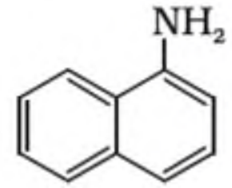
Chapter 13

Amines

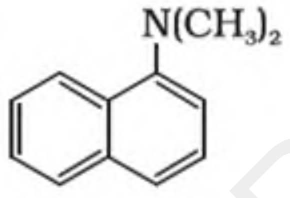
Intext Questions Pg-384

Q. 1 Classify the following amines as primary, secondary or tertiary:

(i)



(ii)



(iii) $(C_2H_5)_2CHNH_2$

(iv) $(C_2H_5)_2NH$

Answer:

(i) Primary. Because the nitrogen atom is attached to the only 1 carbon atom.

Note: The degree of amines depends on the no of atoms attached to the nitrogen atom of amine (except hydrogen).

(ii) Tertiary. Because the Nitrogen atom is attached to the 3 carbon atoms.

(iii) Primary. Because the nitrogen atom is attached to the only 1 carbon atom.

© PRAADIS EDUCATION DO NOT COPY

(iv) Secondary. Because the nitrogen atom is attached to the only 1 carbon.

Q. 2

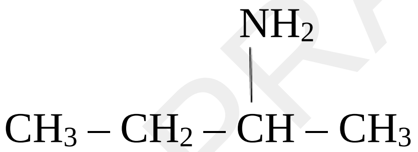
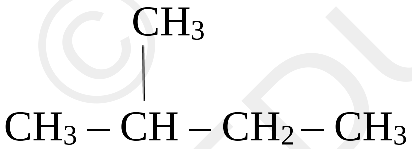
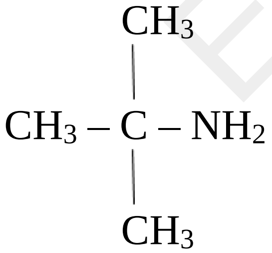
(i) Write structures of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$.

(ii) Write IUPAC names of all the isomers.

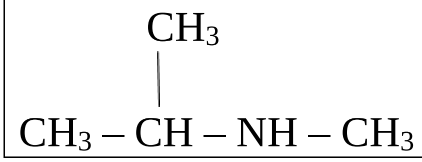
(iii) What type of isomerism is exhibited by different pairs of amines?

Answer:

(i) & (ii) There are total 8 geometrical isomers of the given compound.

Isomers	IUPAC Name
$CH_3-CH_2-CH_2-CH_2-NH_2$	Butan-1-amine or butanamine.
 $CH_3-CH_2-CH(NH_2)-CH_3$	Butan-2-amine.
 $CH_3-CH(CH_3)-CH_2-CH_3$	2 - Methylpropanamine
 $CH_3-C(CH_3)(CH_3)-NH_2$	2 -Methylpropan- 2 - amine
$CH_3-CH_2-NH-CH_2-CH_3$	N -Ethylethanamine

© PRADIS EDUCATION DO NOT COPY

$CH_3\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_3$	N-Methylpropanamine
 $CH_3 - \overset{\overset{CH_3}{\vert}}{C}H - NH - CH_3$	N-Methylprapan- 2 -amin e

(iii) a) Pairs 1,2,6,7 Exhibit Position isomerism; means the change in position of the substituent.

b) Pairs 1,3 and 1,4 and 2,3 and 2,4 exhibit chain isomerism i.e. in this type of isomerism the different structures can be produced by changing the chain of the atoms.

c) Pairs 5,6 and 5,7 exhibit metamerism; i.e. different group on either side of the central atom.

d) All Primary amines exhibit functional isomers. All secondary amines share functional isomerism and same for tertiary. The functional isomerism means same functional group.

<u>Intext Questions Pg-387</u>

Q. 3 A

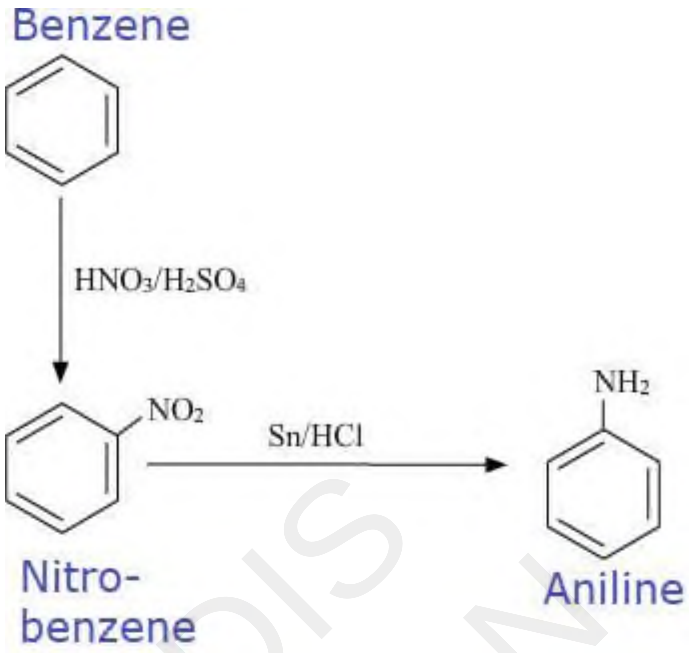
How will you convert Benzene into aniline?

Answer:

Benzene into aniline

When Benzene is treated with HNO_3/H_2SO_4 it forms nitrobenzene. When Nitrobenzene reduced with Sn/HCL it forms Aniline. Because Sn/HCl is a reducing Mixture.

© PRADIS EDUCATION DO NOT COPY

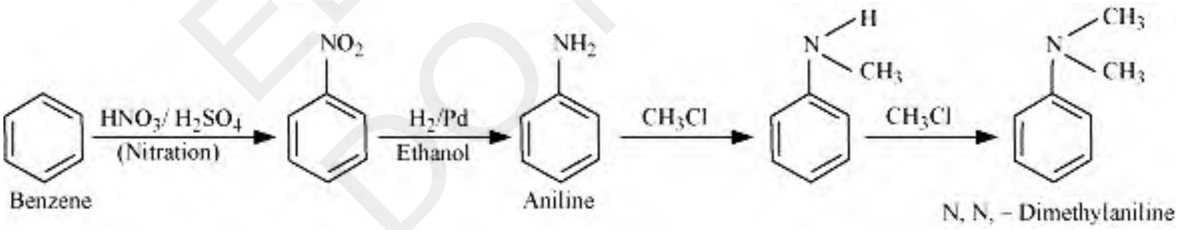


Q. 3 B

How will you convert Benzene into N, N-dimethylaniline?

Answer:

Benzene into N, N-dimethylaniline



When Benzene is reacted with nitrating mixture it forms nitrobenzene. When it Reduced H_2/Pd in ethanol or Sn/HCl, it forms Aniline. When Aniline reacts 2 times with CH_3Cl It forms N, N-dimethylaniline.

© PRAADIS EDUCATION DO NOT COPY

Q. 3 C

How will you convert Cl–$(CH_2)_4$–Cl into hexan-1,6-diamine?

Answer:

Cl–$(CH_2)_4$–Cl into hexan-1,6-diamine?

$$\begin{tikzcd}
Cl - (CH_2)_4 - Cl \arrow[r, "Ethanolic\ NaCN"] & N \equiv C - (CH_2)_4 - C \equiv N \arrow[d, "H_2/Ni"] \\
& H_2N - CH_2 - (CH_2)_4 - CH_2 - NH_2
\end{tikzcd}$$

Hexane – 1, 6 – diamine

When 1,4-dichlorobutane reacts with NaCN it forms Di cyanide compound, After Hydrogenation it forms the Hexane 1,6-Diamine.

Intext Questions Pg-396

Q. 4 A

Arrange the following in increasing order of their basic strength: $C_2H_5NH_2$, $C_6H_5NH_2$, NH_3, $C_6H_5CH_2NH_2$ and $(C_2H_5)_2NH$

Answer:

Alkyl group contribute inductive effect which increases the basic strength of compounds.

$NH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$.

Then $C_6H_5NH_2$ is having –I effect that reduces strength. And $C_6H_5CH_2NH_2$ increases the basic strength but not as much as C_2H_5 group.

© PRAADIS EDUCATION DO NOT COPY

Hence final order will be

$C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$.

Q. 4 B

Arrange the following in increasing order of their basic strength: $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, $C_6H_5NH_2$

Answer:

By taking into consideration –R effect and steric hindrance of groups we can arrange them in the order

$C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$.

Because $(C_2H_5)_3N$ has a lot of steric hindrances that reduces the basic strength.

Q. 4 C

Arrange the following in increasing order of their basic strength:

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

Answer:

In $C_6H_5NH_2$, N is directly attached to the ring that causes delocalization of electrons of the benzene ring. Whereas in case of $C_6H_5CH_2NH_2$ it is not directly connected to benzene ring Hence it has more basic strength.

Due to –I effect of $(CH_3)_3$– a group it has more basic strength than $C_6H_5CH_2NH_2$. Hence final order will be

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

Q. 5 Complete the following acid-base reactions and name the products:

(i) $CH_3CH_2CH_2NH_2 + HCl \rightarrow ?$

(ii) $(C_2H_5)_3N + HCl \rightarrow ?$

Answer:

© PRAADIS EDUCATION DO NOT COPY

(i) $CH_3CH_2CH_2NH_2 + HCl \rightarrow CH_3CH_2CH_2N+H_3Cl-$

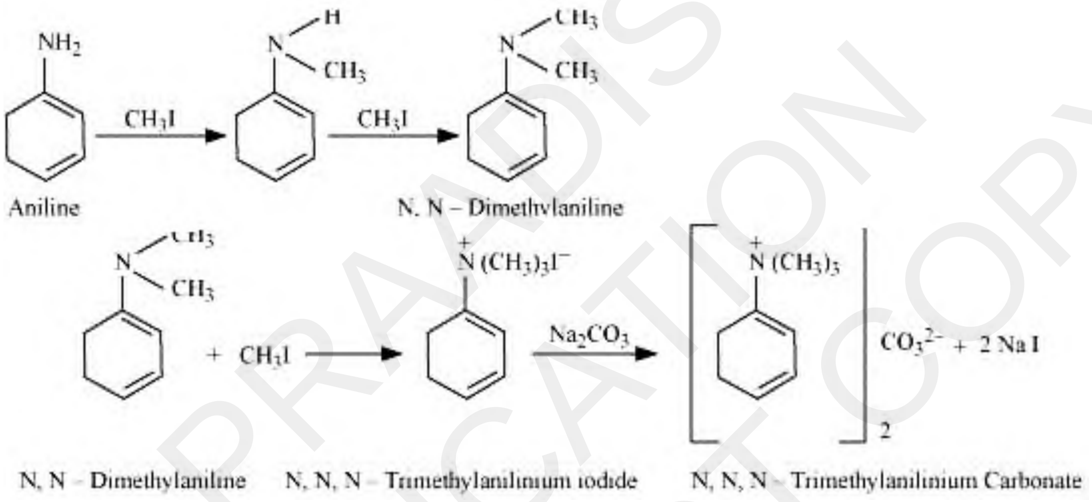
The final product is (N-propyl ammonium chloride.)

(ii) $(C_2H_5)_3N + HCl \rightarrow (C_2H_5)3N+HCl^-$

The final product is (Tri ethyl ammonium chloride)

Q. 6 Write reactions of the final alkylation product of aniline with an excess of methyl iodide in the presence of sodium carbonate solution.

Answer:



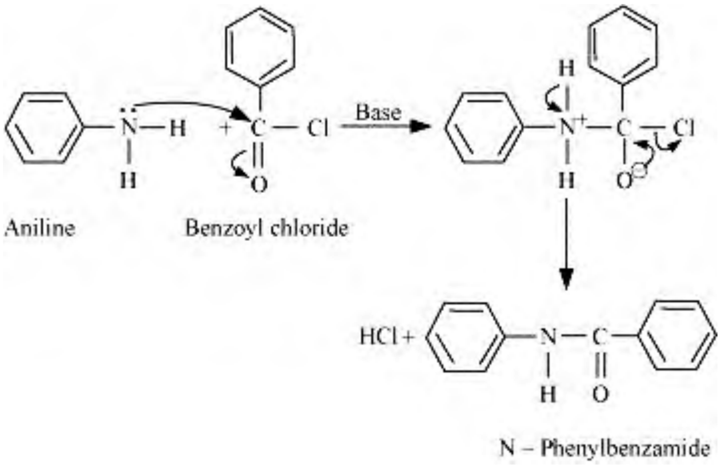
© PRAADIS EDUCATION DO NOT COPY

On excessive alkylation with methyl iodide aniline gets converted into N, N, N-Trimethylanilinium iodide. After reacting it with sodium carbonate it get converted into N, N, N-Trimethylanilinium carbonate.

Q. 7 Write chemical reaction of aniline with benzoyl chloride and write the name of the product obtained.

Answer:

When aniline is treated with benzoyl chloride in the presence of base it gets converted into N-Phenylbenzamide.



Q. 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.

Answer:

The different isomers of the molecular formula: C_3H_9N are given in the table. However only 1° amines will liberate nitrogen gas on the treatment with h=the nitrous acid are given as follows:

	Isomers	IUPAC Name
1° amine	CH3-CH2-CH2-NH2	Propa-1-amine or butanamine.
1° amine	NH2 | CH3-CH-CH3	Pro pan-2-amine.
2° amine	CH3 | CH3-NH-C2H5	2 -Methylethylamine
3° amine	CH3 | CH3-N-CH3	N -N- Dimethy lmethanamine

© PRADIS EDUCATION DO NOT COPY

Note: Only primary amines liberate nitrogen gas on treatment with nitrous acid.

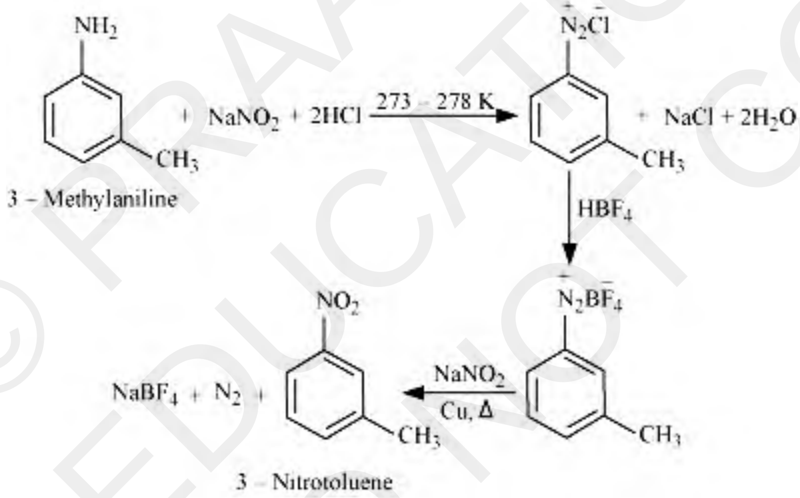
Intext Questions Pg-399

Q. 9 A

Convert 3-Methylaniline into 3-nitrotoluene.

Answer:

When 3-methylaniline treated with $NaNO_2$ + HCl it gets converted into chlorine complex. When that complex reacted with HBF4 It gets converted into Barium Fluoride complex. This complex reacts with $NaNO_2$ in presence of copper to give 3-Nitrotoluene.

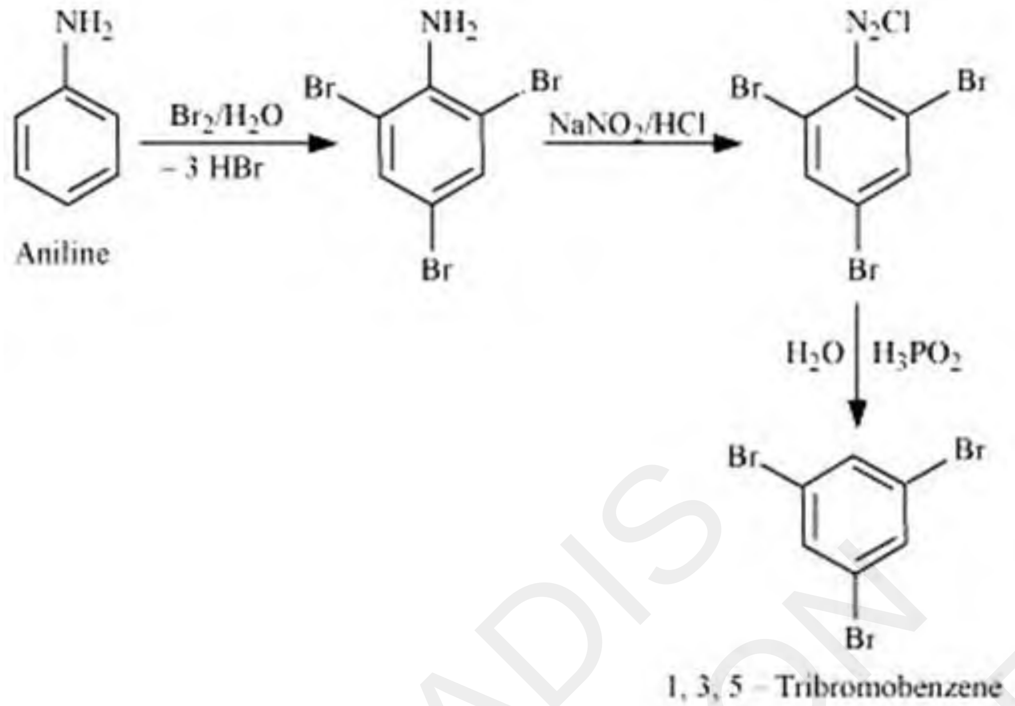


Q. 9 B

Convert Aniline into 1,3,5 – tribromobenzene

Answer:

© PRAADIS EDUCATION DO NOT COPY



When aniline reacts with Br_2 water it gets converted into 2,4,6 tribromobenzamine. When this further reacted with $NaNO_2$/HCl it forms Chloride complex. This complex forms 1,3,5 tribromobenzene after treating with H_3PO_2 in presence of water.

Exercises

Q. 1 A

Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines. $(CH_3)_2CHNH_2$

Answer:

1-Methylethanamine

The root name is based on the longest chain with the $-NH_2$ attached. The chain is numbered so as to give the amine unit the lowest possible number. The longest chain is ethane chain which is further suffixed with ‘amine’.

Q. 1 B

© PRADIS EDUCATION DO NOT COPY

Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines. $CH_3(CH_2)2NH_2$

Answer:

Propan-1-amine

The longest chain here is propane. The naming is such that amine unit should get a lowest possible number. Propane-1-amine can also be written as 1-propylamine.

Q. 1 C

Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines. $CH_3NHCH(CH_3)_2$

Answer:

N−Methyl-2-methylethanamine

The chain is numbered so as to give the amine unit the lowest possible number. The other alkyl group is treated as a substituent, with N as the locant. The N locant is listed before numerical locants. The longest chain is ethane which has a Methyl substituent group.

Q. 1 D

Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines. $(CH_3)_3CNH_2$

Answer:

2-Methylpropan-2-amine

Propane is the longest chain and is joined to the amine group at the 2nd position. Another substituent methyl group is also at the same position.

Q. 1 E

Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines. $C_6H_5NHCH_3$

© PRADIS EDUCATION DO NOT COPY

Answer:

N−Methylbenzamine or N-methylaniline

Aniline is considered as the principle group. The other alkyl group is treated as a substituent, with N as the locant.

Q. 1 F

Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines. $(CH_3CH_2)2NCH_3$

Answer:

N-Ethyl-N-methylethanamine

This is a tertiary group of amine. The root name is based on the longest chain with an amine having the lowest possible number. The alkyl groups are treated as substituents with N as the locant.

Q. 1 G

Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines. m–$BrC_6H_4NH_2$

Answer:

3-Bromobenzenamine or 3-bromoaniline

Benzene is considered as the principle group. The substituent is bromine which is numbered 3. Conventional method of naming is followed.

Q. 2 A

Give one chemical test to distinguish between the following pairs of compounds. Methylamine and dimethylamine

Answer:

The best test for distinguishing methyl amine and dimethylamine is the Carbylamines test.

© PRADIS EDUCATION DO NOT COPY

Carbylamine Test: Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form foul-smelling isocyanides or carbylamines.

In this case, Methylamine (which is an aliphatic primary amine) gives a positive carbylamine test while dimethylamine wont.

Reaction:

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

Methylamine (1°) Methylisocyanide

(foul smell)

$(CH_3)_2NH + CHCl_3 + 3KOH \overset{\Delta}{\rightarrow}$ No reaction

Q. 2 B

Give one chemical test to distinguish between the following pairs of compounds. Secondary and tertiary amines

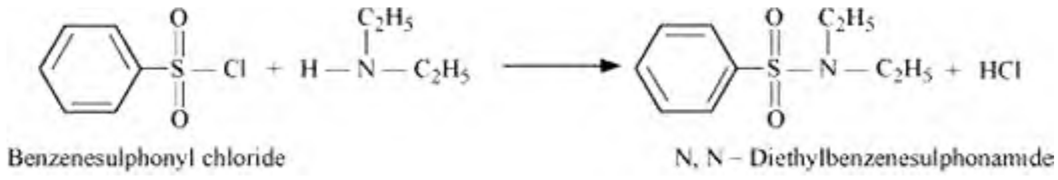
Answer:

Hinsberg's reagent (benzenesulphonyl chloride, $C_6H_5SO_2Cl$). can be used to distinguish secondary and tertiary amines.

Hinsberg Test: Secondary amines react with Hinsberg's reagent to form a product that is insoluble in an alkali. For example, N, N−diethylamine reacts with Hinsberg's reagent to form N,

N−diethylbenzenesulphonamide, which is insoluble in an alkali. Tertiary amines, however, do not react with Hinsberg's reagent.

Reaction:



© PRADIS EDUCATION DO NOT COPY

Q. 2 C

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

Ethylamine and aniline

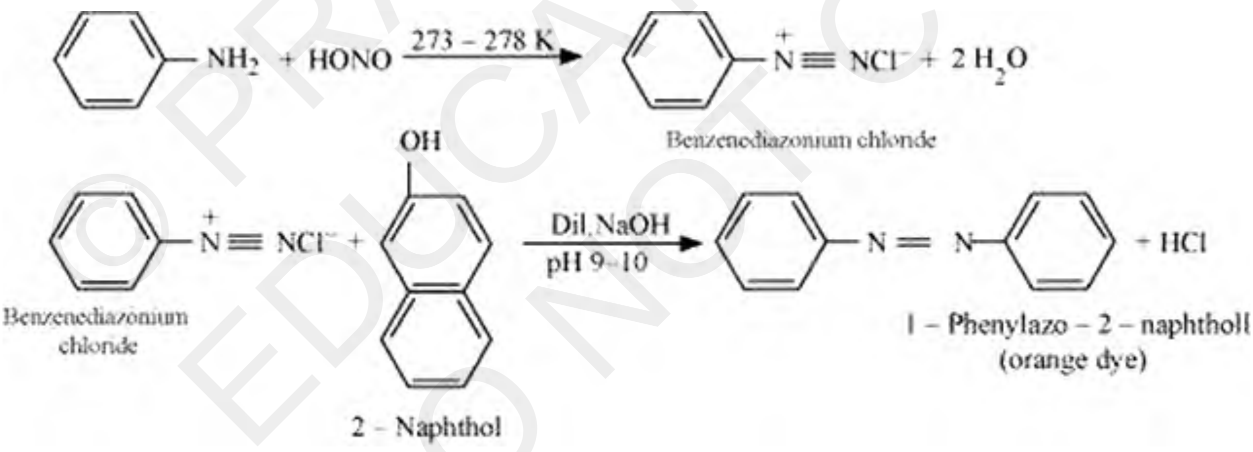
Answer:

Azo-dye test can be used to distinguish ethylamine and aniline.

Azo-dye test: A dye is obtained when aromatic amines react with HNO_2 ($NaNO_2$ + dil. HCl) at 0-5°C, followed by a reaction with the alkaline solution of 2-naphthol. The dye is usually yellow, red, or orange in colour. Aliphatic amines give a brisk effervescence due to the evolution of N_2 gas under similar conditions.

Reaction:

Ethylamine;



Aniline;

$$CH_3CH_2 - NH_2 + HONO \xrightarrow{0.5^\circ C} C_2H_5OH + N_2\uparrow + H_2O$$

Q. 2 D

Give one chemical test to distinguish between the following pairs of compounds. Aniline and benzyl amine

© PRAADIS EDUCATION DO NOT COPY

Answer:

Aniline and benzyl amine can be distinguished with the help of nitrous acid.

Nitrous acid test: Benzyl amine reacts with nitrous acid to form unstable diazonium salt, which in turn gives alcohol with the evolution of nitrogen gas, while aniline reacts with nitrous acid to form a stable diazonium salt without releasing nitrogen gas.

Reaction:

(Benzyl amine)

$$C_6H_5CH_2 - NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [C_6H_5CH_2 \text{ - } N_2^+ Cl^-]$$

(Unstable)

$$\downarrow H_2O$$

$$N_2 \uparrow + C6H_5CH_2 - OH + HCl$$

Benzyl alcohol

(Aniline)

$$C_6H_5NH_2 \xrightarrow[273 - 278\,k]{NaNO_2 + HCl} C_6H_5 - {}^+N_2\,Cl^- + NaCl + 2H_2O$$

Q. 2 E

Give one chemical test to distinguish between the following pairs of compounds. Aniline and N-methylaniline.

Answer:

Carbylamine test can be used to distinguish between Aniline and N-methylaniline.

© PRAADIS EDUCATION DO NOT COPY

Carbylamine Test: Primary amines, on heating with chloroform and ethanolic potassium hydroxide, form foul smelling isocyanides or carbylamines. Aniline, being an aromatic primary amine, gives positive carbylamine test. However, N-methylaniline, being a secondary amine does not.

Reaction:

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

Benzyl amine (1°) Benzylisocyanide

(foul smell)

$$C_6H_6NHCH_3 + CHCl_3 + 3KOH \xrightarrow{\Delta} \text{No reaction}$$

N – Methylaniline

Q. 3 A

Account for the following: pK_b of aniline is more than that of methylamine.

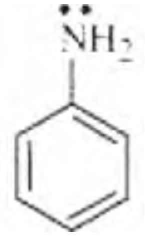
Answer:

Pk_b value is the negative logarithm of the basicity constant (K_b). i.e., $pK_b = -\log K_b$

Evidently, smaller the value of pK_b, stronger is the base (strong tendency to donate electrons)

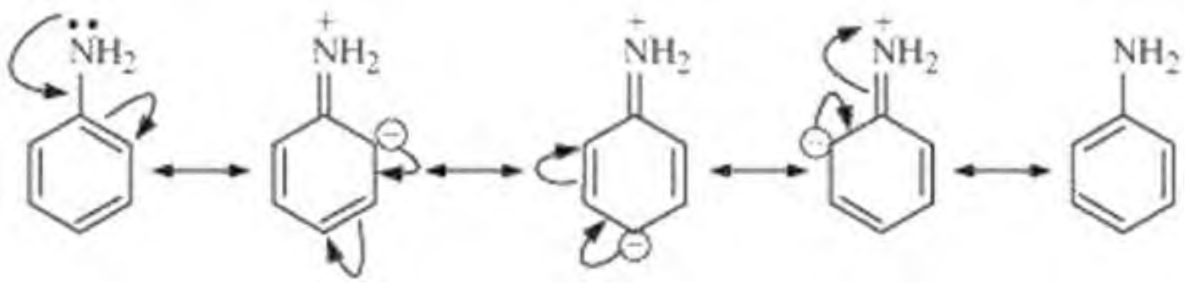
⇒ The structure of methyl amine is CH_3NH_2

⇒ The structure of aniline is:



© PRAADIS EDUCATION DO NOT COPY

Aniline ($C_6H_5NH_2$) shows resonance:



As a result of resonance, the lone pair of electrons on the nitrogen atom gets delocalized over benzene ring. As a result, electron density on the nitrogen decreases and thus is less easily available to donate electrons making it less basic. In contrast, in methyl amine (CH_3NH_2), delocalization of the lone pair of electrons on the nitrogen atom by resonance is not possible. Furthermore, CH_3 being an electron- releasing group, due to which +I effect of CH_3 increases the electron density on the N^- atom and thus is more easily available to donate electrons making it more basic.

CH_3↣N – H
H

+ I effect (pushing electrons)

Therefore, aniline is weaker base than methylamine and hence its pKb value is higher than that of methylamine.

Q. 3 B

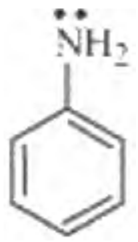
Account for the following: Ethylamine is soluble in water whereas aniline is not.

Answer:

⇒ The structure of ethylamine is $CH_3CH_2NH_2$

⇒ The structure of aniline is:

© PRADIS
EDUCATION
DO NOT COPY



Ethylamine form H-bonds with water. It dissolves in water due to intermolecular H-bonding as shown below:

$$\begin{array}{ccccccccc} & H & & & & H & & & \\ & |\,\delta^- & \delta^+ & \delta^- & \delta^+ & |\,\delta^- & \delta^+ & & \\ \ldots H - & N & \ldots\; H - & O & \ldots\; H - & N & \ldots\; H - & O & \ldots. \\ & | & & | & & | & & | & \\ & C_2H_5 & & H & & C_2H_5 & & H & \end{array}$$

Thus, ethylamine is soluble in water.

However, in aniline, due to the larger hydrophobic part, i.e., hydrocarbon part (C_6H_5 group), which tends to retard the formation of H-bonds. The extent of H-bonding decreases and hence aniline is insoluble in water.

Q. 3 C

Account for the following: Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.

Answer:

⇒ The structure of methylamine is CH_3NH_2

Methylamine is more basic than water due to the presence of CH_3 (electron releasing group) and +I effect (pushing electrons). Being more basic, methylamine accepts a proton from water liberating OH- ions.

© PRAADIS EDUCATION DO NOT COPY

$CH_3\ddot{N}H_2 + H - OH \longrightarrow CH_3 - NH_3 + OH^-$

Dissociation of ferric chloride in water to give Fe^{3+} and Cl^-

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

Now, the liberated OH- ions combine with Fe^{3+} ions present in H_2O to form brown precipitate of hydrated ferric oxide.

$2Fe^{3+} + 6OH^- \longrightarrow 2Fe\,(OH)_3$ or $Fe2O_3.3H_2O$

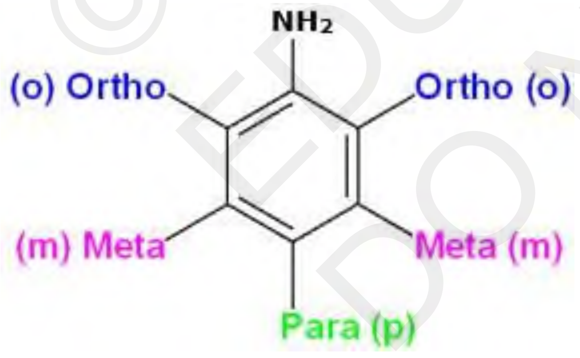
Hydrated ferric oxide (brown ppt)

Q. 3 D

Account for the following: Although amino group is o– and p– directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitro aniline.

Answer:

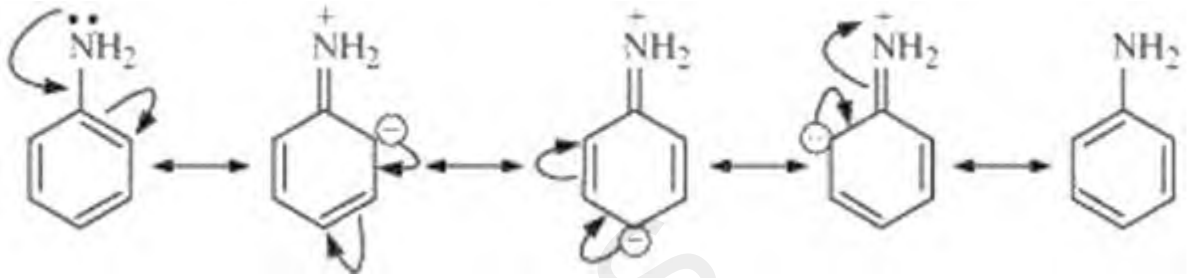
The below diagram shows the position of ortho(o), para(p) and meta(m) derivatives of amino group:



Electrophilic addition reaction of amines: In addition to the reaction of the amino group (NH_2 group), aromatic amines also undergo typical electrophilic substitution reactions of the aromatic ring. In all these reactions, the NH_2 group strongly activates the aromatic ring through

© PRADIS EDUCATION DO NOT COPY

delocalization of the lone pair of electrons of the N-atom over the aromatic ring.

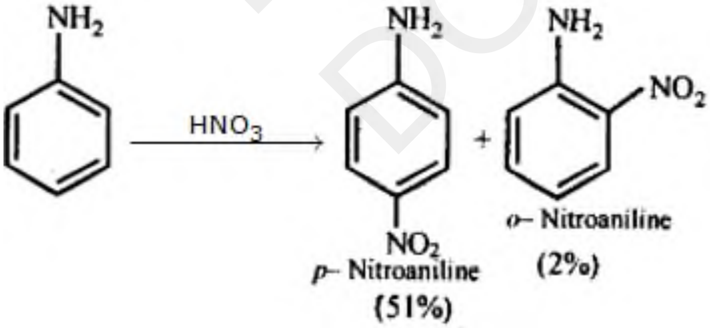


As a result, electron density increases more at ortho and para positions. Therefore, NH_2 group directs the incoming group to ortho and para positions, i.e., NH_2 is an o-, p-directing group.

But it has been observed that on nitration of aniline gives a substantial amount of m-nitrosamine.

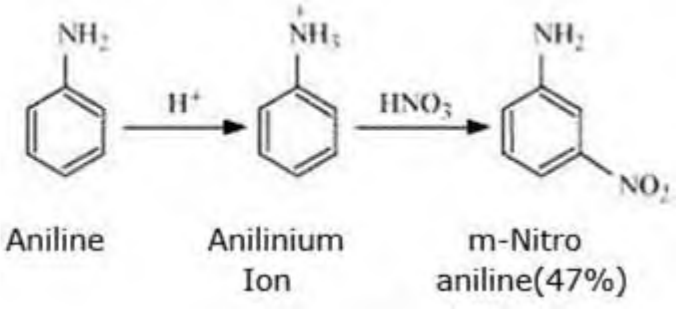
Explanation: Nitration is usually carried out in acidic medium in the presence of concentrated HNO_3 and concentrated H_2SO_4. As a result, most of the aniline is converted into anilinism ion (gets protonated) and since - $^{+}NH_3$ is m-directing group, therefore, an unexpected large amount of m-nitro aniline is obtained.

Nitration of aniline gives mainly p-nitro aniline



Nitration of anilinism ions give m-nitrosamine (due to protonation)

© PRADIS EDUCATION DO NOT COPY



Hence, nitration of aniline gives a mixture of p-nitro aniline and m-nitro aniline in approx. 1:1 ratio.

Q. 3 E

Account for the following: Aniline does not undergo Friedel-Crafts reaction.

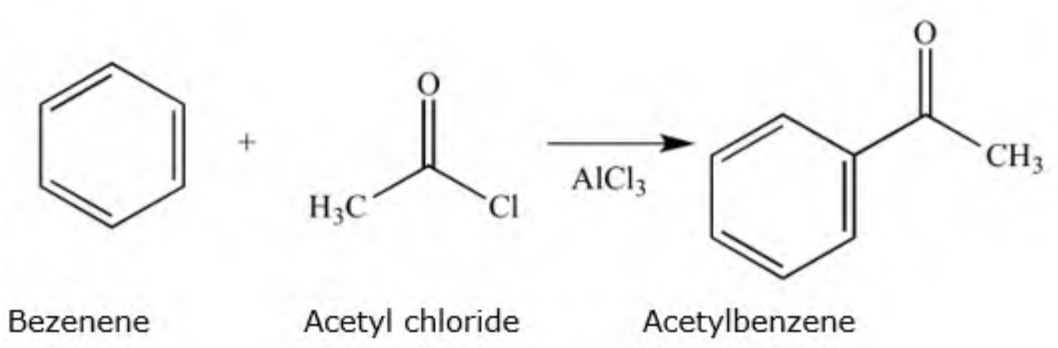
Answer:

Friedel- Crafts reaction: When any benzene or its derivative is treated with alkyl halide (R-X, X=Cl) or acetyl chloride (CH_3-COCl) in the presence of anhydrous aluminium chloride ($AlCl_3$) to form alkyl or acetyl substituted benzene or its derivative, this reaction is called Friedel-Crafts reaction.

⇒ Friedel-Crafts alkylation: When any benzene or its derivative is treated with alkyl halides (R-X, X=Cl, Br) in the presence of anhydrous aluminium chloride ($AlCl_3$) to form alkyl substituted benzene or its derivatives, this reaction is called Friedel-Crafts alkylation. For example:

⇒ Friedel-Crafts acylation: When any benzene or its derivative is treated with acetyl chloride (R-COCl) in the presence of anhydrous aluminium chloride ($AlCl_3$) to form acetyl substituted benzene or its derivatives, this reaction is called Friedel-Crafts acylation. For example:

© PRAADIS EDUCATION DO NOT COPY



Aniline does not undergo Friedel-Crafts reaction.

Explanation: Aniline is a Lewis base (electron-pair acceptor) while $AlCl_3$ is Lewis acid (electron-pair donor). They combine with each to form a salt.

$C_6H_5NH_2 + AlCl_3 \xrightarrow{\hspace{2cm}} C_6H_6N^+H_2AlCl3^-$

Lewis   Lewis   salt

base   acid

Due to presence of positive charge on nitrogen (N) atom in the salt, the group $N^+H_2AlCl^{3-}$ acts as a strong electron withdrawing group (strong deactivating group). As a result, it reduces the electron density in the benzene ring and hence aniline does not undergo Friedel-Crafts (alkylation or acetylation) reaction

Q. 3 F

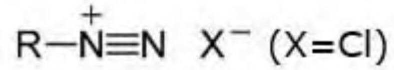
Account for the following: Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

Answer:

Diazonium salts: Diazonium salts have the general formula

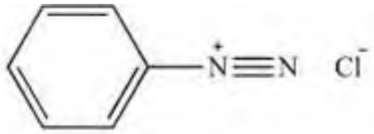
($R/Ar—N^{2+}Cl^-$) where R stands for the alkyl group and Ar stands for the aryl group. The structure is given below:

© PRAADIS EDUCATION DO NOT COPY



$$R-\overset{+}{N}\equiv N\ X^{-}\ (X=Cl)$$

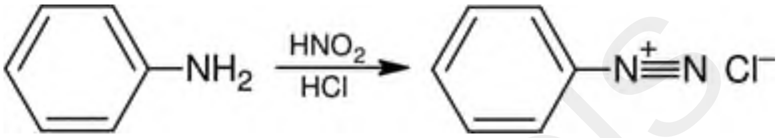
Alkyldiazonium
chloride



Arenediazonium
chloride

Formation of Diazonium salts:

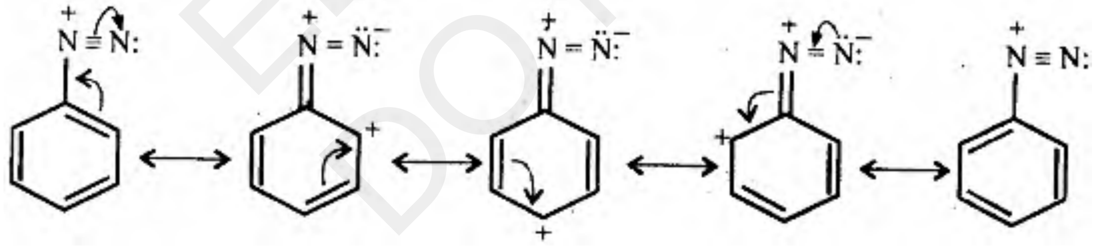
Diazonium salt is obtained by treating aromatic amine(aniline) dissolved in dil. HCl with HNO_2 at 273-278K (0° -5° C)



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

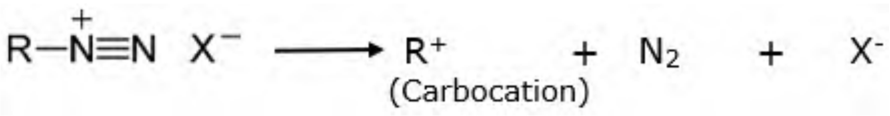
Explanation:

Aromatic amine form arenediazonium salts, which are stable for a short time in solution at low temperature(273-278K). The diazonium salts of aromatic amines are more stable due to the dispersal of the positive charge on the benzene ring (resonance) as shown below:



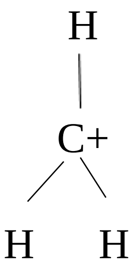
The aliphatic amines, on the other hand, form highly unstable alkane diazonium salt (R—$N^{2+}Cl^{-}$). They rapidly decompose even at low temperature(<272-278K) forming carbocation and nitrogen gas.

© PRAADIS EDUCATION DO NOT COPY



Hence, diazonium salts of aromatic amine are much more stable than aliphatic diazonium salts.

Note: Carbocation is an ion in which carbon atom consists of positive charge



Q. 3 G

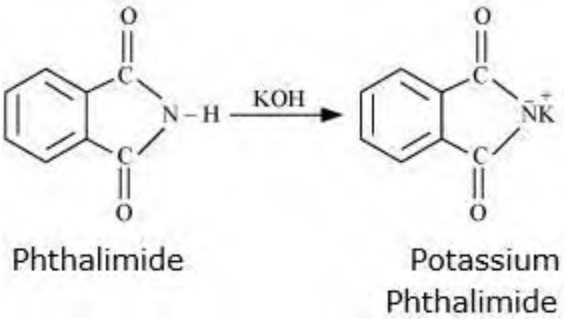
Account for the following: Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

Answer:

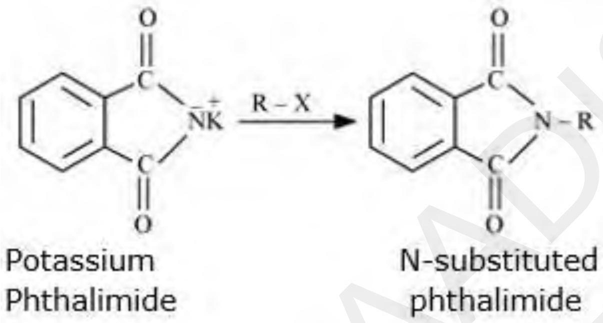
Gabriel phthalimide synthesis is a very convenient method for the preparation of pure aliphatic amines (especially primary amines) Phthalimide on treatment with ethanolic KOH gives potassium phthalimide which on heating with a suitable alkyl halide gives N-substituted phthalimide. These upon subsequent hydrolysis with dil. HCl under pressure or with alkali gives primary amines.

Step 1: Phthalimide is treated with KOH to form potassium phthalimide

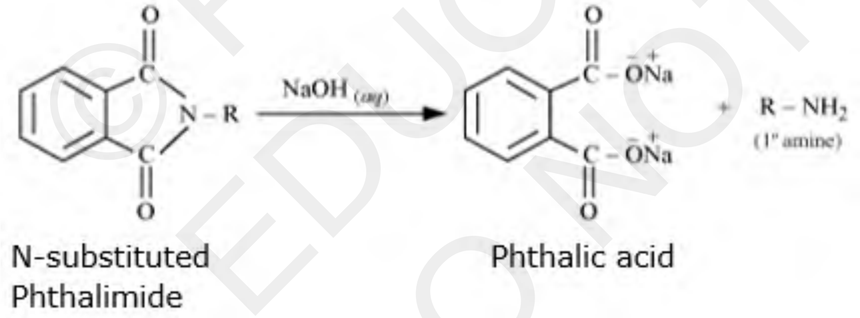
© PRAADIS EDUCATION DO NOT COPY



Step 2: Potassium phthalimide is treated with suitable alkyl halide to form N-substituted phthalimide.

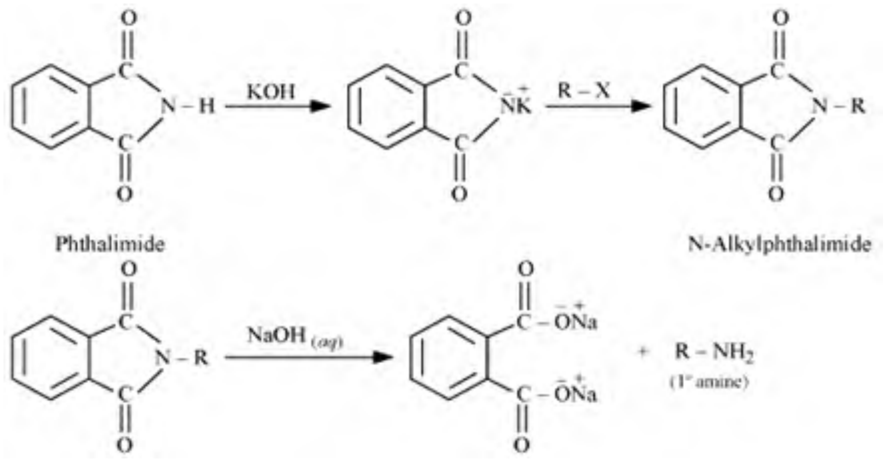


Step 3: N-substituted phthalimide undergoes hydrolysis in the presence of dil HCl or with alkali(NaOH) to give primary amines.



Overall reaction:

© PRANDIS EDUCATION DO NOT COPY



∴ Gabriel phthalimide synthesis results in the formation of primary (1° amine) only. Secondary or tertiary amines are not formed through this synthesis. Hence, Gabriel phthalimide synthesis preferred for the formation of primary amines only.

Q. 4 A

Arrange the following: 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:

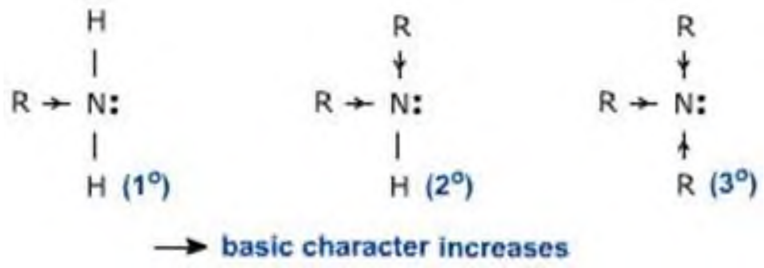
Pk_b value is the negative logarithm of the basicity constant (K_b). i.e., $pK_b = -\log K_b$

Evidently, smaller the value of pK_b, stronger is the base (strong tendency to donate electrons)

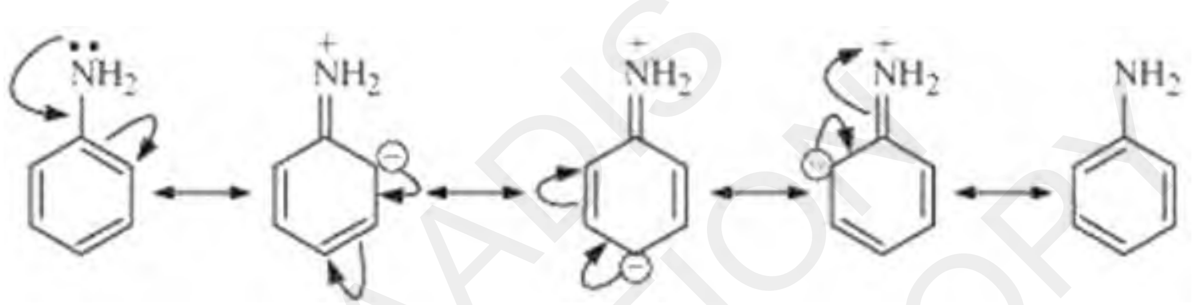
Aliphatic amines($R\text{-}NH_2$) are more basic (tendency to donate electrons) than aromatic amines($C_6H_5NH_2$) because of the following reasons:

⇒ In aliphatic amines, alkyl groups are present. Alkyl groups are electron releasing groups, hence they increase the electron density of N-atom and thus is easily available to donate electrons. This property makes aliphatic amines more basic.

© PRADIS EDUCATION DO NOT COPY



⇒ In aromatic amines, aryl group is present. Aromatic amine shows resonance:



As a result of resonance, the lone pair of electrons on the nitrogen atom gets delocalized over benzene ring. As a result, electron density on the nitrogen decreases and thus is less easily available to donate electrons making it less basic.

Hence aliphatic amines(R-NH_2) are more basic than aromatic amines($C_6H_5NH_2$)

Now, in $C_2H_5NH_2$, one ethyl group(alkyl) is present and in $(C_2H_5)_2NH_2$ two ethyl groups are present. As we know that more alkyl groups are present, more basic will be the amine.

Hence, $(C_2H_5)2NH_2$ is more basic than the $C_2H_5NH_2$

Now in $C_6H_5NH_2$, due to delocalization of lone pair of electrons of the N-atom over the benzene ring, makes it less basic than $(C_2H_5)2NH_2$ and $C_2H_5NH_2$

Now, in $C_6H_5NHCH_3$, due to presence of CH_3 group, makes it more basic than $C_6H_5NH_2$ but less basic than $(C_2H_5)_2NH_2$ and $C_2H_5NH_2$ due to

© PRADIS EDUCATION DO NOT COPY

the presence of aromatic ring which is responsible for the delocalization of lone pair of electrons of N-atom over the benzene ring.

Combining all these facts, the relative basic strength of these four amines decrease in the order:

$(C_2H5)2NH_2 > C_2H_5NH_2 > C_6H_5NHCH_3 > C_6H_5NH_2$

Since, a stronger base has a lower pk_b value, therefore, pKb values decrease in the reverse order:

$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)2NH_2$

Q. 4 B

Arrange the following: 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:

In $(C_2H_5)_2NH_2$, two ethyl groups are present and in CH_3NH_2 one methyl group is present. As we know that more alkyl groups are

present, more basic will be the amine. Hence, $(C_2H_5)_2NH_2$ is more basic than the CH_3NH_2

Now in $C_6H_5NH_2$, due to delocalization of lone pair of electrons of the N-atom over the benzene ring (decreases the electron density of N-atom) makes it less basic than $(C_2H_5)_2NH_2$ and CH_3NH_2

Now, in $C_6H_5N(CH_3)_2$ due to presence of two CH_3 groups (increases the electron density of N-atom) makes it more basic than $C_6H_5NH_2$ but less basic than $(C_2H_5)_2NH_2$ and CH_3NH_2 due to the presence of aromatic ring which is responsible for the delocalization of lone pair of electrons of N-atom over the benzene ring (decreases the electron density of N-atom)

Combining all these facts, the relative basic strength of these four amines increases in the order:

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

© PRADIS EDUCATION DO NOT COPY

Q. 4 C

Arrange the following: In increasing order of basic strength:

(a) Aniline, p-nitro aniline and p-toluidine

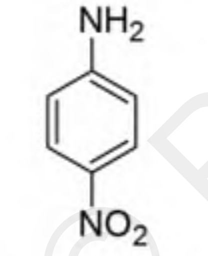
(b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$

Answer:

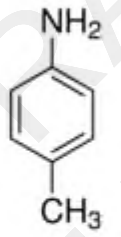
(a) Electron-donating groups such as $–CH_3$, $-OCH_3$, $-NH_2$, etc. increase the basicity and electron-withdrawing groups such as $–NO_2$, -CN, $-SO_3H$, -COOH, -X(halogen), etc. decrease the basicity of amines.

Explanation: Electron-donating groups releases electrons, stabilizes the conjugate acid (cation) and thus increases the basic strength.

Electron-withdrawing groups withdraws electrons, destabilizes the conjugate acid (cation) and thus decreases the basic strength.



p-nitroaniline



p-toluidine

In p-nitro aniline, NO_2 group is present. As we know that NO_2 group is an electron withdrawing group which decreases the basic strength of amine. In p-toluidine, CH_3 group is present and as we know that CH_3 group is an electron donating(releasing) group which increases the basic strength of amine.

Hence, p-toluidine is more basic than p-nitro aniline

Now in $C_6H_5NH_2$ (aniline), due to delocalization of lone pair of electrons of the N-atom over the benzene ring (decreases the electron density of N-atom) makes it less basic than p-toluidine but more basic

© PRADIS EDUCATION DO NOT COPY

than p-nitro aniline (NO_2 group is present which decreases the density of aniline)

Combining all these facts, the relative basic strength of these three amines increases in the order:

p-nitro aniline< aniline < p-toluidine

(b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$

In $C_6H_5NH_2$ and $C_6H_5NHCH_3$, the N-atom is directly attached to the aromatic ring. Hence, they both show resonance in which delocalization of lone pair of electrons N-atom takes place. As a result, the electron density of N-atom decreases. Hence both are weaker bases. However, in $C_6H_5NHCH_3$, CH_3 group (electron withdrawing) is present which increases the overall density of electrons.

Hence, $C_6H_5NHCH_3$ is more basic than $C_6H_5NH_2$

In $C_6H_5CH_2NH_2$, the N-atom is not directly attached to the aromatic ring. As a result, it does not show resonance. There is no effect on the electron density of lone pair of electrons of N-atom. Hence, it is more basic than $C_6H_5NH_2$ and $C_6H_5NHCH_3$

Combining all these facts, the relative basic strength of these three amines increases in the order:

$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

Q. 4 D Arrange the following: In decreasing order of basic strength in gas phase:

$C_6H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3

Answer:

Amines in gas phase or in non-aqueous solvents, there is no solvation effect (getting influenced by the solvent). It means that the stabilization

© PRAADIS EDUCATION DO NOT COPY

of conjugate acid formed due to the formation of hydrogen bonding are absent.

$$CH_3NH_2 + H – OH \xrightarrow{\quad} CH_3 – {}^{+}NH_3 + OH^-$$

(absent)

Hence, the basic strength of amines depends only on the +I effect of the alkyl groups. Alkyl groups are electron releasing groups, they release electron to the nitrogen in amine and increase the overall electron density of electrons and thus is easily available to donate electron. This property makes it more basic. As a result, more alkyl groups are attached, the higher the +I effect. Hence, the higher the +I effect, stronger is the base (high tendency to accept electrons)

In $(C_2H_5)_3N$, 3 alkyl groups are present, hence it is more basic. In $(C_2H_5)_2NH$, 2 alkyl groups are present, hence it is less basic than $(C_2H_5)_3N$. In $C_2H_5NH_2$, only one alkyl group is present, hence it is less basic than $(C_2H_5)_3N$ and $(C_2H_5)2NH$. In NH_3, no alkyl group is present, so there is no +I effect. Hence it is less basic among all the amines.

Combining all these facts, the relative basic strength of these four amines decreases in the order:

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

Q. 4 E

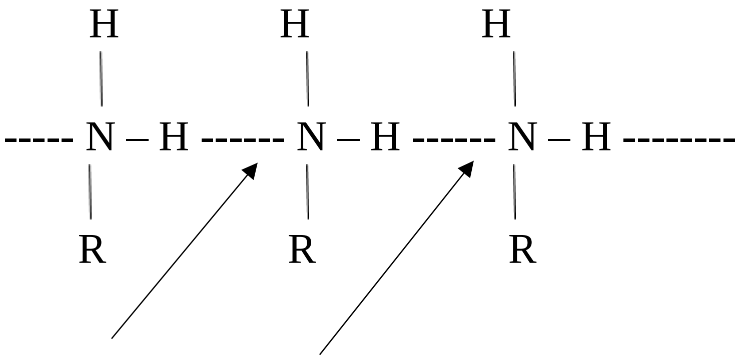
Arrange the following: In increasing order of boiling point:

C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

Answer:

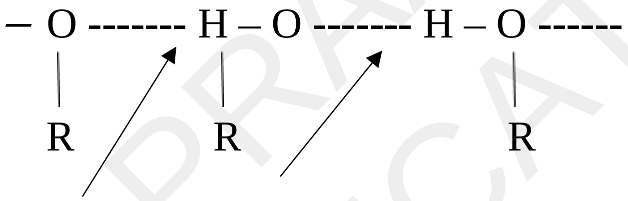
As we know that boiling point of compounds depend upon the formation of H-bonding. Amines have higher boiling points than hydrocarbons of simple molecular masses. This is due to the reason that amines being polar, form intermolecular H-bonding (except tertiary amine which do not have hydrogen atom linked to N-atom, i.e., R_3N)

© PRADIS EDUCATION DO NOT COPY



Intermolecular H – bonding (weak)

Further, since the electronegativity (tendency to attract a shared pair of electrons) of nitrogen in amine is lower (3.0) than that of oxygen (3.5) in alcohol, therefore, amines form weaker H-bonds than electronegative oxygen atom.



Intermolecular H – bonding (strong)

Hence, C_2H_5OH has higher boiling point than $(CH_3)_2NH$ and $C_2H_5NH_2$. Because in C_2H_5OH, the electronegativity of O-atom is higher than H-atom which makes strong intermolecular H-bonding whereas in $(CH_3)_2NH$ and $C_2H_5NH_2$, the electronegativity of N-atom is higher than H-atom but lower than O-atom in C_2H_5OH which makes weak intermolecular H-bonding.

Further, since, the extent of H-bonding depends upon the number of H-atoms on the N-atom. More the no. of H-atoms linked to nitrogen, the higher the boiling point. Since in$(CH_3)_2NH$ have one hydrogen atom and in $C_2H_5NH_2$ have two H-atoms linked to nitrogen, therefore,

$C_2H_5NH_2$ has higher boiling point than $(CH_3)_2NH$.

© PRAADIS EDUCATION DO NOT COPY

Combining all these facts, the boiling point of the given three compounds increases in the order:

$(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

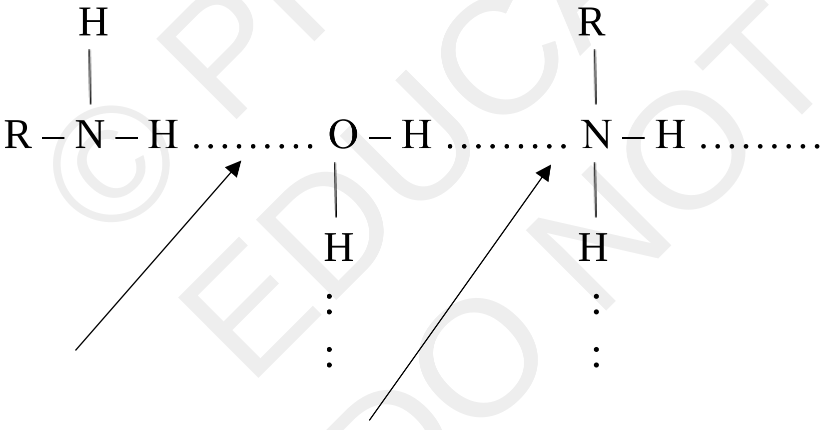
Q. 4 F

Arrange the following: In increasing order of solubility in water:

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

Answer:

All the three classes of aliphatic amines form H-bonds with water. As the size of alkyl group increases, the solubility decreases due to a corresponding increase in the hydrophobic part (hydrocarbon part) of the molecule. On the other hand, aromatic amines are insoluble in water due to presence of larger hydrocarbon part (C_6H_5-group) which tends to retard the formation of H-bonds.



$$R - \overset{H}{\overset{|}{N}} - H \cdots\cdots\cdots \underset{\underset{\vdots}{H}}{\underset{|}{O}} - H \cdots\cdots\cdots \overset{R}{\overset{|}{\underset{\underset{\vdots}{H}}{\underset{|}{N}}}} - H \cdots\cdots\cdots$$

Intermolecular H – bonding with water

Now, among the given compounds, $C_6H_5NH_2$ is insoluble in water due to presence of C_6H_5-group (hydrocarbon part). In $(C_2H_5)_2NH$, two alkyl groups are present and in $C_2H_5NH_2$ only one alkyl group is present, hence $C_2H_5NH_2$ is more soluble in water than $(C_2H_5)_2NH$.

© PRADIS EDUCATION DO NOT COPY

Combining all these facts, solubility of the given three compounds increases in the order:

$C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

Q. 5 A

How will you convert: Ethanoic acid into methanamine?

Answer:

$$CH_3COOH \xrightarrow{SOCl_2} CH_3COCl \xrightarrow{NH_3(excess)} CH_3CONH_2$$

Ethanoic acid

$$\Big\downarrow \; Br_2 / NaOH$$

$$CH_3NH_2$$

Methanamine

Explanation:

To convert ethanoic acid into methanamine (CH_3NH_2), we need ethanamide (amide group-$RCONH_2$) and we can get ethanamide from ethanoyl chloride (acid chloride group- RCOCl).

Step-1: Convert ethanoic acid into ethanoyl chloride

Ethanoic acid (CH_3COOH) reacts with thionyl chloride ($SOCl_2$) or PCl5 or PCl_3 to form ethanoyl chloride (CH_3COCl) by the replacement of OH group by Cl atom.

Step-2 Convert ethanoyl chloride into ethanamide

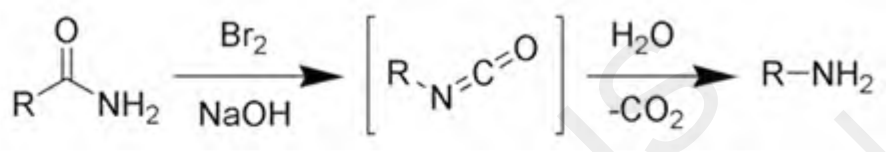
Ethanoyl chloride (CH_3COCl) reacts with ammonia (in excess) to form ethanamide (CH_3CONH_2) by removal of NH_4Cl

Step-3: Convert ethanamide into methanamine (Hoffman Bromamide reaction)

© PRAADIS EDUCATION DO NOT COPY

Ethanamide (CH_3CONH_2) is treated with an aqueous or ethanolic solution of potassium hydroxide (KOH) and bromine (Br_2), it gives ethanamine (CH_3NH_2-final product)

Note: Hoffman Bromide Reaction is a reaction in which a primary amide is treated with an aqueous KOH or NaOH and bromine, it gives a primary amine which has one carbon atom less than the original amide.



Q. 5 B

How will you convert: Hexanenitrile into 1-aminopentane?

Answer:

$$\begin{tikzcd} C_5H_{11}CN \arrow[r, "H^+/H_5O"] & C_5H_{11} - COOH \arrow[r, "SOCl_2"] & C_5H_{11} - COCl \arrow[d, "NH_3\ (excess)"] \\ & C_2H_{11} - NH_2 & C_5H_{11} - CONH_2 \arrow[l, "Br_2/KOH"'] \end{tikzcd}$$

Hexanenitrile

1- Aminopentane

Explanation:

The structure of Hexanenitrile is $CH_3CH_2CH_2CH_2CH_2CN$ or $C_5H_{11}CN$. To convert Hexanenitrile into 1-aminopentane, first we need hexanamide (amide group-$RCONH_2$) and we can get hexanamide from

© PRADIS EDUCATION DO NOT COPY

hexanoyl chloride (acid chloride group – RCOCl) and we can get hexanoyl chloride from hexanoic acid.

Step 1: Convert Hexanenitrile into Hexanoic acid

Hexanenitrile ($C_5H_{11}CN$) undergoes hydrolysis to form Hexanoic acid ($C_5H_{11}COOH$)

Step 2: Convert Hexanoic acid into hexanoyl chloride

Hexanoic acid ($C_5H_{11}COOH$) reacts with thionyl chloride ($SOCl_2$) or PCl_5 or PCl_3 to form hexanoyl chloride ($C_5H_{11}COCl$) by the replacement of OH group by Cl atom.

Step 3: Convert Hexanoyl chloride into hexanamide

Hexanoyl chloride ($C_5H_{11}COCl$) reacts with excess ammonia to form hexanamide ($C_5H_{11}CONH_2$) by the removal of NH_4Cl.

Step 4: Convert hexanamide into 1- amino pentane by Hoffman Bromamide reaction)

Hexanamide ($C_5H_{11}CONH_2$) is treated with an aqueous or ethanolic solution of potassium hydroxide (KOH) and bromine (Br_2), it gives 1-aminopentane (final product) which has one carbon atom less than the hexanamide.

Q. 5 C

How will you convert: Methanol to ethanoic acid?

Answer:

$$\begin{tikzcd}
CH_3OH \arrow[r, "PCl_5"] & CH_3Cl \arrow[r, "Ethanolic\ NaCN"] & CH_3CN \arrow[d, "H+/H_2O"] \\
 & & CH_3COOH
\end{tikzcd}$$

© PRANDIS EDUCATION DO NOT COPY

Explanation:

The structure of methanol is CH_3OH. To convert methanol to ethanoic acid (the number of carbon atoms is increasing from one carbon atom to two carbon atoms) we need ethanenitrile and we can get ethanenitrile from methyl chloride.

Note: If the number of carbon atoms is increasing, we need a nitrile group and if the number of atoms is decreasing, we need an amide group (Hoffman Bromamide reaction)

Step 1: Convert methanol into methyl chloride

Methanol (CH_3OH) reacts with thionyl chloride ($SOCl_2$) or PCl_5 or PCl3 to form methyl chloride (CH_3Cl) by the replacement of OH group by Cl atom.

Step 2: Convert methyl chloride into ethanenitrile

Methyl chloride (CH_3Cl) reacts with ethanolic NaCN/ KCN to form ethanenitrile (CH_3CN) by the removal of NaCl / KCl

Step 3: Convert ethanenitrile into ethanoic acid

Ethanenitrile (CH_3CN) undergoes hydrolysis to form ethanoic acid (final product) which has one carbon atom more than the ethanenitrile.

Q. 5 D

How will you convert: Ethanamine into methanamine?

Answer:

Ethanamine into methanamine (ethylamine to methylamine)

$$CH_3 - CH_2 - NH_2 \xrightarrow{NaNO_2/HCl} [CH_3 - CH_2 - N_2^+ Cl^- \xrightarrow{H_2O} CH_3 - CH_2 - OH$$

Ethanamine

$$\downarrow$$

© PRADIS EDUCATION DO NOT COPY

$KMnO^4$ / H^+

$$CH_3 - NH_2 \xleftarrow{Br_2/NaOH} CH_3CONH_2 \xleftarrow{NH_3(excess)} CH_3COOH$$

Methanamine

Explanation:

The structure of ethanamine is $CH_3CH_2NH_2$. To convert ethanamine into methanamine (the number of carbon atoms is decreasing from two carbon atoms to one carbon atom), first we need ethanamide (amide group- $RCONH_2$) and we can get acetamide from acetic acid. By oxidation of ethanol, we can get ethanoic acid.

Step 1: Convert Ethanamine into ethanol with the help of diazonium salt

Ethanamine ($CH_3CH_2NH_2$) reacts with $NaNO_2$ and HCl to give Diazonium salt (R--N2+Cl-) which undergoes hydrolysis to form ethanol.

Note: The diazonium salts or diazonium compounds are the class of organic compounds with general formula $R-N^{2+}X-$ where X is an organic or inorganic anion (for example, Cl^-, Br^-, BF^{4-}, etc.) and R is an alkyl or aryl group. Hence, they have two nitrogen atoms with one being charged. Example - Benzenediazonium chloride ($C_6H_5N^{2+}Cl^-$)

Step 2: Convert ethanol to ethanoic acid by oxidation

Ethanol (CH_3CH_2OH) undergoes oxidation in the presence of strong oxidizing agent $KMNO_4$ to form ethanoic acid (CH_3COOH)

Step 3: Convert ethanoic acid into ethanamide (amide group)

Ethanoic acid (CH_3COOH) is treated with ammonia (in excess) to form ethanamide (CH_3CONH_2)

Step 4: Convert ethanamide into methanamine by Hoffman Bromamide Reaction

© PRADEEP EDUCATION DO NOT COPY

Ethanamide (CH_3CONH_2) is treated with alc. NaOH or KOH in the presence of bromine, it gives methanamine (CH_3NH_2 - final product) which has one carbon atom less than the ethanamide.

Q. 5 E

How will you convert: Ethanoic acid into Propanoic acid?

Answer:

$$\begin{tikzcd}
CH_3COOH \arrow[r, "\frac{(i)LiAlH_4}{ether}", "(ii)H_3O^+"'] & CH_3CH_2OH \arrow[r, "PCl_5"] & CH_3CH_2Cl \arrow[dd, "\text{Ethanolic NaCN}"] \\
\text{Ethanoic acid} & & \\
& CH_3CH_2COOH & CH_3CH_2CN \arrow[l, "H^+/H_2O"'] \\
& \text{Propanoic acid} &
\end{tikzcd}$$

Explanation:

To convert ethanoic acid into Propanoic acid (the number of carbon atoms are increasing from two carbon atoms to three carbon atoms), we need propionitrile (CH_3CH_2CN) and we can get propionitrile from ethyl chloride. To get ethyl chloride, we need ethanol which can be formed by the reduction of ethanoic acid.

Step 1: Convert ethanoic acid into ethanol by reduction

Ethanoic acid (CH_3COOH) undergoes reduction in the presence of lithium aluminium hydride ($LiAlH_4$) to form ethanol (CH_3CH_2OH)

Step 2: Convert ethanol into ethyl chloride

Ethanol (CH_3CH_2OH) reacts with PCl_5 to form ethyl chloride (CH_3CH_2Cl) by the replacement of OH group by Cl atom.

Step 3: Convert ethyl chloride into ethyl cyanide/ propionitrile

© PRADIS EDUCATION DO NOT COPY

Ethyl chloride (CH_3CH_2Cl) reacts with ethanolic NaCN / KCN to give ethyl cyanide/ propionitrile (CH_3CH_2CN)

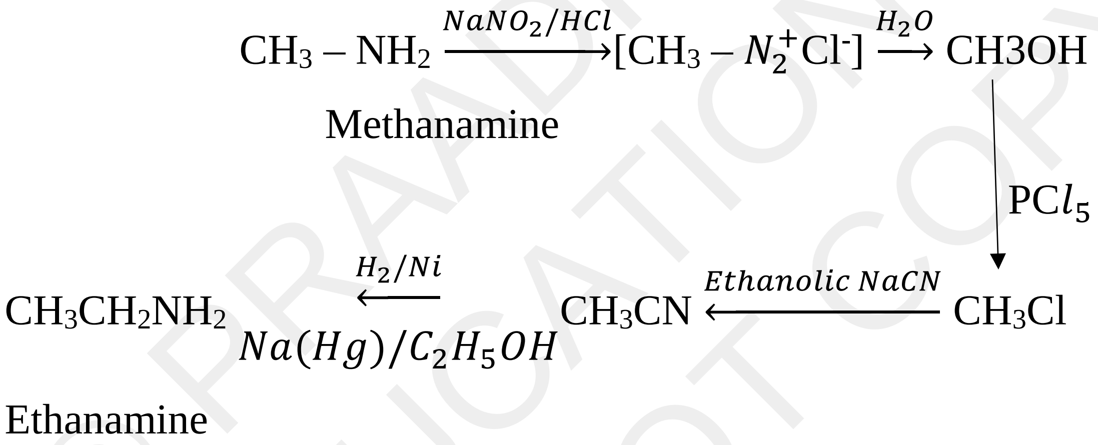
Step 4: Convert ethyl cyanide/ propionitrile into Propanoic acid

Ethyl cyanide (CH_3CH_2CN) undergoes hydrolysis to form a Propanoic acid (CH_3CH_2COOH-final product) which has one carbon atom more than the propionitrile.

Q. 5 F

How will you convert: Methanamine into ethanamine?

Answer:



$$\begin{tikzcd}
\underset{\text{Methanamine}}{CH_3-NH_2} \arrow[r, "NaNO_2/HCl"] & {[CH_3-N_2^+Cl^-]} \arrow[r, "H_2O"] & CH3OH \arrow[d, "PCl_5"] \\
\underset{\text{Ethanamine}}{CH_3CH_2NH_2} & CH_3CN \arrow[l, "H_2/Ni"', "Na(Hg)/C_2H_5OH"] & CH_3Cl \arrow[l, "Ethanolic\ NaCN"']
\end{tikzcd}$$

Explanation:

The structure of methanamine is CH_3NH_2 and the structure of ethanamine is $CH_3CH_2NH_2$. To convert methanamine into ethanamine (the number of carbon atoms are increasing from one carbon atom two carbon atoms) so we need ethanenitrile which we can get from ethyl chloride. We can obtain ethyl chloride from alcohol which can be obtained from diazonium salt (R^--$N^{2+}Cl^-$)

Step 1: Convert methyl amine to methanolMethyl amine (CH_3NH_2) is first treated with HNO_2 and HCl, which gives a fresh diazonium salt (R--$N^{2+}Cl^-$) and then diazonium salt undergoes hydrolysis to form methanol.

Step 2: Convert methanol to methyl chloride

© PRADIS EDUCATION DO NOT COPY

Methanol is treated with PCl5 or thionyl chloride, gives ethanenitrile (CH_3Cl) by the replacement of OH atom by Cl atom.

Step 3: Convert methyl chloride to ethanenitrile

Methyl chloride (CH_3Cl) is treated with ethanolic NaCN or KCN, gives ethanenitrile (CH_3CN)

Step 4: Convert ethanenitrile to ethanamine

Ethanenitrile (CH_3CN) undergoes a reduction in the presence of sodium and ethyl alcohol to form ethanamine ($CH_3CH_2NH_2$ – final product) which has one carbon atom more than the ethanenitrile.

Q. 5 G

How will you convert: Nitromethane into dimethylamine?

Answer:

$$\begin{tikzcd}
CH_3 - NO_2 \arrow[r, "Sn/HCl"] & CH_3 - NH_2 \arrow[r, "CHCl_3/KOH/\Delta", "(Carbylamine\ reaction)"'] & CH_3 - NC \text{ Nitromethane} \arrow[dd] \\
Na/C_2H_5OH & & \\
 & & CH_3 - NH - CH_3
\end{tikzcd}$$

Explanation:

The structure of Nitromethane is CH_3NO_2 and structure of dimethylamine (CH_3NHCH3), as dimethylamine is a secondary amine so to obtain this, we need methyl isocyanide (CH_3NC) which we can get from methanamine through carbylamine reaction.

Step 1: Convert nitromethane to methanamine

© PRAADIS EDUCATION DO NOT COPY

Nitromethane (CH_3NO_2) undergoes reduction in the presence of Sn and HCl to form methanamine (CH_3NH_2)

Step 2: Convert methanamine to methyl isocyanide by Carbylamine reaction

Methanamine (CH_3NH_2) is heated with alcoholic potassium hydroxide and chloroform, the methyl isocyanide (CH_3NC) is formed.

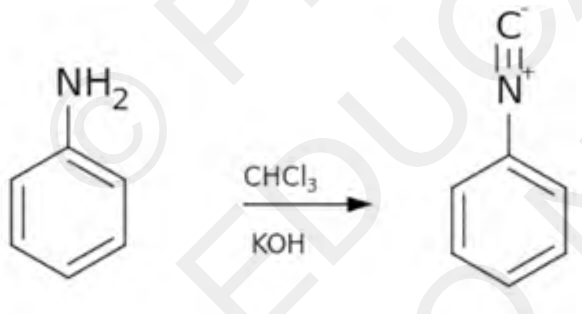
Note: Carbylamine reaction is given only by primary amines

Primary amines when heated with chloroform and alcoholic potassium hydroxide give isocyanides (carbylamines) having very unpleasant smell, which can be easily detected.

$R – NH2 + CHCl3 + 3KOH\ (alc.) \xrightarrow{\Delta} R – NC + 3KCl + 3H2O$

Primary Chloroform Potassium Carbylamine

Amine hydroxide



Step 3: Convert methyl isocyanide to diethylamine

Methyl isocyanide (CH_3NC) undergoes reduction in the presence of sodium and ethyl alcohol to form diethylamine (CH_3NHCH_3-final product)

Q. 5 H

How will you convert: Propanoic acid into ethanoic acid?

© PRADIS EDUCATION DO NOT COPY

Answer:

Propanoic acid to Ethanoic acid/ acetic acid

$$CH_3CH2COOH \xrightarrow[\Delta]{NH_3(excess)} CH_3CH_2CONH_2 \xrightarrow{Br_2/KOH} CH_3CH_2NH_2$$

Propanoic acid (Hoffmann bromamide reaction)

$$\downarrow$$

$$CH_3COOH \xleftarrow{KMnO_4/H^+} CH_3CH_2OH \xleftarrow{H_2O} [CH_3CH_2^+N_2Cl^-]$$

Ethanoic acid

Explanation:

The structure of Propanoic acid is CH_3CH_2COOH and the structure of ethanoic acid is CH_3COOH. To convert Propanoic acid to ethanoic acid (the number of carbon atoms are decreasing), we need propionamide (amide group-$RCONH_2$). Then propionamide undergoes Hoffman Bromamide reaction to form methylamine. Then methylamine formed can be converted to ethanol to form ethanoic acid by oxidation.

Step 1: Convert Propanoic acid to propionamide

Propanoic acid (CH_3CH_2COOH) reacts with ammonia (in excess) to form propionamide ($CH_3CH_2CONH_2$)

Step 2: Convert propionamide to ethyl amine by Hoffman Bromamide reaction

Propionamide ($CH_3CH_2CONH_2$) reacts with potassium hydroxide and bromine to form ethylamine ($CH_3CH_2NH_2$) which has one carbon atom less than the propionamide (Hoffman Bromamide reaction)

Step 3: Convert ethyl amine to methanol by forming diazonium salt

© PRADIS EDUCATION DO NOT COPY

Ethyl amine ($CH_3CH_2NH_2$) reacts with $NaNO_2$ and HCl to form diazonium salt (R^{-}-$N^{2+}Cl^{-}$) then diazonium salt undergoes hydrolysis to from ethanol (CH_3CH_2OH)

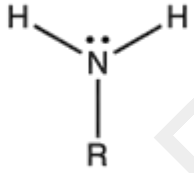
Step 4: Convert ethanol to ethanoic acid by oxidation

Ethanol (CH_3CH_2OH) undergoes oxidation in the presence of strong oxidizing agent $KMNO_4$ to form ethanoic acid (CH_3COOH-final product)

Q. 6 Describe the method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reaction involved.

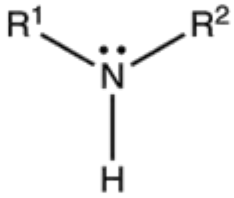
Answer:

Primary amine: A primary (1°) amine is an amine that has the following general structural formula.



R= alkyl or aryl group

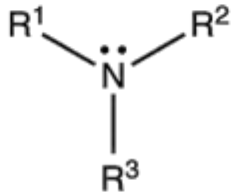
Secondary amine: A secondary (2°) amine is an amine that has the following general structural formula.

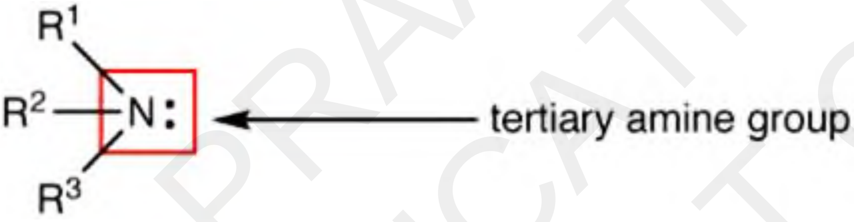


© PRADIS EDUCATION DO NOT COPY

R1 and R2= alkyl or aryl group

Tertiary amine: A tertiary amine is an amine that has the following structure





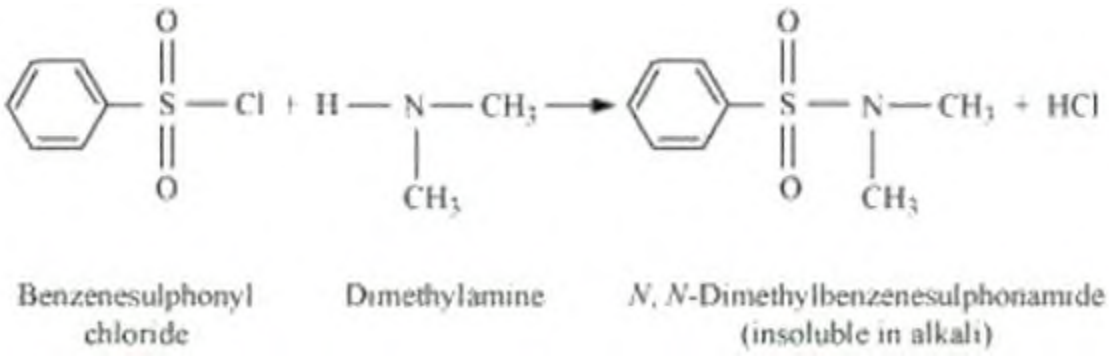
© PRAADIS EDUCATION DO NOT COPY

R_1, R_2 and R_3 are alkyl or aryl groups

Identification of Primary, Secondary and Tertiary amines

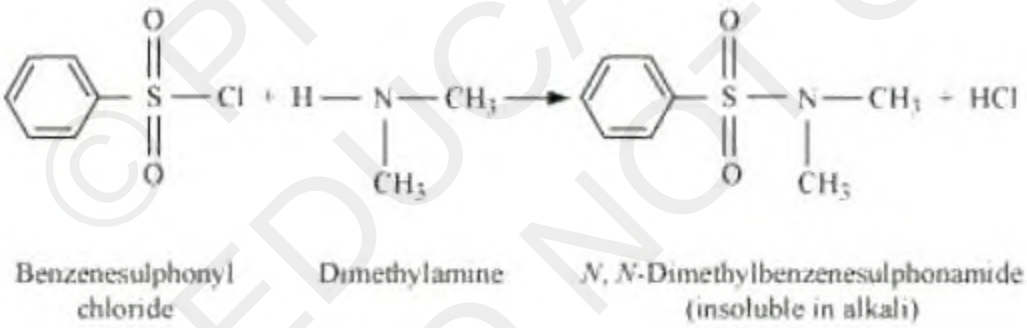
Primary, secondary and tertiary amines can be identified by the following test:

Hinsberg’s test: This is an excellent test for the identification of primary, secondary and tertiary amines. In this test, the amine is shaken with benzenesulphonyl chloride (Hinsberg’s reagent) in the presence of an excess of aqueous KOH solution when



(i) A primary amine gives a clear solution which on acidification gives an N-alkylbenzene sulphonamide which is soluble in alkali.

Due to the presence of strong electron withdrawing sulphonyl group in the sulphonamide, the H-atom attached to nitrogen can be easily released as a proton. So it is acidic and dissolves in alkali.



© PRADIS EDUCATION DO NOT COPY

(ii) A secondary amine reacts with Hinsberg's reagent to give a sulphonamide which is soluble in water.

There is no H-atom attached to the N-atom in the sulphonamide Therefore it is not acidic and soluble in alkali.

(iii) A Tertiary amine does not react with Hinsberg’s reagent at all

Q. 7 A

Write short notes on Carbylamine reaction

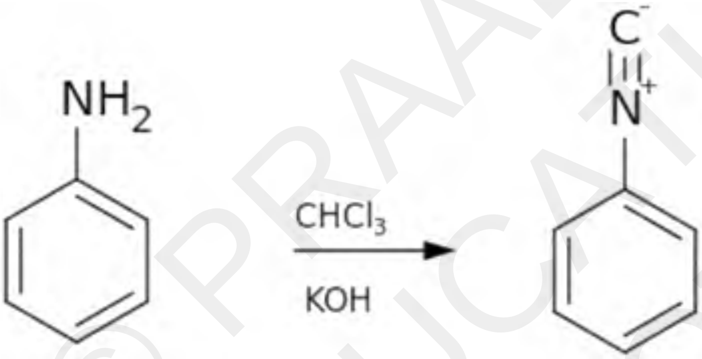
Answer:

Carbylamine reaction is given only by primary amines. Primary amines when heated with chloroform and alcoholic potassium hydroxide give isocyanides (carbylamines) having a very unpleasant smell, which can be easily detected.

$R - NH_2 + CHCl + 3LPH\ (alc.) \xrightarrow{\Delta} R - NC + 3KCl + 2H_2O$

Primary   Chloroform Potassium   Carbylamine

Amine   hydroxide

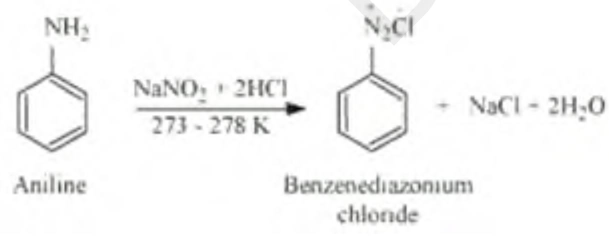


© PRAADIS EDUCATION DO NOT COPY

Q. 7 B

Write short notes on Diazotization

Answer:

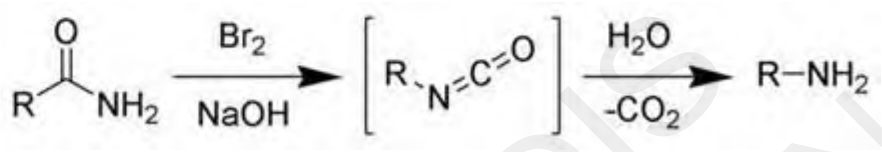


Aromatic primary amines react with nitrous acid (prepared in situ from NaNO2 and a mineral acid such as HCl) at low temperatures 273-278K to form Diazonium salts ($Ar^-N^{2+}Cl^-$) This process of conversion of a primary aromatic amine into its diazonium salt is called Diazotization.

Q. 7 C

Write short notes on Hoffman Bromamide Reaction

Answer:



Hoffman Bromamide Reaction is a reaction in which a primary amide is treated with an aqueous KOH or NaOH and bromine, it gives a primary amine which has one carbon atom less than the original amide. This reaction involves the migration of alkyl or aryl group from the carbonyl carbon atom amide to the nitrogen atom.

For example:

$$CH_3 - \overset{\overset{O}{\parallel}}{C} - NH_2 + Br_2 + 4NaOH \longrightarrow CH_3 - NH_2 + Na_2CO_3 +$$

Ethanamine Methanamine 2NaBr+ $2H_2O$

$C6H5 - C - NH2 + Br2 + 4NaOH \longrightarrow C6H5 - NH2 + Na2CO3$

Benzamide Aniline + 2NaBr+ 2H2O

Q. 7 D

© PRADIS EDUCATION DO NOT COPY

Write short notes on Coupling Reaction

Answer:

The reaction of joining two aromatic rings through the --N=N—bond is known as coupling reaction.

Arenediazonium salts (Ar-N2+Cl-) such as benzene diazonium salts (C_6H_5-N_2+Cl-) react with phenol or aromatic amine (C_6H_5-NH_2) to form coloured Azo compounds.

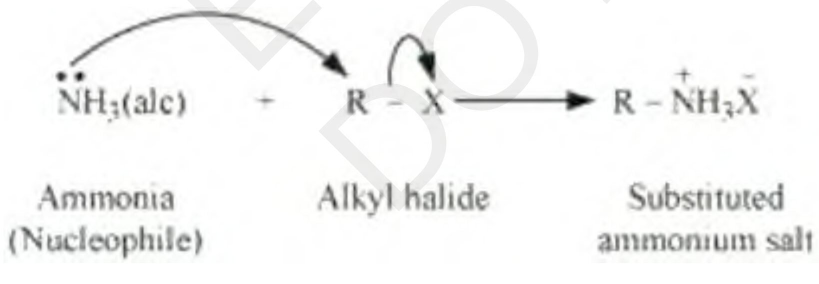
The coupling reaction is an example of electrophilic substitution reaction in which the diazonium cation with the positive charge on the terminal nitrogen acts as the electrophile while the electron rich compounds such as phenols and amines act as the nucleophiles.

Note: Electrophilic substitution reaction is a chemical reaction in which an electrophile (electron loving) displaces a group in a compound. For example:

Q. 7 E

Write short notes on Ammonolysis

Answer:



When an alkyl or benzyl halide allowed to react with an ethanolic solution of ammonia, it undergoes nucleophilic substitution reaction in

© PRADIS EDUCATION DO NOT COPY

which the halogen atom is replaced by amino (-NH_2 group) The process of cleavage of the C-X bond by ammonia is called Ammonolysis.

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

$$R\ \text{-} + NH_3X^- + NaOH \longrightarrow R - NH_2 + H_2O + NaX$$

Amine

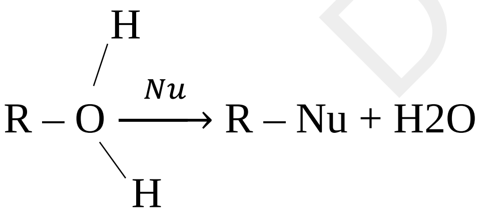
Though primary amine is produced as the major product, this process produces a mixture of primary, secondary and tertiary amines and also quaternary ammonium salts as shown below:

$$RNH_2 \xrightarrow{RX} R_2NH \xrightarrow{RX} R_3N \xrightarrow{RX} R_4{}^{+}NX^-$$

(1°) (2°) (3°) Quanternary ammonium salt

This method cannot be used for the preparation of aryl amines (aniline) since aryl halides are much less reactive than alkyl halides towards nucleophilic substitution reaction.

Note: Nucleophilic substitution reaction is the reaction of an electron pair donor (Nu, the nucleophile) with the electron pair acceptor (the electrophile) For example:



$$R - \overset{H}{\underset{H}{O}} \xrightarrow{Nu} R - Nu + H2O$$

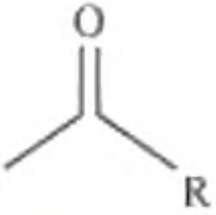
Q. 7 F

© PRADIS EDUCATION DO NOT COPY

Write short notes on Acetylation

Answer:

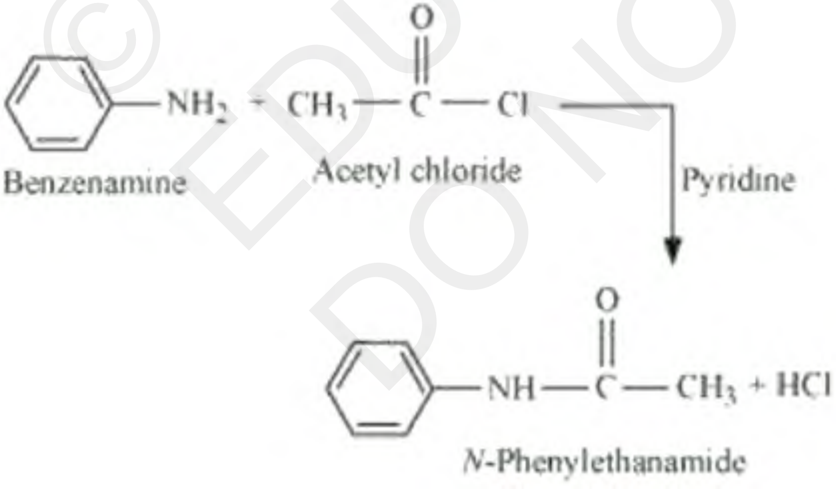
Acetylation is the process of introducing an acetyl group into a molecule.



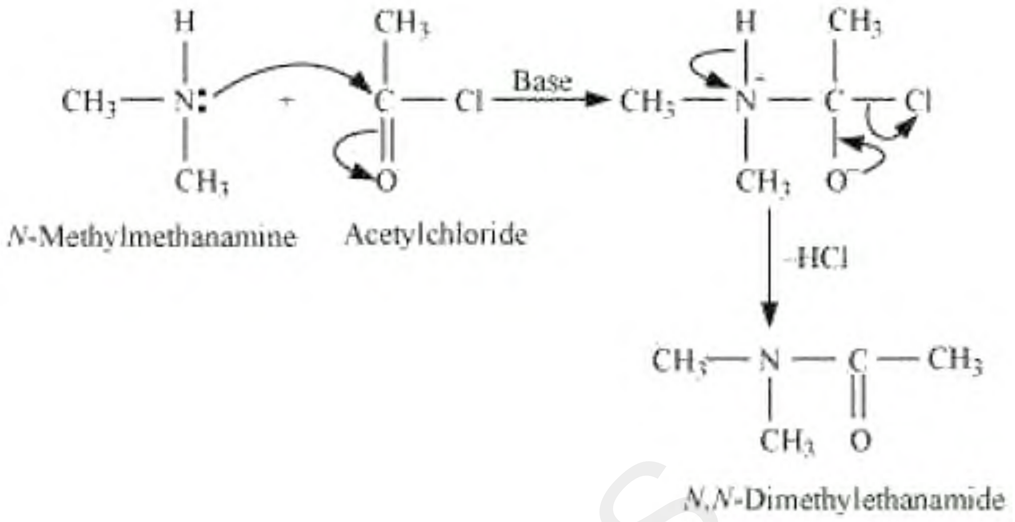
Acetyl group

With aliphatic amines: Primary and secondary amines (but not tertiary amines because they do not contain an H-atom on the N-atom) undergo nucleophilic substitution reaction when treated with acid chlorides to form N- substituted amides.

This reaction involves the replacement of Hydrogen atom of NH_2 or NH group of acetyl group which in turn leads to the production of amides.

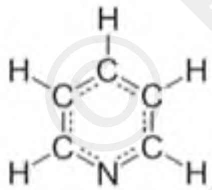


© PRADIS EDUCATION DO NOT COPY



With aromatic amine: Acylation of aromatic amines is usually carried out in the presence of a catalyst. For example, acetylation with acetyl chloride is carried out in the presence of a base stronger than the amide, like pyridine, which removes HCl formed during the reaction and shifts the equilibrium in the forward direction.

Note: Pyridine is a basic heterocyclic organic compound with the chemical formula C_5H_5N.



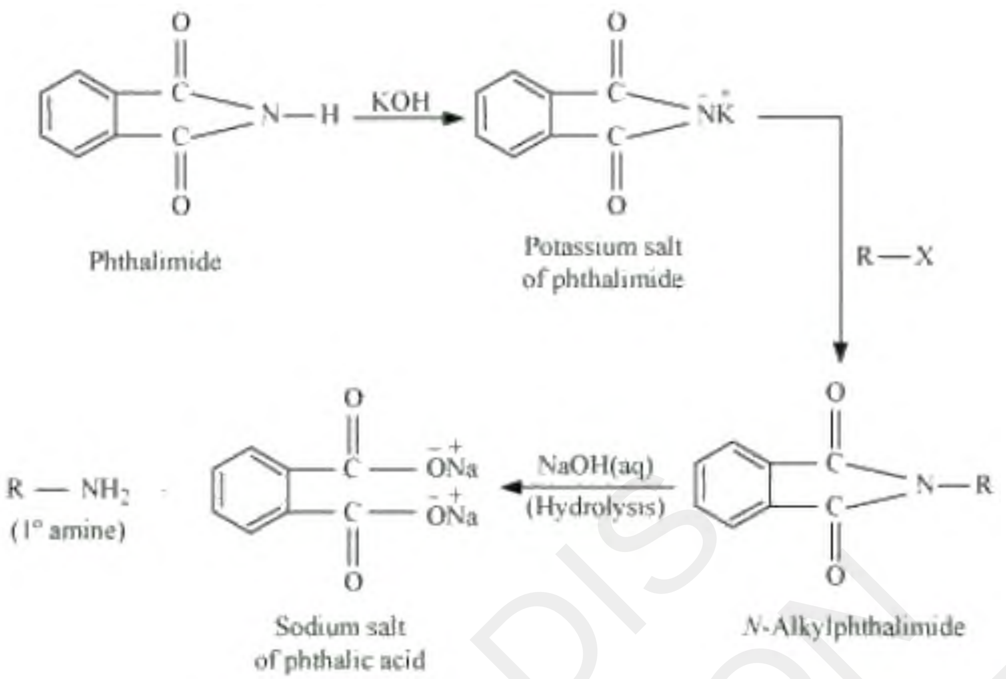
Q. 7 G

Write short notes on Gabriel phthalimide reaction

Answer:

This is a very convenient method for the preparation of pure aliphatic primary amines. Phthalimide on treatment with ethanolic KOH gives potassium phthalimide which on heating with a suitable alkyl halide gives an N- substituted phthalimide followed by the subsequent hydrolysis to give corresponding primary amines.

© PRADIS EDUCATION DO NOT COPY



Note: Aromatic primary amines such as aniline cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution reaction with potassium phthalimide under mild conditions

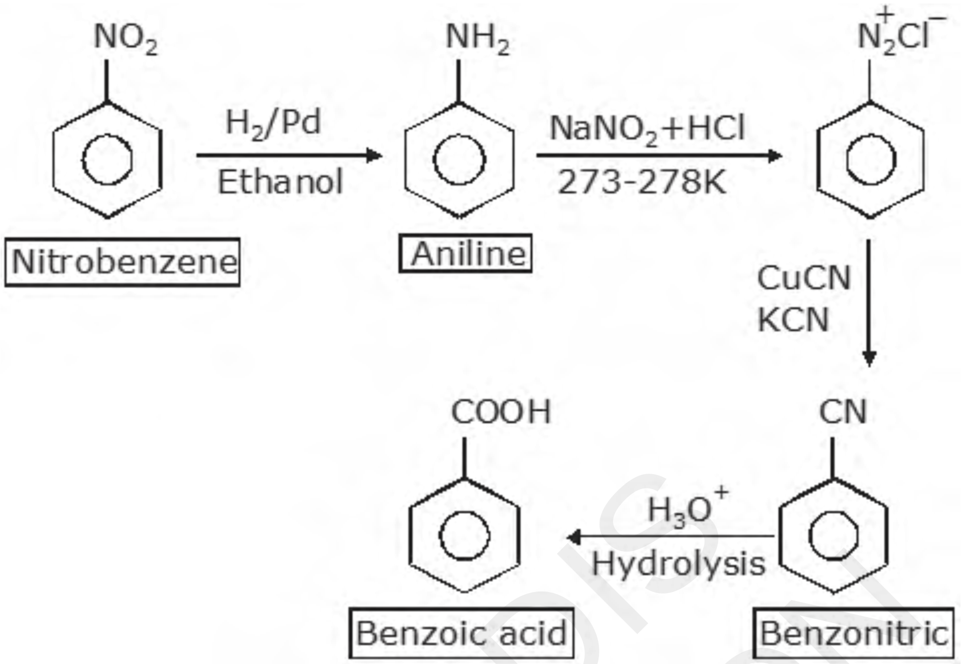
Q. 8 A

Accomplish the following conversions: Nitrobenzene to benzoic acid

Answer:

First nitrobenzene is reduced to aniline by reduction with hydrogen gas with palladium catalyst followed by nitration and substitution and final hydrolysis by acid by a proton yields benzoic acid.

© PRAADIS EDUCATION DO NOT COPY



Q. 8 B

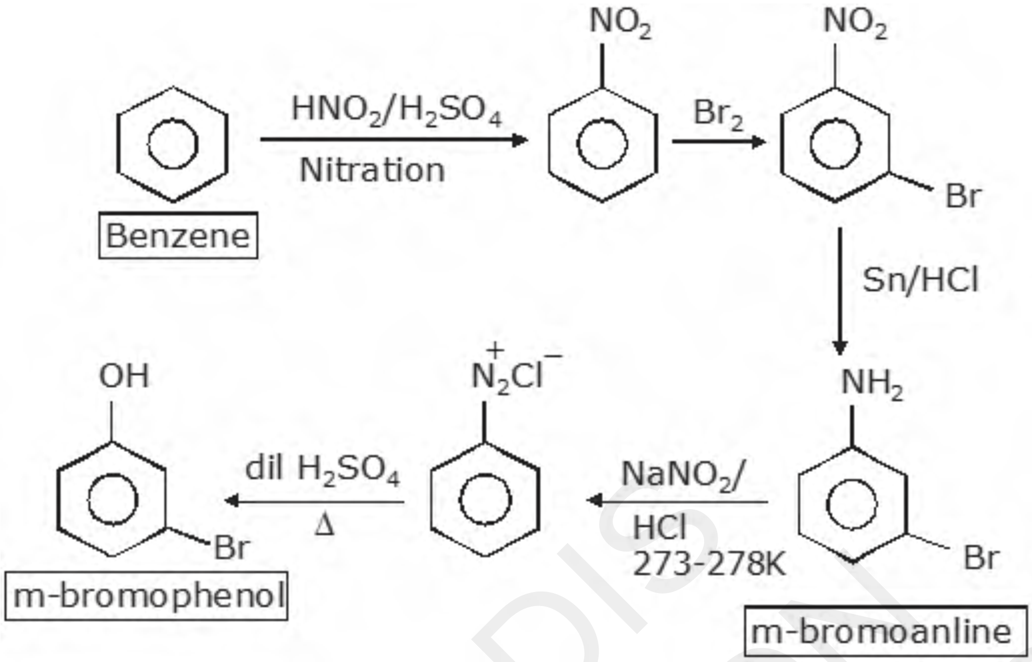
Accomplish the following conversions: Benzene to m-bromophenol

Answer:

Benzene by nitration with conc. hydrochloric acid and nitrous acid gives nitrobenzene which on reaction with bromine liquid gives m-bromobenzene.

Upon reduction with tin and acid followed by heating with diluted hydrochloric acid gives m-bromophenol.

© PRAADIS EDUCATION DO NOT COPY

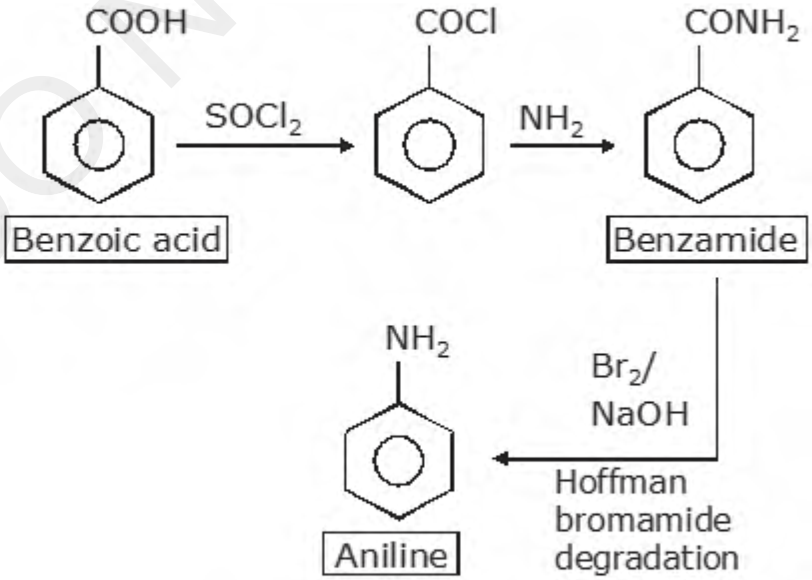


Q. 8 C

Accomplish the following conversions: Benzoic acid to aniline

Answer:

Benzoic acid, reacted with sulphonyl chloride undergoes reaction, followed by ammine and bromine liquid in presence of sodium hydroxide gives aniline. This reaction is called as Hoffman bromamide degradation.



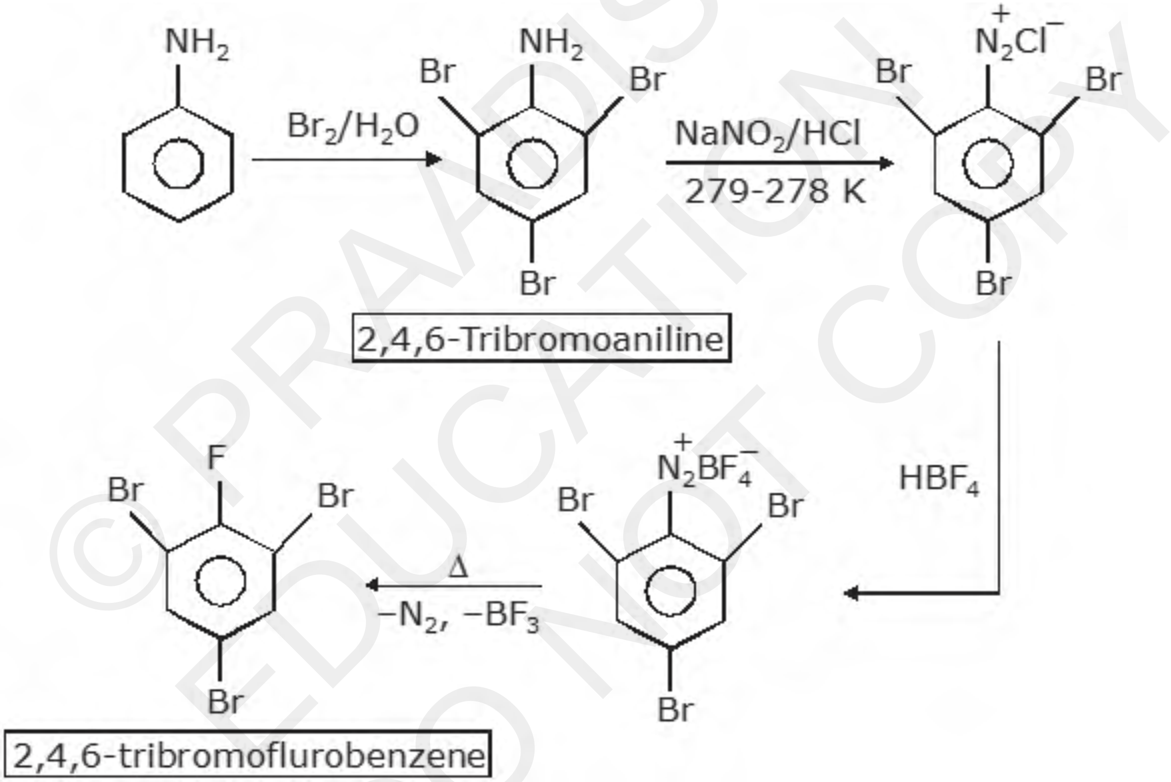
© PRADIS EDUCATION DO NOT COPY

Q. 8 D

Accomplish the following conversions: Aniline to 2,4,6-tribromofluorobenzene

Answer:

Aniline reaction with bromine water, followed by sodium nitrite gives 2,4,6- tribromodiazoniumchloride, which is very reactive gives 2,4,6-tribrmofluorobenzene upon treatment with hydrofluoroburic acid.



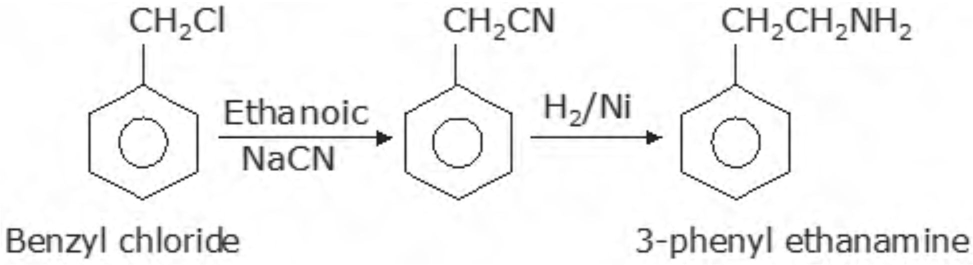
© PRAADIS EDUCATION DO NOT COPY

Q. 8 E

Accomplish the following conversions: Benzyl chloride to 2-phenylethanamine

Answer:

Benzyl chloride reacted with alcoholic NaCN and reduction gives 3-phenylethananmine.



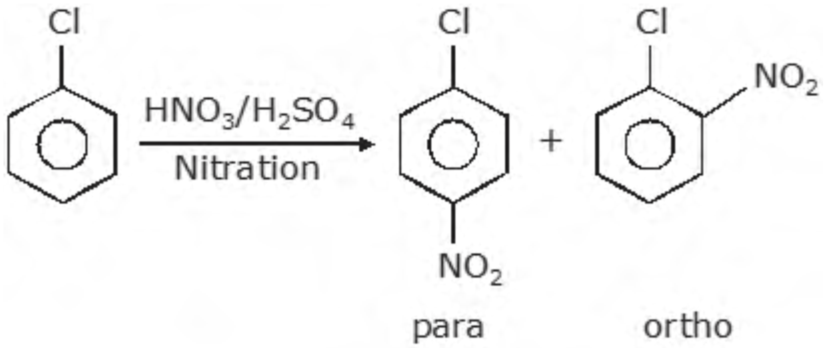
Q. 8 F

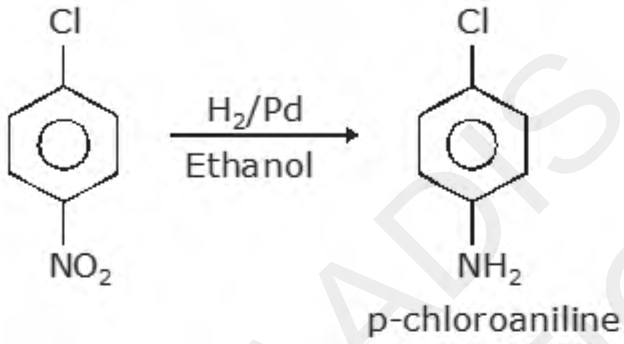
Accomplish the following conversions: Chlorobenzene to p-chloroaniline

Answer:

Chlorobenzene upon nitration with nitronium ion and para product obtained undergoes reduction to give p-chloroaniline.

© PRADIS EDUCATION DO NOT COPY





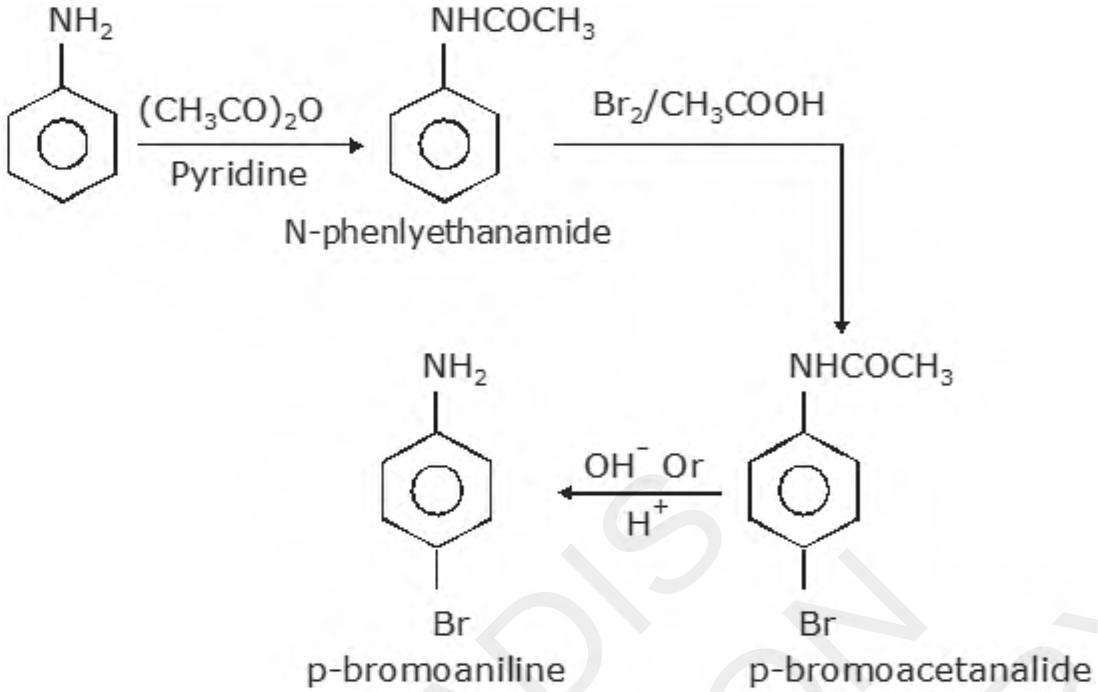
Q. 8 G

Accomplish the following conversions: Aniline to p-bromoaniline

Answer:

As aniline is a very activating group, it is first reacted with anhydride to make it less activating, which on reaction with bromine in acetic acid, followed by acid hydrolysis gives p-bromoaniline.

© PRAADIS EDUCATION DO NOT COPY



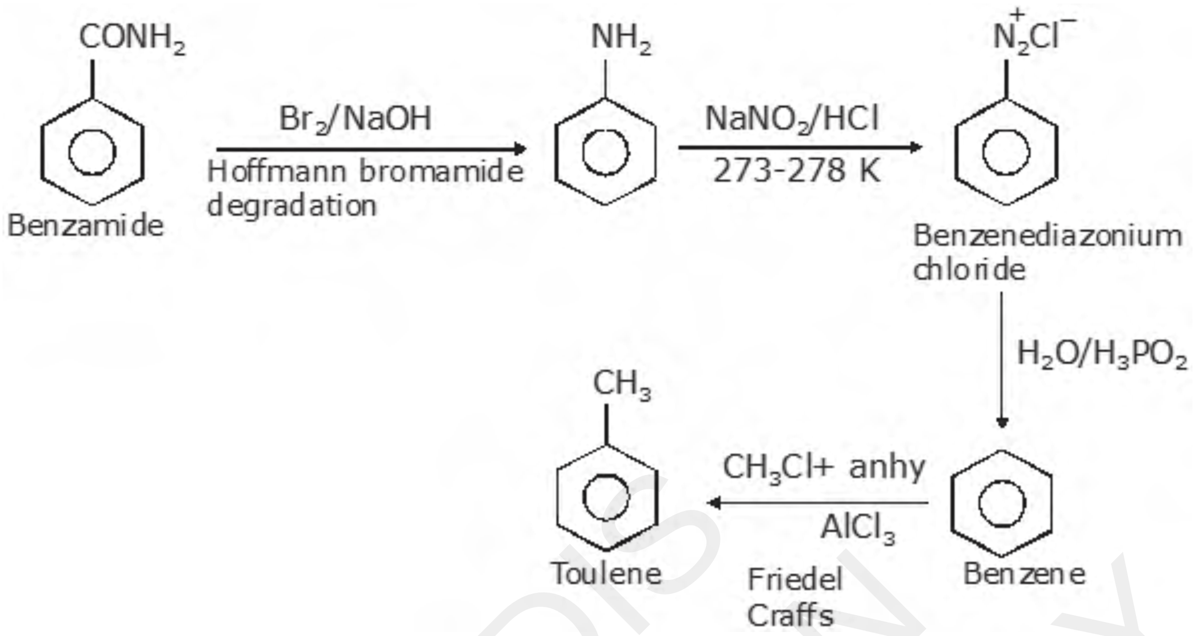
Q. 8 H

Accomplish the following conversions: Benzamide to toluene

Answer:

Benzamide undergoes Hoffman bromamide degradation to give aniline upon treatment with sodium nitrite gives benzenediazonium chloride, reacts with phosphoric acid, followed by Friedel crafts reaction with methyl chloride in solvent gives toluene.

© PRAADIS EDUCATION DO NOT COPY

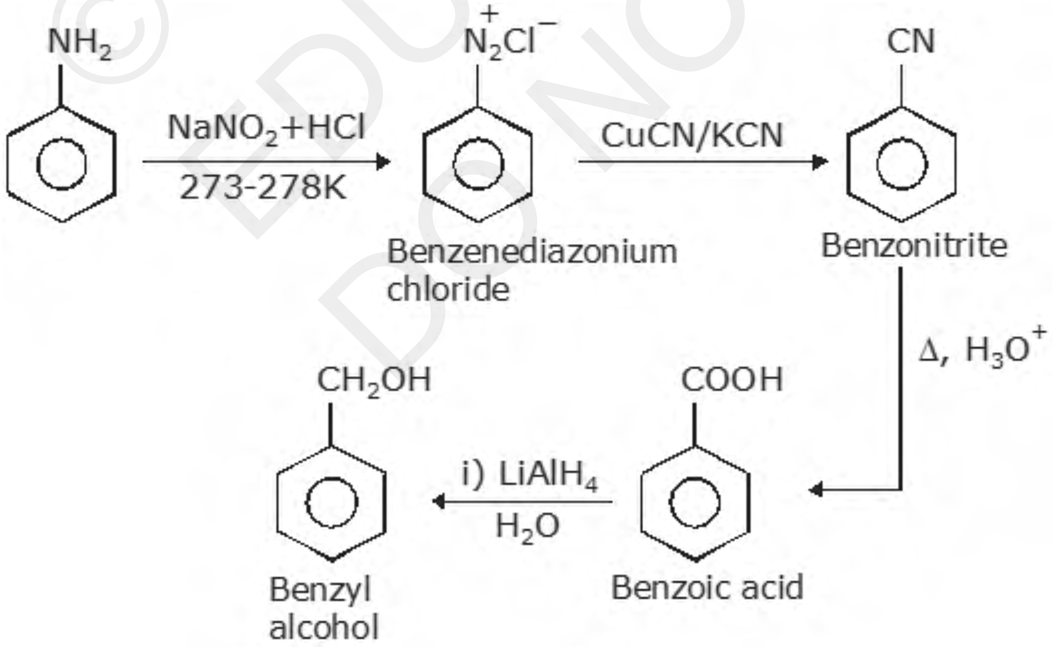


Q. 8 I

Accomplish the following conversions: Aniline to benzyl alcohol.

Answer:

Aniline reacts with sodium nitrite following by substitution reaction with KCN, by acid hydrolysis gives benzoic acid which upon treatment with reducing agent gives benzyl alcohol.



© PRAADIS EDUCATION DO NOT COPY

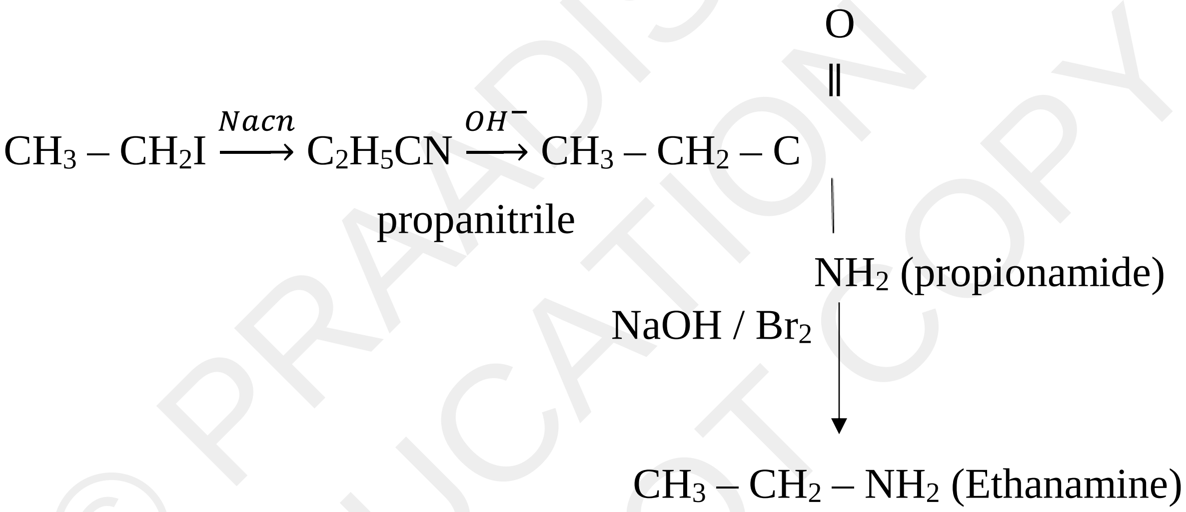
Q. 9 A

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

$$\mathrm{CH3CH2l} \xrightarrow{NaCN} \mathrm{A} \xrightarrow[Partial\ hydrolysis]{OH^-} \mathrm{B} \xrightarrow{NaOH+Br_2} \mathrm{C}$$

Answer:

Ethyl iodide reacts with NaCN gives a substitution reaction to give propanitrile upon partial hydrolysis gives B, upon reaction with sodium hydroxide gives C.



$$CH_3 - CH_2I \xrightarrow{Nacn} \underset{\text{propanitrile}}{C_2H_5CN} \xrightarrow{OH^-} CH_3 - CH_2 - \overset{\overset{O}{\|}}{\underset{\underset{NH_2}{|}}{C}}\ \text{(propionamide)}$$

$$\xrightarrow{NaOH / Br_2} CH_3 - CH_2 - NH_2\ \text{(Ethanamine)}$$

Q. 9 B

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

$$C_6H_5N_2Cl \xrightarrow{CuCN} \mathrm{A} \xrightarrow{\frac{H_2O}{H^+}} \mathrm{B} \xrightarrow[\Delta]{NH_3} \mathrm{C}$$

Answer:

Benzenediazoniumchloride gives nucleophilic substitution reactions gives A, upon hydrolysis the CN ion is replaced by OH ion which is less good leaving group gives B upon heating with ammonia gives C.

© PRADIS EDUCATION DO NOT COPY

$$C_6H_5N_2Cl \xrightarrow{CuCN} C_6H_5CN \xrightarrow{H_2O/H^+} C_6H_5COH$$

Cyanobenzene (A) Benzoic acid (B)

$$\Delta \Big\downarrow NH_3$$

$$C_6H_5CONH_2$$

Benzamide (C)

Q. 9 C

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

$$CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow{HNO_2} C$$

Answer:

Ethyl bromide gives nucleophilic substitution reactions gives B, upon reduction gives B followed by reacting with nitrous acid, i.e. oxidation gives propanol.

$$CH_3CH_2Br \xrightarrow{KCN} CH_3CH_2CN \xrightarrow{LiAlH_4} CH_3CH_2CH_2NH_2$$

Cyanoethane propanamine

$$\Big\downarrow HNO_2$$

$$CH_3CH_2CH_2OH$$

Propanol

Q. 9 D

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

$$C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{NaNO_2+HCl} B \xrightarrow{H_2O/H^+} C$$

© PRADIS EDUCATION DO NOT COPY

Answer:

Nitrobenzene upon reduction with iron/acid gives A, reacting with sodium nitrite gives benzenediazonium chloride, followed by complete Hydrolysis gives phenol.

$$\begin{tikzcd}
C_6H_5NO_2 \arrow[r, "Fe/HCl"] & C_6H_5NH_2 \arrow[r, "NaNO_2+HCl", "273\ K"'] & C6H5 - N_2^+Cl^- \arrow[d, "H_2O/\ H^+", "\Delta"'] \\
 & & C_6H_5OH
\end{tikzcd}$$

Aniline Benzene diazonium chloride

Phenol

Q. 9 E

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

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

Answer:

Acetic acid upon heating with ammonia gives A, which is an amide. This amide reacts with NaOBr which extracts the carbonyl carbon giving B, followed by reacting with sodium nitrite gives methanol.

© PRAADIS EDUCATION DO NOT COPY

$$\begin{tikzcd} CH_3COOH \arrow[r, "NH_3", "\Delta"'] & CH3CONH2 \arrow[r, "NaOBr"] & CH_3NH_2 \arrow[d, "NaNO_2 / HCl"] \\ & & CH_3OH \end{tikzcd}$$

Ethanamide Methanamine

Methanol

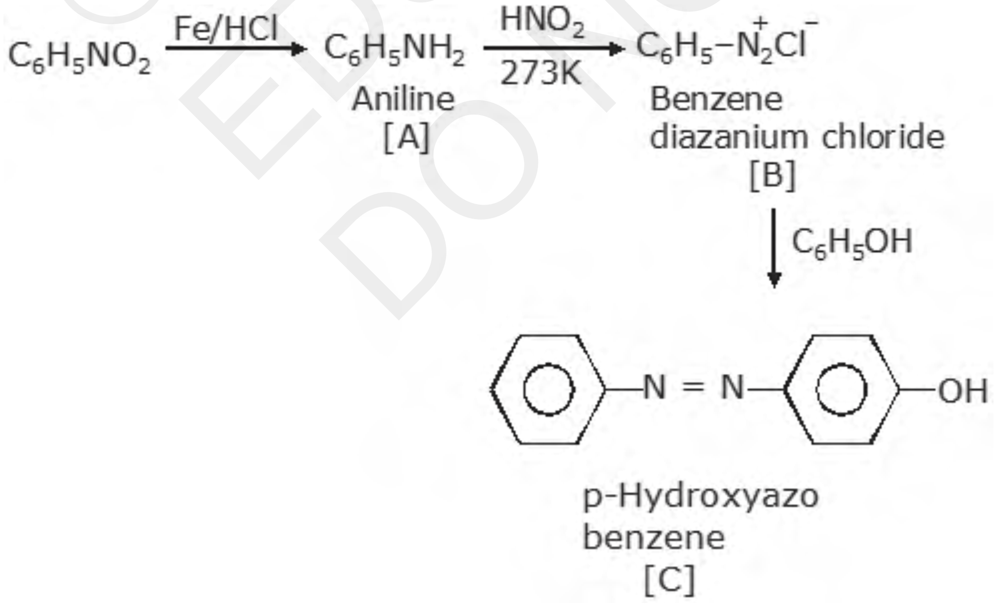
Q. 9 F

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

$$C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\ K]{HNO_2} B \xrightarrow{C_2H_5OH} C$$

Answer:

Nitrobenzene upon reduction with iron/acid mixture gives A, followed by oxidation with nitrous acid gives B and reacting with phenol undergoes addition reaction to give C.

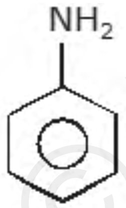


© PRADIS EDUCATION DO NOT COPY

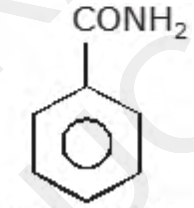
Q. 10 An aromatic compound ‘A’ on treatment with aqueous ammonia and heating forms compound ‘B’ which on heating with Br_2 and KOH forms a compound ‘C’ of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

Answer :

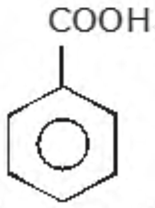
It is given that compound 'C' having the molecular formula, C_6H_7N is formed by heating compound 'B' with $Br_2$and KOH. This is a Hoffmann bromamide degradation reaction (in which isicyanide compound is formed). Therefore, compound 'B' is an amide and compound 'C' is an amine. The only amine having the molecular formula, C_6H_7N is aniline, Therefore, compound 'B' (from which 'C' is formed) must be benzamide, Further, benzamide is formed by heating compound 'A' with aqueous ammonia. Therefore, compound 'A' must be benzoic acid. The given reactions can be explained with the help of the following equations:



[A]

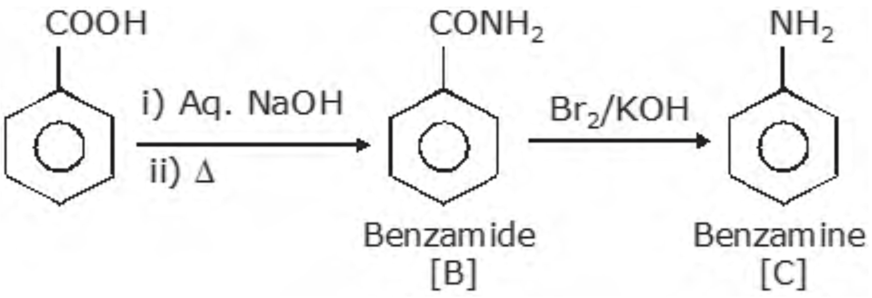


Benzamide
[B]



Benzoic acid

© PRADIS EDUCATION DO NOT COPY



Q. 11 A→

Complete the following reactions: $C_6H_5NH_2 + CHCl_3 + alc.KOH \rightarrow$

Answer:

It is a carbylamine reaction in which a isocyanide compound is form along with side products of potassium chloride. Basically the name of reaction is given is due to formation of a foul smelling compound called as isocyanide.

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

Phenyl – isocyanide

Q. 11 B

Complete the following reactions: $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$

Answer:

Benzenediazonium chloride is a very reactive compound which oxidizes hypophosphorous acid to hypophosphoric acid and the reactant is reduced to benzene.

$$C_6H_5N2Cl + H_3PO_2 + H_2O \longrightarrow C_6H_5 + N_2 + H_3PO_3 + HCl$$

Benzenediazonium chloride

Q. 11 C

Complete the following reactions: $C_6H_5NH_2 + H_2SO_4(conc.) \rightarrow$

© PRAADIS EDUCATION DO NOT COPY

Answer:

aniline undergoes sulphonation to anillium hydrogensulphate.

$C_6H_5NH_2$ + conc. → $C_6H_5NH^+3SO^-{}_4$

Anillium hydrogen sulphate

Q. 11 D

Complete the following reactions: $C_6H_5N_2Cl + C_2H_5OH \rightarrow$

Answer:

aniline is very activating group which undergoes reaction to give ortho and para product. But in acidic medium aniline acquires positive charge on N atom which is misdirecting group and hence the product.

$$C_6H_5N_2Cl + C_2H_5OH \longrightarrow C_6H_5 + CH_3CHO + N_2 + HCl$$

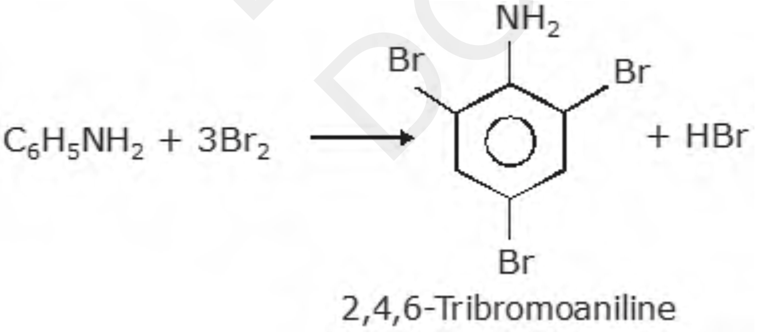
Benzene

Q. 11 E

Complete the following reactions: $C_6H_5NH_2 + Br_2(aq) \rightarrow$

Answer:

It is clubbing reaction of a very reactive compound undergoing addition to give benzene.



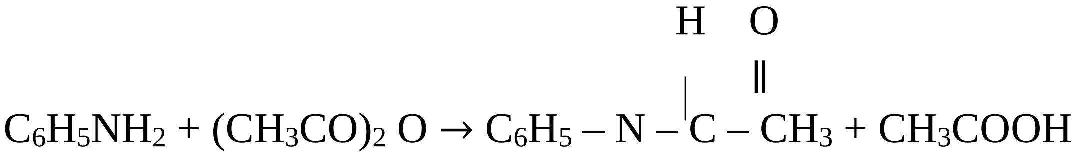
Q. 11 F

© PRADIS EDUCATION DO NOT COPY

Complete the following reactions: $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow$

Answer:

As mentioned aniline is very activating group, so to reduce its activity it is reacted with anhydride to give n-phenylethanamine.



$$C_6H_5NH_2 + (CH_3CO)_2\,O \rightarrow C_6H_5 - \overset{\overset{H}{|}}{N} - \overset{\overset{O}{\|}}{C} - CH_3 + CH_3COOH$$

Acetic Anhydride

N – phenyl ethanamide

Q. 11 G

Complete the following reactions:

$$C_6H_5N_2Cl \xrightarrow[(ii)NaO_2/Cu\Delta]{(i)HBF_4}$$

Answer:

Hydrofluroburic acid reacts with benzenediazonium chloride along with sodium nitrite to give a reduced product as Nitrobenzene.

$$C_6H_5N_2Cl \xrightarrow[(ii)NaNO_2/HCl]{(i)HBF_4} C_6H_5NO_2 + N_2 + NaBF_4$$

Nitrobenzene

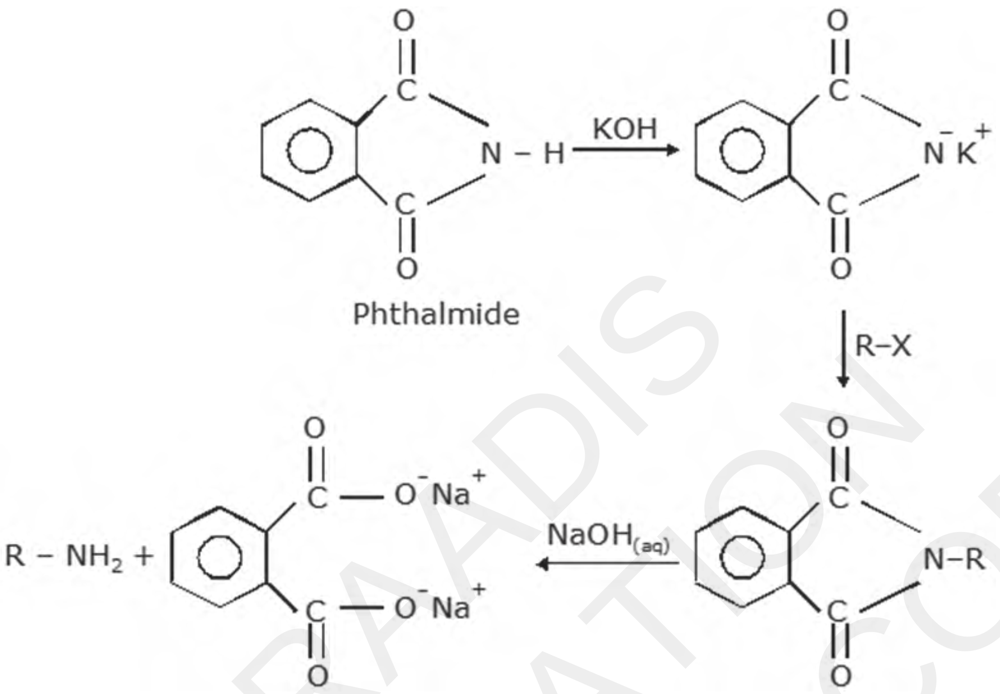
Q. 12 Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

Answer:

Gabrielphthalimide synthesis is used for the preparation of aliphatic primary amines. It involves nucleophilic substitution (SN2) of alkyl halides by the anion formed by the phthalimide. But aryl halides do not undergo nucleophilic substitution with the anion formed by the phthalimide.

© PRADIS EDUCATION DO NOT COPY

Therefore, aromatic primary amines cannot be formed by gabriel phthalimide process.

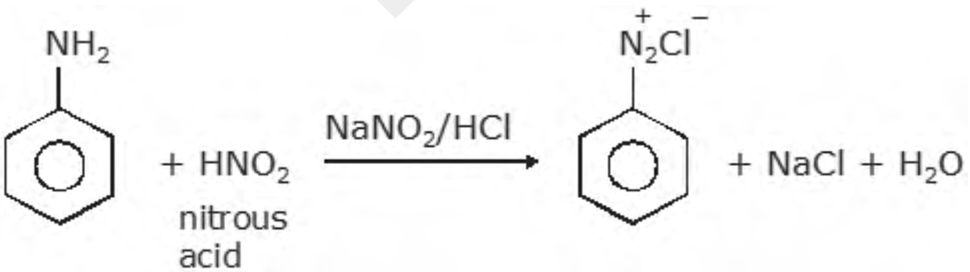


© PRAADIS EDUCATION DO NOT COPY

Q. 13 Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.

Answer:

(i) Aromatic amines react with nitrous acid (prepared in situ from$NaNO_2$ and a mineral acid such as HCl) at 273 - 278 K to form stable aromatic diazonium salts i.e., NaCl and water. This reaction is widely used for preparation of variety of compounds.



(ii) Aliphatic primary amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) to form unstable aliphatic diazonium salts, which is very reactive, which further produce alcohol and HCl with the evolution of nitrogen gas.

$$R - NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [R - N_2^+ Cl\text{-}]$$

Aliphatic Nitrous Aliphatic

Primary acid diazonium salt

Alcohol

$$\downarrow H_2O$$

$$N_2 \uparrow + HCl + ROH$$

Alcohol

Q. 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?

Answer:

i) Amines undergo protonation to give amide ion.

$R\text{-}NH_2$ --> R-NH + H^+

Similarly, alcohol loses a proton to give alkoxide ion.

R-OH --> R-O + H

© PRAADIS EDUCATION DO NOT COPY

In an amide ion, the negative charge is on the N-atom whereas, an alkoxide ion, the negative charge is on the O-atom. Since O is more electronegative than N, O can accommodate the negative charge more easily than N. As a result, the amide ion is less stable than the alkoxide ion. Hence, amines are less acidic than alcohols of comparable molecular masses.

ii) In a molecule of a tertiary amine, there are no H−atoms whereas, in primary amines, two hydrogen atoms are present. Due to the presence of H−atoms, primary amines undergo extensive intermolecular H−bonding.

As a result, extra energy is required to separate the molecules of primary amines. Hence, primary amines have higher boiling points than tertiary amines.

iii)Due to the −R effect of the benzene ring, the electrons on the N- atom are less available in case of aromatic amines. Therefore, the electrons on the N-atom in aromatic amines cannot be donated easily. This explains why aliphatic amines are stronger bases than aromatic amines.

© PRADIS EDUCATION DO NOT COPY