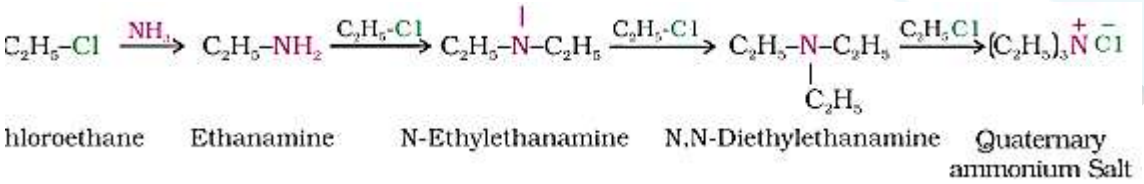
Examples

Example 13.1 Write chemical equations for the following reactions:

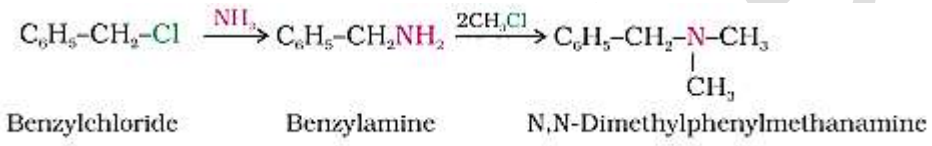
(i) Reaction of ethanolic NH_3 with C_2H_5Cl.

Solution:



(ii) Ammonolysis of benzyl chloride and reaction of amine so formed with two moles of CH_3Cl.

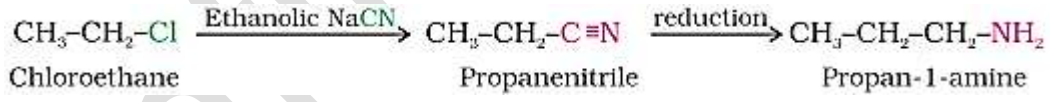
Solution:



Example 13.2 Write chemical equations for the following conversions:

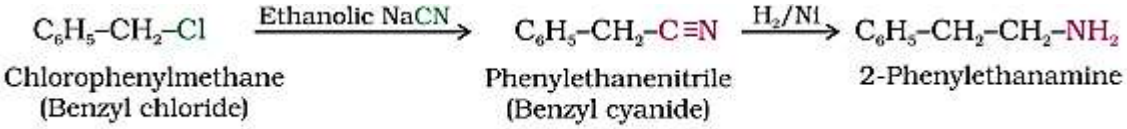
(i) CH_3-CH_2-Cl **into** $CH_3-CH_2-CH_2-NH_2$

Solution:



(ii) $C_6H_5-CH_2-Cl$ **into** $C_6H_5-CH_2-CH_2-NH_2$

Solution:



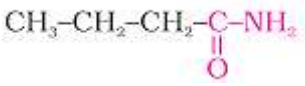
Example 13.3 Write structures and IUPAC names of

(i) the amide which gives propanamine by Hoffmann bromamide reaction.

Solution: Propanamine has three carbon atoms.

As a result, the amide molecule must have four carbon atoms.

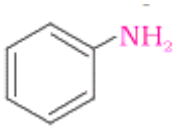
The following is the structure and IUPAC nomenclature of the beginning amide with four carbon ato ms:



(ii) the amine produced by the Hoffmann degradation of benzamide.

Solution: Benzamide is a carbon-containing aromatic amide with seven carbon atoms.

As a result, the amine produced from benzamide is an aromatic primary amine with six carbon atoms.



Example 13.4 Arrange the following in decreasing order of their basic strength:

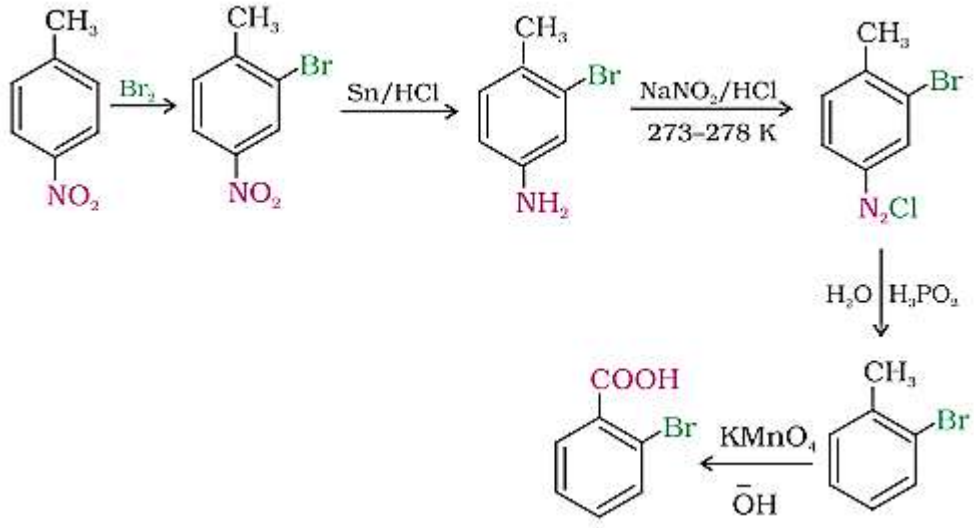
$C_6H_5NH_2, C_2H_5NH_2, (C_2H_5)_2\ NH, NH_3$

Solution: The following is the decreasing order of basic strength of the amines and ammonia listed above:

$(C_2H_5)_2\ NH > C_2H_5NH_2 > NH_3 > C_6H_5NH_2$

Example 13.5 How will you convert 4 – nitrotoluene to 2 – bromobenzoic acid?

Solution:



EXERCISES

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

(i) $(CH_3)_2CHNH_2$

Answer: $1-$Methylethanamine (1^0 amine)

(ii) $CH_3(CH_2)_2NH_2$

Answer: Propan-1-amine (1^0 amine)

(iii) $CH_3NHCH(CH_3)_2$

Answer: $N-$Methyl-2-methylethanamine (2° amine)

(iv) $(CH_3)_3CNH_2$

Answer: $2-$Methylpropan-2-amine (1^0 amine)

(v) $C_6H_5NHCH_3$

Answer: $N-$Methylbenzamine or $N-$methylaniline (2° amine)

(vi) $(CH_3CH_2)_2NCH_3$

Answer: $N-$Ethyl-$N-$methylethanamine (3^0 amine)

(vii) $m-BrC_6H_4NH_2$

Answer: $3-$Bromobenzenamine or $3-$bromoaniline (1^0 amine)

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

(i) Methylamine and dimethylamine

Answer: The carbylamine test can discriminate between methylamine and dimethylamine.

Carbylamine test: Aliphatic and aromatic primary amines create foul-smelling isocyanides or carbylamines when heated with chloroform and ethanolic potassium hydroxide.

Methylamine causes a positive carbylamine test, whereas dimethylamine does not.

$$CH_3-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} CH_3-NC + 3KCl + 3H_2$$

Methylamine (1°) — Methyl isocyanide (foul smell)

$$(CH_3)_2NH + CHCl_3 + 3KOH \xrightarrow{\Delta} \text{No reaction}$$

(ii) Secondary and tertiary amines

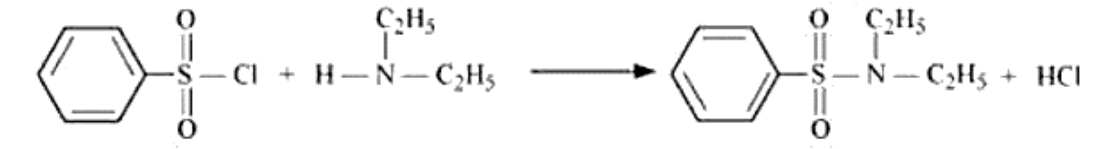
Answer:

Secondary and tertiary amines can be distinguished by reacting with Hinsberg's reagent (benzenesulphonyl chloride, $C_6H_5SO_2Cl$).

Secondary amines react with Hinsberg's reagent to generate an alkali-insoluble product.

For instance, N,N — diethylamine combines with Hinsberg's reagent to create N , $N-$ iethylbenzenesulphonamide, which is insoluble in alkalis.

Tertiary amines, on the other hand, are unaffected by Hinsberg's reagent.



Benzenesulphonyl chloride — N, N – Diethylbenzenesulphonamide

(iii) Ethylamine and aniline

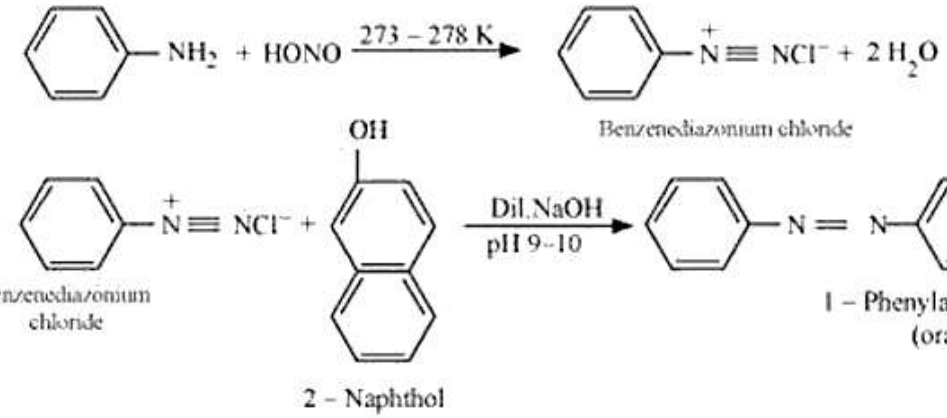
Answer: The azo-dye test can differentiate between ethylamine and aniline.

Aromatic amines react with HNO_2 ($NaNO_2 + \text{dil. HCl}$ at $0-5^{\circ}C$,

followed by a reaction with an alkaline solution of 2 -naphthol to produce a dye.

Typically, the dye is yellow, red, or orange in colour.

Under identical conditions, aliphatic amines produce a rapid effervescence due to the development of N_2 gas.

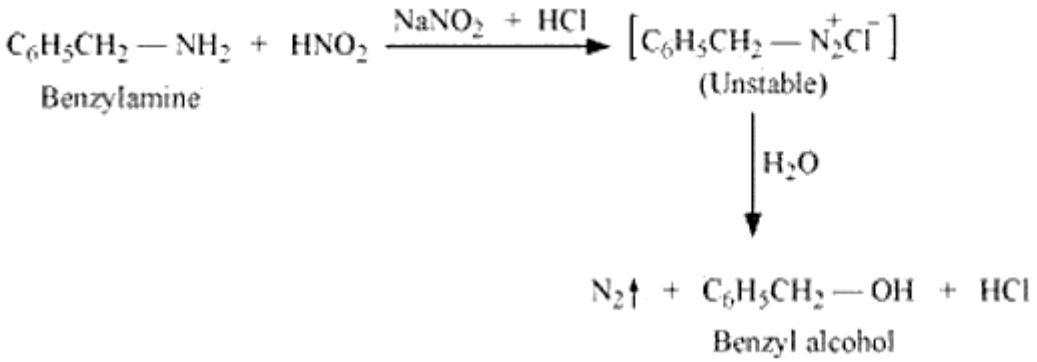


$$CH_3CH_2 - NH_2 + HONO \xrightarrow{0\text{-}5^\circ C} C_2H_5OH + N_2\uparrow + H_2O$$

(iv) Aniline and benzylamine

Answer:
The reactions of aniline and benzylamine with nitrous acid, which is produced in situ from a mineral a cid and sodium nitrite, differentiate them.

When benzylamine interacts with nitrous acid, it forms an unstable diazonium salt, which produces al cohol with the release of nitrogen gas.



Also,

$$C_6H_5NH_2 \xrightarrow[273\text{–}278K]{NaNO_2 + HCl} C_6H_5 - \overset{+}{N}_2\,\overset{-}{Cl} + NaCl + 2H_2O$$

(v) Aniline and N-methylaniline.

Answer: The Carbylamine test can tell the difference between aniline and N -methylaniline.

When heated with chloroform and ethanolic potassium hydroxide, primary amines generate foul-smelling isocyanides or carbylamines.

Aniline, being an aromatic primary amine, results in a positive carbylamine test.

N -methylaniline, on the other hand, being a secondary amine, does not.

$$C_6H_5-NH_2+CHCl_3+3KOH \xrightarrow{\Delta} C_6H_5-NC+3KCl+3H_2O$$

Benzylamine (1^0) — Benzylisocyanide (foul smell)

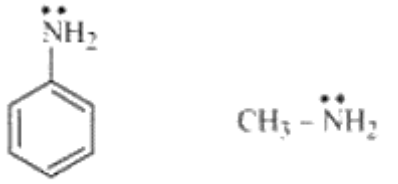
$$C_6H_5NHCH_3+CHCl_3+3KOH \xrightarrow{\Delta} \text{No reaction}$$

N-Methylaniline

13.3 Account for the following:

(i) pK_b of aniline is more than that of methylamine.

Answer:

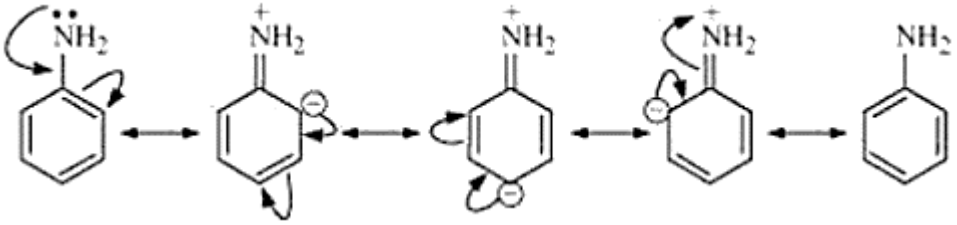


Aniline

Methylamine

Aniline undergoes resonance, and the electrons on the N-atom get delocalized over the benzene ring as a result.

As a result, there are less electrons available to donate on the N-atom.



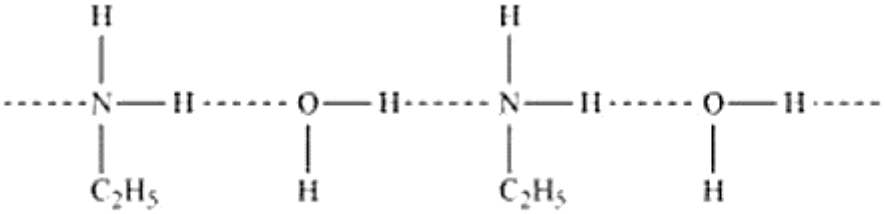
In the case of methylamine, however, the electron density on the $N-$ atom is enhanced due to the $+1$ action of the methyl group.

As a result, aniline has a lower basicity than methylamine.

As a result, aniline has a higher pK_b than methylamine.

(ii) Ethylamine is soluble in water whereas aniline is not.

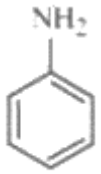
Answer: When ethylamine is introduced to water, it creates intermolecular H-bonds with the water. As a result, it dissolves in water.



Ethylamine

However, aniline does not undergo significant $H-$ bonding with water due to the existence of a large hydrophobic $-C_6H_5$ group.

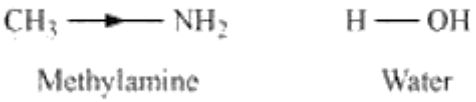
As a result, aniline is insoluble in water.



Aniline

(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.

Answer:



Methylamine Water

$$CH_3-NH_2+H-OH \longrightarrow CH_3-\overset{+}{N}H_3+OH^-$$

$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$$

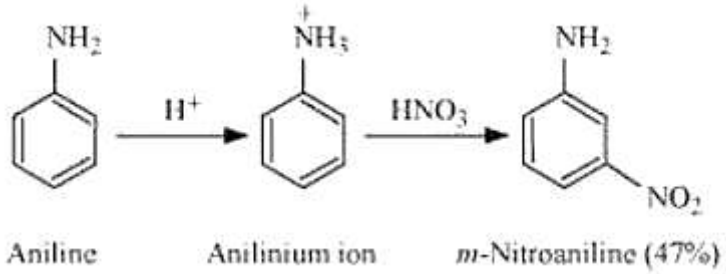
$$2Fe^{3+} + 6OH^- \longrightarrow Fe_2O_3 \cdot 3H_2O$$

Hydrated ferric oxide

(iv) Although amino group is and p – directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m – nitroaniline.

Answer: Nitration takes place in an acidic media.

Aniline is protonated in an acidic media to produce anilinium ion (which is meta-directing).



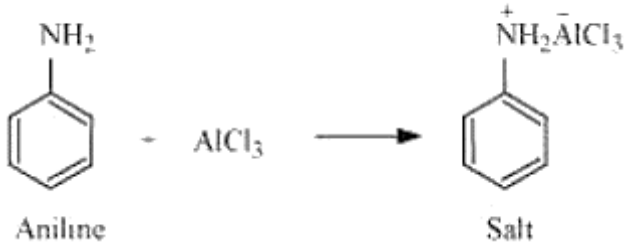
As a result, aniline on nitration yields a significant quantity of m-nitroaniline.

(v) Aniline does not undergo Friedel-Crafts reaction.

Answer: In the presence of $AlCl_3$, a Friedel-Crafts reaction is carried out.

However, $AlCl_3$ is acidic in nature, whereas aniline is a strong base.

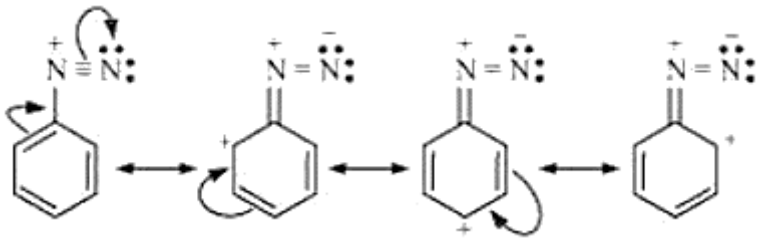
As a result, aniline interacts with $AlCl_3$ to generate a salt (as shown in the following equation).



Electrophilic substitution in the benzene ring is deactivated due to the positive charge on the N-atom. As a result, aniline is not subjected to the Friedel-Crafts reaction.

(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

Answer:



This resonance is responsible for the diazonium ion's stability.

As a result, aromatic amine diazonium salts are more stable than aliphatic amine diazonium salts.

(vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

Answer: The single product of Gabriel phthalimide synthesis is 1° amine.

This synthesis does not produce 2° or 3° amines.

As a result, a pure 1° amine may be produced.

As a result, Gabriel phthalimide synthesis is favoured for the production of primary amines.

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** $C_6H_5NH_2$

Answer: $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

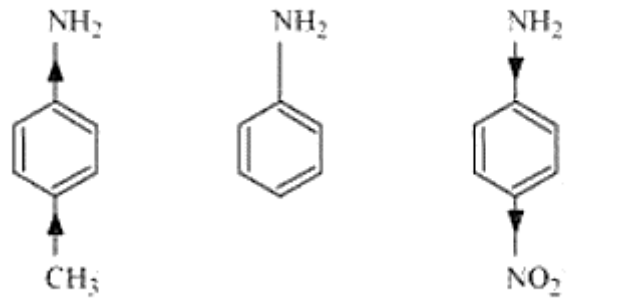
(ii) In increasing order of basic strength: $C_6H_5NH_2, C_6H_5N(CH_3)_2, (C_2H_5)_2NH$ **and** CH_3NH_2

Answer: $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$

(iii) In increasing order of basic strength:

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

Answer:



p-Toluidine Aniline *p*-Nitroaniline

p-Nitroaniline < Aniline < *p*-Toluidine

(b) $C_6H_5NH_2, C_6H_5NHCH_3, C_6H_5CH_2NH_2$.

Answer: $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

(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.

Answer: $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$

(v) In increasing order of boiling point: $C_2H_5OH_+ (CH_3)_2NH, C_2H_5NH_2$

Answer: $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

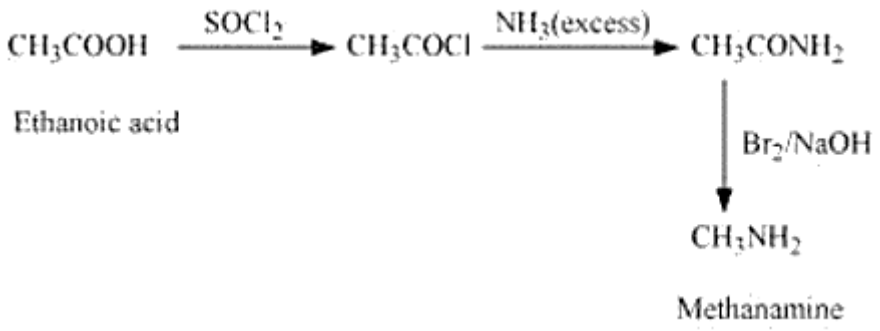
(vi) In increasing order of solubility in water: $C_6H_5NH_2, (C_2H_5)_2NH, C_2H_5NH_2$.

Answer: $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

13.5 How will you convert:

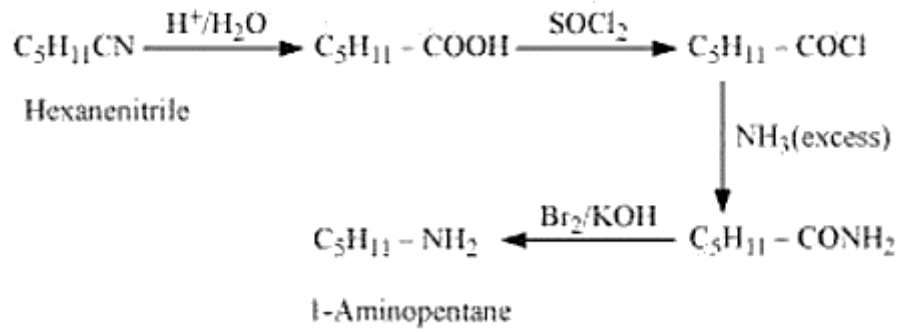
(i) Ethanoic acid into methanamine

Answer:



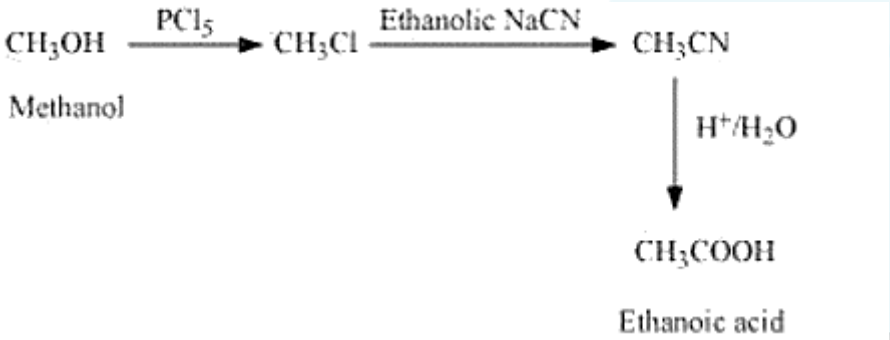
(ii) Hexanenitrile into 1–aminopentane

Answer:



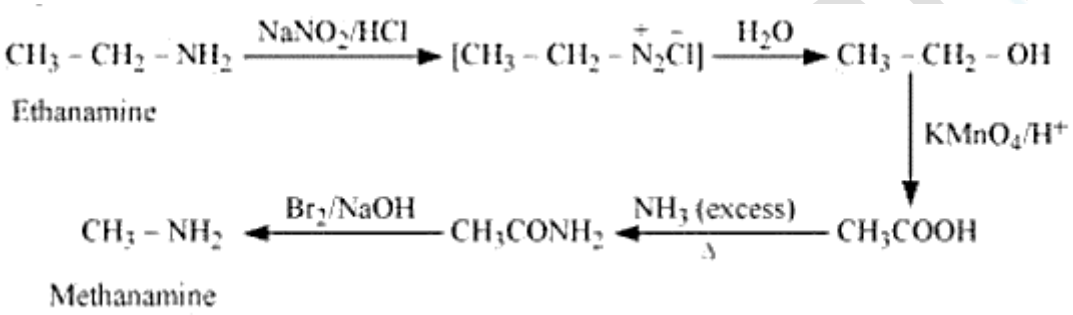
(iii) Methanol to ethanoic acid

Answer:



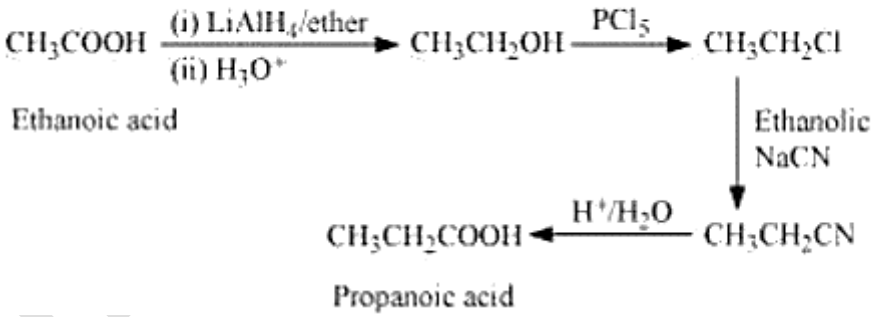
(iv) Ethanamine into methanamine

Answer:



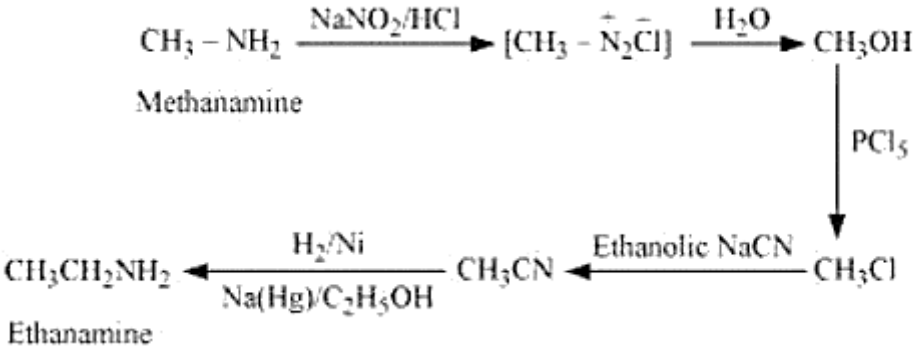
(v) Ethanoic acid into propanoic acid

Answer:



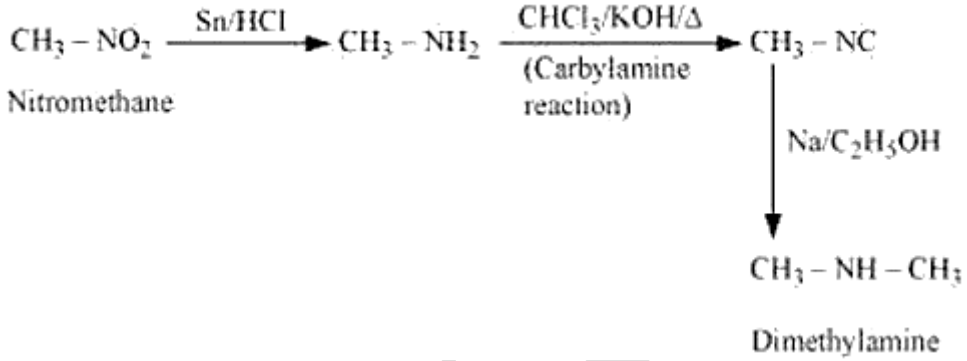
(vi) Methanamine into ethanamine

Answer:



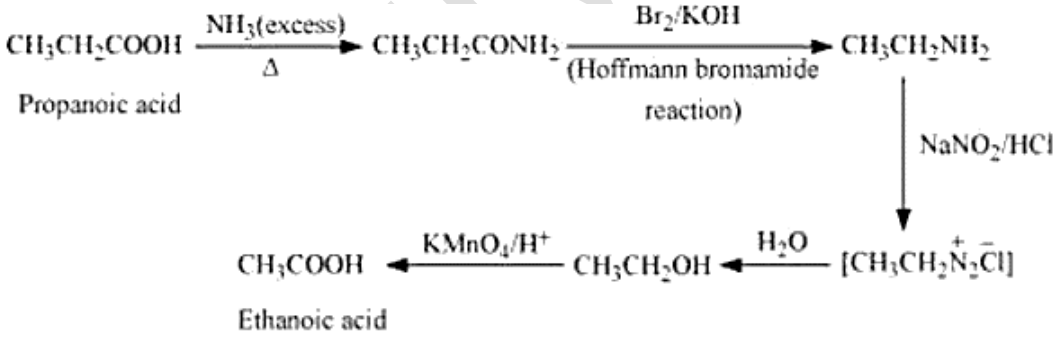
(vii) Nitromethane into dimethylamine

Answer:



(viii) Propanoic acid into ethanoic acid?

Answer:



13.6 Describe a method for the identification of primary, secondary and tertiary amines.

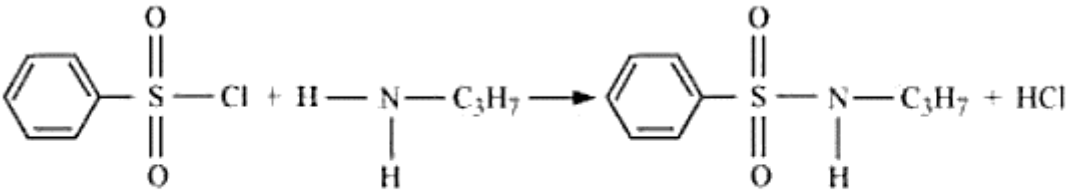
Also write chemical equations of the reactions involved.

Answer: Hinsberg's test distinguish between primary, secondary, and tertiary amines.
Allow the amines to react with Hinsberg's reagent, benzenesulphonyl chloride, $\left(C_6H_5SO_2Cl\right)$ in this test.

Hinsberg's reagent reacts differently with the three kinds of amines.

As a result, Hinsberg's reagent can easily identify them.

When primary amines react with benzenesulphonyl chloride, an alkali soluble N-alkylbenzenesulphonyl amide is produced.

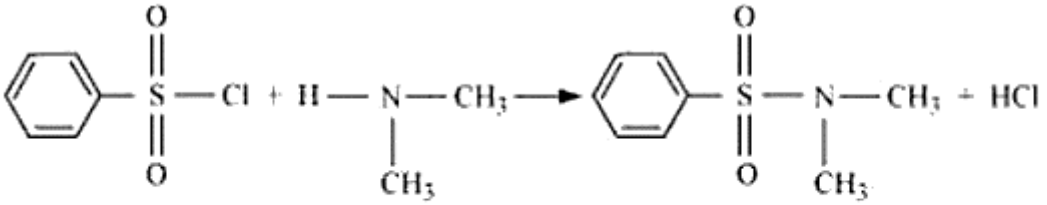


Benzenesulphonyl chloride | Propanamine | *N*-Propylbenzenesulphonamide

Because the sulphonamide has a strong electron-withdrawing sulphonyl group, the H -atom linked to nitrogen may be easily released as a proton.

As a result, it's acidic and dissolves in alkali.

Secondary amines react with Hinsberg's reagent to form an alkali-insoluble sulphonamide.



Benzenesulphonyl chloride | Dimethylamine | *N*, *N*-Dimethylbenzenesulphonamide (insoluble in alkali)

In the sulphonamide, there is no H -atom linked to the N -atom.

As a result, it is not acidic and is insoluble in alkali.

Tertiary amines, on the other hand, have no reaction with Hinsberg's reagent.

13.7 Write short notes on the following:

(i) Carbylamine reaction

Answer: The carboxylamine reaction is a test for identifying primary amines.

Carbylamines (or isocyanides) are generated when aliphatic and aromatic primary amines are cooked with chloroform and ethanolic potassium hydroxide.
The odours of these carbylamines are quite unpleasant.

This test has no effect on secondary or tertiary amines.

$$R-NH_2 + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta} R-NC + 3KCl + 3H_2O$$

Primary amine — Chloroform — Potassium hydroxide — Carbylamine

$$CH_3-NH_2 + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta} CH_3-NC + 3KCl + 3H_2O$$

Methanamine — Methyl carblylamine or methyl isocyanide

(ii) Diazotisation

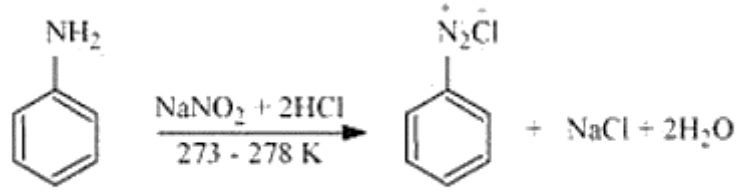
Answer:

At low temperatures ($273-278K$),

aromatic primary amines react with nitrous acid (made in situ from $NaNO_2$ and a mineral acid such as HCl) to create diazonium salts.

Diazotization is the process of converting aromatic primary amines into diazonium ions.

For example, aniline produces benzenediazonium chloride when treated with $NaNO_2$ and HCl at $273-278K$, with $NaCl$ and H_2O as byproducts.



Aniline — Benzenediazonium chloride

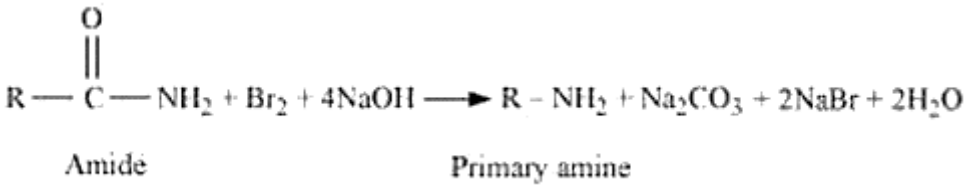
(iii) Hofmann's bromamide reaction

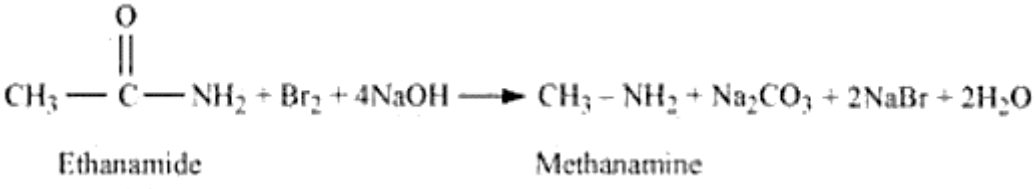
Answer:

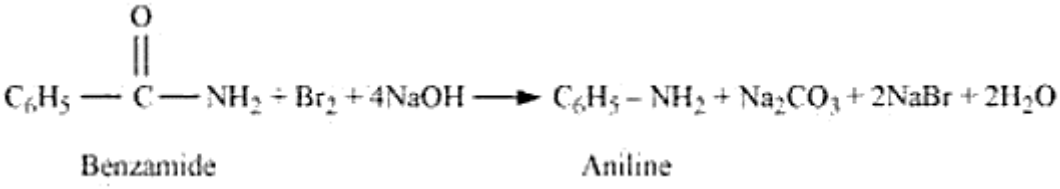
When an amide is treated with bromine in an aqueous or ethanolic sodium hydroxide solution, a prima ry amine with one less carbon atom than the original amide is formed.

The Hoffmann bromamide reaction is the name given to this degradation process.

The migration of an alkyl or aryl group from the carbonyl carbon atom of the amide to the nitrogen at om is involved in this reaction.



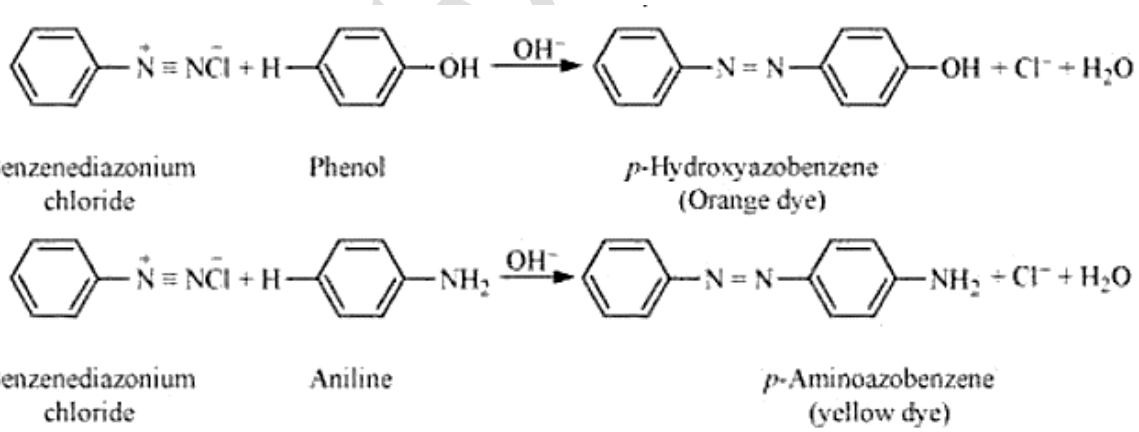




(iv) Coupling reaction

Answer: The coupling reaction is the merging of two aromatic rings via the $-N=N-$ bond.

Colored azo compounds are formed when arenediazonium salts, such as benzene diazonium salts, co mbine with phenol or aromatic amines.



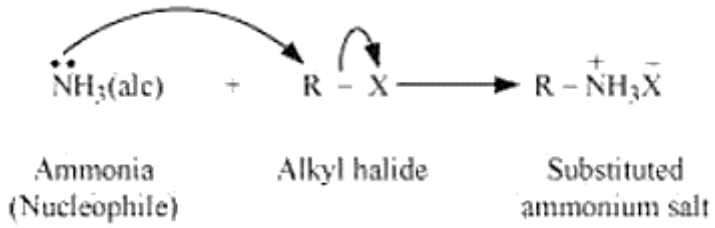
The para-positions of phenol and aniline are seen to be linked with the diazonium salt.

Electrophilic substitution is used in this process.

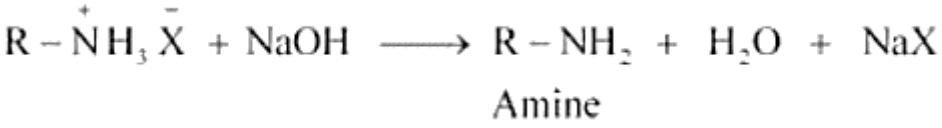
(v) Ammonolysis

Answer: When an alkyl or benzyl halide reacts with an ethanolic solution of ammonia, a nucleophilic substitution process takes place in which the halogen atom is replaced by an amino $\left(-NH_2\right)$ group.

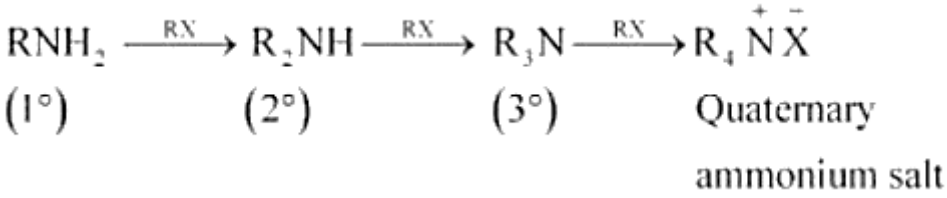
Ammonolysis is the process of cleaving the carbon-halogen bond.



When a strong base, such as sodium hydroxide, is applied to this substituted ammonium salt, amine is formed.

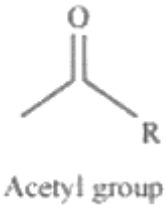


Though primary amine is the main result, this procedure also yields a combination of primary, secondary, and tertiary amines, as well as a quaternary ammonium salt, as illustrated.



(vi) Acetylation

Answer:

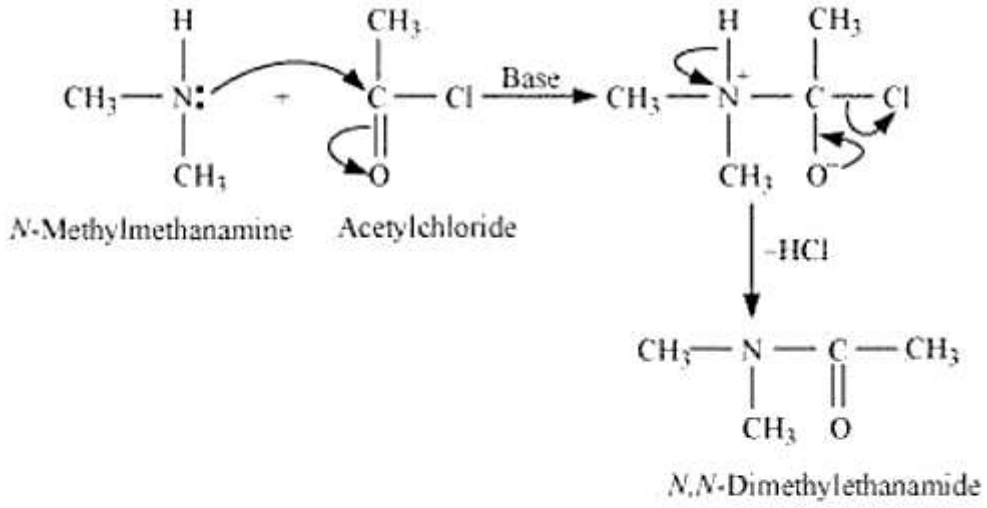


When handled with acid chlorides, anhydrides, or esters, aliphatic and aromatic primary and secondary amines undergo acetylation by nucleophilic substitution.

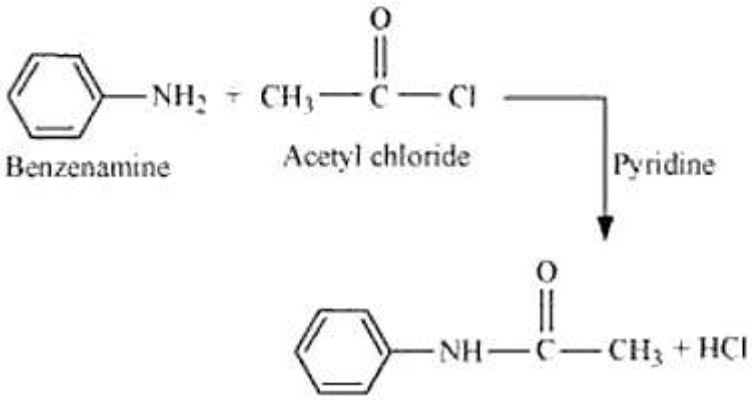
This reaction includes the replacement of the hydrogen atom of the $-NH_2$ or $>NH$ group with the acetyl group, resulting in the formation of amides.

The HCl generated during the reaction is eliminated as soon as it is created to shift the equilibrium to the right.

This reaction takes place in the presence of a stronger base (such as pyridine) than the amine.



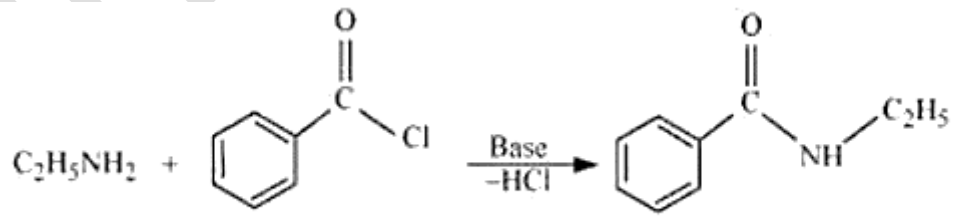
N-Methylmethanamine Acetylchloride *N,N*-Dimethylethanamide



Benzenamine Acetyl chloride *N*-Phenylethanamide

The process that occurs when amines react with benzoyl chloride is known as benzoylation.

As an example,



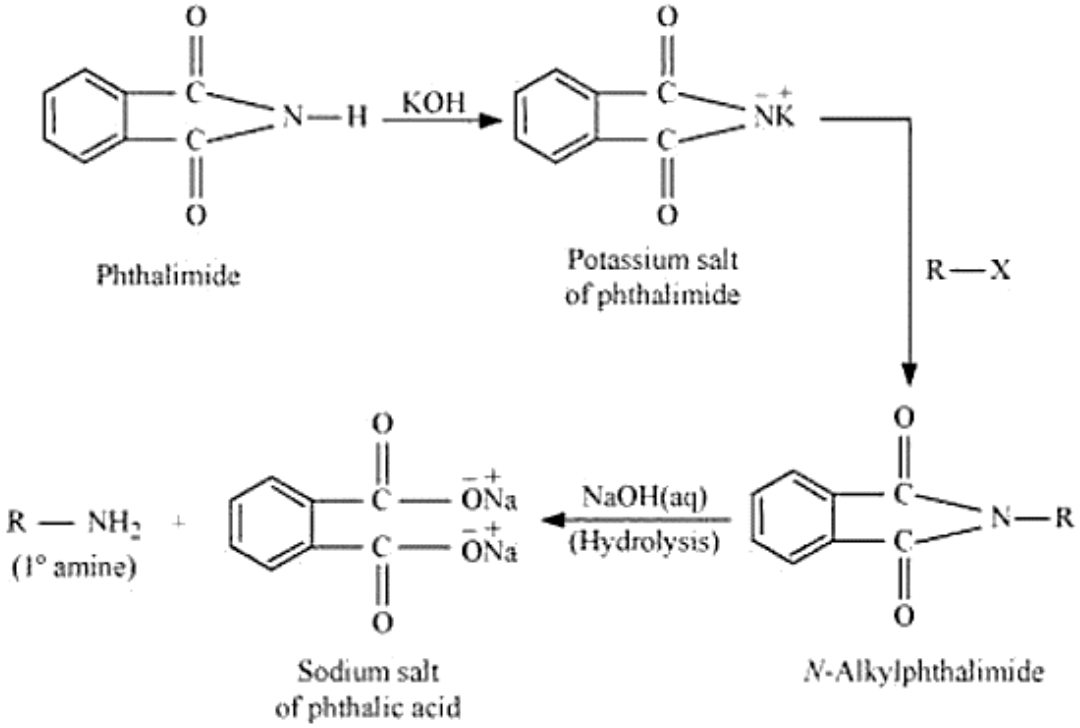
Ethanamine Benzoyl chloride *N*-Ethylbenzamide

(vii) Gabriel phthalimide synthesis.

Answer:

Gabriel phthalimide synthesis is a very helpful technique for producing aliphatic primary amines.

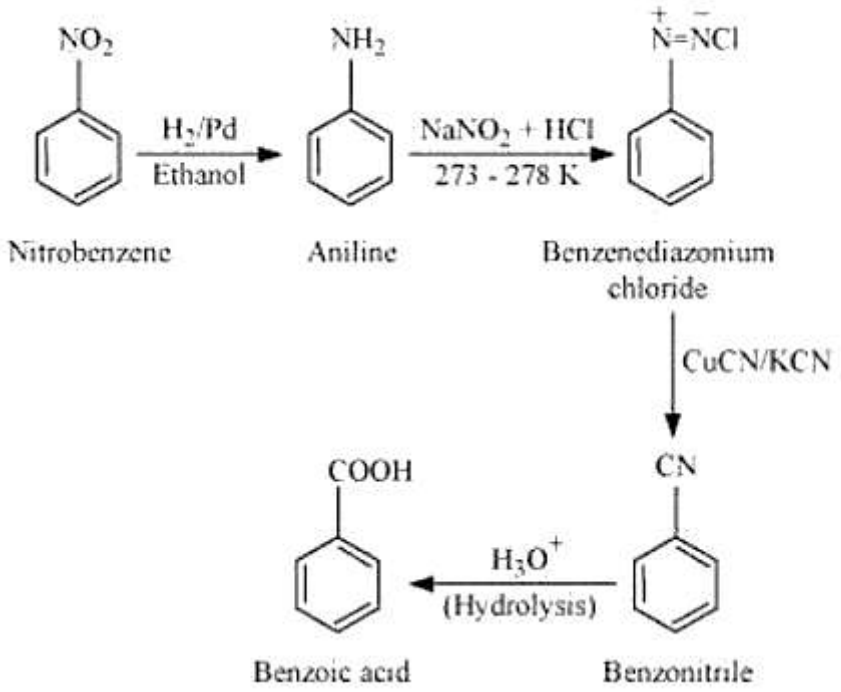
It entails treating phthalimide with ethanolic potassium hydroxide to generate phthalimide potassium s alt. This salt is then heated with alkyl halide before being alkaline hydrolyzed to produce the matching primary amine.



13.8 Accomplish the following conversions:

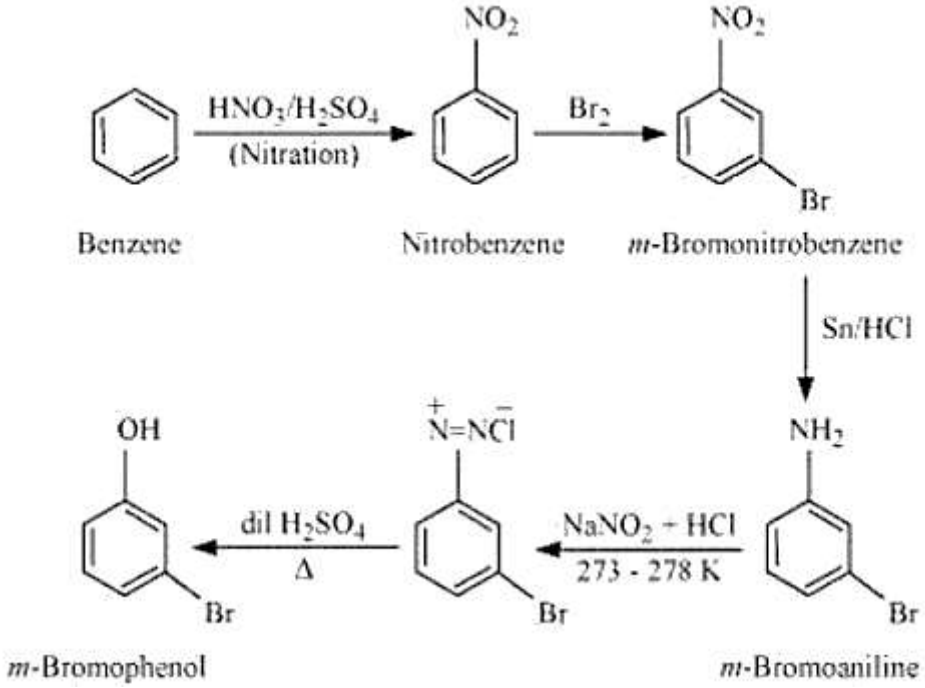
(i) Nitrobenzene to benzoic acid

Answer:



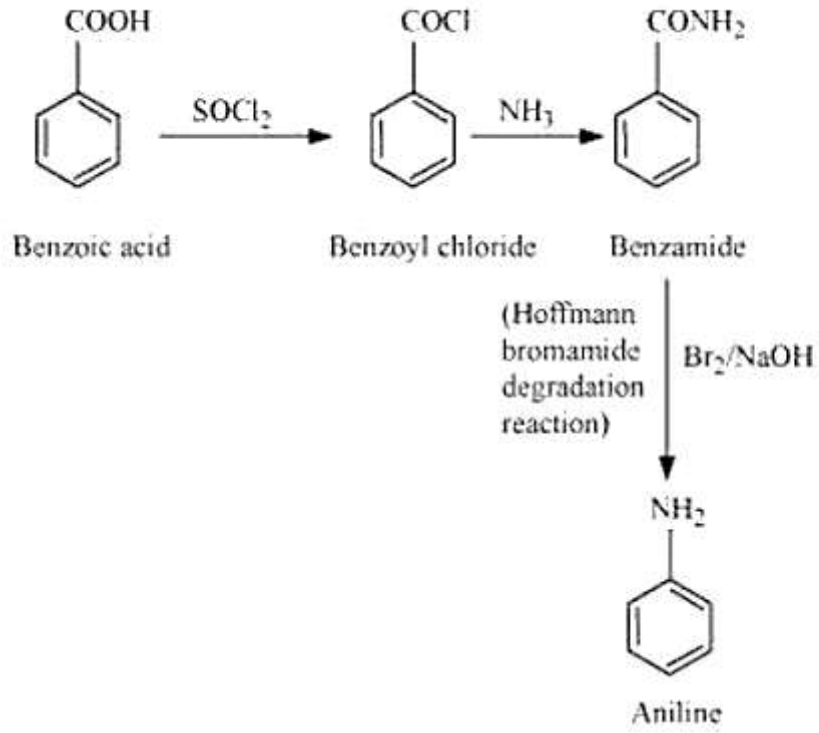
(ii) Benzene to m-bromophenol

Answer:



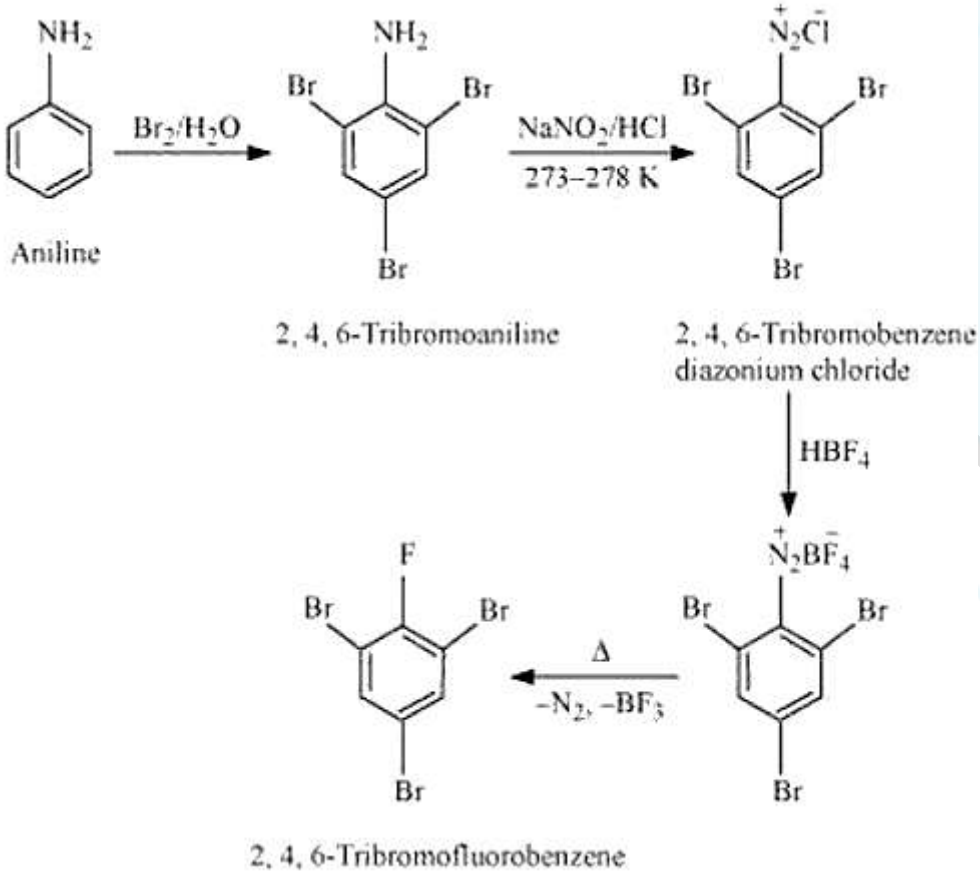
(iii) Benzoic acid to aniline

Answer:



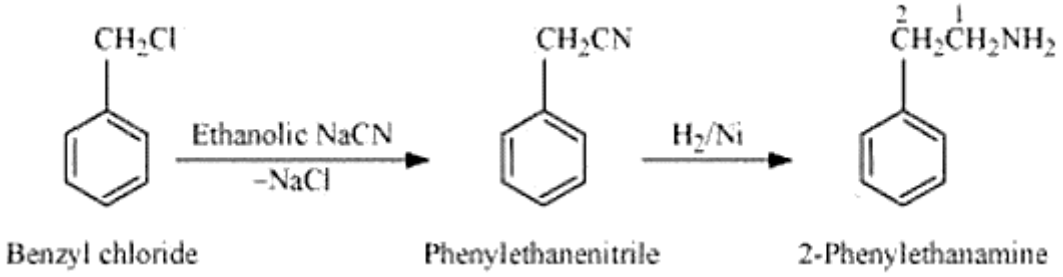
(iv) Aniline to $2,4,6$-tribromofluorobenzene

Answer:



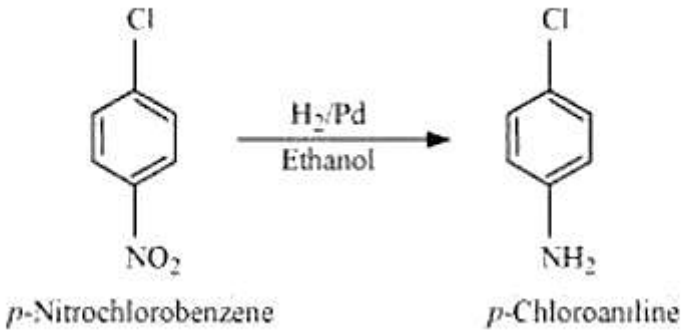
(v) Benzyl chloride to 2 -phenylethanamine

Answer:



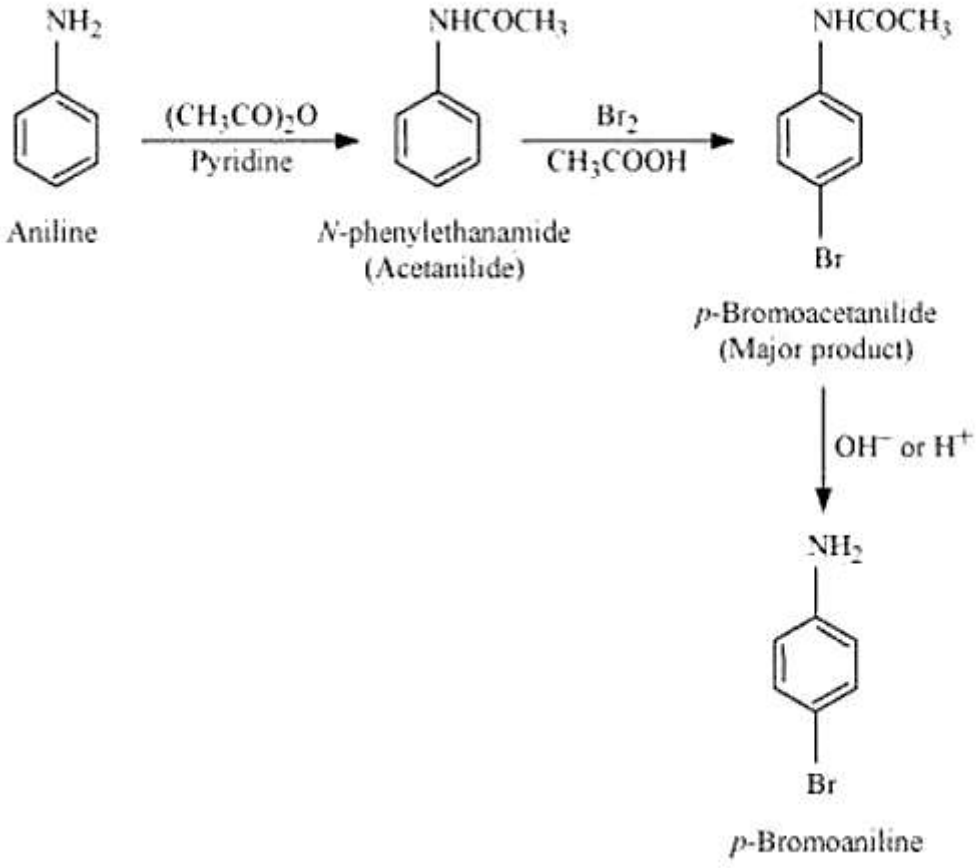
(vi) Chlorobenzene to p-chloroaniline

Answer:



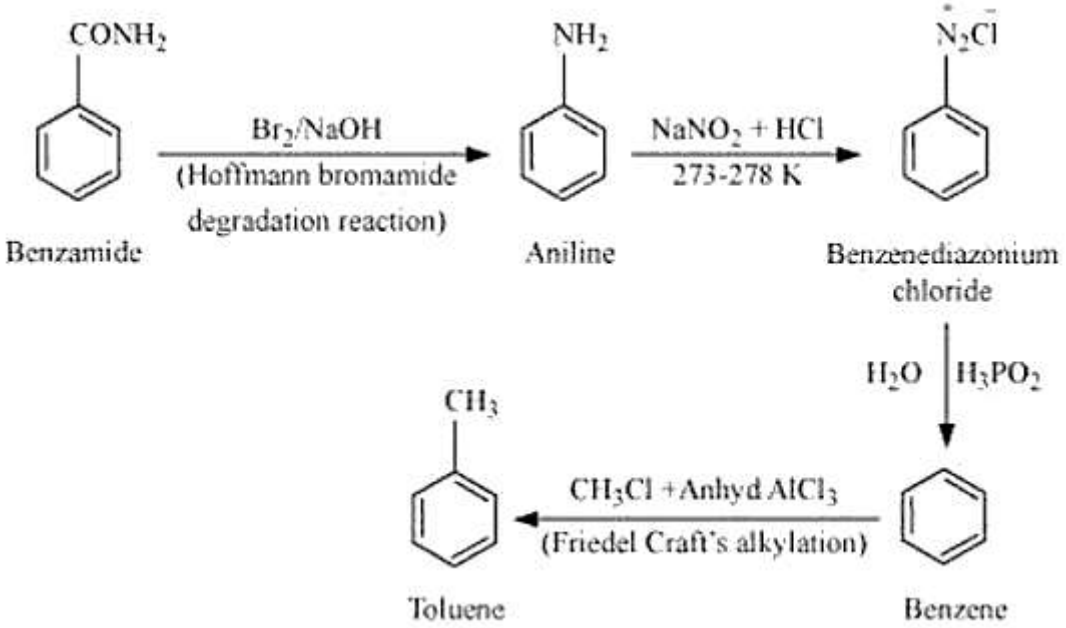
(vii) Aniline to p-bromoaniline

Answer:



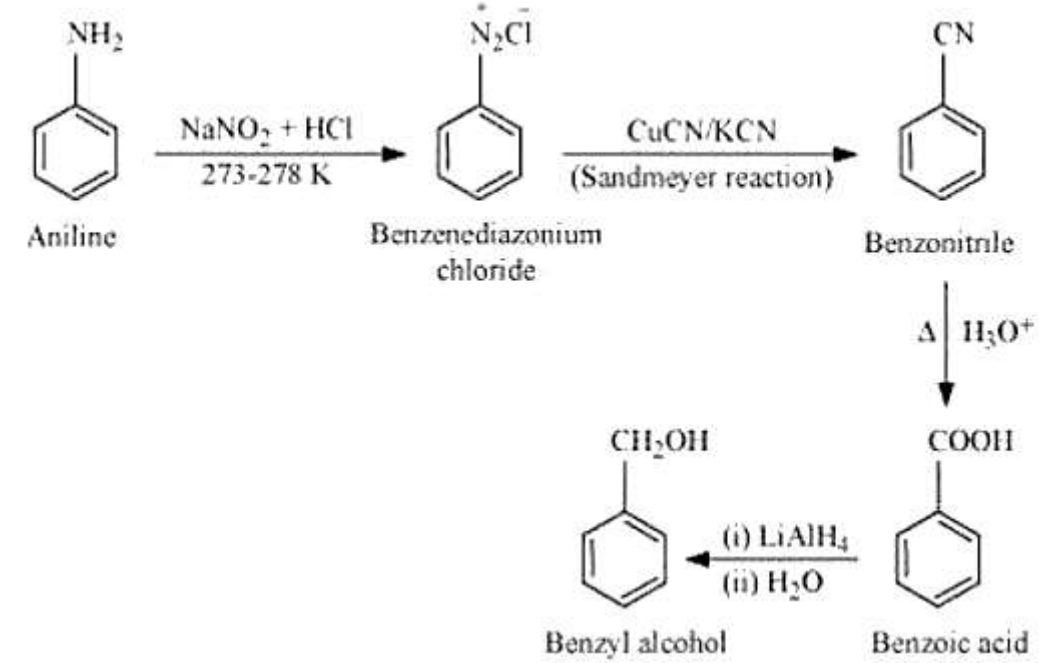
(viii) Benzamide to toluene

Answer:

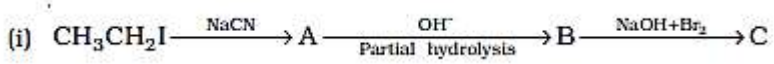


(ix) Aniline to benzyl alcohol.

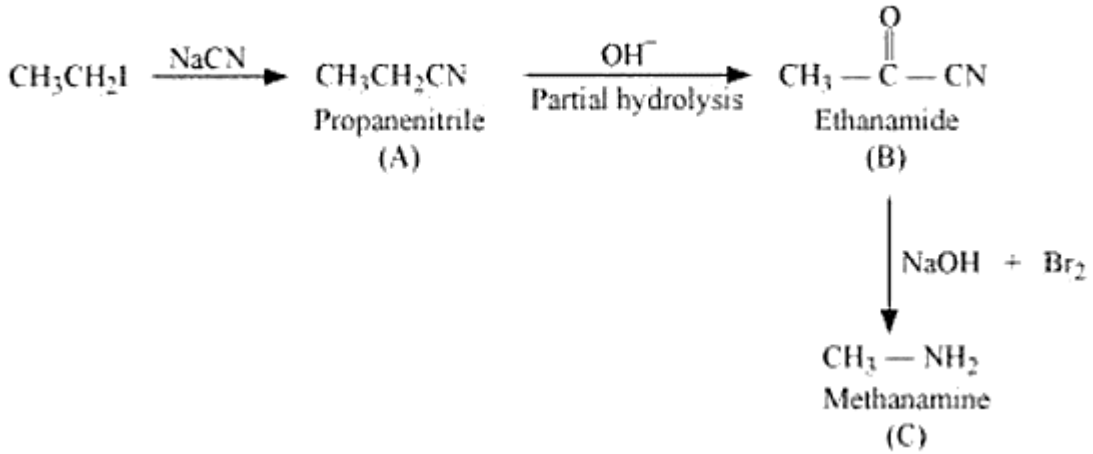
Answer:



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

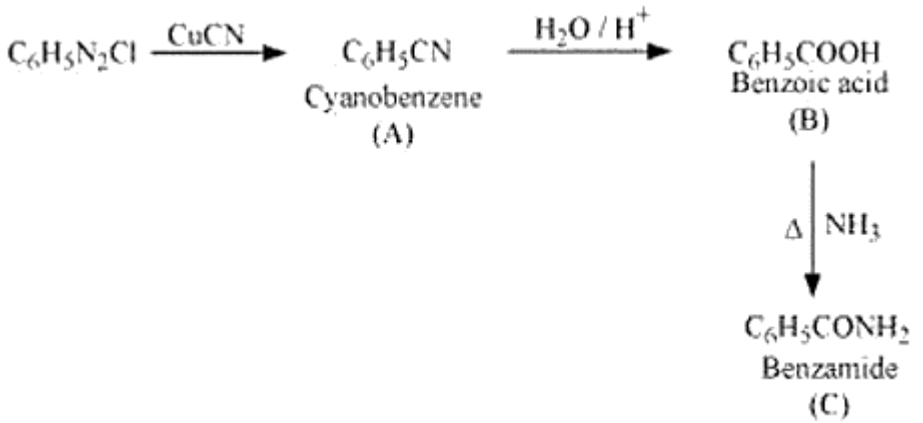


Answer:



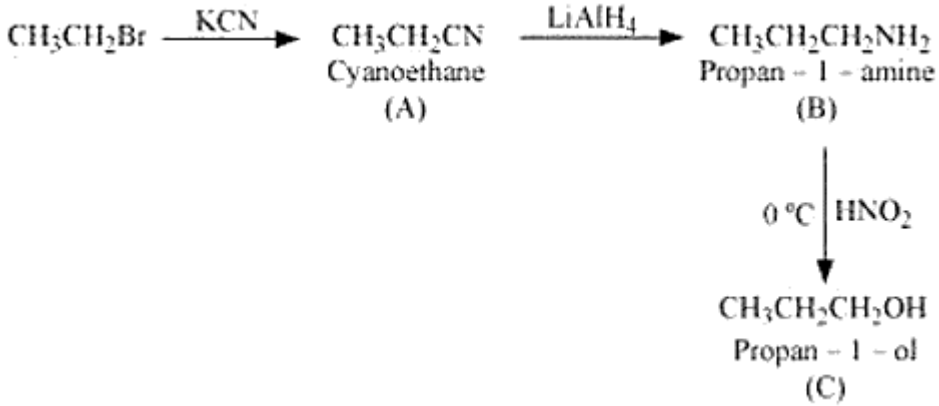
(ii) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

Answer:



(iii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0°C]{HNO_2} C$

Answer:



(iv) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{NaNO_2+HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$

Answer:

$C_6H_5NO_2 \xrightarrow{Fe/HCl} \underset{\text{Aniline (A)}}{C_6H_5NH_2} \xrightarrow[273\ K]{NaNO_2+HCl} \underset{\text{Benzenediazonium chloride (B)}}{C_6H_5-\overset{+}{N}_2\overset{-}{Cl}} \xrightarrow[\Delta]{H_2O/H^+} \underset{\text{Phenol (C)}}{C_6H_5OH}$

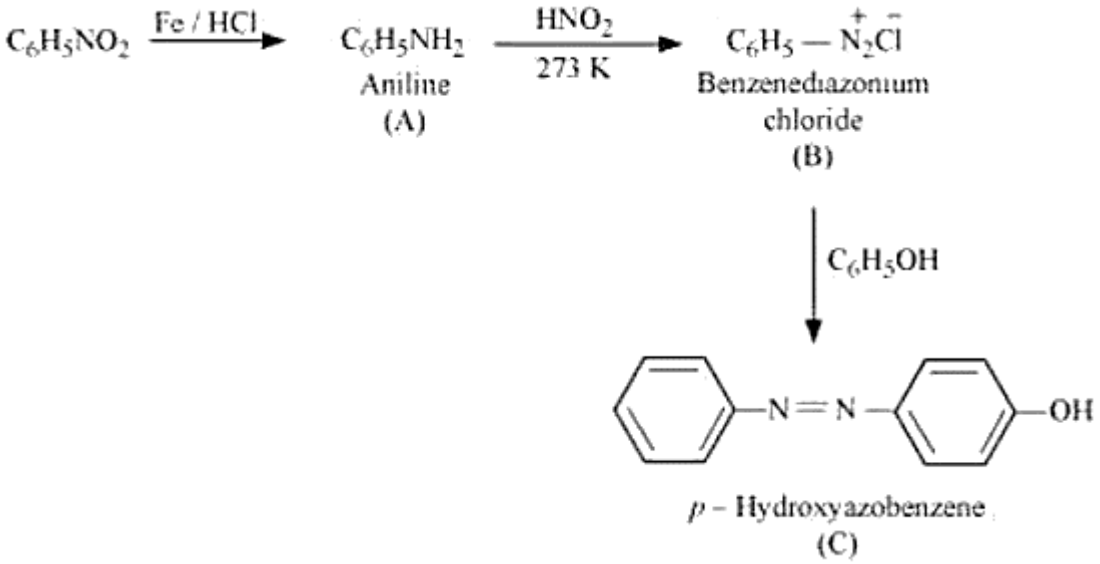
(v) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

Answer:

$CH_3COOH \xrightarrow[\Delta]{NH_3} \underset{\text{Ethanamide (A)}}{CH_3CONH_2} \xrightarrow{NaOBr} \underset{\text{Methanamine (B)}}{CH_3NH_2} \xrightarrow{NaNO_2/HCl} \underset{\text{Methanol (C)}}{CH_3OH}$

(vi) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{HNO_2} B \xrightarrow{C_6H_5OH} C$

Answer:



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 .

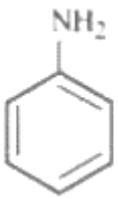
Answer:

It is said that compound 'C' is generated by heating compound 'B' with Br_2 and KOH to form the molecular formula, C_6H_7N .

This is an example of a Hoffmann bromamide degradation process.

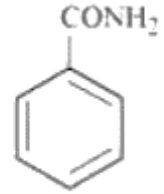
As a result, compound 'B' is an amide, while compound 'C' is an amine.

The only amine with the molecular formula, C_6H_7N , is aniline, $(C_6H_5NH_2)$.



Aniline

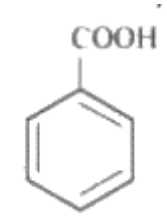
As a result, compound 'B' (from which compound 'C' is generated) must be benzamide, $(C_6H_5CONH_2)$



Benzamide

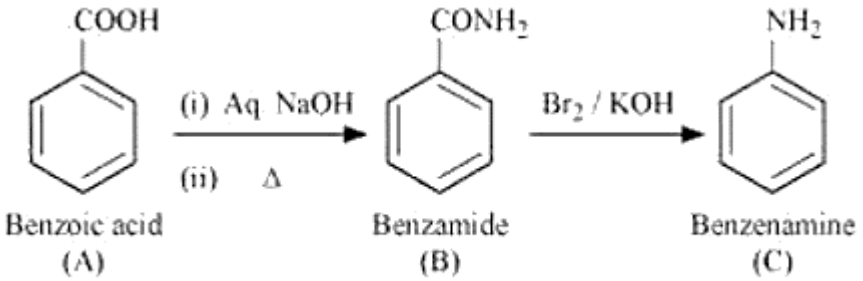
By heating chemical 'A' with aqueous ammonia, benzamide is produced.

As a result, component 'A' must be benzoic acid.



Benzoic acid

Now,



13.11 Complete the following reactions:

(i) $C_6H_5NH_2 + CHCl_3 + \text{alc.KOH} \rightarrow$

Answer:

$$C_6H_5NH_2 + CHCl_3 + 3\text{alc. KOH} \xrightarrow[\text{reaction}]{\text{Carbylamine}} 3H_2O + 3KCl + C_6H_5-NC$$

Aniline — Phenyl isocyanide

(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$

Answer:

$$C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow C_6H_6 + N_2 + H_3PO_3 + HCl$$

Benzenediazonium chloride — Benzene

(iii) $C_6H_5NH_2 + H_2SO_4\,(conc.) \rightarrow$

Answer:

$$C_6H_5NH_2 + conc.H_2SO_4 \rightarrow C_6H_5\overset{+}{N}H_3\overset{-}{H}SO_4$$

Aniline — Anilinium hydrogen sulphate

(iv) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$

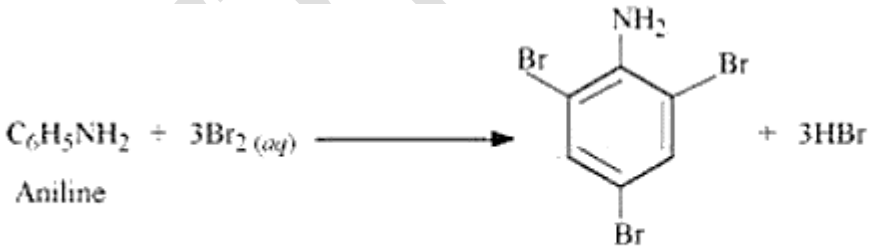
Answer:

$$C_6H_5N_2Cl + C_2H_5OH \rightarrow C_6H_6 + CH_3CHO + N_2 + HCl$$

Benzenediazonium chloride — Ethanol — Benzene — Ethanal

(v) $C_6H_5NH_2 + Br_2\,(aq) \rightarrow$

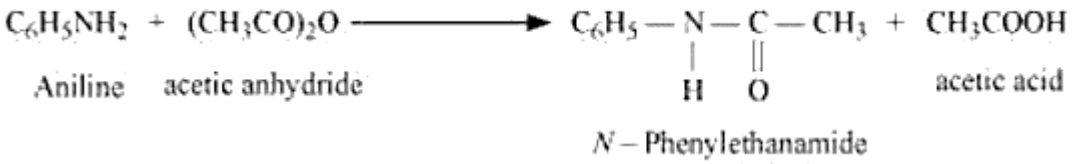
Answer:



2,4,6 - Tribromoaniline

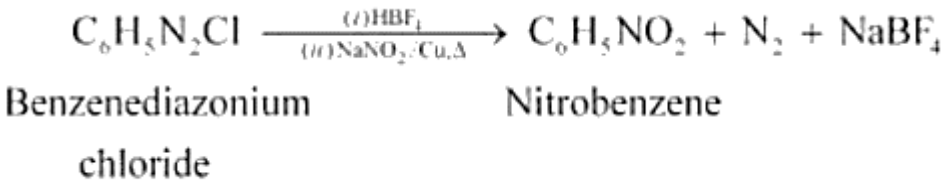
(vi) $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow$

Answer:



(vii) $C_6H_5N_2Cl \xrightarrow[(ii)NaNO_2/Cu,\Delta]{(i)HBF_4}$

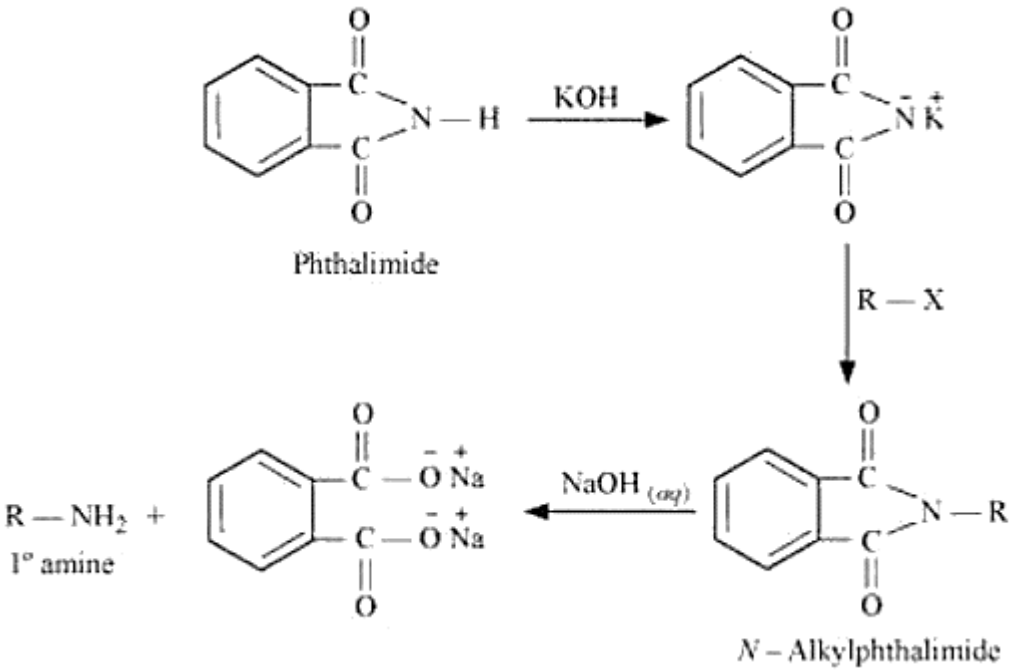
Answer:



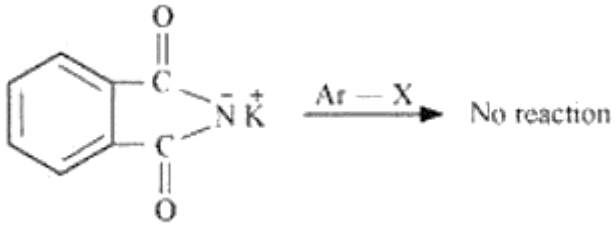
13.12 Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

Answer: Gabriel phthalimide synthesis is used to make aliphatic primary amines.

It entails nucleophilic replacement of alkyl halides by the anion produced by the phthalimide (S_N2).



Aryl halides, on the other hand, do not undergo nucleophilic substitution with the phthalimide anion.

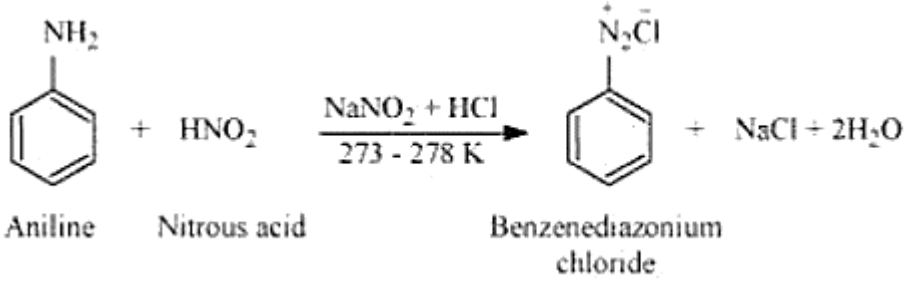


As a result, aromatic primary amines cannot be produced using this method.

13.13 Write the reactions of

(i) Aromatic

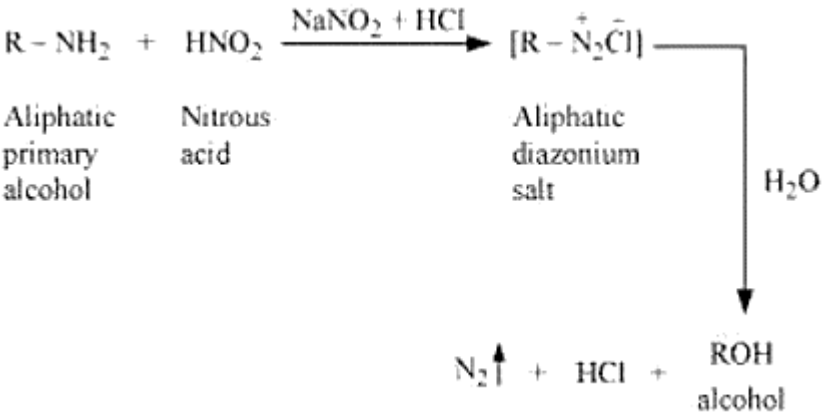
Answer: At $273-278\,K$, aromatic amines react with nitrous acid (made in situ from $NaNO_2$ and a mineral acid such as HCl) to generate stable aromatic diazonium salts, $NaCl$ and H_2O.



(ii) Aliphatic primary amines with nitrous acid.

Answer: Aliphatic primary amines react with nitrous acid (made in situ from $NaNO_2$ and a mineral acid such as HCl) to make unstable aliphatic diazonium salts,

which then react with alcohol and HCl to produce alcohol and HCl via the evolution of N_2 gas.



13.14 Give plausible explanation for each of the following:

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

Answer:

$$R-NH_2 \longrightarrow \underset{\text{Amide ion}}{R-\bar{N}H} + H^+$$

$$\underset{\text{Alcohol}}{R-OH} \longrightarrow \underset{\text{Alkoxide ion}}{R-\bar{O}} + H^+$$

The negative charge in an amide ion is on the N-atom, whereas the negative charge in an alkoxide ion is on the O-atom.

Because O is more electronegative than N, it can more readily tolerate the negative charge.

As a result, the amide ion has a lower stability than the alkoxide ion.

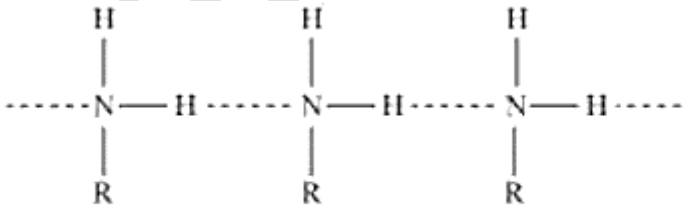
As a result, amines are less acidic than equivalent molecular mass alcohols.

(ii) Why do primary amines have higher boiling point than tertiary amines?

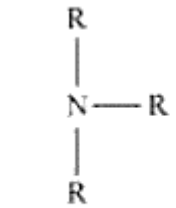
Answer: There are no H-atoms in a tertiary amine molecule,

whereas two hydrogen atoms are present in a primary amine molecule.

Primary amines have substantial intermolecular H-bonding due to the presence of H-atoms.



Primary amine



Tertiary amine

As a result, it takes more energy to separate the molecules of basic amines.

As a result, the boiling points of primary amines are greater than those of tertiary amines.

(iii) Why are aliphatic amines stronger bases than aromatic amines?

Answer: In aromatic amines, electrons on the N atom are less accessible due to the $-R$ effect of the benzene ring.

As a result, the electrons on the $N-$atom in aromatic amines cannot be readily given.

This explains why aliphatic amines have a higher base potential than aromatic amines.