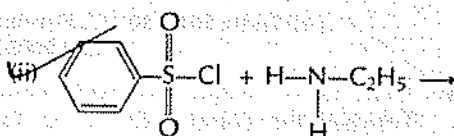
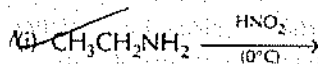
[All India 2013]

44. Write the main products of the following reactions.



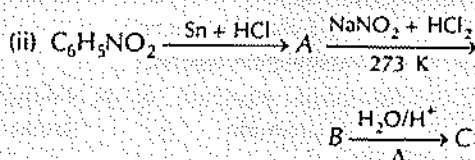
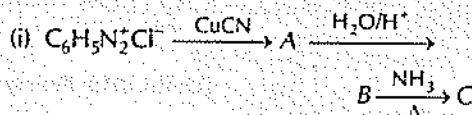
[All India 2013]

45. Write the main products of the following reactions



[All India 2013]

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



[Delhi 2013]

47. Write chemical equation for the following conversions.

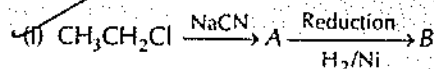
(i) Nitrobenzene to benzoic acid

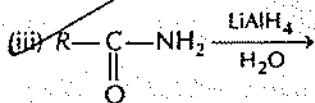
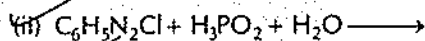
(ii) Benzyl chloride to 2-phenylethanamine

(iii) Aniline to benzyl alcohol

[Delhi 2012]

48. Complete the following reactions.





[Delhi 2011; All India 2010; Foreign 2010]

49. State reasons for the following.

- $pK_b$  value for aniline is more than that for methylamine.
- Ethylamine is soluble in water whereas aniline is not soluble in water.
- Primary amines have higher boiling points than tertiary amines.

[All India 2011, 2010C; Foreign 2010; Delhi 2009C; 2008]

50. Give one the chemical test each to distinguish between the compounds in the following pairs.

- Methylamine and dimethylamine
- Aniline and benzylamine
- Ethylamine and aniline

[All India 2010, 2011; Foreign 2008, 2009]

51. Complete the following reactions.

- $C_6H_5N_2Cl + C_6H_5NH_2 \longrightarrow$
- $C_6H_5N_2Cl + CH_3CH_2OH \longrightarrow$
- $RNH_2 + CHCl_3 + KOH \longrightarrow$

[Delhi 2010; Foreign 2010]

52. (i) Write one chemical reaction for each.

- Carbylamine reaction
- Acetylation reaction
- Write structure of N,N-ethylmethyl ethanamide

[Delhi 2010C]

53. Giving an example for each describe the following reactions

- Hofmann's bromamide reaction
- Gattermann reaction
- Coupling reaction

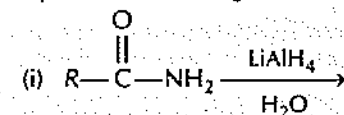
[Delhi 2009, 2008C; Foreign 2008]

54. Complete the following reaction equations.

- $C_6H_5NH_2 + CH_3COCl \longrightarrow$
- $C_2H_5NH_2 + C_6H_5SO_2Cl \longrightarrow$
- $C_2H_5NH_2 + HNO_2 \longrightarrow$

[All India 2009]

55. Complete the following reaction equations.



- $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$
- $C_6H_5NH_2 + Br_2(aq) \longrightarrow$

[All India 2012]

56. How are the following conversions carried out?

- Aniline to nitrobenzene
- Ethanamine to N-ethylethanamide
- Chloroethane to propan-1-amine

[Foreign 2009]

57. State the reactions and reaction conditions for the following conversions.

- Benzene diazonium chloride to nitrobenzene
- Aniline to benzene diazonium chloride
- Ethylamine to methylamine

[Foreign 2008]

58. How could you achieve the following conversions?

- Nitrobenzene to aniline
- An alkyl halide to a quaternary ammonium salt.
- Aniline to benzonitrile

[Delhi 2007]

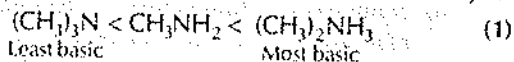
59. Give complete reaction in each case.

- Preparation of ethylamine from acetaldehyde.
- Preparation of benzonitrile from aniline.
- Preparation of ethyl isonitrile from ethylamine.

[Delhi 2006C]

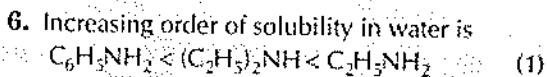
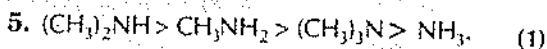
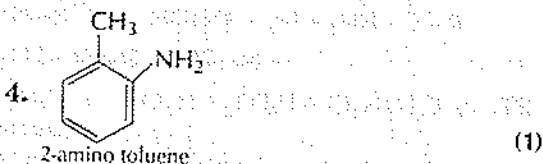
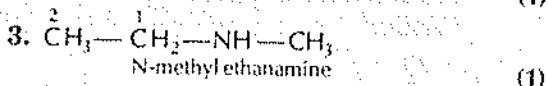
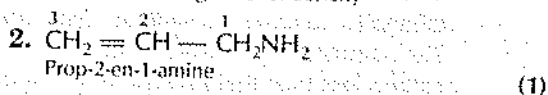
## Step-by-Step Solutions

1. Basicity increases with increase in the no. of R groups but 3° amine are least basic due to steric hindrance. Thus, the order of basicity is

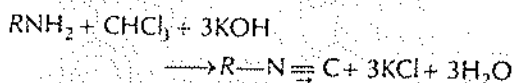


Least basic Most basic

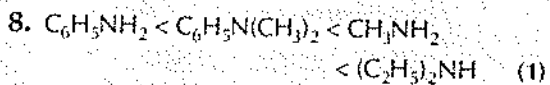
—————> Increasing order of basicity



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



It is the test for primary amines. (1)

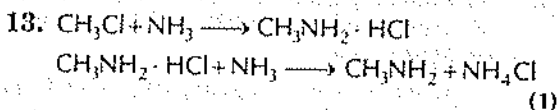


9. Ethylamine and aniline can be distinguished by azo dye test. When aniline is treated with  $\text{HNO}_2$  followed by treatment with alkaline solution of 2-naphthol, an orange dye is obtained but ethylamine gives  $\text{N}_2$  gas with the formation of 1° alcohols. (1)

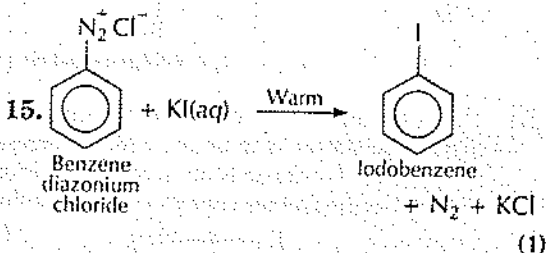
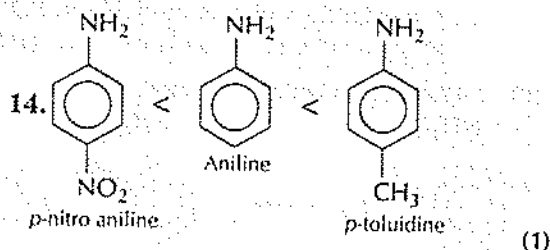
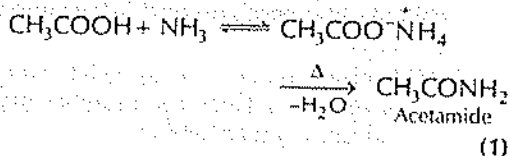


11. On adding  $\text{CHCl}_3$  and  $\text{KOH}$ , aniline will give offensive smell due to formation of phenyl carbylamine (phenyl isocyanide), while N-methylaniline will not react. (1)

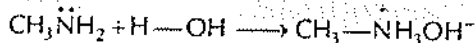
12. Due to strong activating effect of the  $-\text{NH}_2$  group, aromatic amines undergo electrophilic substitution reactions readily and it is difficult to stop the reaction at the monosubstitution stage. (1)



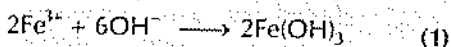
OR



16. Methylamine being more basic than water accepts a proton from water liberating  $\text{OH}^-$  ions.



These  $\text{OH}^-$  ions combine with  $\text{Fe}^{3+}$  ions present in  $\text{H}_2\text{O}$  to form a brown ppt. of hydrated ferric hydroxide.



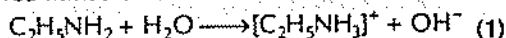
17. It is used as a raw material in the preparation of a number of dyes. (1)

18. Due to the presence of lone pair of electrons on nitrogen atom, amines can donate them and act as nucleophiles. (1)

19.  $RX + NH_3 \longrightarrow RNH_2 + HX$  (1)

20. 3-bromo-N-methyl butanamide. (1)

21. Aqueous ethylamine is basic in nature because of the presence of free  $OH^-$  ions, hence it turns red litmus blue.

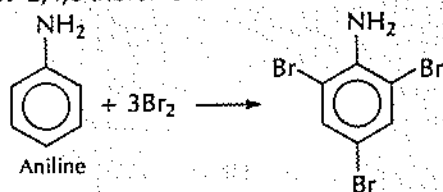


22. The amine is treated with benzene sulphonyl chloride (Hinsberg's reagent) in the presence of aq. KOH.

(i) A clear solution in aq. KOH which on acidification gives an insoluble material indicates primary amine. (1/2)

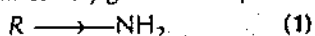
(ii) A precipitate which is insoluble in KOH solution indicates secondary amine. (1/2)

23. 2,4,6-tribromo aniline is formed.

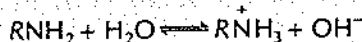


2, 4, 6-tribromoaniline (1)

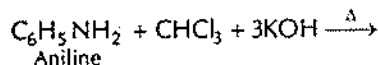
24. This is because of the electron releasing effect of the alkyl group in an amine which increases the electron density on N atom of amino group. This makes the amines very good nucleophiles.



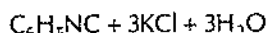
25. In aqueous solution, amines accept a proton from water and liberate  $OH^-$  ions. Because of the presence of these  $OH^-$  ions, their aqueous solution is basic. (1)



26. (i) Carbylamine reaction Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamine which are foul smelling substances. This reaction is known as carbylamine reaction. (1)

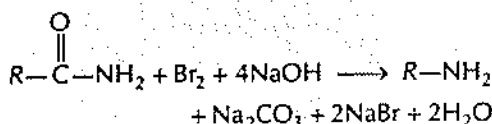


Aniline



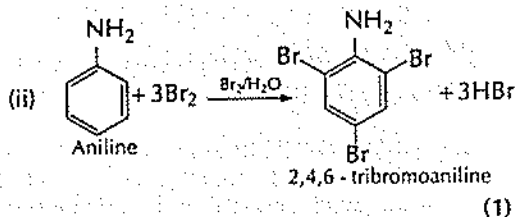
This reaction is used as a test for primary amine.

(ii) Hofmann's bromamide degradation reaction It is a method for the preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. The amines so formed contains one carbon less than that present in the parent amide. (1)

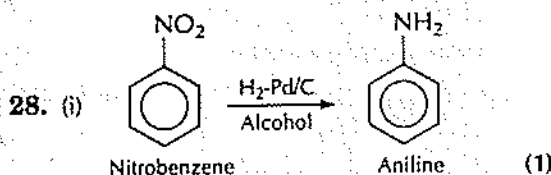


27. (i)  $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow C_6H_6 + N_2 + H_3PO_3 + HCl$  (1)

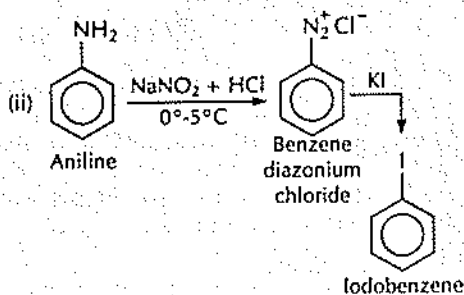
Benzene



(1)



(1)

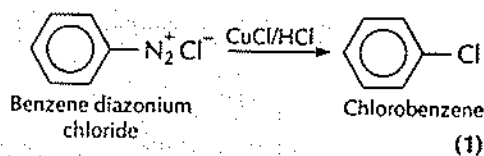


(1)

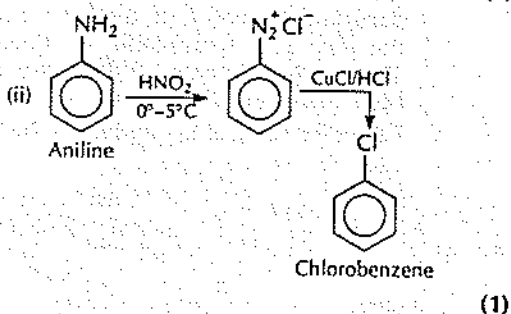
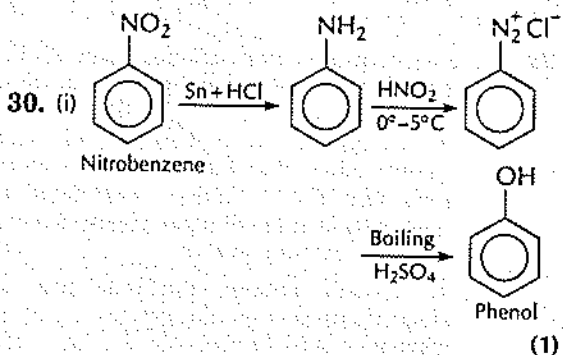
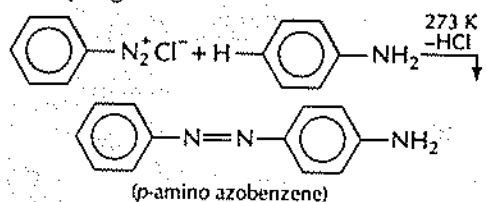
29. (i) Sandmeyer reaction By this reaction nucleophiles like  $Cl^-$ ,  $Br^-$ ,  $CN^-$  etc., can easily be introduced in the benzene ring

## Amines

by treating the diazonium salt solution with corresponding halogen acid in the presence of Cu(I) ion.



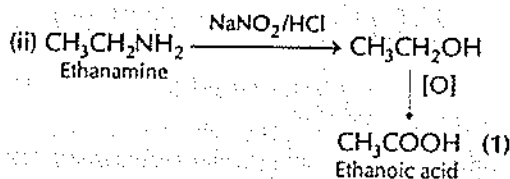
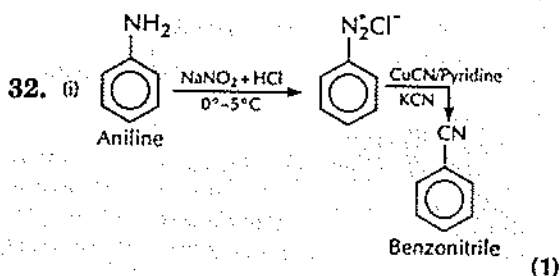
- (ii) **Coupling reaction** Benzene diazonium chloride reacts with aniline, in which the molecule at its *para* position is coupled with the diazonium salt to form *p*-amino azobenzene. This is an example of coupling reaction.



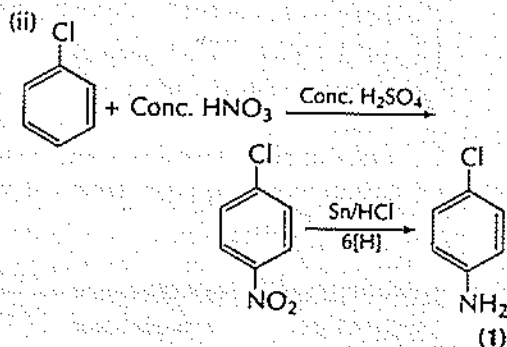
31. (i) It is due to resonance stabilization possible in diazonium salts of aromatic amines, which is not possible in diazonium salts of

aliphatic amines, which is not possible in diazonium salts of aliphatic amines.. (1)

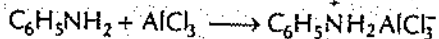
- (ii) Since 'N' is less electronegative than 'O', therefore, lone pair of electrons are easily available. (1)



33. (i)  $\text{CH}_3\text{NH}_2 + \text{HNO}_2 \longrightarrow \text{CH}_3\text{OH} \xrightarrow{\text{P/I}_2} \text{CH}_3\text{I}$  (1)

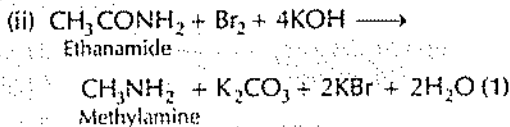
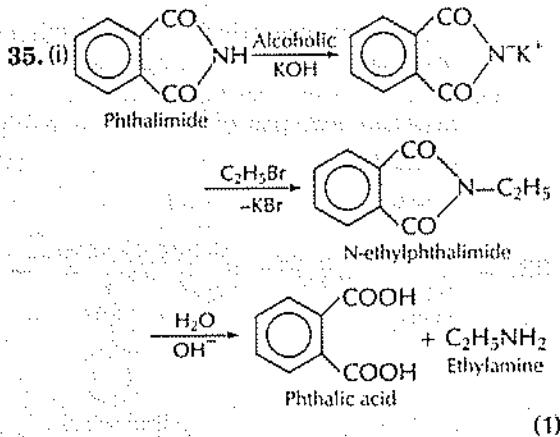


34. (i) Aniline being a Lewis base reacts with Lewis acid ( $\text{AlCl}_3$ ) to form a salt.

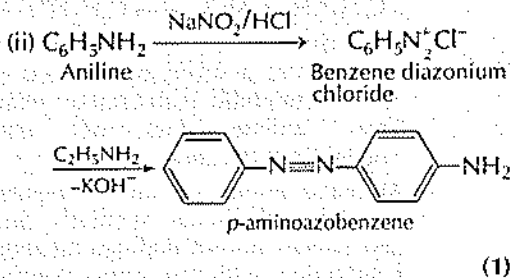
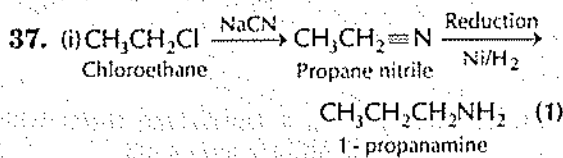


As a result, N acquires a positive charge so it acts as a strong deactivating group for electrophilic substitution reaction. Thus, aniline does not undergo Friedel-Crafts reaction. (1)

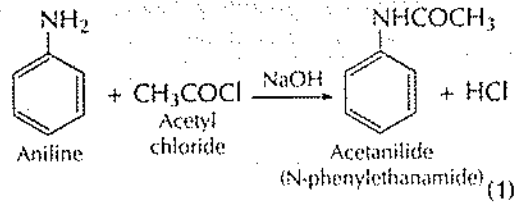
- (ii) Aromatic amines cannot be prepared by Gabriel phthalimide synthesis because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide. (1)



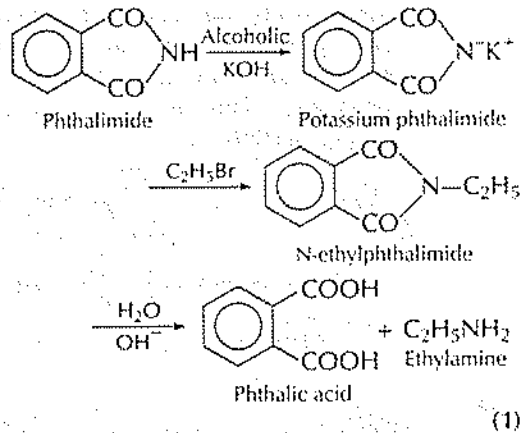
36. (i) Methyl amine gives carbylamine test, i.e., on treatment with alc. KOH and chloroform, followed by heating it gives offensive odour of methyl isocyanide. Dimethyl amine does not give this test. (1)
- (ii) Aniline gives carbylamine test i.e., on treatment with alc. KOH and chloroform followed by heating it gives offensive odour of phenylisocyanide but N-methyl aniline being secondary amine, does not show this test. (1)



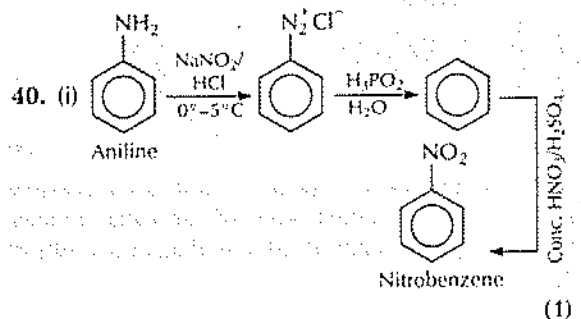
38. (i) Acetylation



- (ii) Gabriel phthalimide synthesis

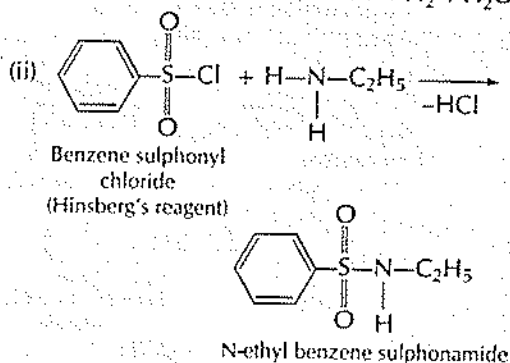
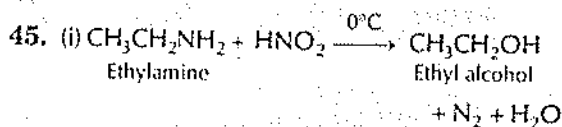
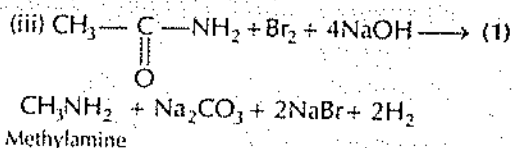
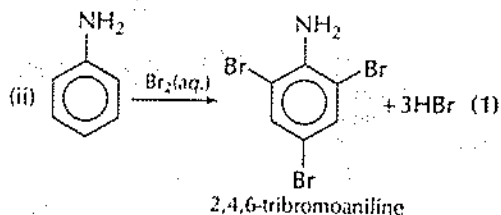
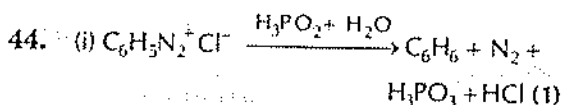
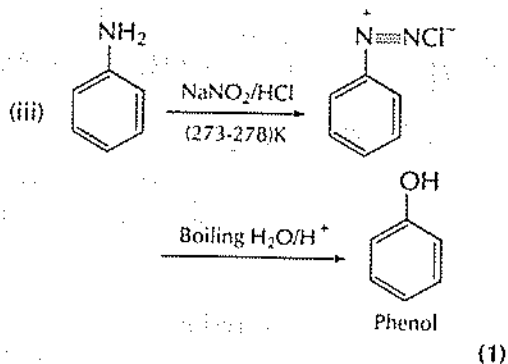
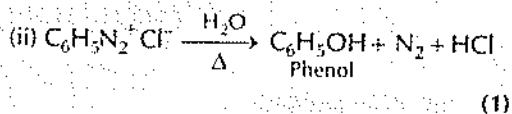
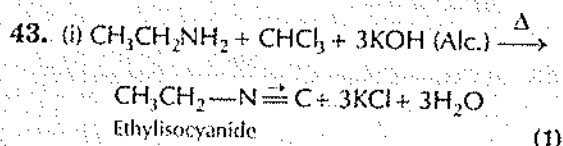
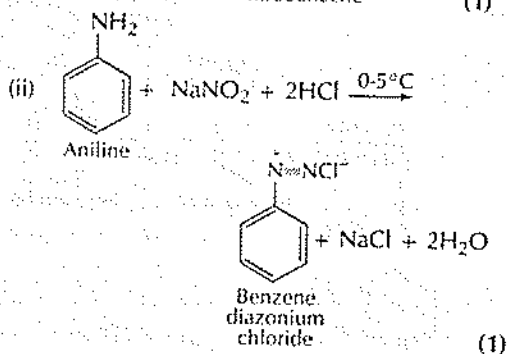
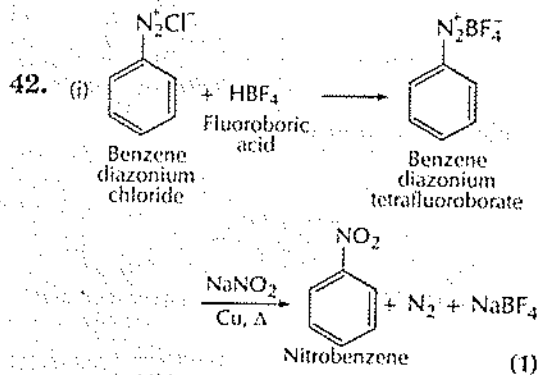
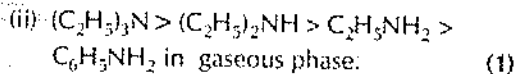
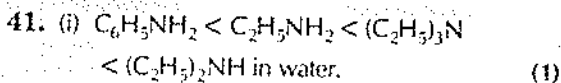
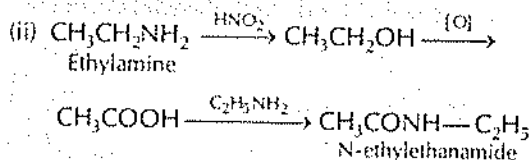


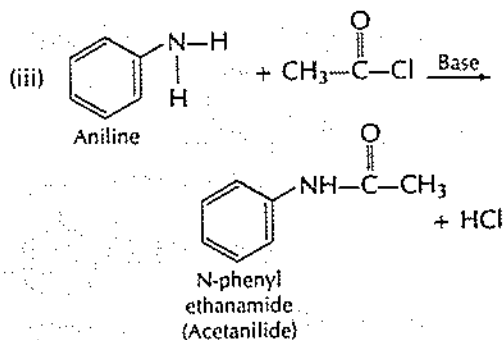
39. (i) Loss of proton from amines gives  $\text{RNH}^-$  ion whereas loss of proton from alcohol forms alkoxide ion. Since, O is more electronegative than N therefore,  $\text{RO}^-$  can accommodate the negative charge more easily than  $\text{RNH}^-$ . Further O—H bond is more polar than N—H bond. Hence, amines are less acidic than alcohol. (1)
- (ii) In aromatic amines, the lone pair of electrons present on nitrogen takes part in resonance and hence, not available for donation. However, in aliphatic amines, the lone pair is available for donation. That's why aliphatic amines are more basic than aromatic amines. (1)
- Larger the value of  $K_b$ , stronger is the base.



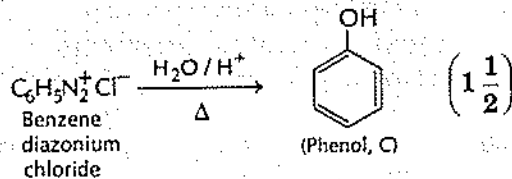
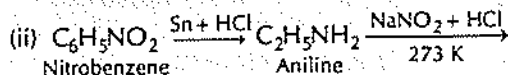
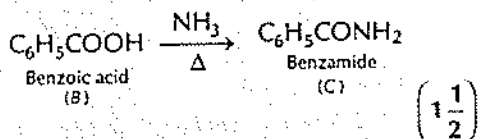
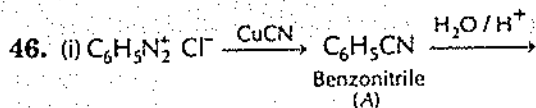


# Amines

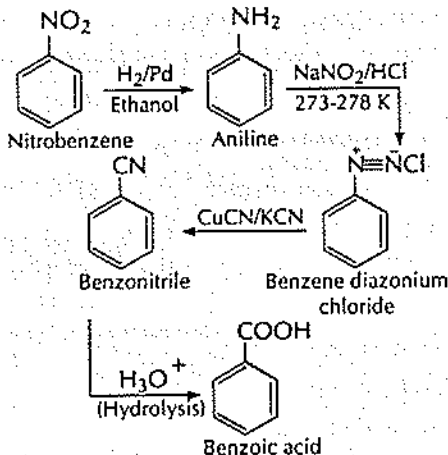




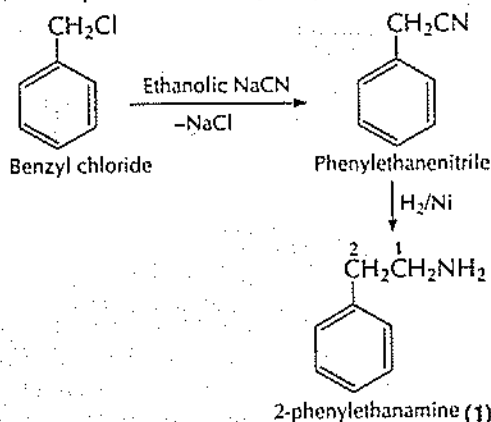
(1 × 3 = 3)



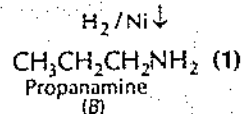
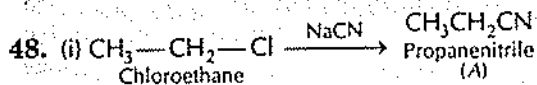
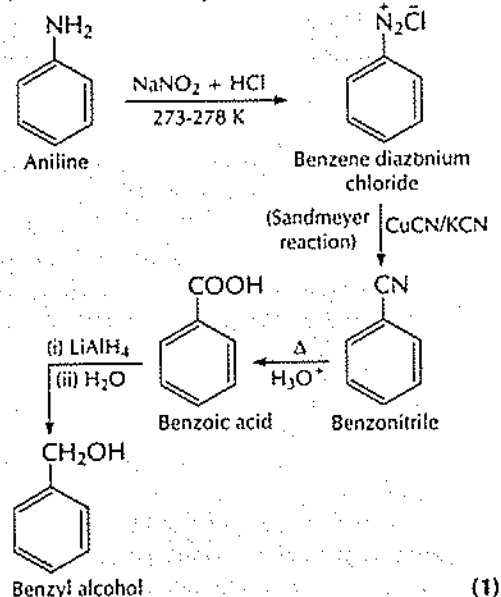
47. (i) Nitrobenzene to benzoic acid



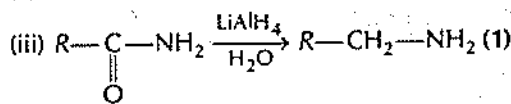
(ii) Benzyl chloride to 2-phenylethanamine



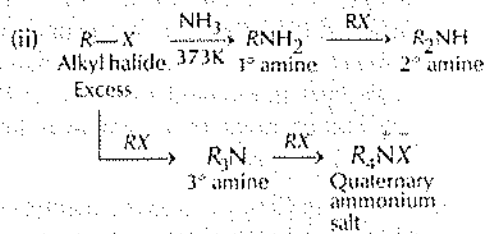
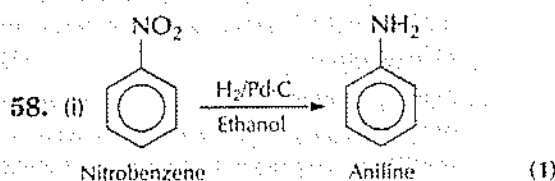
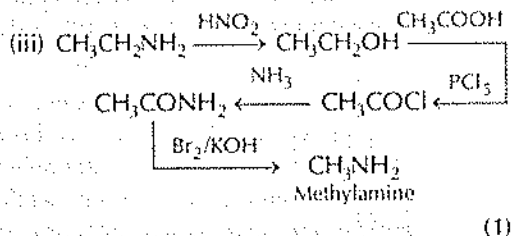
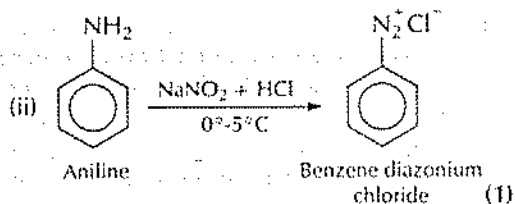
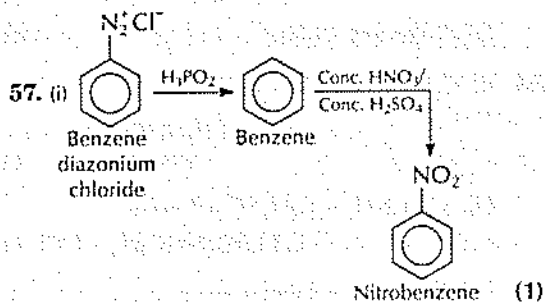
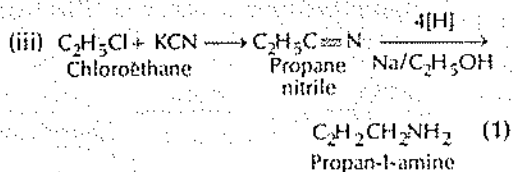
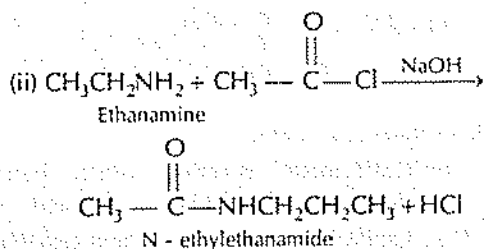
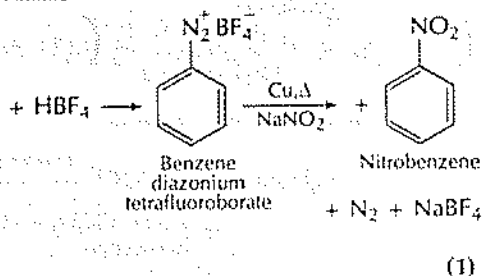
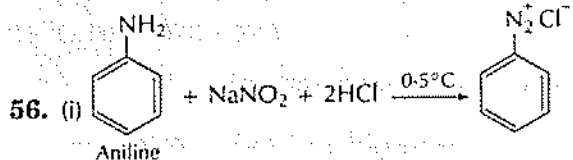
(iii) Aniline to benzyl alcohol



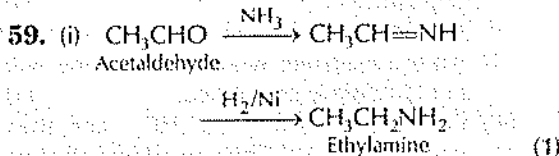
(ii) Refer ans 44(i) (1)







(iii) Refer ans. 29 (i).



(ii) Refer ans. 29 (i).

