

UNIT 13

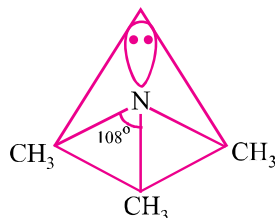
AMINES

Points to Remember

- Amines are alkyl and/or aryl derivatives of $\ddot{\text{N}}\text{H}_3$.
- Functional groups of 1°, 2° and 3° amines are respectively as given below :

$$-\ddot{\text{N}}\text{H}_2, -\ddot{\text{N}}\text{H}- \text{ and } -\ddot{\text{N}}-$$
- Gabriel phthalimide synthesis can't be used for the preparation of 2° and 3° amines. It gives aliphatic primary amine only.
- Hoffmann's bromamide reaction gives 1° amines having one carbon atom less than parent primary amide.
- The order of basic strength of aliphatic amines is :
 - Aliphatic amines are more basic than $\ddot{\text{N}}\text{H}_3$.
 - In aqueous solution medium, the order is $2^\circ > 1^\circ > 3^\circ$ (for $-\text{CH}_3$ group) and $2^\circ > 3^\circ > 1^\circ$ for $-\text{C}_2\text{H}_5$ group.
 - In non-aqueous medium or gaseous phase, the order is $3^\circ > 2^\circ > 1^\circ$.
- Basic strength of aromatic amines :
 - Aromatic amines are weaker bases than $\ddot{\text{N}}\text{H}_3$.
 - ERGs like $-\text{CH}_3$, $-\text{OR}$, $-\text{NH}_2$ etc. increase basic strength while EWGs like $-\text{NO}_2$, $-\text{CN}$ etc. decrease the basic strength. The effect of substituents is more at para positions and less at meta position.
- Basic strength of amines is expressed in terms of K_b or $\text{p}K_b$.
- 1°, 2° and 3° amines can be distinguished by Hinsberg's test.
- Hinsberg's reagent is benzenesulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$).
- 3° amines like trimethylamine are used as insect attractants.
- Diazonium salts are represented by the general formula $[\text{Ar N} \equiv \text{N}]^+ \text{X}^-$.

12. **Structure of amines :** Pyramidal for trimethyl amine $(\text{CH}_3)_3 \ddot{\text{N}}$. They are Lewis bases.



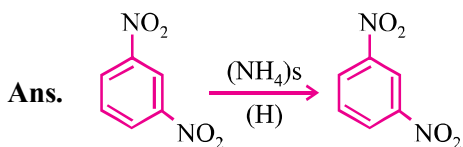
13. Aliphatic amines are known as amino alkanes.
14. Aliphatic amines are more basic than NH_3 .
i.e., $\text{CH}_3\text{NH}_2 > \text{NH}_3$
15. Aniline is less basic than NH_3 (*i.e.*, $\text{C}_6\text{H}_5\text{NH}_2 < \text{NH}_3$).
16. Carbylamine test only given by 1° amines.
17. Manich reaction involves the reaction of ketones with HCHO and NH_3 (or amine) in acidic medium to form Manich bases.
18. 1° amines give effervescence with HNO_2 .
19. $-\text{NH}_2$ group in aniline is *o*- and *p*- directing and is highly activating in nature.
20. Acylation of aniline is done before subjecting it to nitration or halogenation.
21. Aliphatic diazonium salts are very unstable and do not exist while aromatic salts are relatively stable.
22. These salts are prepared from 1° aryl amines by diazotization reactions.
23. Diazotised salts (diazonium salts) are used to prepare a variety of aromatic compounds.
24. $\text{R}-\text{C}\equiv\text{N}$ have generally pleasant odours but alkyl isocyanides have highly unpleasant odours.
25. Alkyl isocyanides have lower boiling points than that of isomeric alkyl cyanides due to lower dipole moments.
26. Arenediazonium salts are highly reactive compounds and reactivity is due to excellent leaving ability of diazo group as N_2 gas.

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

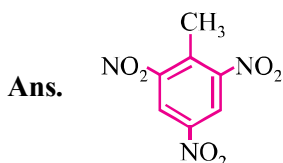
Q. 1. Write IUPAC name of CH_3NC .

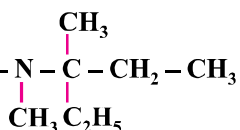
Ans. Methane carbylamine.

Q. 2. Convert m-dinitrobenzene to m-nitro aniline.



Q. 3. Draw structure of TNT, an explosive.



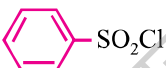
Q. 4. Write IUPAC name of $\text{CH}_3 - \text{N} - \text{C} - \text{CH}_2 - \text{CH}_3$


Ans. 3-N-Methyl-N,N-dimethyl pentanamine

Q. 5. Give one use of quaternary ammonium salts.

Ans. It is used as detergents, e.g., $[\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_2]^+\text{Cl}^-$.

Q. 6. What is Hinsberg's reagent ?

Ans. Benzene sulphonyl chloride, 

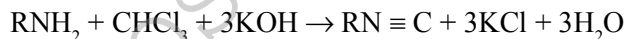
Q. 7. Why aniline dissolves in HCl ?

Ans. $\text{C}_6\text{H}_5\text{NH}_2 + \text{HCl} \rightarrow [\text{C}_6\text{H}_5\text{NH}_3]^+\text{Cl}^-$

It dissolves due to its basic nature.

Q. 8. How will you test the presence of primary amine ?

Ans. By carbyl amine test.



Q. 9. What is vapour phase nitration ?

Ans. $\text{CH}_4 + \text{HNO}_3 \xrightarrow{623 \text{ K}} \text{CH}_3\text{NO}_2$
 (High temperature and nitration in vapour phase only)

Q. 10. Write one use of dopamine and atropine alkaloid.

Ans. Dopamine : Neurotransmitter

Atropine alkaloid : 0.5-1.0% solution ophthalmic examination.

Q. 11. Direct nitration of aniline is not carried out. Explain.

Ans. ($\text{H}_2\text{SO}_4 + \text{HNO}_3$) easily oxidized aniline into tarry complex product due to high e^- density on the benzene ring of aniline.

Q. 12. Among the compounds as following which will react with $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ to give product containing $> \text{C} = \text{N} -$?

(i) $\text{C}_6\text{H}_5\text{NH}_2$

(ii) $(\text{CH}_3)_3\text{N}$

(iii) $\text{C}_6\text{H}_5\text{NHC}_6\text{H}_5$

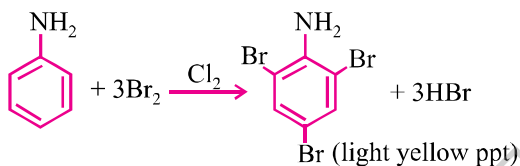
(iv) $\text{C}_6\text{H}_5\text{NHNH}_2$

Ans. $\text{C}_6\text{H}_5\text{NH}_2$ and $\text{C}_6\text{H}_5\text{NHNH}_2$.

Q. 13. How will you give expression for K_b to indicate its basic strength ?

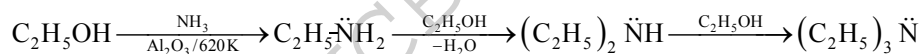
Ans.
$$K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{R}-\text{NH}_2]}$$

Q. 14. What happens when aniline is treated with bromine ?

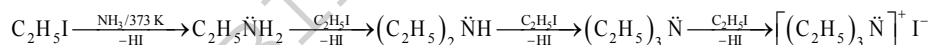
Ans. 

Q. 15. Write a chemical equation to illustrate the ammonolysis.

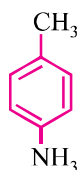
Ans. For alcohols :



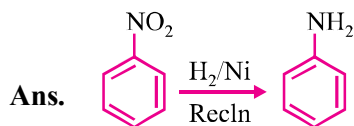
For alkyl halides :



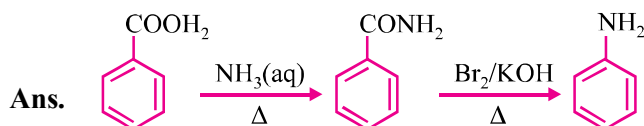
Q. 16. Write the structure of p-toluene.

Ans. 

Q. 17. Prepare/convert nitrobenzene into aniline.



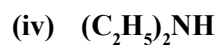
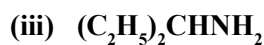
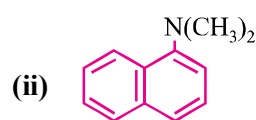
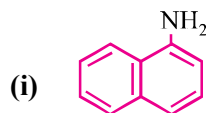
Q. 18. Convert C_6H_5COOH to $C_6H_5NH_2$.



Q. 19. Write isomerism exhibited by different amines.

Ans. Chain, position, metamerism, functional.

Q. 20. Classify the following as 1° , 2° and 3° amines :



Ans. (i) 1°

(ii) 3°

(iii) 1°

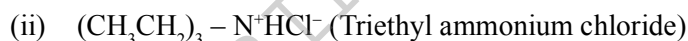
(iv) 2°

SHORT ANSWER TYPE QUESTIONS (2 Marks)

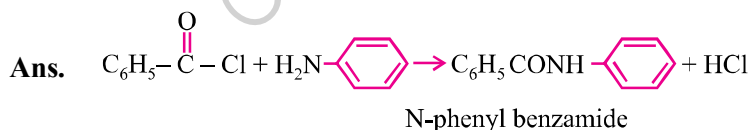
Q. 1. Complete the following acid-base reactions and name the products :



Ans. (i) $CH_3CH_2CH_2N^+H_3Cl^-$ (n-propyl ammonium chloride)



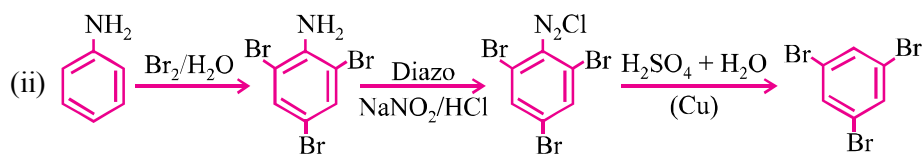
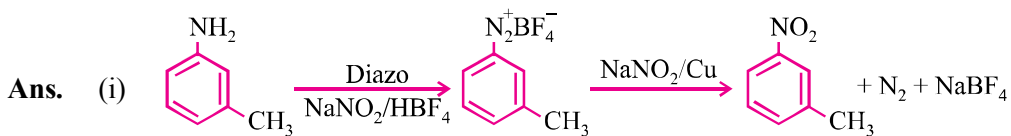
Q. 2. Write chemical reaction of $C_6H_5NH_2 + C_6H_5COCl$ and name product obtained.



Q. 3. How will you convert :

(i) **3-methylaniline** → **3-nitrotoluene**

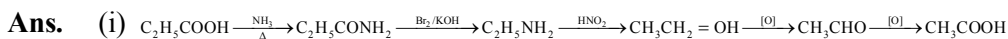
(ii) **Aniline** → **1, 3, 5-tribromobenzene**



Q. 4. How will you convert :

(i) **Propanoic acid** → **Ethanoic acid**

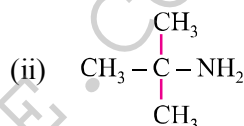
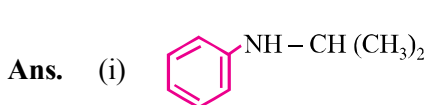
(ii) **Nitromethane** → **Dimethylamine**



Q. 5. Draw the structures of the following compounds :

(i) **N-isopropylaniline**

(ii) **t-butylamine**



Q. 6. Why $C_6H_5N^+(CH_3)_3OH^-$ a stronger base than NH_4OH ?

Ans. Due to EW – I effect of phenyl group, it decreases e^- density on nitrogen atom but no such group in NH_4OH .

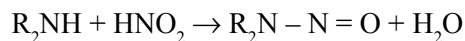
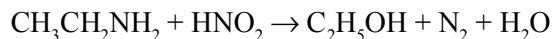
Q. 7. Explain K_b order : $Et_2NH > Et_3N > EtNH_2$ in aqueous solution.

Ans. Basicity of amines in aqueous solution depends upon :

- + I effect of an alkyl group.
- Extend of hydrogen bonding with H_2O .
- Steric effects of alkyl groups.

Q. 8. Distinguish between 1°, 2° and 3° amines by HNO₂ acid test.

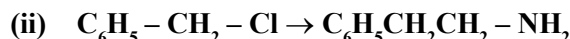
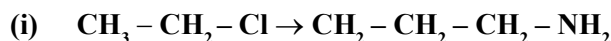
Ans. 1° gives N₂ gas. 2° gives yellow oily compound. 3° form water soluble salts.



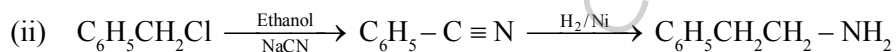
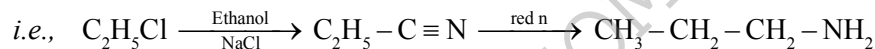
Q. 9. A compound 'A' having molecular formula C₃H₇ON reacts with Br₂ in presence of NaOH to give compound 'B'. This compound 'B' reacts with HNO₂ to form alcohol and N₂ gas. Identify compound 'A' and 'B' and write the reaction involved.

Ans. 'A' is CH₃CH₂CONH₂ $\xrightarrow[\text{NaOH}]{\text{Br}_2}$ CH₃CH₂NH₂ $\xrightarrow{\text{HNO}_2}$ C₂H₅OH + N₂ + H₂
(B)

Q. 10. Write chemical equation for the following conversions :



Ans. (i) With NaCN and reduction.



Q. 11. Account for :

(i) **Amino group in aniline is *o*- and *p*- directing in aromatic electrophilic substitution reactions. Aniline on nitration gives a substantial amount of *m*-nitroaniline.**

(ii) **Aniline does not go Friedel Crafts reaction.**

Ans. (i) It is because aniline is formed by protonation with NH_3^{\oplus} *i.e.*, EWG hence it is *m*-directing *i.e.*, 47%.

(ii) It is because aniline is basic, can form adduct with AlCl₃, electrophile cannot be generated.

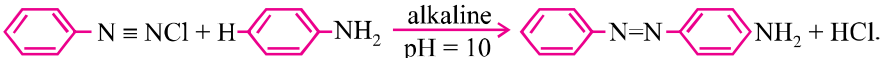
Q. 12. Account for the following :

- (i) Electrophilic substitution in aromatic amines takes place more readily than benzene.
- (ii) Nitro compounds have higher boiling points than hydrocarbons having almost same molecular mass.

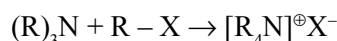
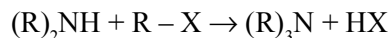
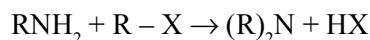
Ans. (i) $-\text{NH}_2$ is ERG, electrophilic substitution takes place faster.
 (ii) Nitro compounds are more polar than hydrocarbons therefore have more van der Waal's forces of attraction.

Q. 13. Write short notes on :

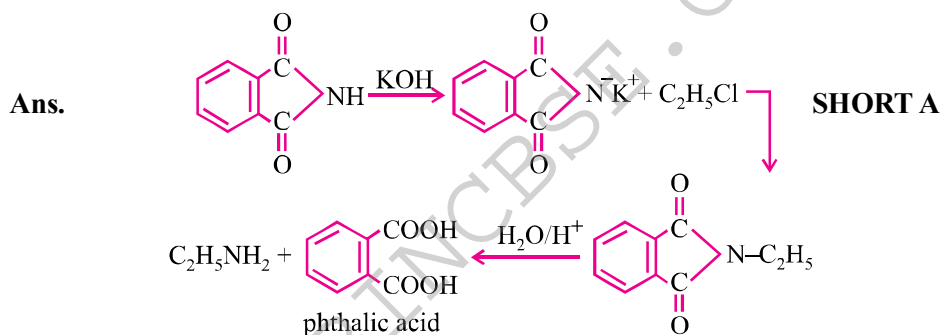
- (i) Coupling reaction
- (ii) Ammonolysis

Ans. (i) 

(ii) Ammonolysis : $\text{R} - \text{X} + \text{NH}_3 \rightarrow \text{R} - \text{NH}_2 + \text{HX}$



Q. 14. Prepare pure sample of 1° amine from 1° alkyl halide.



ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. What happens when :

- (i) An alkyl halide reacts with AgNO_2 and product is reduced.
- (ii) An alkyl halide is treated with AgCN and product is hydrolysed.
- (iii) Methyl magnesium is treated with cyanogens chloride.

- Ans.** (i) $R - X + AgNO_2 \rightarrow R - NO_2 \rightarrow R - NH_2$
- (ii) $R - X + AgCN \rightarrow RNC \rightarrow RNH_2 + HCOOH$
- (iii) $CH_3MgBr + CN - Cl \rightarrow CH_3CN + MgCl$

Q. 2. How would you prepare :

- (i) $C_6H_5NH_2$ from $C_6H_5NO_2$
- (ii) CH_3NH_2 from $C_2H_5NH_2$
- (iii) $C_2H_5NH_2$ from CH_3NH_2

Ans. (i)

- (ii) $C_2H_5NH_2 \xrightarrow{CH_3COOH} CH_3COONH_4 \xrightarrow{CH_3CONH_2} CH_3NH_2$
- (iii) $CH_3NH_2 \xrightarrow{CH_3OH} CH_3Cl \xrightarrow{CH_3CN} CH_3CH_2NH_2$

Q. 3. Write the structure of the products in each case :

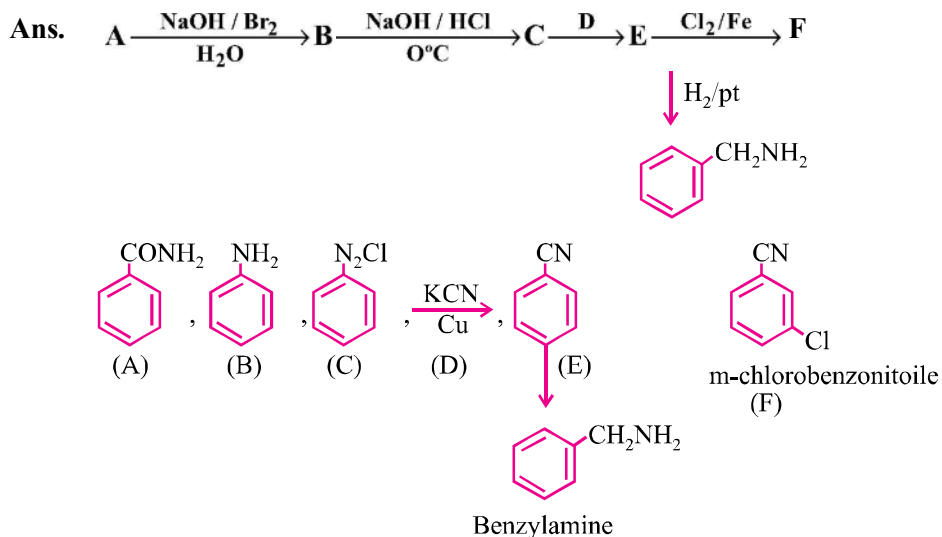
- (i) $CH_3CH_2NH_2$
- (ii) $CH_3CONHC_6H_5$
- (iii) CH_3CH_2CN

Ans. (i) $CH_3CH_2NHCOCH_3, CH_3COOH$

(ii)

(iii) $CH_3CH_2COOH + NH_4^+$

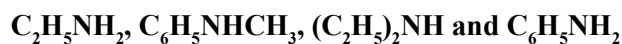
Q. 4. Write the structure of reagents/organic compounds 'A' to 'F':



LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. Arrange the following :

(i) In decreasing order of pK_b values :

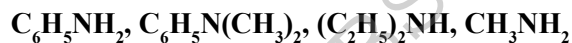


(ii) In increasing order of basic strength :

(a) Aniline, p-nitroaniline and p-toluidine



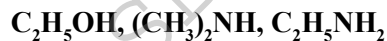
(iii) In decreasing order of basic strength :



(iv) Decreasing order of basic strength in gas phase :



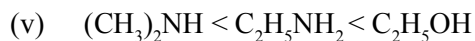
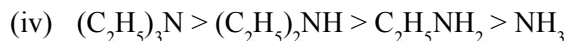
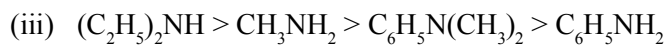
(v) Increasing order of boiling point :



Ans. (i) $\text{C}_2\text{H}_5\text{NH}_2 > \text{C}_6\text{H}_5\text{NHCH}_3 > \text{C}_6\text{H}_5\text{NH}_2 > (\text{C}_2\text{H}_5)_2\text{NH}$

(ii) (a) p-nitroaniline < aniline < p-toluidine





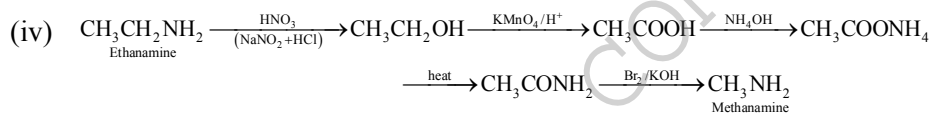
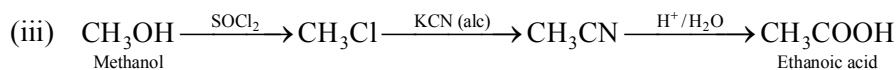
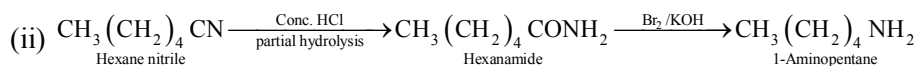
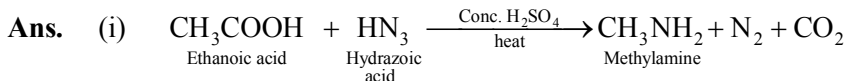
Q. 2. How will you convert :

(i) Ethanoic acid into methanamine

(ii) Hexane nitrile into 1-aminopentane

(iii) Methanol into ethanoic acid

(iv) Ethanamine into methanamine



Q. 3. Write short note on the following :

(i) Carbylamine reaction

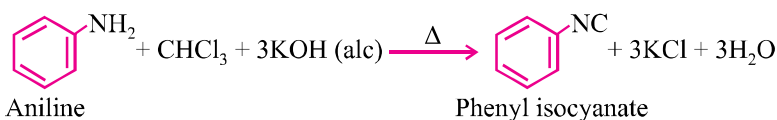
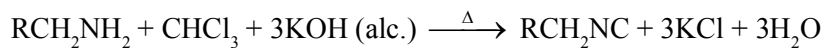
(ii) Diazotization

(iii) Hoffmann's bromide reaction

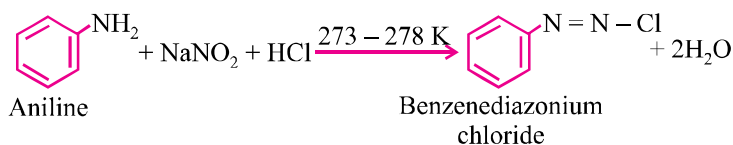
(iv) Coupling reaction

(v) Ammonolysis

Ans. (i) **Carbylamine reaction :** When primary amine (aromatic or aliphatic) warmed with chloroform and alc. KOH, isocyanides are formed which can be identified by their offensive smell. This test is used to identify the presence of primary amine or chloroform.

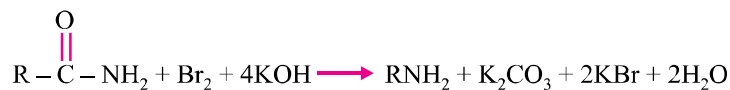


- (b) **Diazotization** : When primary aromatic amine is treated with $NaNO_2$ and HCl at 273-278 K, diazonium salt is obtained. This reaction is known as diazotization.



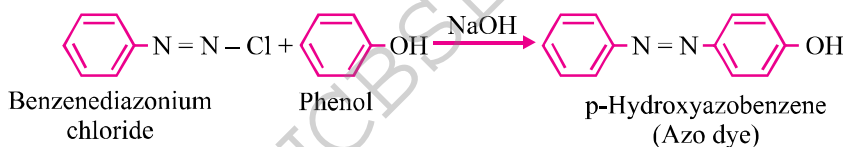
Benzenediazonium chloride is a very important synthetic compound, which can be changed into haloarenes, phenol, cyanobenzene, benzene etc.

- (c) **Hoffmann's bromide reaction** : When any primary amide (aliphatic or aromatic) is treated with bromine and alkali, it gives the amine of one carbon atom less.

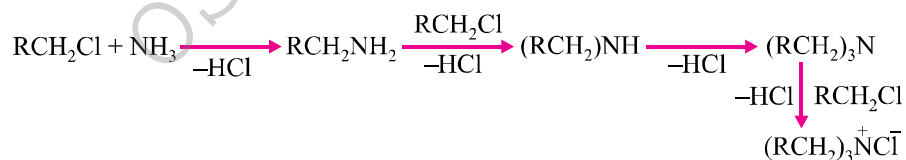


This reaction is used to reduce one carbon atom from a compound.

- (d) **Coupling reaction** : When benzenediazonium chloride is treated with phenols or aromatic amines, azo dyes are produced in which diazo ($-N=N-$) group is retained. Coupling reactions generally take place at p-position of phenol or aromatic amines.

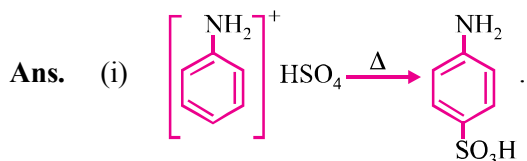


- (e) **Ammonolysis** : Reaction of alkyl halides with ammonia is known as ammonolysis. Ammonolysis generally gives the mixture of 1°, 2°, 3° amines and quaternary ammonium salt.



Q. 4. Complete the following reactions :

- (i) $C_6H_5NH_2 + H_2SO_4$ (conc.) \rightarrow
 (ii) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$
 (iii) $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow$
 (iv) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$
 (v) $C_6H_5NH_2 + CHCl_3 + 3KOH$ (alc.) \rightarrow



- (ii) $C_6H_6 + N_2 + HCl + CH_3CHO$
 (iii) $C_6H_5NHCOCH_3 + CH_3COOH$
 (iv) $C_6H_6 + H_3PO_3 + HCl + N_2$
 (v) $C_6H_5NC + 3KCl + 3H_2O$

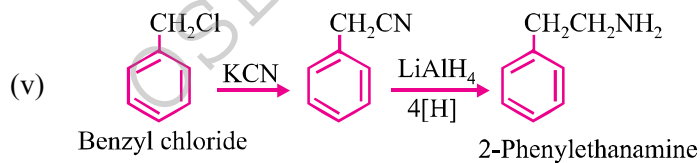
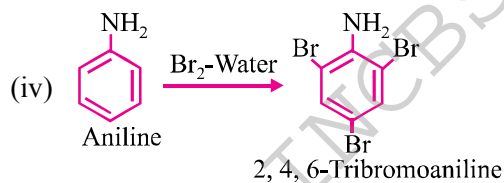
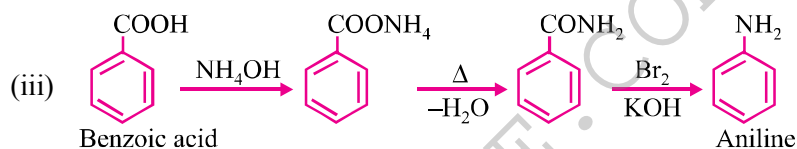
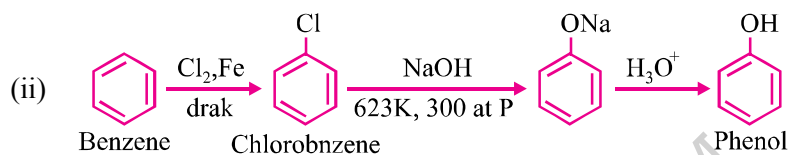
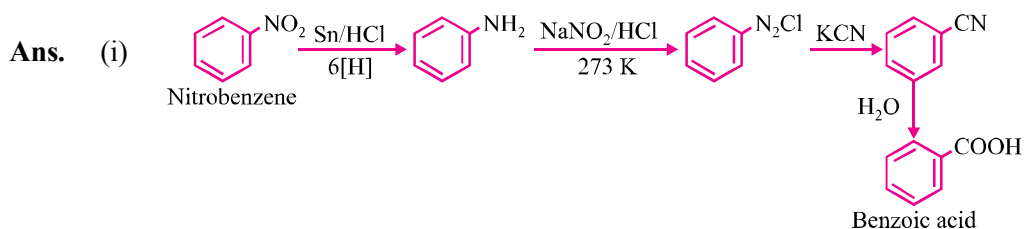
Q. 5. Write A, B and C in the given reactions :

- (i) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow{NH_3} C$
 (ii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0^\circ C]{HNO_2} C$
 (iii) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273 K]{HNO_2} B \xrightarrow[2\Delta]{H_2O/H^+} C$
 (iv) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$
 (v) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{partial hydrolysis}]{OH^-} B \xrightarrow{NaOH/Br_2} C$

- Ans.** (i) $C_6H_5CN, C_6H_5COOH, C_6H_5CONH_2$
 (ii) $CH_3CH_2CN, CH_3CH_2NH_2, CH_3CH_2OH$
 (iii) $C_6H_5NH_2, C_6H_5N_2Cl, C_6H_5OH$
 (iv) $CH_3CONH_2, CH_3NH_2, CH_3NH_3^+Cl^-$
 (v) $CH_3CH_2CN, CH_3CH_2CONH_2, CH_3CH_2NH_2$

Q. 6. Accomplish the following conversions :

- (i) $C_6H_5NO_2 \rightarrow C_6H_5 - COOH$
- (ii) Benzene \rightarrow m-bromophenol
- (iii) $C_6H_5COOH \rightarrow C_6H_5NH_2$
- (iv) Aniline \rightarrow 2, 4, 6 tribromoaniline
- (v) Benzylchloride \rightarrow 2-phenyl ethanamine



VALUE BASED QUESTIONS (4 Marks)

Q. 1. Sushil's friend want to play Holi with synthetic colours. Ramesh persuades his friends to play Holi with natural colours as synthetic colours may cause skin allergy. Sushil's friends agreed and prepared natural colours using flowers and leaves.

How are following dyes prepared from phenol :

- (i) p-hydroxyazobenzene
- (ii) p-aminoazobenzene
- (iii) Write the name of one pigment present in natural colours.
(Hint : Carotenoids)
- (iv) Mention the values shown by Sushil.

Q. 2. Neetu and Asha took organic compound synthesis as their chemistry project. They prepared benzene diazonium chloride and stored it at room temperature. Due to holiday, they start preparing azo dye but it cannot be prepared. Then, their friend Reena told them to prepare benzene diazonium chloride again and to use it immediately to prepare azo dye and they proceed accordingly and prepared azo dye successfully.

- (i) Write the chemical reaction involved in azo dye formation.
- (ii) Write the values associated with the suggestion given by Reena.

How is diazonium salt used in the preparation of following dyes :

- (iii) p-hydroxyazobenzene
- (iv) p-aminoazobenzene