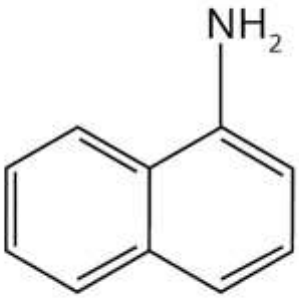
NCERT Solutions for Class 12 Chemistry

Chapter 9 – Amines

Intext Questions – Class 12 Chemistry Chapter 9 Amines NCERT Solutions

9.1

Classify the following amines as primary, secondary or tertiary:

(i) 

(ii) 

(iii) $(C_2H_5)_2CHNH_2$

(iv) $(C_2H_5)_2NH$

Ans – (i) 1°
(ii) 3°
(iii) 1°
(iv) 2°

9.2

(i) Write structures of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$.

(ii) Write IUPAC names of all the isomers.

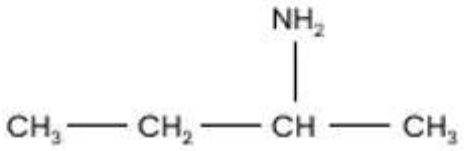
(iii) What type of isomerism is exhibited by different pairs of amines?

Ans – Structures and IUPAC names of different isomeric amines:-

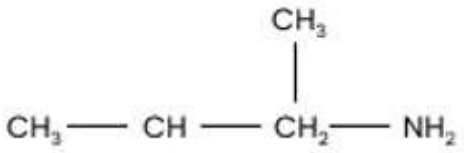
a) Butanamine (1^0)

$CH_3 - CH_2 - CH_2 - CH_2 - NH_2$

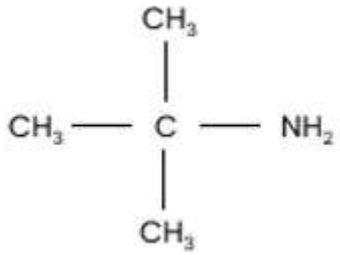
b) Butan-2-amine (1^0)



c) 2-methyl propanamine (1^0)



d) 2-methylpropan-2-amine (1^0)



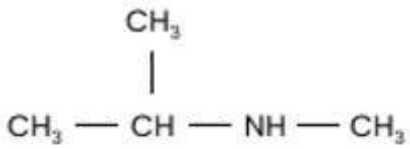
e) N-ethylethanamine (2^0)

$CH_3 - CH_2 - CH_2 - NH - CH_3$

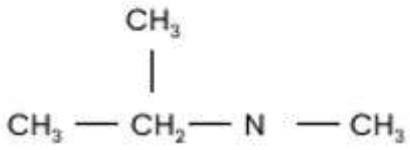
f) N-methylpropananmine (2^0)

$CH_3 - CH_2 - NH - CH_2 - CH_3$

g) N-methylpropan-2-amine (2^0)



h) N,N, Dimethylethanamine (3^0)



(iii) Position Isomers:

Butanamine (1^0) and Butan-2-amine (1^0);

N-ethylethanamine (2^0) and N-methylpropan-2-amine (2^0)

Chain Isomers:

Butanamine (1^0) and 2-methyl propanamine (1^0);

Butanamine (1^0) and 2-methylpropan-2-amine (1^0);

Butan-2-amine (1^0) and 2-methyl propanamine (1^0)

Butan-2-amine (1^0) and 2-methylpropan-2-amine (1^0)

Metamers:

N-ethylethanamine (2^0) and N- methylpropananmine (2^0)

N- methylpropananmine (2^0) and N-methylpropan-2-amine (2^0)

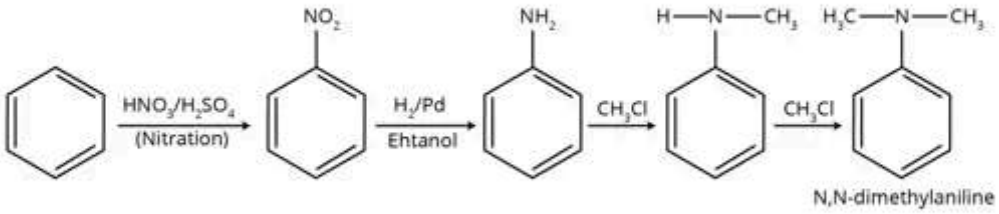
Functional Isomers: All 1^0 amines are functional isomers of 2^0 and 3^0 amines and vice-versa

9.3

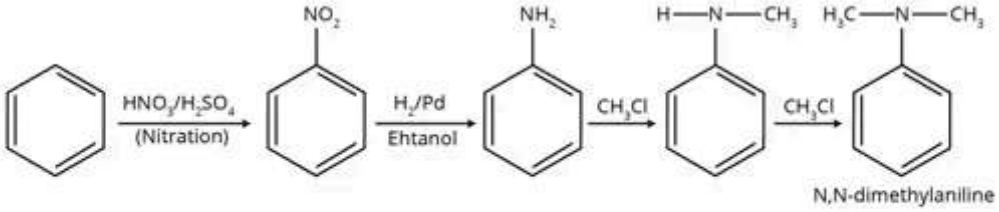
How will you convert

(i) Benzene into aniline (ii) Benzene into N, N-dimethylaniline (iii) $Cl–(CH_2)_4–Cl$ into hexan-1,6-diamine?

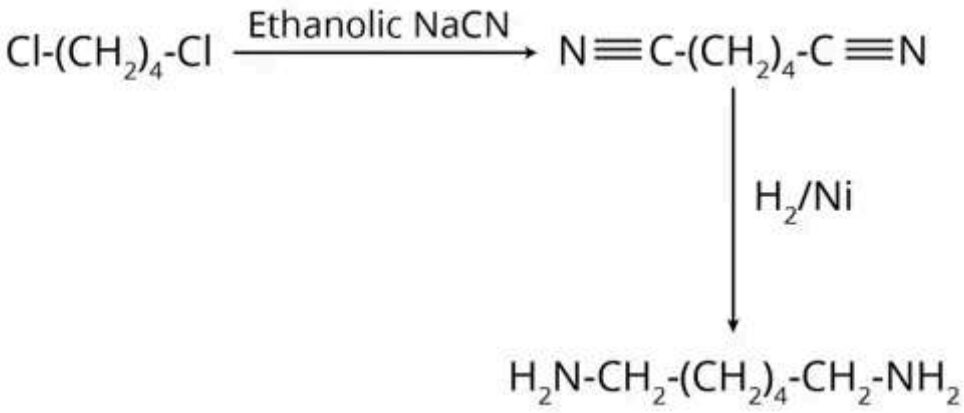
Ans - (a)



(b)



(c)



9.4

Arrange the following in increasing order of their basic strength:

(i)$C_2H_5NH_2$, $C_6H_5NH_2$, NH_3 , $C_6H_5CH_2NH_2$ and $(C_2H_5)_2NH$

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

(iii) CH_3NH_2 , $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$.

📌 ***Key Points to Note from Question***

Key Concept:

- **Electron-donating alkyl groups** increase basic strength by stabilizing the positive charge on nitrogen after accepting a proton.
- **Aromatic rings (C_6H_5-)** delocalize the lone pair on nitrogen, decreasing basicity.
- **Steric hindrance** in tertiary amines reduces accessibility to protons, lowering basicity in some cases.

What to Calculate:

- Inductive effect (alkyl groups)
- Resonance (aryl amines)
- Steric hindrance (bulkier alkyl groups)

Ans – (i) Given each of the alkyl-based compounds $C_2H_5NH_2$, $(C_2H_5)_2NH$'s & NH_3 inductive action, they can be ranked in an ascending sequence of fundamental potency as mentioned below:

$NH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$

Once more, NH_3 has more proton acceptance compared to $C_6H_5NH_2$. Consequently, we have the following characteristics: $C_6H_5NH_2 < NH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$

The density of electrons on the N-atom surrounding $C_6H_5CH_2NH_2$ is greater compared to the one in NH_3, but much smaller than the one found on the N-atom within $C_2H_5NH_2$ because of the −I impact created by the C_6H_5- group. As a result, the compounds that come next can be ranked according to their fundamental attributes:$C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$

(ii) By considering the fact of steric restriction alongside the inductive impact of the alkyl compounds $C_2H_5NH_2$ & $(C_2H_5)_2NH$ along with their basic reaction can be described in the following manner: $C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$

Once more, the overall electron density regarding the nitrogen atom present in $C_6H_5NH_2$ is significantly less when compared to that around the N atom in $C_2H_5NH_2$ due to the −R impact occurring inside the C_6H_5- band. Consequently, $C_6H_5NH_2$ consists of declined fundamental features as opposed to $C_2H_5NH_2$ compounds.

As a result, the compounds that come next can be grouped in ascending hierarchy based on their basic physical properties: $C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$

(iii) By considering the fact of the steric constraint & inductive impact of alkyl divisions, the CH_3NH_2, $(CH_3)_2NH$ & $(CH_3)_3N$ compounds are capable of being ranked in ascending sequence based on their fundamental qualities in the following way:

$(CH_3)_3N < (CH_3)_2NH < CH_3NH_2$

N is joined straight with the benzene ring through $C_6H_5NH_2$. Consequently, the N-atom's single set of electrons becomes dispersed across the benzene ring. N is not bonded completely with the benzene ring around $C_6H_5CH_2NH_2$. Its single couple is therefore not decentralized across the benzene ring.

As a result, $C_6H_5CH_2NH_2$ happens to be more base compared to $C_6H_5NH_2$ due to the electrons that exist on the atom of nitrogen, which is easier to acquire for protonation to occur in the former case.

Once more, the density of electrons on the N-atom in $C_6H_5CH_2NH_2$ is relatively lower compared to the one present on the N-atom in $(CH_3)_3N$ due to the −I impact caused by the C_6H_5 molecular compound. Consequently, compared to $C_6H_5CH_2NH_2$, $(CH_3)_3N$ remains more basic. As a result, the following is an arrangement for rising basic potency for the substances mentioned.

$C_6H_5NH_2 < C_6H_5CH_2NH_2 < (CH_3)_3N < (CH_3)_2NH < CH_3NH_2$

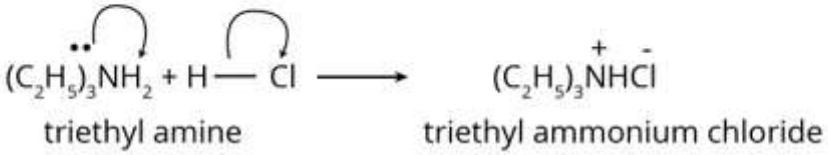
9.5

Complete the following acid-base reactions and name the products:

(i) $CH_3CH_2CH_2NH_2 + HCl \longrightarrow$ (ii) $(C_2H_5)_3N + HCl \longrightarrow$

Ans - (i)

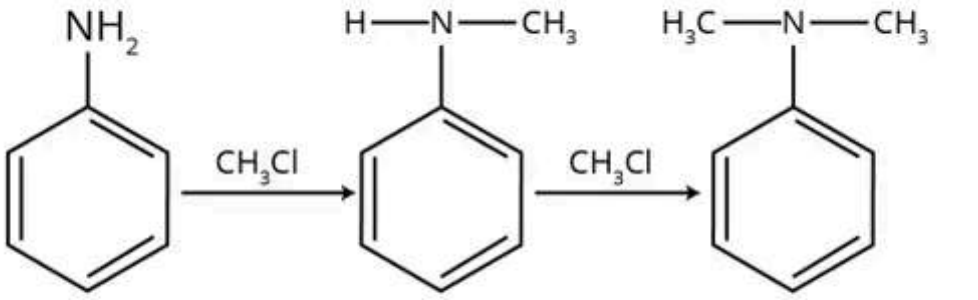
(ii)



9.6

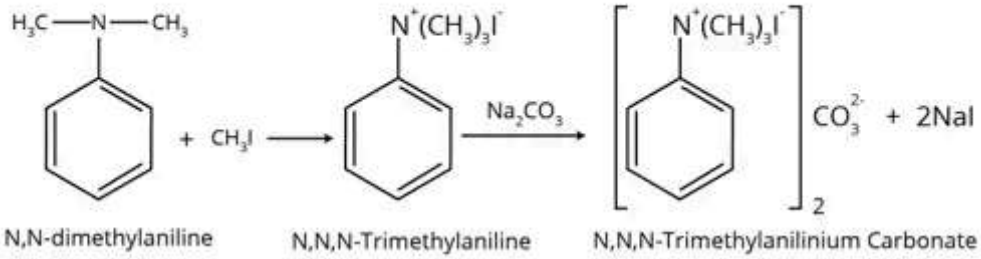
Write reactions of the final alkylation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.

Ans - Aniline undergoes reaction with methyl iodide to yield N,N-dimethylaniline.



N,N-dimethylaniline

In the presence of Na_2CO_3 solution, excess methyl iodide reacts with N,N-dimethylaniline to yield N,N,N-trimethylanilinium carbonate.

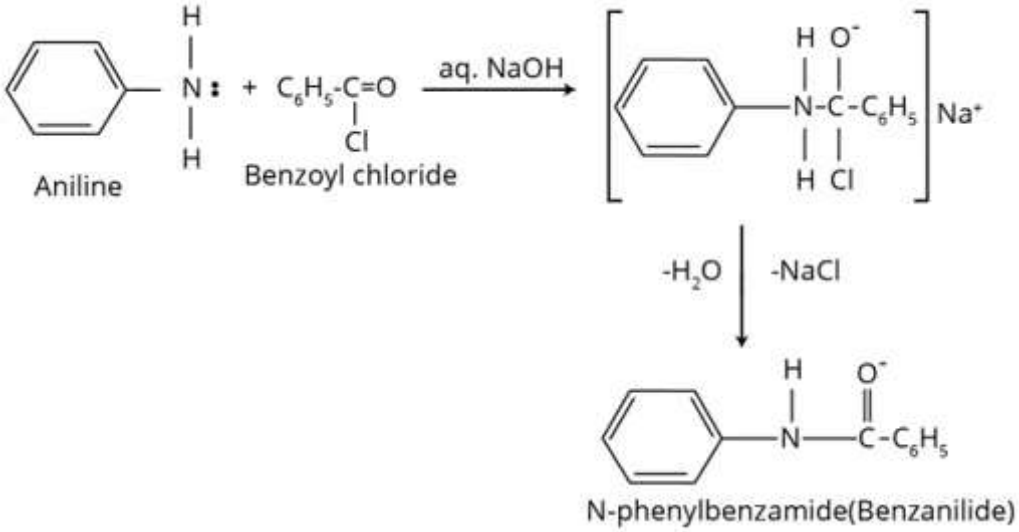


N,N-dimethylaniline N,N,N-Trimethylaniline N,N,N-Trimethylanilinium Carbonate

9.7

Write chemical reaction of aniline with benzoyl chloride and write the name of the product obtained.

Ans –



9.8

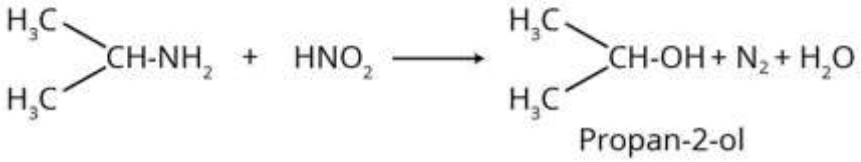
Write structures of different isomers corresponding to the molecular formula, C_3H_9N. Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.

Ans - Four structural isomers are possible. They are:

only 1^0 amines react with HNO_2 to liberate N_2 gas

only 1^0 amines react with HNO_2 to liberate N_2 gas

$$\underset{Propan-1-amine}{CH_3CH_2CH_2NH_2} + HNO_2 \rightarrow \underset{Propan-1-ol}{CH_3CH_2CH_2OH} + N_2 + H_2O$$



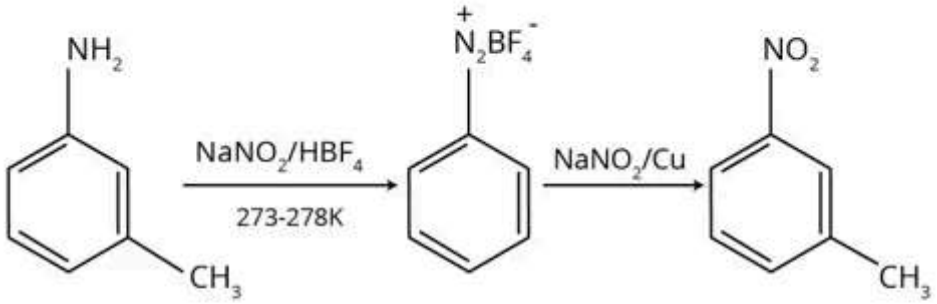
9.9

Convert

(i) 3-Methylaniline into 3-nitrotoluene.

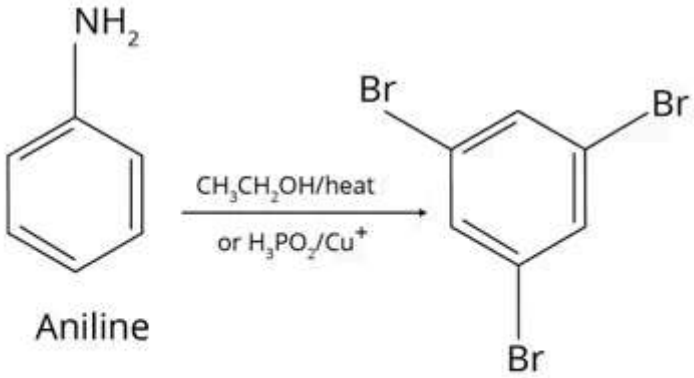
(ii) Aniline into 1,3,5 - tribromobenzene.

Ans - (i)



3-nitrotoluene

(ii)



Aniline

1,3,5- tri bromo benzene

Exercise Questions – Class 12 Chemistry Chapter 9 Amines NCERT Solutions

9.1

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

(i)$(CH_3)_2CHNH_2$ (ii) $CH_3(CH_2)_2NH_2$ (iii) $CH_3NHCH(CH_3)_2$

(iv) $(CH_3)_3CNH_2$ (v) $C_6H_5NHCH_3$ (vi) $(CH_3CH_2)_2NCH_3$

(vii) m–$BrC_6H_4NH_2$

Ans – (i) Propan-2-amine(1°)
(ii) Propan-1-amine (1°),
(iii) N-Methylpropan-2-amine (2°).
(iv) 2-Methylpropan-2-amine(l°)
(v) N-Methylbenzenamine or N-methylaniline(2°)

(vi) N-Ethyl-N-methylethanamine (3°)
(vii) 3-Bromobenzenamine or 3-bromoaniline (1°)

9.2

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) Methylamine and methylamine can be distinguished by using the carbylamine test.

$$CH_3NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} CH_3NC + 2KCl + 3H_2O$$

$$(CH_3)_2NH \xrightarrow{CHCl_3/KOH(alc)} \text{No reaction}$$

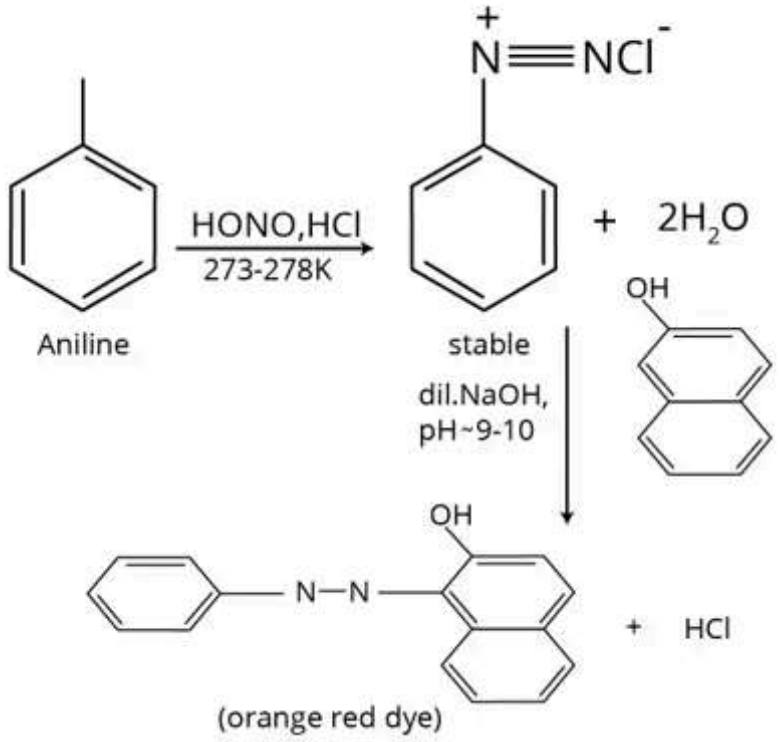
(ii) Secondary and tertiary amine can be distinguished by using the Liebermann's nitrosamine test.

$$(CH_3CH_2)_2NH + HO-N=O \xrightarrow{HCl+NaNO_2} \underset{\text{Yellow colour}}{(CH_3CH_2)_2N-N=O} + H_2O$$

$$(CH_3CH_2)_3N + HNO_2 \rightarrow \underset{\text{Triethylammonium nitrate (soluble)}}{[(CH_3CH_)_3NH]^+NO_2^-}$$

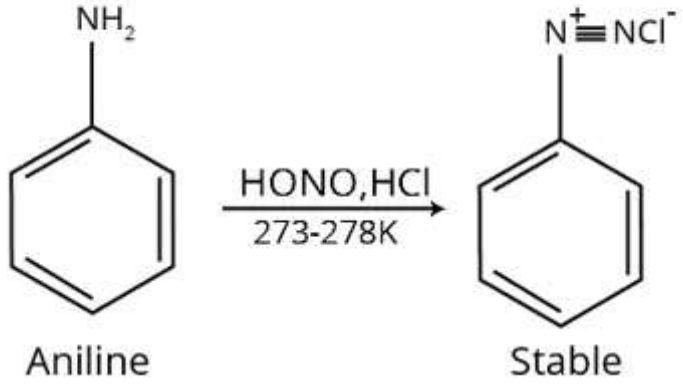
(iii) Ethylamine and aniline can be distinguished by using the azo test

$$C_2H_5NH_2 + HONO + HCl \xrightarrow{273-278K} C_2H_5OH + CH_2 = CH_2 + CH_3CH_2Cl + N_2$$



(iv) Aniline and benzylamine can be distinguished by using the nitrous acid test.

$$C_6H_5CH_2NH_2 \xrightarrow[HCl]{HONO} [C_6H_5CH_2N_2^+Cl^-] \xrightarrow[Decompose]{H_2O} C_6H_5CH_2OH + N_2\uparrow + HCl$$



(v) Aniline and N-methylaniline can be distinguished by using the carbylamine test.

$$\underset{Aniline}{C_6H_5NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\text{Offensive smell}}{C_6H_5NC} + 3KCl + 3H_2O$$

$$C_6H_5 - NH - CH_3 \xrightarrow{CHCl_3+3KOH} \text{No reaction}$$

9.3

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.

📌 *Key Points to Note from Question*

Key Concept:

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

In aniline, the lone pair on nitrogen delocalizes into the benzene ring, reducing its availability for protonation and thus lowering basicity.

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

Ethylamine can form stronger hydrogen bonds with water due to the absence of a bulky hydrophobic phenyl ring, unlike aniline.

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

Methylamine is a strong base, increases OH^- in solution, causing Fe^{3+} to precipitate as $Fe(OH)_3$.

(iv) Aniline on nitration gives substantial m-nitroaniline

Acidic nitration conditions protonate the $–NH_2$ group, converting it into $–NH_3^+$, which is meta-directing.

(v) Aniline does not undergo Friedel–Crafts reaction

Aniline forms a Lewis acid-base complex with $AlCl_3$, deactivating the ring for further substitution.

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

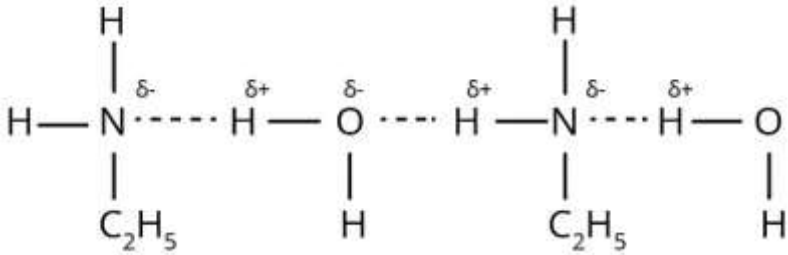
Aromatic diazonium salts are resonance-stabilized by the benzene ring, unlike their aliphatic counterparts.

(vii) Gabriel phthalimide synthesis is preferred for synthesizing primary amines

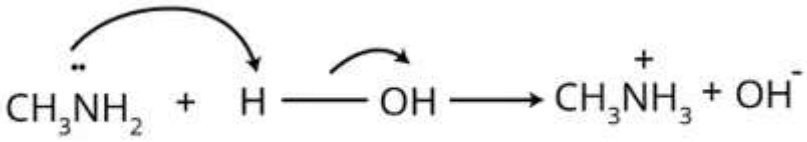
It avoids formation of secondary or tertiary amines, giving selectively primary amines via nucleophilic substitution.

Ans – (i) The previous N-atom's singular set of electrons in order becomes decentralized across the benzene ring within the case of aniline. The nitrogen atoms of electrons therefore drop. In contrast, the $-CH_3$ group's +I action in CH_3NH_2 raises the N-atom's abundance of electrons. Consequently, aniline has a greater pK_b ratio compared to methylamine since it constitutes a less effective base material.

(ii) The H-bond between molecules causes ethylamine to dissociate in fluids. Nevertheless, aniline has become impermeable in water because of its significant hydrophobic portion, or hydrocarbon portion, which results in relatively little H-bonding.



(iii) Since methylamine is more fundamental compared to water, it may take a proton coming from it and release OH^- ions. When these OH^- ions mix together with the Fe^{+3} ions in H_2O, a brown compound of properly hydrated ferric oxide is created.



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

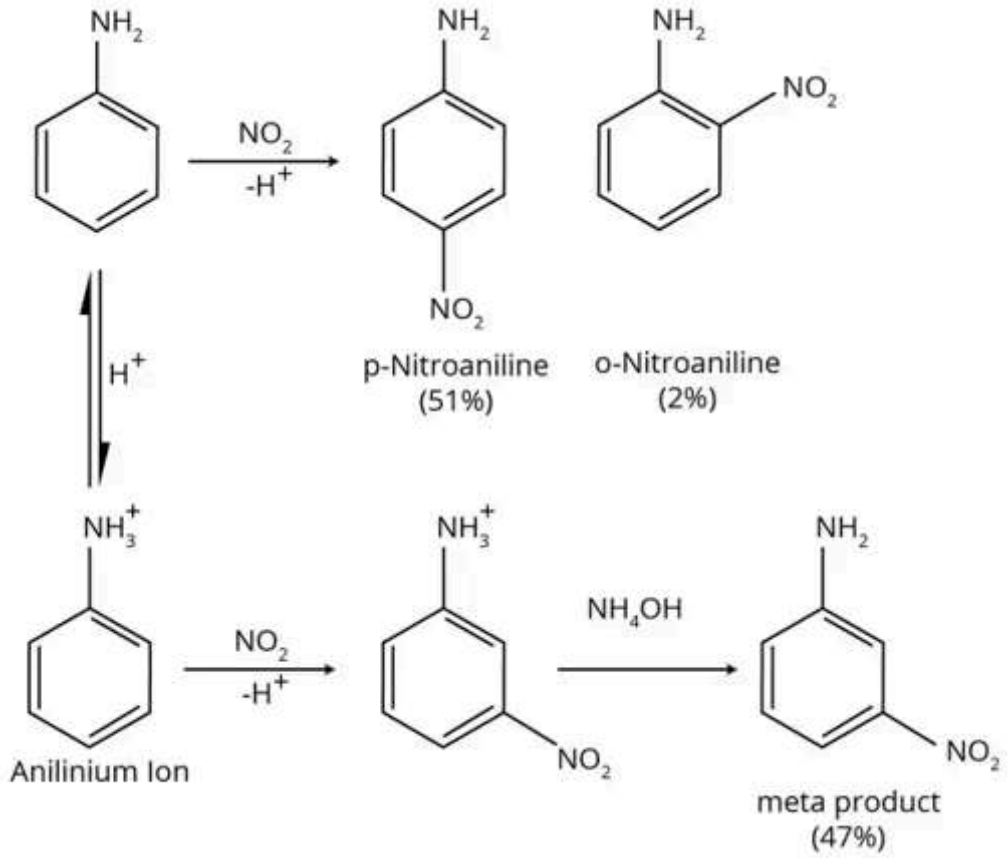
$$2Fe^{+3} + 6OH^- \rightarrow \underset{\text{Brown ppt}}{2Fe(OH)_3 or Fe_2O_3.3H_2O}$$

(iv) Typically, a combination of conc HNO^{3+} conc H_2SO_4 is used for nitration. The majority of the aniline is protonated to create the anilinium ion when acidic substances are present. Meanwhile, aniline alongside anilinium ions makes up the outcome of the solution when acidic substances are readily available in the compound.

At this point, the element that gained NH^{3+} ions within the anilinium-charged particles might tend to be eliminating & m-directing, whereas the $-NH_2$ compound around aniline gets activated alongside o, p-directing: Because of steric resistance at the o-region, aniline nitration mostly yields p-nitroaniline, while anilinium ion nitration yields m-nitroaniline.

In real life, p-nitroaniline & m-nitroaniline are mixed roughly around a 1:1 ratio. As a result of the

chain of amino acids being protonated, nitration of aniline yields a significant quantity of m-nitroaniline.

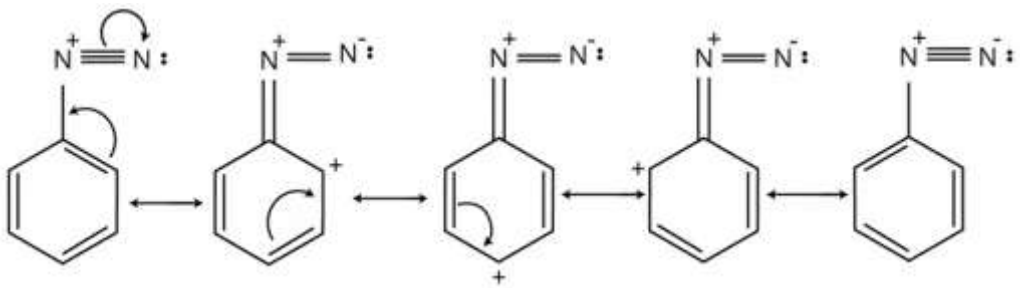


(v) The study of organic chemistry method called the Friedel-Crafts reaction adds substituted molecules to aromatic ring structures. It's also defined as an electrophilic aromatic replacement process (EAS). A substance that is salty when created due to the presence of aniline, a base gained from the Lewis formula gets merged with the Lewis acid $AlCl_3$.

It acts as a robust deactivating reagent for an electrophilic replacement mechanism, created when the N of aniline attains a positive value. Therefore, Aniline doesn't experience the Friedel Crafts response.

$C_6H_5NH_2 + AlCl_3 \rightarrow C_6H_5NH_2{}^+AlCl_3{}^-$

(vi) Because of resonant frequencies, the positive electrical charge around the benzene ring is dispersed, making the diazonium salts containing aromatic amines of greater stability as opposed to those containing aliphatic amines.



(vii) The Gabriel synthesis is a type of chemical process that converts primary alkyl halides to basic amines. Historically, potassium phthalimide can be employed in this process. In the field of organic chemistry, it's a vital aspect of developing amine-based substances. Siegmund Gabriel, a German chemist, gave the process its name. Clean primary amines are produced using Gabriel's phthalimide responses, free of both tertiary & secondary amine interference. As a result, it is recommended during the synthesis of primary amines.

9.4

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) While there are two $-C_2H_5$ compounds present in $(C_2H_5)_2NH$, there is one sole pair of compounds available in $C_2H_5NH_2$. As a result, $(C_2H_5)_2NH$ has a greater +I impact as opposed to $C_2H_5NH_2$ & $(C_2H_5)_2NH$ consists of a maximum electron density throughout the entire N-atom compared to $C_2H_5NH_2$. Therefore, $(C_2H_5)_2NH$ remains more basic in nature as compared to $C_2H_5NH_2$.

Additionally, because the only pair of molecules in $C_6H_5NHCH_3$ & $C_6H_5NH_2$ is delocalized, they are both more fundamental than $(C_2H_5)_2NH$ & $C_2H_5NH_2$. Furthermore, due to the significant presence of the $-CH_3$ group's +I action, $C_6H_5NHCH_3$ is expected to be relatively much easier compared to $C_6H_5NH_2$. Therefore, the below factor will be the sequence in which the basic features of supplied molecular compounds get increased:
$C_6H_5NH_2 < C_6H_5NHCH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$

We are aware that pK_b readings will decrease while increasing the basic force.

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

(ii) $(C_2H_5)_2NH$ tends to be highly basic as opposed to CH_3NH_2, mainly because of the larger +I impact of two separate $-C_2H_5$ molecules over a single $-CH_3$ unit. The individual pair of charged particles that surround the N-atom become dispersed around the benzene ring throughout both $C_6H_5NH_2$ & $C_6H_5N(CH_3)_2$, but the +I impact of the 2 $-CH_3$ groupings makes $C_6H_5N(CH_3)_2$ a more fundamental compound.

$(C_2H_5)_2NH > CH_3NH_2 > C_6H_5N(CH_3)_2 > C_6H_5NH_2$

(iii) a) The fundamental stability of amines reduces when the electron-withdrawing NO_2 compound is present, but the electron-donating $-CH_3$ compound rises.

p−nitroaniline < aniline < p−toluidine

(iii) b) The element nitrogen is joined immediately with the benzene ring around $C_6H_5NH_2$ & $C_6H_5NHCH_3$. The N-atom's single set of electrons is thus decentralized underneath the benzene ring. Consequently, compared to $C_6H_5CH_2NH_2$, both $C_6H_5NH_2$ & $C_6H_5NHCH_3$ are less effective bases, among others. With regard to the +1 impact of the $-CH_3$ category, $C_6H_5NHCH_3$ is considered a far more fundamental compound as opposed to $C_6H_5NH_2$.

$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

(iv) The solvation consequences, especially the stability of the conjugate acids owing to H-bonding, cannot be observed in the gas state or in solvents that are not water-based like chlorobenzene, etc. As a result, the alkyl compounds' +I action is the sole element influencing basic potency. The more pairs of alkyl groups there are the greater the +I impact. Therefore, in the gas period, the proper sequence for reducing basic intensity has become,

$(C_2H_5)_3N > (C_2H_5)_2N > C_2H_5NH_2 > NH_3$

(v) Alcohols generate more robust H-bonds compared to amines because oxygen has an increased electronegativity as opposed to nitrogen. Furthermore, the degree of H-bonding is higher in basic amines compared with secondary amines because it is dependent on the amount of H-atoms surrounding the N-atom.

$(CH_3)_2NH_2 < C_2H_5NH_2 < C_2H_5OH$

(vi) As amino acids' molecular weight increases, their solubility reduces given that the water-resistant hydrocarbon portion is bigger and since there are fewer hydrogen atoms adjacent to the N-atom that form H-bonds.

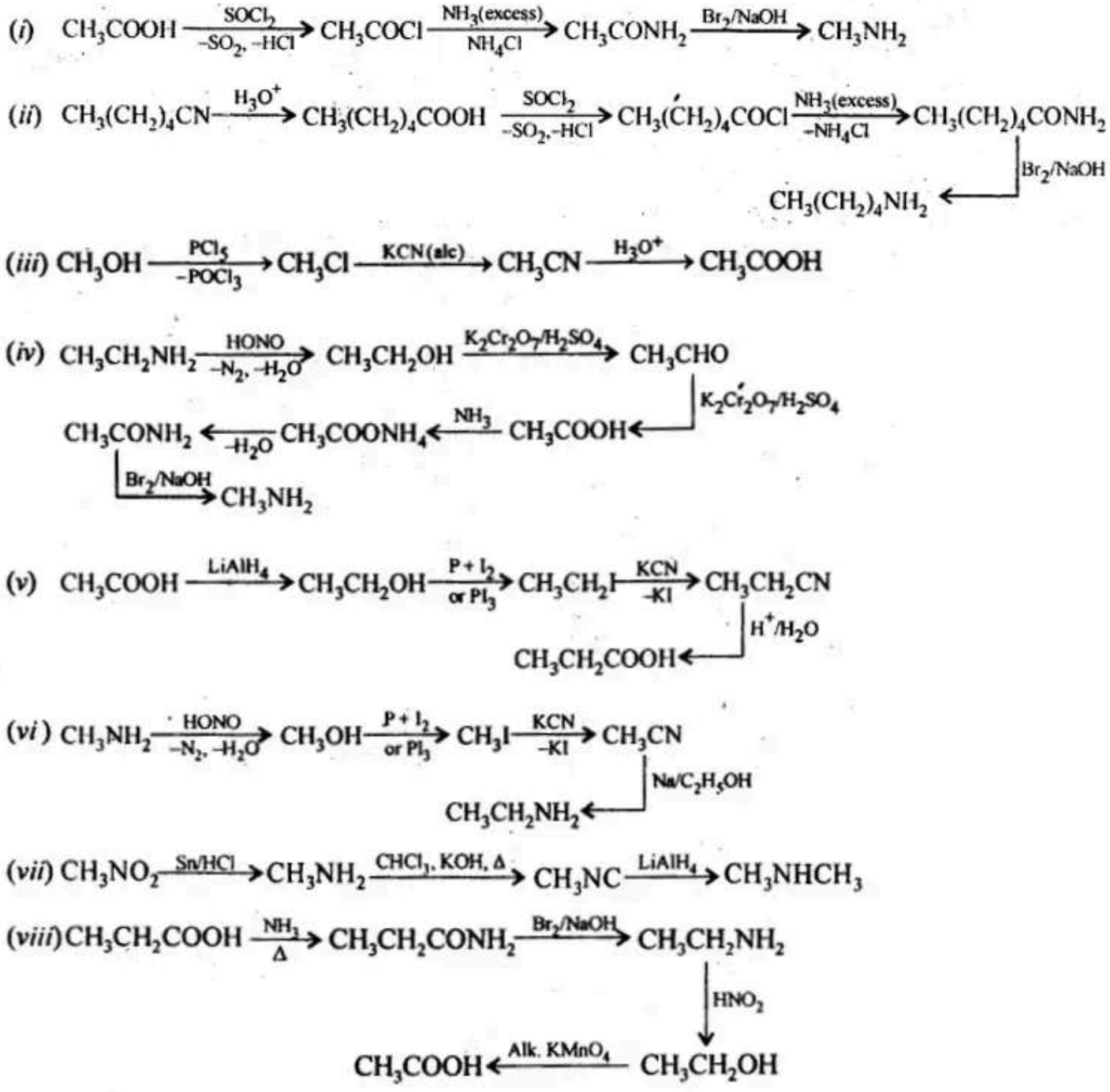
$C_6H_5NH_2 < (C_6H_5)_2NH < C_2H_5NH_2$

9.5

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?

Ans –



9.6

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

Ans – The Heinsberg method can be utilized to differentiate between all three categories of amines that exist. The procedure involves shaking the amine using benzene sulphonyl chloride ($C_6H_5SO_2Cl$) when there is too much aqueous NaOH or KOH present. An impenetrable substance is produced when a primary amine interacts to produce a transparent liquid that becomes more acidic.

$$RNH_2 + C_6H_5SO_2Cl \xrightarrow[-HCl]{OH^-} C_6H_5SO_2NHR \xrightarrow{KOH} C_6H_5SO_2N^-RK^+$$

$$\downarrow H^+$$

$$\underset{\text{Insoluble}}{C_6H_5SO_2NHR}$$

An impervious chemical substance is created by a secondary amine and stays that way regardless of being acidified.

$$R_2NH + C_6H_5SO_2Cl \xrightarrow[-HCl]{OH^-} \underset{\text{Insoluble}}{C_6H_5SO_2NR_2} \xrightarrow{H^+} No\ reaction$$

A ternary amine evaporates forming an acidic substance instead of reacting against the chemical reagents.

$$C_6H_5SO_2Cl + R_3N \xrightarrow{OH^+} \text{No reaction}$$

$$R_3N + H^+ \rightarrow \underset{\text{clear solution}}{[R_3NH]^+}$$

9.7

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 consists of the inclusion of amine in the middle reaction developed from the dehydrohalogenation of chloroform substances. This intermediate chain reaction is defined as dichlorocarbene. This process is called Hofmann isocyanide synthesis or carbylamine reaction. It's a fundamental assessment to find the composition of primary amines-based compounds. When heated with chloroform & an alcohol-based KOH aqueous solution

both aliphatic & fragrant basic amines yield isocyanides or carbylamines, which possess a highly disagreeable smell.

$R-NH_2 + CHCl_3 + 3KOH(alc) \rightarrow R-N\equiv C + 3KCl + 3H_2O$

(ii) In 1858, Peter Griess, a German-based industrial scientist, became the first to record this sort of reaction. Diazotization is a technique by which a primary aromatic amino molecule is changed to produce a diazonium salt. These diazonium salts are often made by reacting an aromatic amine combined with nitrous acid when an additional acid is present.

This procedure involves mixing a water-based solution that comprises sodium nitrite into a principal existing component of aromatic amine (such as aniline) fluid that contains a substantial amount of HCl components around an approximate temperature lower than 5°C.

$$\underset{1^0\text{amine}}{ArNH_2} + NaOH_2 + 2HX \xrightarrow{273-278K} \underset{\text{Arene Diazonium salt}}{ArN_2{}^+X^-} + NaX + 2H_2O$$

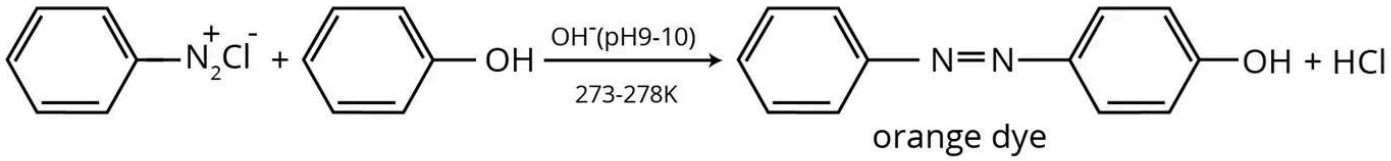
(iii) August Wilhelm Von Hoffmann has successfully presented Hoffmann's explanation of the bromamide degradation process. The Hoffmann Rearrangement Reaction is another name given to this process, that is deployed to generate primary amines. To penetrate the amide compound & cause deprotonation followed by the resulting formation of an anion, the Hoffmann bromamide reaction process often involves the application of an alkali representing a powerful base.

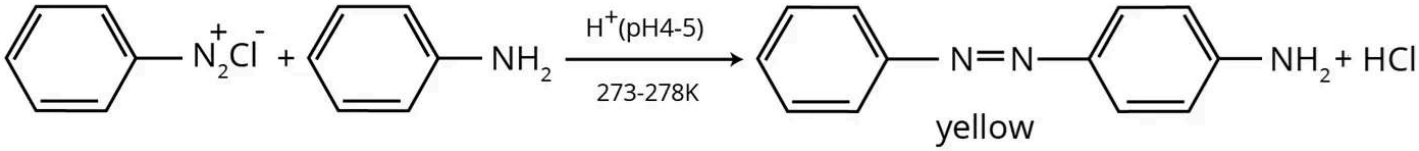
During the creation, the basic amine consists of one less carbon atom, as opposed to the primary amide. The subsequent occurrence happens whenever an amide undergoes treatment alongside bromine under an alkali-based environment. This phenomenon is defined as Hoffmann's bromamide degradation process.

$$C_6H_5CONH_2 \xrightarrow{Br_2+NaOH} C_6H_5NH_2$$

(iv) A chemical-based event known as a coupling reaction occurs when a new molecular structure merges with two or more molecular components. In the field of organic chemistry, it's an essential process that turns basic compounds into more complicated ones. Luminously coloured azo-based substances are created when arenediazonium salt combines alongside either phenol (in an alkaline solution) or aromatic amino acid compounds (in a slightly acidic environment).

In most cases, the chain reaction occurs within the para location that contains an amino or hydroxyl category in the protein. The ortho region is where the para slot is immobilized, and no interaction arises when both the ortho & para locations are engaged.





(v) Ammonolysis is a detailed reaction mechanism where ammonia is deployed in a process that incorporates chemicals to develop compounds such as amines or nitrides. This phenomenon happens only when an amino group (NH_2) gets linked along with ammonia (NH_3) under an ethanolic solution by replacing the presence of halogen atoms with an alkyl or benzyl halide compound.

Ammonolysis additionally refers to the method by which a group of amino substances replaces the hydroxyl group within alcoholic substances (or phenols) or the halogen atom around alkyl halides (or aryl halides). Alcoholic ammonia was the compound employed during the ammonolysis process. Tertiary, secondary & primary amines typically interact while producing a complex combination.

These methods can additionally employ hydroammonolysis, which uses the hydrogenation process as a trigger movement alongside an ammonia-hydrogen combination to seamlessly generate amines via carbonyl compounds without any external factors.

$$ROH + NH_3 \xrightarrow[\text{Hightemp., Pressure}]{Al_2O_3,\Delta} RNH_2 + H_2O$$

$$\underset{1^0}{R-NH_2} \xrightarrow[-H_2O]{ROH} \underset{2^0}{R_2NH} \xrightarrow[-H_2O]{ROH} \underset{3^0}{R_3N} \xrightarrow{ROH} R_4N^+OH^-$$

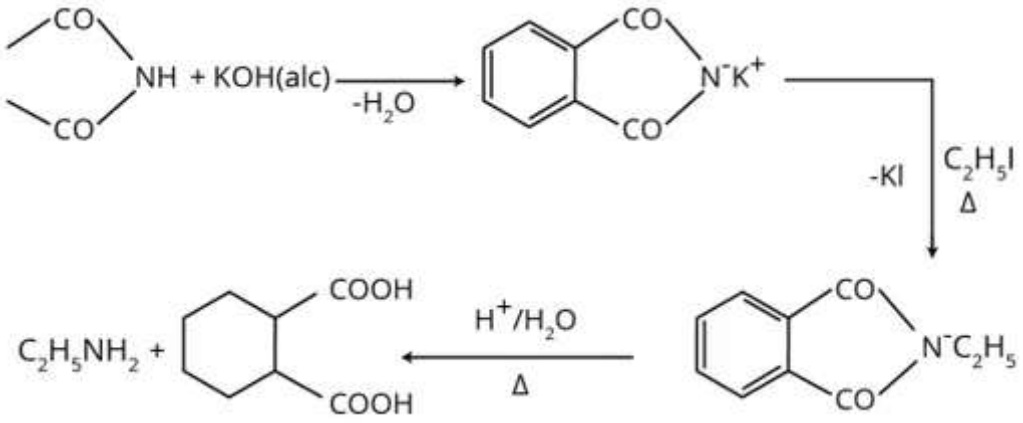
(vi) According to the internationally recognized IUPAC terminology, ethanoylation refers to the chemical process of acetylation. It explains the process by which a chemical molecule acquires an acetyl group with functional properties. Deacetylation, or the elimination of the acetyl category, is a reverse chemical process.

This can also be characterized when an acetyl group ($CH_3C{=}O$ component) in a molecule is replaced with an atom of hydrogen. Acetoxy functional groups are commonly found in the results of acetylation processes. Acetylation is an approach in which one employs acetyl chloride or acetic anhydride to add another acetyl (CH_3CO-) compound to an existing molecule.

(vii) A German chemist named Siegmund Gabriel gave this process as Gabriel synthesis. It's a mode of chemical process that converts primary alkyl halides to basic amines. Historically, potassium phthalimide is used in the process.

In the field of organic chemistry, it's a crucial process for making amine substances. Pure aliphatic along with aralkyl amines that are primary may be prepared using this procedure.

Potassium phthalimide is produced when a phthalimide substance has been treated using ethanolic KOH.
When heated with an appropriate alkyl or aralkyl halide molecular compound, N-substituted phthalimides are produced, which hydrolyse with either HCl or an alkaline solution to produce the principal amines.

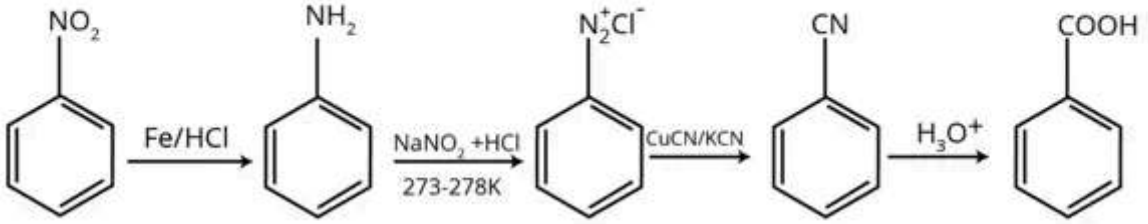


9.8

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.**

Ans - (i)



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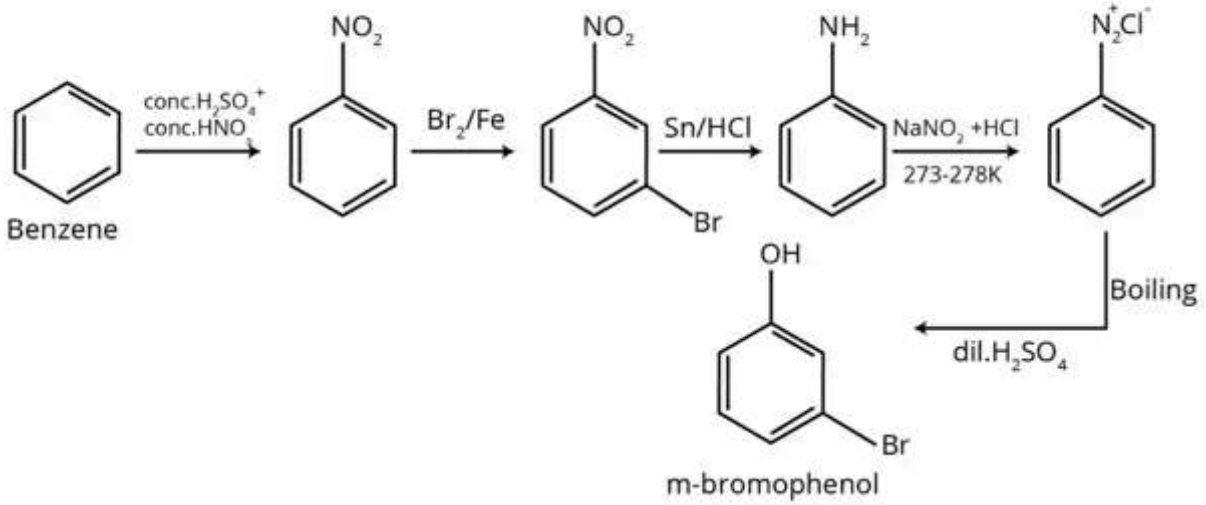

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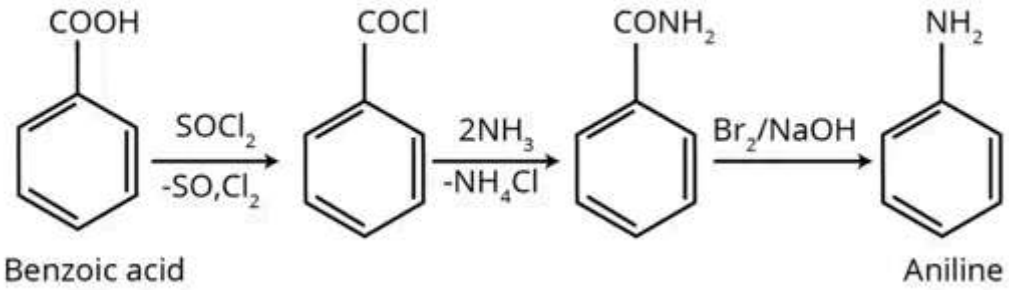

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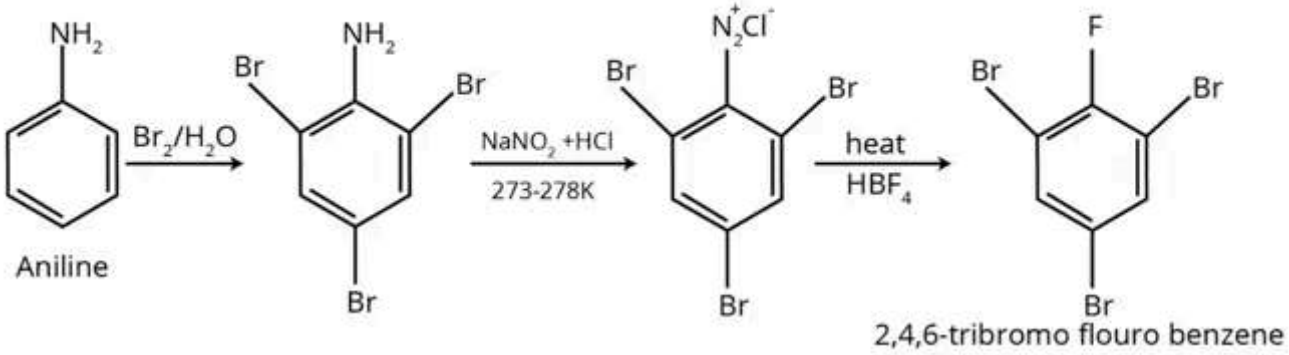

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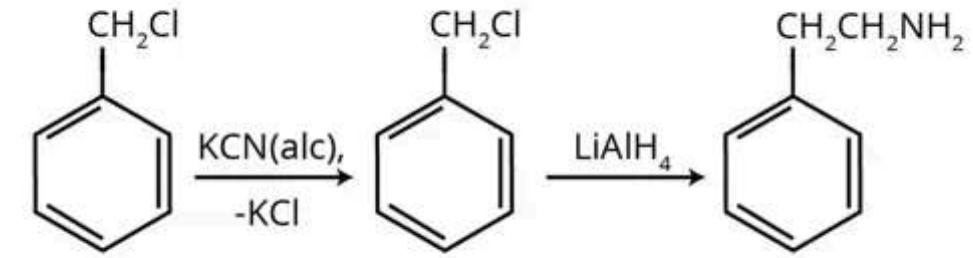
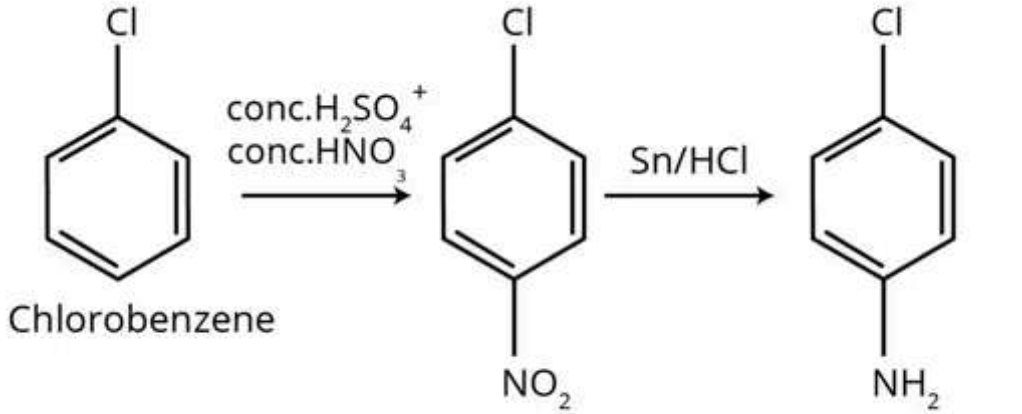


benzyl chloride

2 phenylethanamine

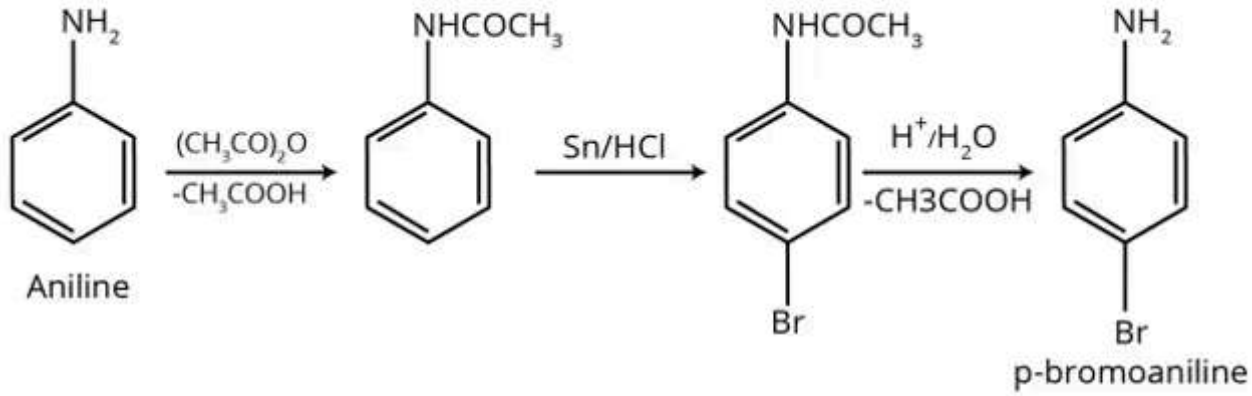
(vi)



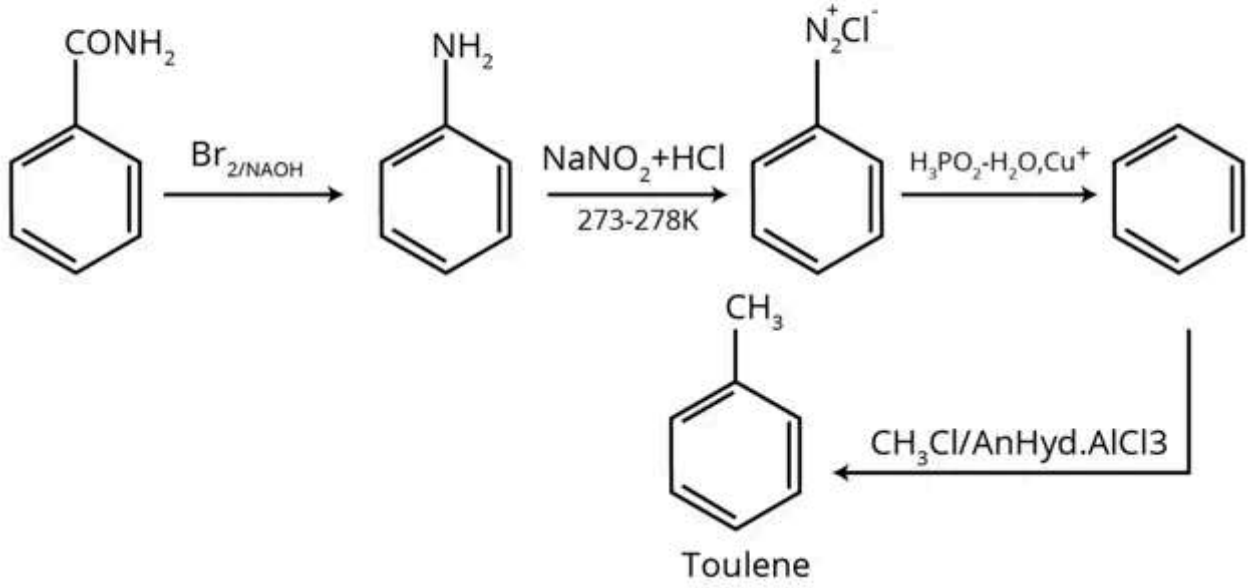
Chlorobenzene

p-chloroaniline

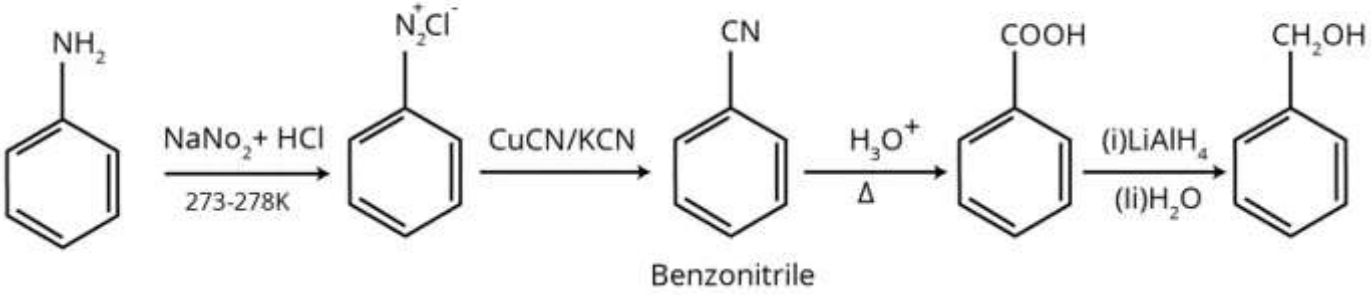
(vii)



(viii)



(ix)



9.9

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

(i) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH+Br_2} C$

(ii) $C_6H_5Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

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

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

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

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

Ans – (i) A = CH_3CH_2CN, B = $CH_3CH_2CONH_2$, C = $CH_3CH_2NH_2$

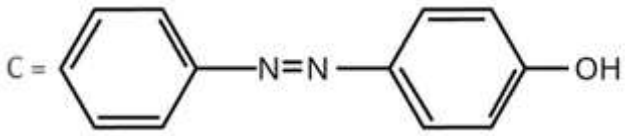
(ii) A = C_6H_5CN, B = C_6H_5COOH, C = $C_6H_5CONH_2$

(iii) A = CH_3CH_2CN, B = $CH_3CH_2CH_2NH_2$, C = $CH_3CH_2CH_2OH$

(iv) A = $C_6H_5NH_2$, B = $C_6H_5N_2Cl^-$, C = C_6H_5OH

(v) A = CH_3CONH_2, B = CH_3NH_2, C = CH_3OH

(vi) A = $C_6H_5NH_2$, B = $C_6H_5N_2{}^+Cl^-$,



9.10

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.

📌 ***Key topics to focus***

Nucleophilic Substitution Reactions of Aromatic Compounds

- Especially **aromatic nucleophilic substitution of halogenated compounds** (e.g., chlorobenzene derivatives like chloronitrobenzene).

Amination using Aqueous Ammonia

- How aryl halides react with aqueous ammonia under heating to form **anilines** (amino-substituted benzenes).

Hofmann Bromamide Degradation Reaction

- Conversion of amides to **amines** with one fewer carbon atom using **Br_2 and KOH**.
- Understand the **mechanism** and structural implications of this reaction.

Determining Molecular Formula and Structure

- Using molecular formula (e.g., C_6H_7N) to deduce possible structures of **aromatic amines**.

Basic IUPAC Nomenclature for Aromatic Amines and Amides

Ans – Component "B" should be an amide along with component "C" which is also amine similar to component C, which has the chemical structure C_6H_7N. This substance is produced from component B upon processing with Br_2 & KOH compounds. Aniline is the sole known amine with the chemical structure C_6H_7N, or $C_6H_5NH_2$.

Considering "C" represents an aniline, benzamide ($C_6H_5CONH_2$) must belong to the amide compound that is used when it comes into existence. Component "B" is therefore benzamide. Because component 'B' is created from a substance created using liquid ammonia by heating. Thus, component 'A' has to contain benzoic acid by definition.

9.11

Complete the following reactions:

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

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

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

(iv) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$

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

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

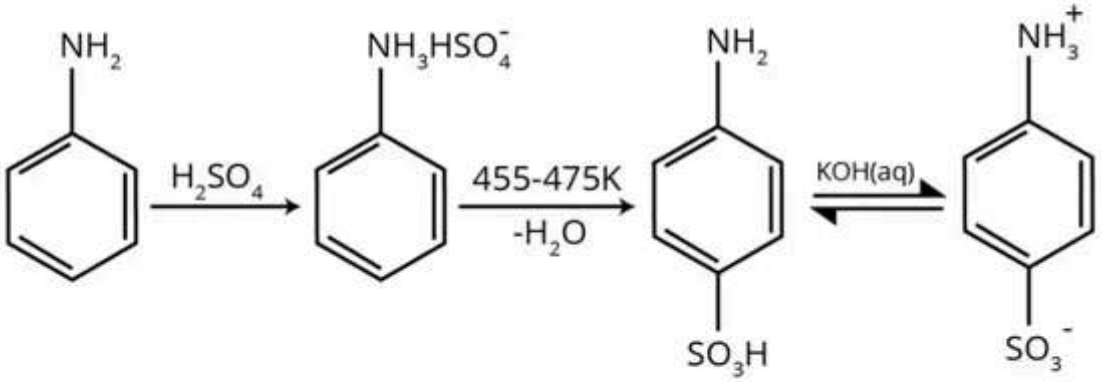
(vii) $C_6H_5N_2Cl \xrightarrow[(ii)NaNO_2/Cu.\Delta]{(i)HBF_4}$

Ans -

(i) $C_6H_5NH_2 + CHCl_3 + \text{alc.KOH} \xrightarrow{\Delta} C_6H_5NC + 3KCl + 3H_2O$

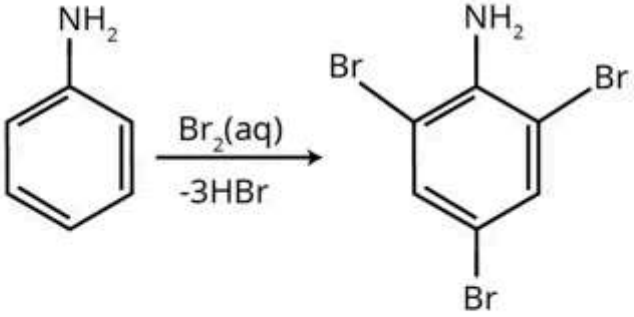
(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \xrightarrow{Cu^+} C_6H_6 + N_2 + H_3PO_3 + HCl$

(iii)



(iv) $C_6H_5N_2Cl + C_2H_5OH \rightarrow C_6H_6 + CH_3CHO + N_2 + HCl$

(v)



(vi) $C_6H_5N_2Cl \xrightarrow[(ii)NaNO_2/Cu.\Delta]{(i)HBF_4} C_6H_5NO_2 + N_2 + NaBF_4$

9.12

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

📌 ***Key Concepts to Learn***

Gabriel Phthalimide Synthesis Mechanism

Understand how **phthalimide reacts with alkyl halides** to form **primary amines** via nucleophilic substitution, followed by hydrolysis.

Reaction Limitations with Aryl Halides

Learn why **aryl halides (like bromobenzene)** do **not readily undergo nucleophilic substitution** due to:

- **Partial double bond character** in the C–X bond (due to resonance).

- The **planar structure** of the benzene ring which resists SN2 attack.
- Lack of reactivity under standard Gabriel synthesis conditions.

Inapplicability of SN2 Mechanism to Aryl Halides

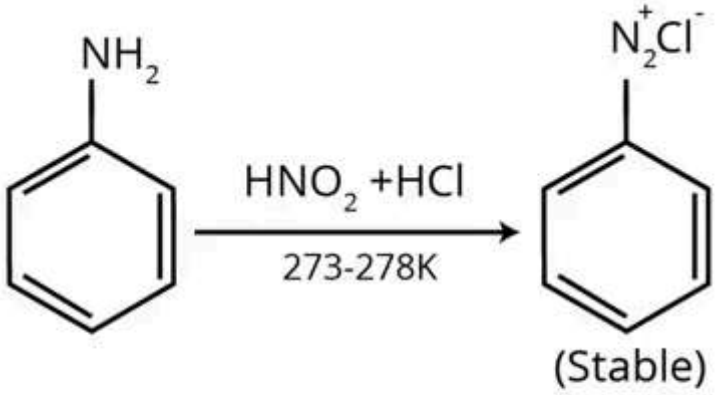
SN2 mechanism works best with **aliphatic halides**, not **aromatic** ones.

Ans – The phthalimide anion turns nucleophilic when there is an assault against the organic compounds of halogen molecules is what makes Gabriel's phthalimide synthesis successful. The Gabriel phthalimide process cannot be used to create arylamines, or aromatic primary amines, given that aryl halides are very difficult to serve as substitutes nucleophilically.

9.13

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

Ans – Between 273-278 K, aliphatic & aromatic main amines interact using HNO_2 to produce aliphatic & aromatic diazonium sodium chloride, correspondingly. Nevertheless, when exposed to this extremely low temperature, aliphatic diazonium salts become volatile and easily break down into a variety of chemical substances. The following is the reaction between HNO_2, highly aromatic & aliphatic principal amines.



$$CH_3CH_2NH_2 + HONO + HCl \xrightarrow[-2H_2O]{273-278\,K} \underset{\text{(Unstable)}}{[CH_3CH_2 - N^+ \equiv NCl^-]} \xrightarrow[273-278\,K]{\text{Decomposes}} CH_3CH_2OH + CH_2 = CH_2 + CH_3CH_2Cl + N_2$$

9.14

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?**

📌 *Key Concepts to Learn*

Acidity and Basicity Concepts:
Understand how electronegativity, conjugate base stability, and solvation effects influence acidity. Learn why O–H bond in alcohols is more acidic than N–H bond in amines due to greater electronegativity of oxygen.

Hydrogen Bonding in Amines:
Study intermolecular hydrogen bonding in primary, secondary, and tertiary amines. Understand how the number of hydrogen atoms on nitrogen affects the extent of hydrogen bonding and thus boiling points.

Basic Strength of Amines:
Learn about inductive effects, resonance effects, and availability of the lone pair on nitrogen. Understand how alkyl groups increase electron density on nitrogen in aliphatic amines, while resonance delocalization in aromatic amines (like aniline) reduces the basicity.

Ans – (i) An amide ion is produced when an amine loses its proton charge, whereas an alkoxide ion is produced when a substance like alcohol loses its proton charge.

$R–NH_2 \rightarrow R–NH^- + H^+$

$R–O–H \rightarrow R–O– + H^+$

O is likely to draw positively charged substances with greater force to N due to the fact it happens to be more of an electronegative compound. RO is considered extremely stable as opposed to RNH^- as a result. Alcohols therefore have a higher acidity compared to amines. Alcoholic compounds are considerably more acidic instead of amines as a result.

(ii) The solution is that O is going to draw positive creatures far more effectively as opposed to N because the former happens to be more electronegative in nature. Meanwhile, RNH^- seems more volatile compared to RO. Alcohols therefore have a higher acidity rather than amines. On the other hand, alcoholic substances are more acidic in nature compared to amines.

(iii) For a few different causes, amines that are aromatic are significantly less basic as opposed to aliphatic & ammonia amines-based compounds. It includes,

(a) The isolated pair of electron particles present inside the nitrogen atom becomes decentralized around the benzene ring because of the resonating frequency experienced in aniline along with other aromatic amines, making it less readily accessible for protonation to occur Because of this consequence, aliphatic amines & ammonia are somewhat stronger bases compared to aromatic amines.
(b) Aromatic amine compounds have a lower basic compound as opposed to comparable protonated charged particles simply because they have a greater persistence while exhibiting an extremely small tendency to interact with another proton to generate similar protonated ionic substances.