
LESSON AT A GLANCE

- **Amines:** Derivatives of ammonia obtained by replacement of hydrogen atoms with alkyl or aryl groups.
- **Primary amine:** Characterised by the structure.
—→ $R\text{NH}_2$
- **Secondary amine:** Characterised by the structure.
—→ $R_2\text{NH}$
- **Tertiary amine:** Characterised by the structure —→ $R_3\text{N}$
- Amines are classified as primary, secondary or tertiary amines 1° , 2° and 3° , according to the number of alkyl groups attached to the nitrogen atom.
- **Primary amine (1°):** A primary amine has only one alkyl group directly attached to the nitrogen.
- **Secondary amine (2°):** A secondary amine has two alkyl groups directly attached to the nitrogen.
- **Tertiary amine (3°):** Amine has three alkyl groups directly attached to the nitrogen.
- **Hoffmann's Degradation of Amides:** This is a good laboratory method for the conversion of an amide to a pure primary amine. The amide is warmed with bromine and concentrated NaOH solution.
- **Basicity of Amines:** Amines are basic in nature. This is because they possess an unshared pair (lone pair) of electrons on nitrogen. This lone pair of electrons is available for the formation of a new bond with a proton or Lewis acids. Thus amines react with acids to form salts.
- **Basicity Constants:** Strong bases (e.g., NaOH or KOH) completely ionise in aqueous solution. Amines are weak bases. They are only partially ionised in aqueous solution.

and an equilibrium exists between the ionised and unionised forms.

- **Relative Basicities:** Aliphatic amines are stronger bases than ammonia. This is because the alkyl groups are electron-releasing. They increase the electron density around the nitrogen, thereby increasing the availability of lone pair of electrons.

The greater the number of electron releasing alkyl groups, the greater the availability of nitrogen's lone pair and stronger the base.

- **Diazonium Salts:** The diazonium salts have the general formula RN_2^+X^- where R stand for an aryl group and X^- ion may be Cl^- , Br^- , HSO_4^- , BF_4^- etc.

They are named by suffixing diazonium to the name of the parent hydrocarbon from which they are formed, followed by the name of anion such as chloride, hydrogen sulphate etc. The N_2^+ group is called diazonium group. For example, $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$ is named as benzene diazonium chloride.

TEXTBOOK QUESTIONS SOLVED

13.1 Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines:

- | | |
|---|---|
| (i) $(\text{CH}_3)_2\text{CHNH}_2$ | (ii) $\text{CH}_3(\text{CH}_2)_2\text{NH}_2$ |
| (iii) $\text{CH}_3\text{NHCH}(\text{CH}_3)_2$ | (iv) $(\text{CH}_3)_3\text{CNH}_2$ |
| (v) $\text{C}_6\text{H}_5\text{NHCH}_3$ | (vi) $(\text{CH}_3\text{CH}_2)_2\text{NCH}_3$ |
| (vii) $m\text{-BrC}_6\text{H}_4\text{NH}_2$ | |

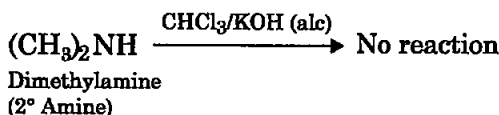
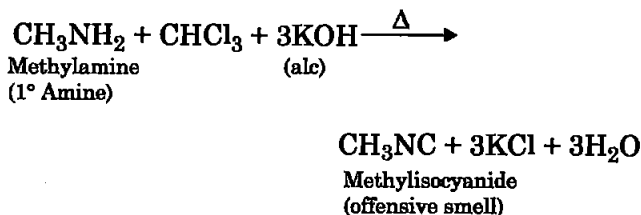
- Ans.**
- (i) Propan-2-amine (1° amine)
 - (ii) Propan-1-amine (1° amine)
 - (iii) N-Methylpropan-2-amine (2° amine)
 - (iv) 2-Methylpropan-2-amine (1° amine)
 - (v) N-Methylaniline or N-Methylbenzenamine (2° amine)
 - (vi) N-Ethyl-N-Methylethanamine (3° amine)
 - (vii) 3-Bromoaniline or 3-Bromobenzenamine (1° amine)

13.2 Give one chemical test to distinguish between the following pairs of compounds:

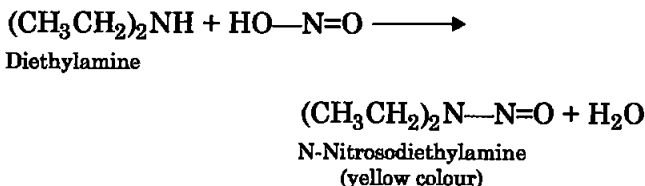
- (i) Methylamine and dimethylamine
- (ii) Secondary and tertiary amines

- (iii) *Ethylamine and aniline*
 (iv) *Aniline and benzylamine*
 (v) *Aniline and N-methylaniline*

Ans. (i) These can be distinguished by the carbylamine test.



- (ii) These can be distinguished by Libermann nitrosoamine test since 2° amine gives Libermann nitrosoamine test while 3° does not.



Tertiary amines do not give this test.

- (iii) **Azodye test:** It involves the reaction of any aromatic primary amine with HNO_2 ($\text{NaNO}_2 + \text{dil. HCl}$) at 273–278K followed by treatment with an alkaline solution of 2-naphthol (b-naphthol) when a brilliant yellow, orange or red coloured dye is obtained. Aliphatic primary amine like ethylamine under these condition give a brisk evolution of N_2 gas with the formation of primary alcohol.
- (iv) **Nitrous acid test:** Benzylamine reacts with nitrous acid to form a diazonium salt which being unstable even at low temperature, decomposes with evolution of N_2 gas. Aniline, on the other hand, reacts with HNO_2 to form benzene diazonium chloride which is stable at 273–278 K and hence does not decompose to evolve N_2 gas.

(v) **Carbylamine test:** Aniline being a primary amine gives carbylamine test, *i.e.* when heated with an alcoholic solution of KOH and CHCl_3 , it gives offensive smell of phenyl isocyanide.

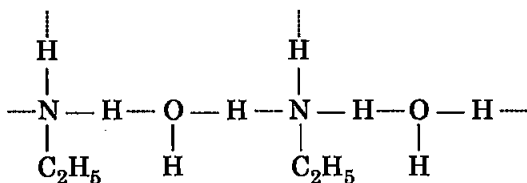
In contrast N-methylamine being a secondary amine does not give this test.

13.3 Account for the following:

- (i) pK_b of aniline is more than that of methylamine.
- (ii) Ethylamine is soluble in water whereas aniline is not.
- (iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.
- (iv) Although amino group is *o*- and *p*-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline.
- (v) Aniline does not undergo Friedel-Crafts reaction.
- (vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
- (vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

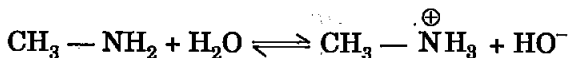
Ans. (i) Higher value of pK_b for aniline indicates it to be a weaker base than methylamine. In methylamine, the electron releasing effect of $-\text{CH}_3$ group increases the electron density on nitrogen atom of amine group. Whereas in aniline, the electron density is decreased due to the delocalisation of the lone-pair of electron over the benzene ring. Therefore, aniline is a weaker base than methylamine.

(ii) Ethylamine is soluble in water because it forms hydrogen bonding with water molecules.

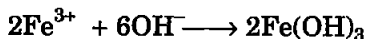


Although, the $-\text{NH}_2$ group present in aniline can also form hydrogen bonding with water molecules but the benzene ring is a water repelling group and net hydrogen bonding occurs to a very small extent. That makes aniline insoluble in water.

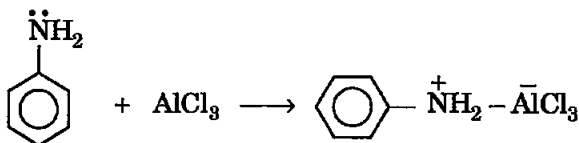
- (iii) Methylamine forms some hydroxide ions when dissolved in water due to the following acid-base equilibrium.



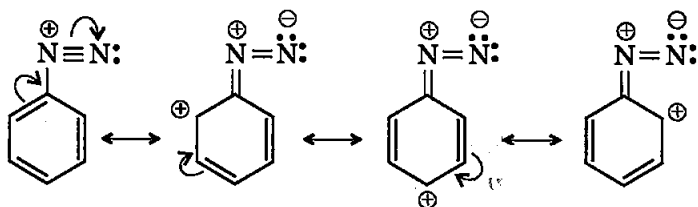
These OH^- ions react with Fe^{3+} ions to form ferric hydroxide.



- (iv) Nitration is carried out with conc. HNO_3 in the presence of conc. H_2SO_4 . In the presence of these acids, the $-\text{NH}_2$ group of aniline gets protonated and is converted into $-\overset{\oplus}{\text{N}}\text{H}_3$ group. This positively charged group acts as a strong electron withdrawing group. Hence, the incoming electrophile goes to m -position.
- (v) In Friedel-Crafts reaction, AlCl_3 is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge. This positively charged nitrogen acts as a strong deactivating group, hence aniline does not undergo Friedel-Crafts reaction.



- (vi) Diazonium salts of aromatic amines are more stable due to dispersal of positive charge due to resonance that leads to stability.



- (vii) Gabriel phthalimide synthesis involves the nucleophilic attack on alkyl halide and during the reaction, the alkyl group attaches to the attacking nitrogen atom. Since further attack on a second molecule of alkyl halide is

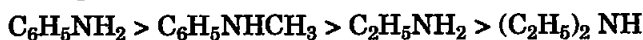
not possible, so pure primary amines are formed in this reaction.

13.4 Arrange the following:

- (i) In decreasing order of the pK_b values:
 $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$
- (ii) In increasing order of basic strength:
 $C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2
- (iii) In increasing order of basic strength:
 (a) Aniline, *p*-nitroaniline and *p*-toluidine
 (b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$
- (iv) In decreasing order of basic strength in gas phase:
 $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3
- (v) In increasing order of boiling point:
 C_2H_5OH , $(CH_3)_2NH$, $C_2H_5NH_2$
- (vi) In increasing order of solubility in water:
 $C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$.

Ans. (i) Decreasing order of pK_b is as follows:

(Low pK_b value indicates a stronger base)



(ii) $C_6H_5NH_2 < C_6H_5NHCH_3 < CH_3NH_2 < (C_2H_5)_2NH$

(iii) (a) *p*-Nitroaniline < aniline < *p*-toluidine



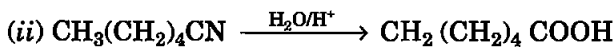
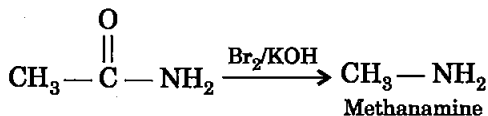
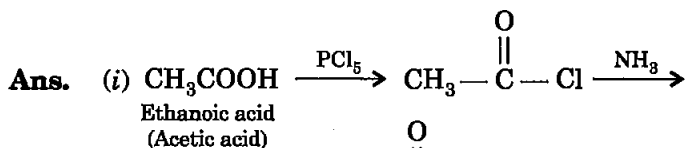
(iv) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$

(v) $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

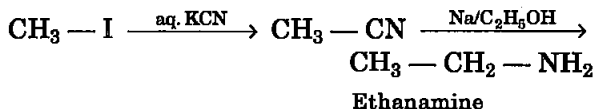
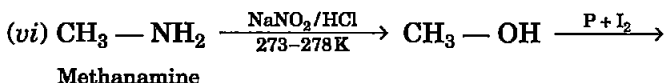
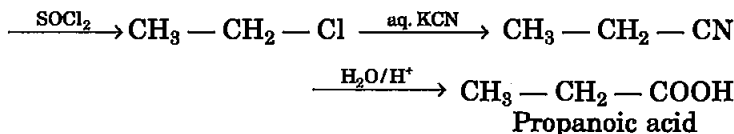
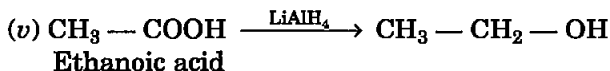
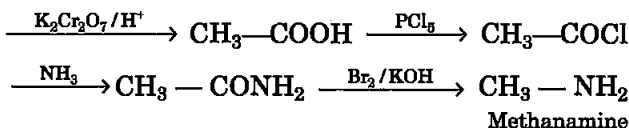
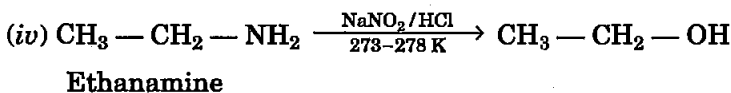
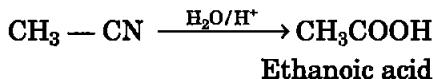
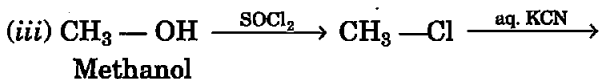
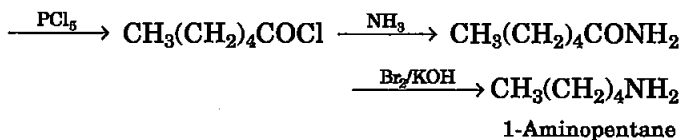
(vi) $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

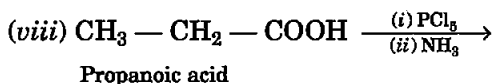
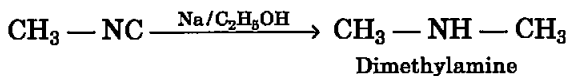
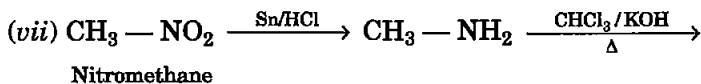
13.5 How will you convert:

- (i) Ethanoic acid into methanamine
 (ii) Hexanenitrile into 1-aminopentane
 (iii) Methanol to ethanoic acid
 (iv) Ethanamine into methanamine
 (v) Ethanoic acid into propanoic acid
 (vi) Methanamine into ethanamine
 (vii) Nitromethane into dimethylamine
 (viii) Propanoic acid into ethanoic acid?



Hexanenitrile

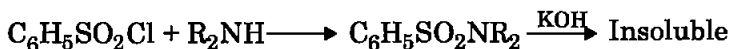
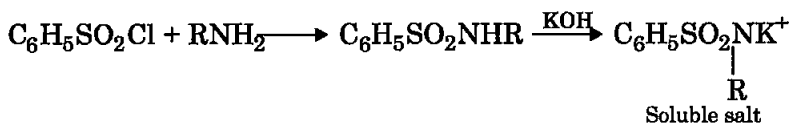




Ethanoic acid

13.6 Describe a method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved.

Ans. Add Hinsberg reagent, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$. Primary amines will react to form a compound soluble in KOH. 2° amines will form a salt insoluble in KOH while 3° amines will not react.

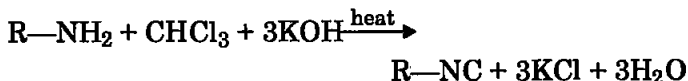


13.7 Write short notes on the following:

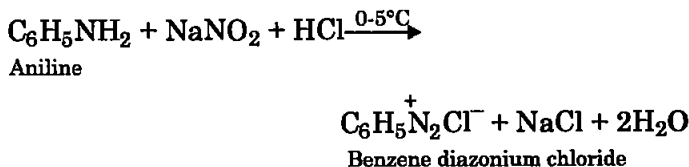
- (i) Carbylamine reaction
- (ii) Diazotisation
- (iii) Hofmann's bromamide reaction
- (iv) Coupling reaction
- (v) Ammonolysis
- (vi) Acetylation
- (vii) Gabriel phthalimide synthesis.

Ans. (i) **Carbylamine reaction:** Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or

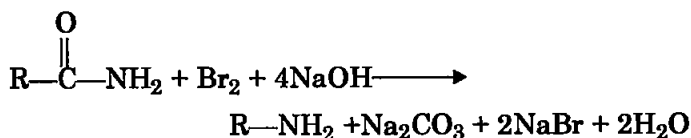
carbonyl amines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test, and is used as a test for primary amines.



(ii) **Diazotisation:** The process of converting an amine to the diazonium salt is called diazotisation.



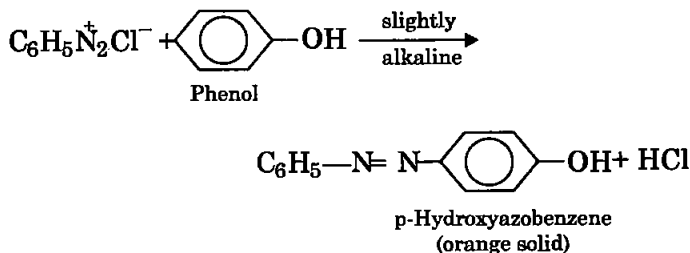
(iii) **Hoffmann's bromide reaction:** Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom.



(iv) **Coupling reaction:** Diazonium salts react readily with phenols and dialkylanilines ($\text{C}_6\text{H}_5\text{NR}_2$) to form highly coloured derivatives known as Azo compounds.



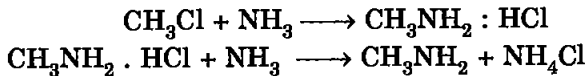
For example,



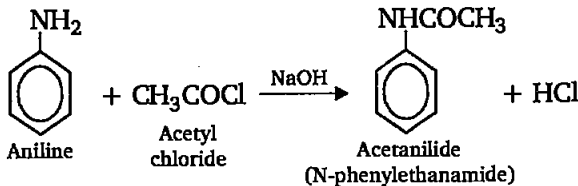
Such reaction in which the diazonium ion is joined or coupled to the ring of a phenol or an aromatic amine are called Diazo coupling reactions.

(v) Ammonolysis:

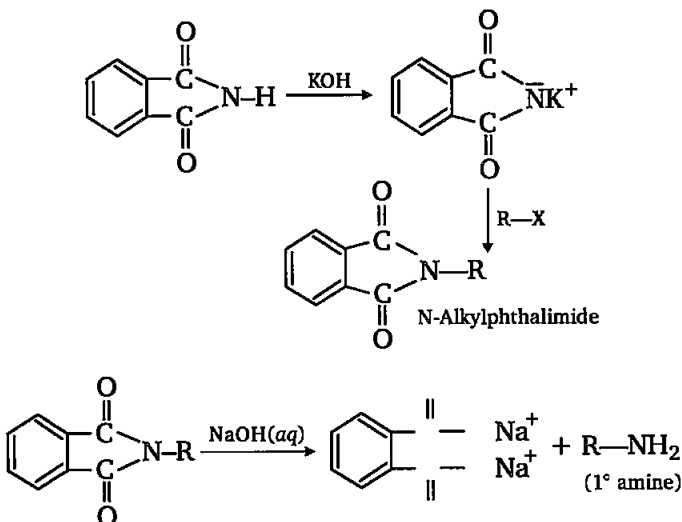
Alkyl halide reacts with ammonia to form primary amine. The reaction of ammonia with alkyl halide is known as ammonolysis.

**(vi) Acetylation:**

The process in which acetyl group ($\text{CH}_3\text{—}\overset{\text{O}}{\parallel}{\text{C—}}$) is introduced is called acetylation. It is done by reaction with acetyl chloride or acetic anhydride.

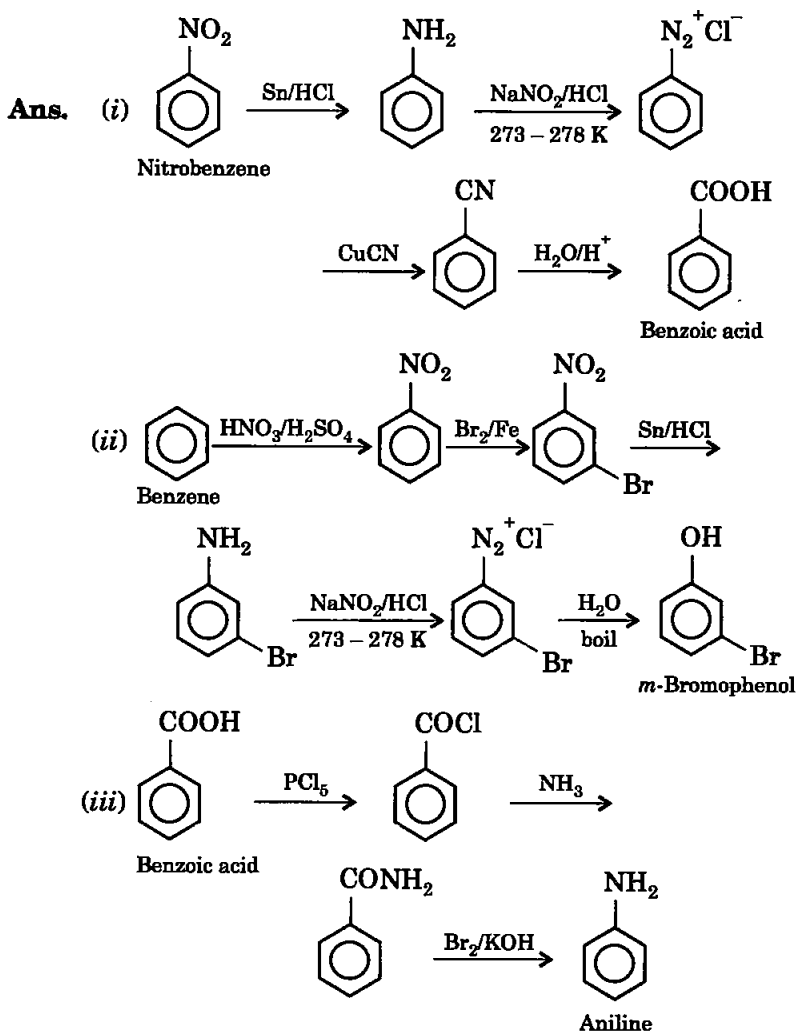
**(vii) Gabriel phthalimide synthesis:**

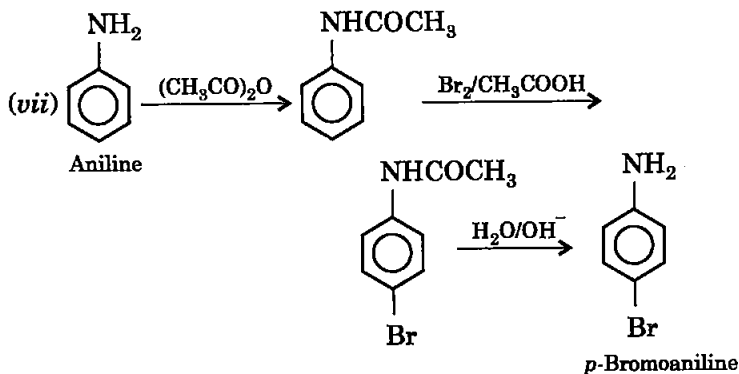
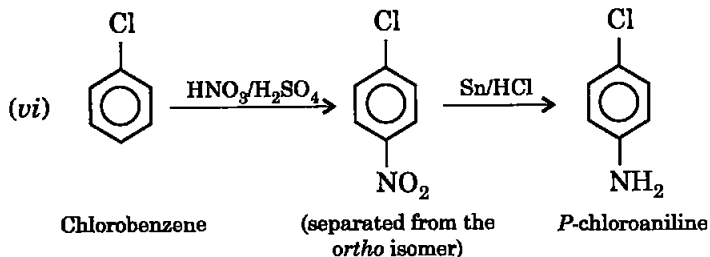
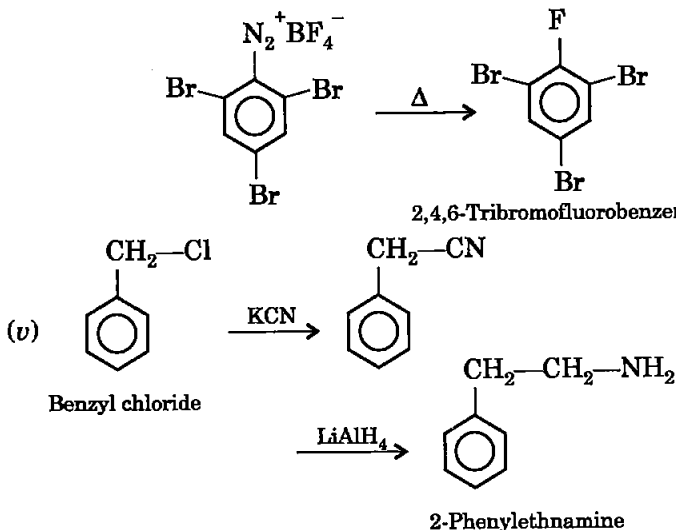
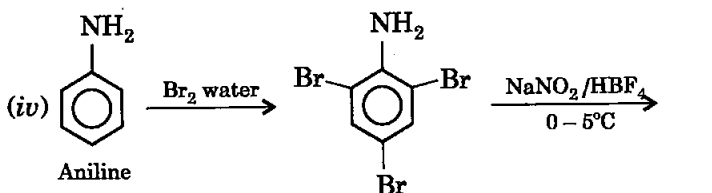
Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine.

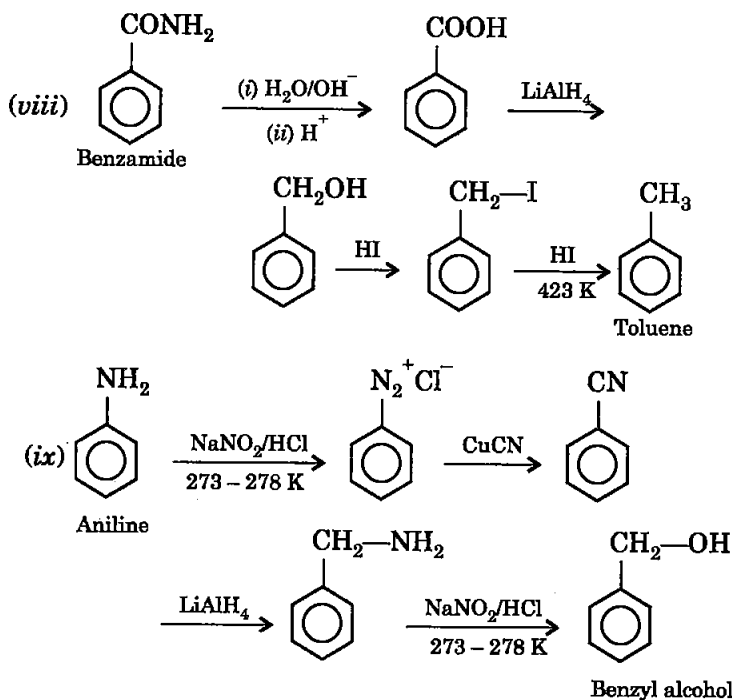


13.8 Accomplish the following conversions:

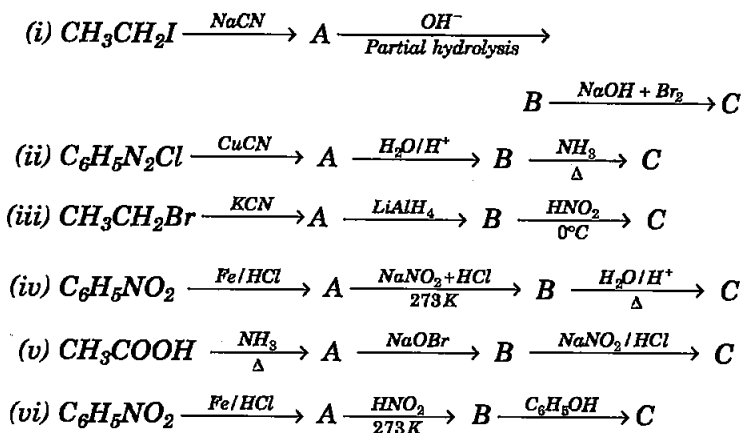
- (i) Nitrobenzene to benzoic acid
- (ii) Benzene to *m*-bromophenol
- (iii) Benzoic acid to aniline
- (iv) Aniline to 2,4,6-tribromofluorobenzene
- (v) Benzyl chloride to 2-phenylethanamine
- (vi) Chlorobenzene to *p*-chloroaniline
- (vii) Aniline to *p*-bromoaniline
- (viii) Benzamide to toluene
- (ix) Aniline to benzyl alcohol.





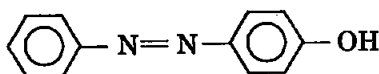


13.9 Give the structures of A, B and C in the following reactions:



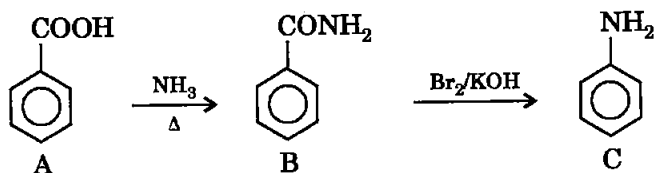
Ans. (i) A = $\text{CH}_3 - \text{CH}_2 - \text{CN}$ (Propanenitrile)
 B = $\text{CH}_3 - \text{CH}_2 - \text{CONH}_2$ (Propanamide)
 C = $\text{CH}_3 - \text{CH}_2 - \text{NH}_2$ (Ethanamine)

- (ii) $A = C_6H_5 - CN$ (Benzonitrile)
 $B = C_6H_5 - COOH$ (Benzoic acid)
 $C = C_6H_5 - CONH_2$ (Benzamide)
- (iii) $A = CH_3 - CH_2 - CN$ (Propanenitrile)
 $B = CH_3 - CH_2 - CH_2 - NH_2$ (Propan-1-amine)
 $C = CH_3 - CH_2 - CH_2 - OH$ (Propan-1-ol)
- (iv) $A = C_6H_5NH_2$ (Aniline)
 $B = C_6H_5N_2^+Cl^-$ (Benzene diazonium chloride)
 $C = C_6H_5OH$ (Phenol)
- (v) $A = CH_3 - CONH_2$ (Ethanamide)
 $B = CH_3 - NH_2$ (Methanamine)
 $C = CH_3 - OH$ (Methanol)
- (vi) $A = C_6H_5NH_2$ (Aniline)
 $B = C_6H_5N_2^+Cl^-$ (Benzene diazonium chloride)
 $C = C_6H_5 - N = N - C_6H_5OH$

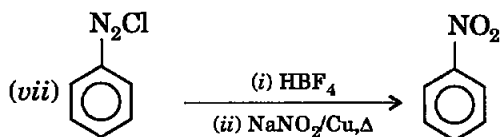
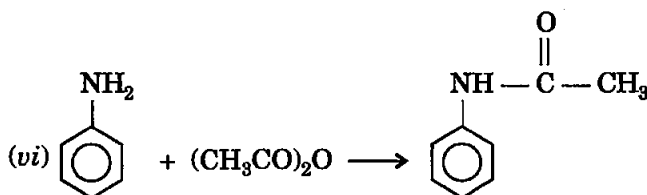
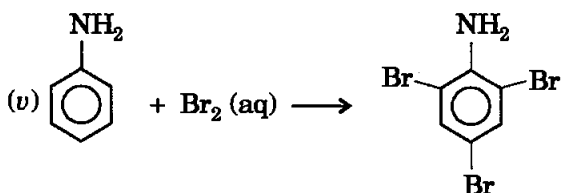
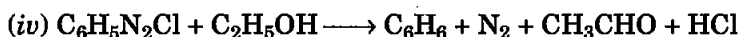
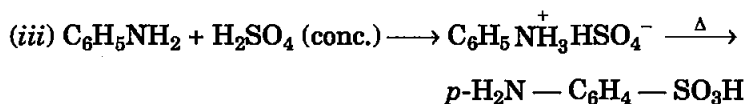
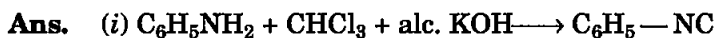
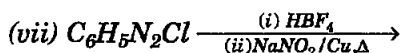
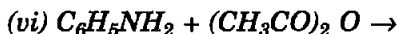
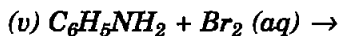
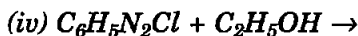
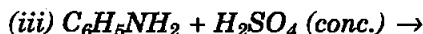
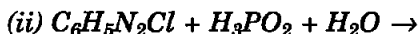


13.10 An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N . Write the structures and IUPAC names of compounds A, B and C.

Ans. Formula of the compound 'C' indicates it to be an amine. Since it is obtained by the reaction of Br_2 and KOH with the compound 'B' so compound 'B' can be an amide. It is also indicated because 'B' is obtained from compound 'A' by reaction with ammonia followed by heating. So compound 'A' could be an aromatic acid. Formula of compound 'C' shows it to be aniline, then 'B' is benzamide and compound 'A' is benzoic acid. The sequence of reactions can be written as follows:



13.11 Complete the following reactions:



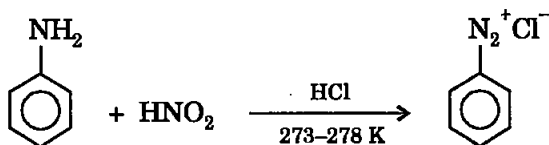
13.12 Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

Ans. The Gabriel phthalimide reaction involves the nucleophilic attack of the phthalimide anion on alkyl halide and the alkyl

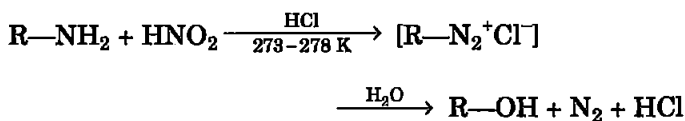
group is attached to nitrogen. Since aryl halides do not undergo nucleophilic substitution, therefore, aromatic primary amines cannot be prepared by this reaction.

13.13 Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.

Ans. (i) Aromatic primary amines react with nitrous acid to form diazonium salts.



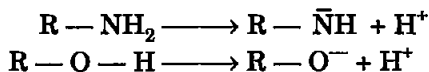
(ii) Aliphatic primary amines also form diazonium salts on reaction with nitrous acid but they are unstable and decompose to give the corresponding alcohols as the major product with the evolution of nitrogen.



13.14 Give plausible explanation for each of the following:

- (i) Why are amines less acidic than alcohols of comparable molecular masses?
- (ii) Why do primary amines have higher boiling point than tertiary amines?
- (iii) Why are aliphatic amines stronger bases than aromatic amines?

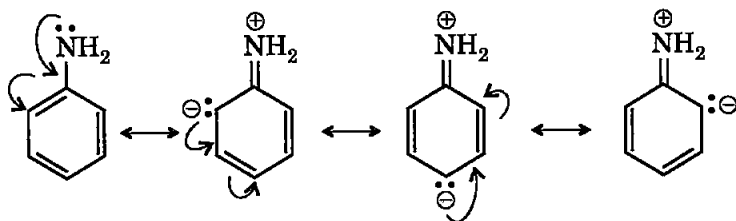
Ans. (i) In alcohols, the hydrogen atom is attached to more electronegative oxygen atom whereas nitrogen of amines is less electronegative. After the loss of H^+ ion, the negative charge is more easily accommodated on oxygen than in case of nitrogen in amines. Hence, amines have lesser tendency to lose H^+ ions, so they are less acidic than alcohols.



(ii) Primary amines (R-NH_2) have two hydrogen atoms on nitrogen which can undergo intermolecular hydrogen

bonding whereas no such hydrogen bonding is present in tertiary amines (R_3N). So primary amines boil at a higher temperature than tertiary amines.

(iii) In aromatic amines, the lone-pair of electrons on nitrogen atom is involved in resonance with the benzene ring as shown below for aniline.



It shows that this pair of electrons is less available in comparison to that in case of aliphatic amines where alkyl groups are also electron releasing. So, aliphatic amines are stronger bases than aromatic amines.

□□□