

**CHEMISTRY**

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**BIOLOGY**

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**ADVANTAGE KOTA**

11 - 12 SCI

IIT - JEE

GUJCET

GSEB

CBSE

Eng - Med / Guj - Med

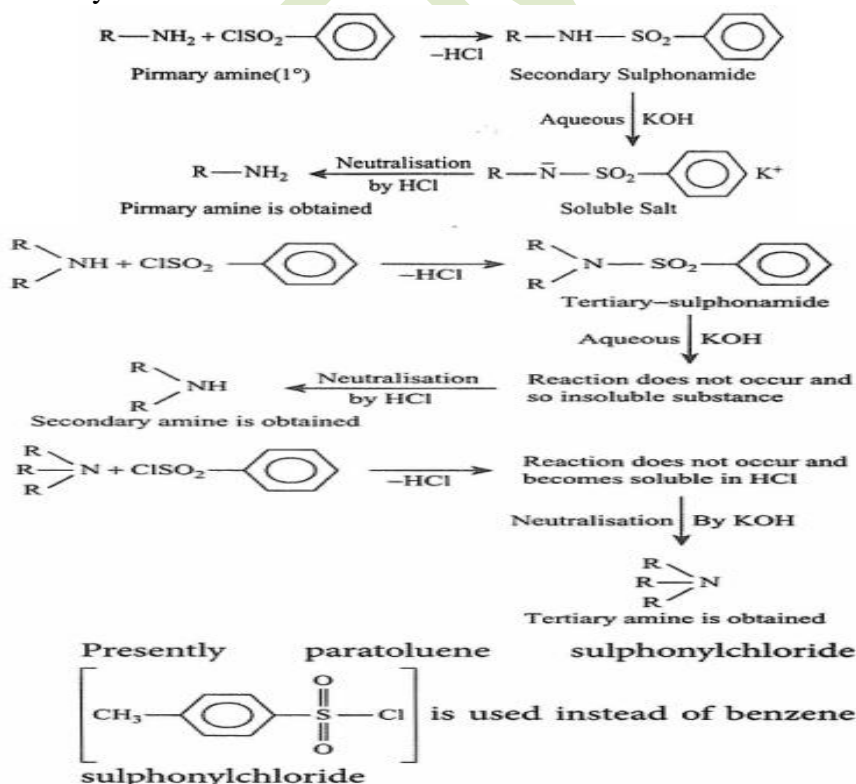
**\*(1) Explain separation of 1°, 2° and 3° amines.**

**Sol:** Separation of primary, secondary and tertiary amines: Benzene sulphonyl chloride or



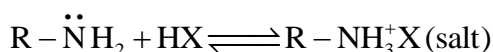
In the mixture of primary, secondary and tertiary alkyl (aliphatic) and aryl (aromatic) amines, if benzene sulphonyl chloride is added, then by the chemical reaction of primary and secondary amine, secondary sulphonamide and tertiary sulphonamide are formed respectively; while tertiary amine does not react. To this mixture when dilute hydrochloric acid (HCl) is added the unreacted tertiary amines become soluble and the secondary sulphonamide being insoluble in acid are obtained as residue by filtration. By neutralization of filtrate, tertiary amine is separated.

In the residue of secondary and tertiary sulphonamide, aqueous solution of potassium hydroxide (KOH) is added so that secondary sulphonamide becomes soluble. This reaction mixture is filtrated and by neutralization of the filtrate with acid, primary amine and secondary amine from residue gets separated by neutralization.

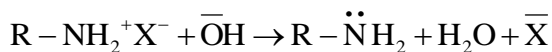


(2) **Explain basicity of aliphatic amines.**

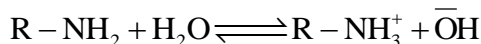
**Sol:** (1) Basic characteristic of amine compounds: In amine compounds, the nitrogen atom has a nonbonding electron pair, so amine compound behave as Lewis base. As amine compounds possess basic property, they reacts with acid and form salt.



These amine salts are soluble in water but insoluble in organic (nonpolar) solvents like ether. By reaction of amine salts with base like NaOH, the original amine compound is obtained back.



The strength of amine as base can be explained easily as follows according to  $K_b$  or  $pK_b$  values.



$$K = \frac{[\text{R}-\text{NH}_3^+][\overline{\text{OH}}]}{[\text{R}-\text{NH}_2][\text{H}_2\text{O}]}$$

$$K(\text{H}_2\text{O}) = \frac{[\text{R}-\text{NH}_3^+][\overline{\text{OH}}]}{[\text{R}-\text{NH}_2]}$$

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

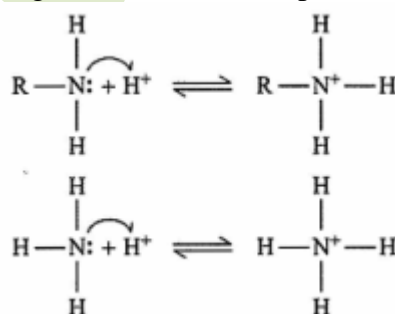
or  $pK_b = -\log K_b$

Higher the value of  $K_b$  (or lower the value of  $pK_b$ ) shows more basicity of amine. For ammonia the value of  $pK_b$  is 4.75. The values of  $pK_b$  of aliphatic amines are between 3 to 4.22 and so they are stronger base than ammonia; while the values of  $pK_b$  of aromatic amines are higher than 4.22 and so they are weak base.

The basicity of amines is related with their structures. The basicity of amine depends on the tendency to form positive ion easily by receiving proton from acid. If the corresponding positive ion of amine is more stable then, amine is more basic.

**(a) Basicity of aliphatic amine (alkanamine):**

(i) Comparison of alkanamine with ammonia: The basicity of alkanamine and ammonia are compared by taking into considering their reaction with proton  $[\text{H}^+]$



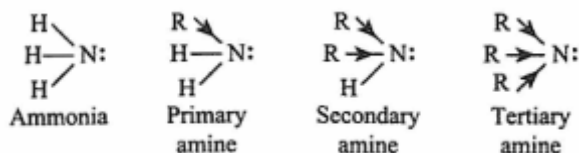
Because of the electron donating property of alkyl group, in alkanamine, alkyl group produces +1 effect

(You have studied +1 effect in semester 1).

Hence, in alkanamine the non-bonding electron pair is easily available for sharing with proton. In addition, they attain stability because of +1 effect of alkyl group, the displaced ammonium ion formed from amine by, spreading of positive charge. Hence, alkanamine are stronger base than ammonia.

**(ii) Comparison of primary, secondary and tertiary alkanamine:**

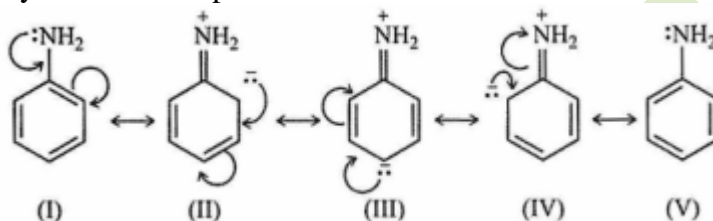
Going from tertiary amine to primary amine, the +1 effect of alkyl group is decreasing because of these groups attached with nitrogen atom in primary, secondary and tertiary amines having one, two and three alkyl groups are attached respectively.



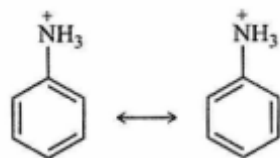
Alkyl group is electron releasing group and so it sends the electrons of bond towards N. Thus the electron density of N atom increases. As there are more number of alkyl groups in tertiary amine, N atom will have more electron density in the compound. So such compounds can easily donate electron pair. Hence, the order of basicity of ammonia, primary amine, secondary amine and tertiary amine in gaseous phase is Tertiary amine > secondary amine > primary amine > ammonia.

(3) **Explain basicity of aromatic amines.**

**Sol:** (i) The basicity of aryl amine is less than that of ammonia because of the resonance of aniline as follows: the non-bonding electron pair on N delocalises on benzene ring. Hence, the non-bonding electron pair is not easily available for protonation on N.



Also, the anilinium ion that is obtained by protonation of aniline possesses two resonance structures.



So, the stability of aniline is more than anilinium ion. Hence, the tendency of aniline or aromatic amine to receive proton is less. The resonance structures are not available in ammonia and aliphatic amines compounds, like aniline, so the electron pair on their N atom is localized. Hence, these compounds can easily donate electron pairs so that their basicity is more than that of aniline. As discussed in the earlier points, keeping in mind the order of basicity of amine compounds can be written as follows:

Tertiary amine > secondary amine > primary amine > ammonia > aniline

(ii) In the case of substituted aniline, it is found that because of the presence of electron donating groups like  $-OCH_3$ ,  $-CH_3$  the strength as base increases. While because of the presence of electron attracting groups like  $-NO$ ,  $-SO_3H$ ,  $-COOH$  its strength as a base decreases.

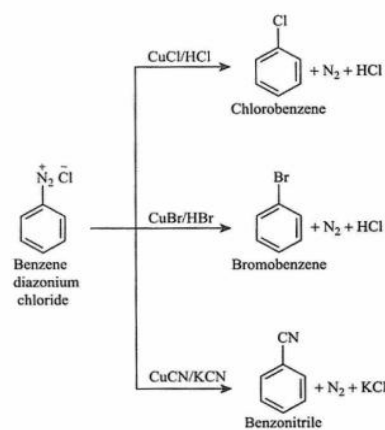
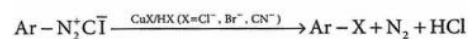
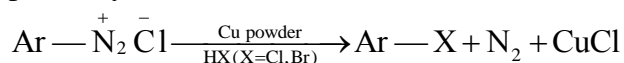
(4) **Explain chemical reaction of benzene diazonium chloride.**

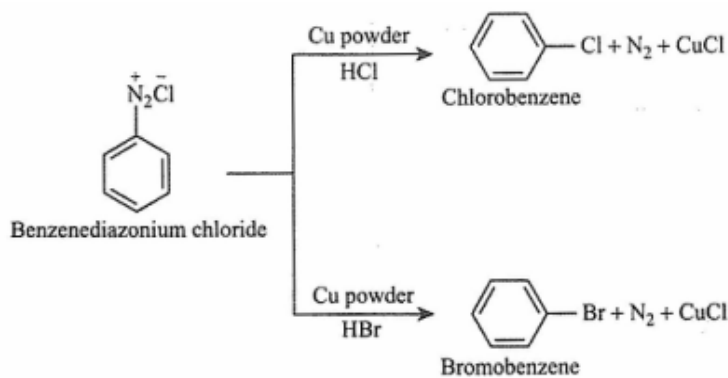
**Sol:** Chemical reactions:

(A) **Displacement of nitrogen:** Diazonium group ( $-N^+ \equiv N^-$ ) can be substituted by groups like  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $CN^-$ ,  $OH^-$  and dinitrogen ( $N_2$ ) is removed in the form of gas because of substitution reaction.

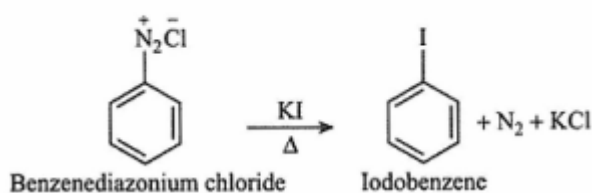
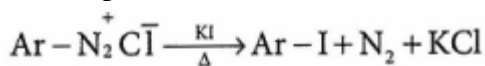
(i) Diazonium salt reacting with cuprous chloride in HCl gives chlorobenzene, with cuprous bromide in HBr gives bromobenzene and with cuprous cyanide in KCN gives benzonitrile (cyanobenzene). These reactions are called Sandmeyer reactions.

(ii) On reaction of diazonium salt in presence of copper powder with HCl or HBr, chlorobenzene or bromobenzene are respectively obtained. This is called Gatterman reaction.



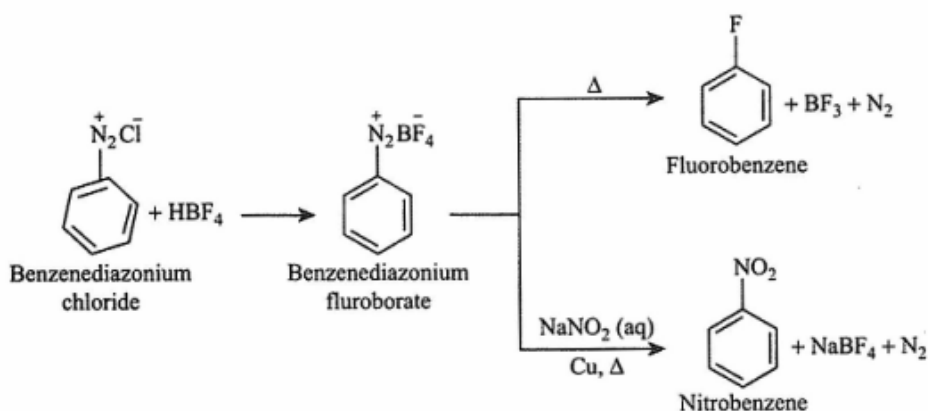
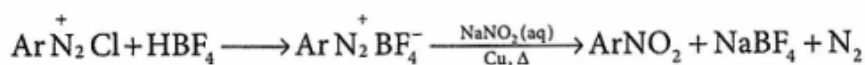
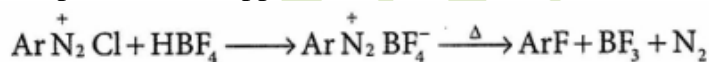


(iii) On heating diazonium salt with potassium iodide, iodobenzene is formed.

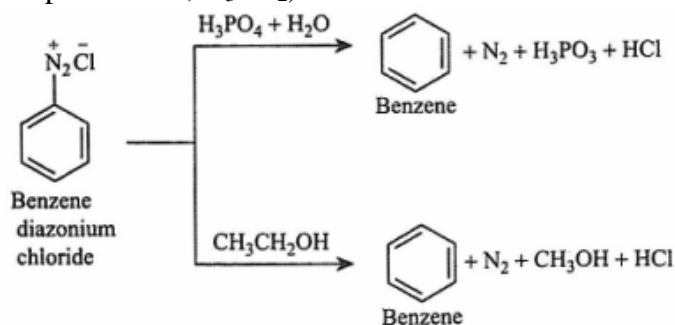


(iv) Precipitates of diazonium fluoroborate are obtained by reaction of diazonium salt with fluoroboric acid (HBF<sub>4</sub>). On heating, it decomposes and gives fluorobenzene.

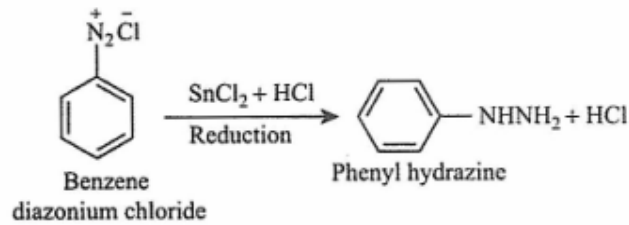
In addition, nitrobenzene is obtained by heating diazonium fluoroborate with aqueous solution of sodium nitrate (NaNO<sub>2</sub>) in presence of copper metal.



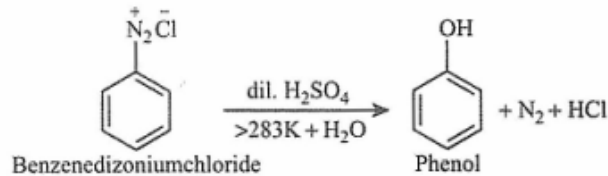
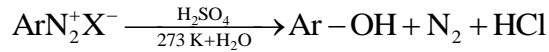
(v) Benzene is obtained by reduction of diazonium salt with weak reducing agent like hypophosphorus acid (phosphinic acid, H<sub>3</sub>PO<sub>2</sub>) or ethanol.



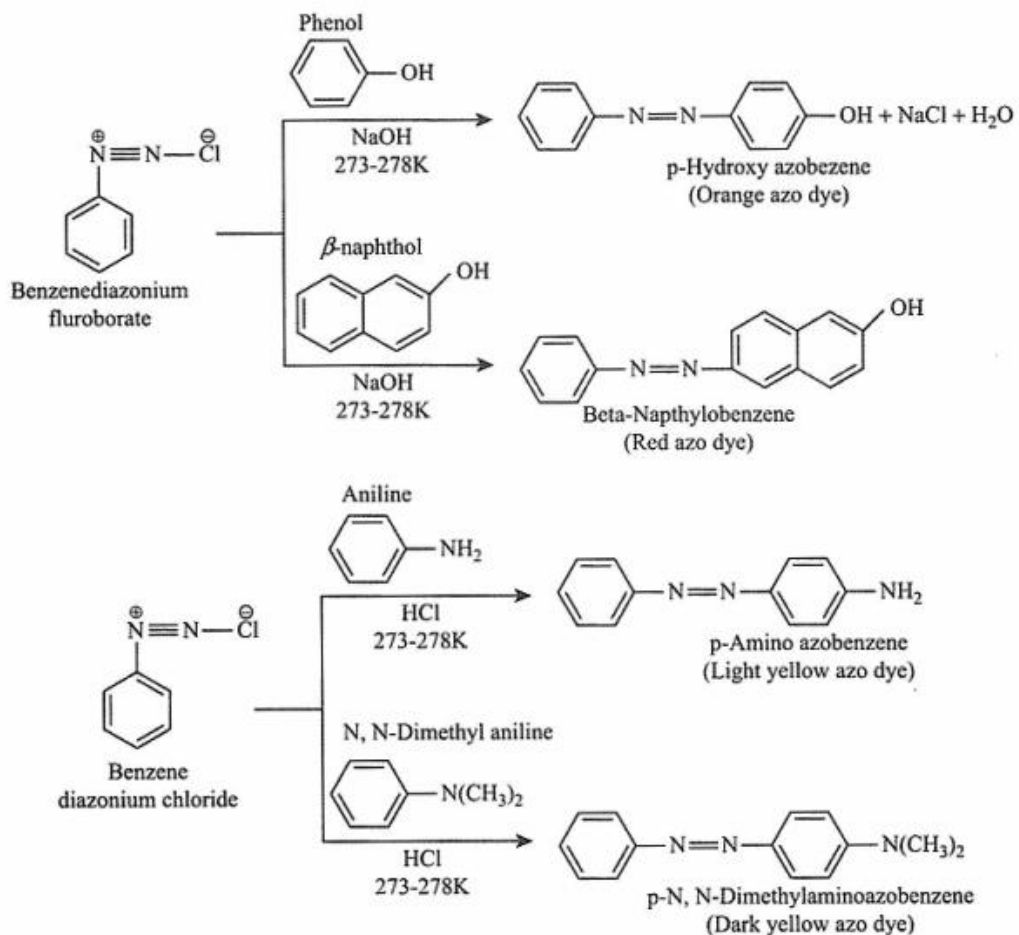
When diazonium salt is reduced with stannous chloride and hydrochloric acid, it gives phenyl hydrazine. (Here diazonium salt is not substituted).



(vi) Phenol is obtained by heating diazonium salt with dil.  $\text{H}_2\text{SO}_4$  at temperature higher than 283 K

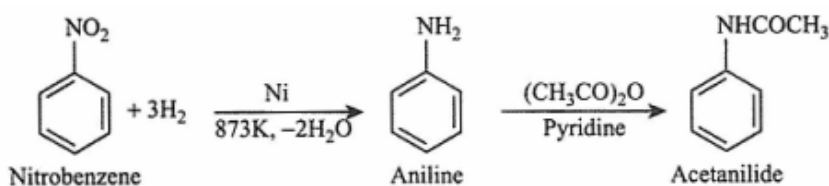


(B) Azo coupling reaction: Solution of phenol or beta naphthol ( $\beta$ -naphthol) in sodium hydroxide when reacts with benzene diazonium chloride at 273–278K temperature, orange and red color azo dyes are obtained. Also, light yellow and dark yellow colored azo dyes are respectively obtained when solutions of aniline or N, N dimethyl aniline in HCl reacts with benzene diazonium chloride.



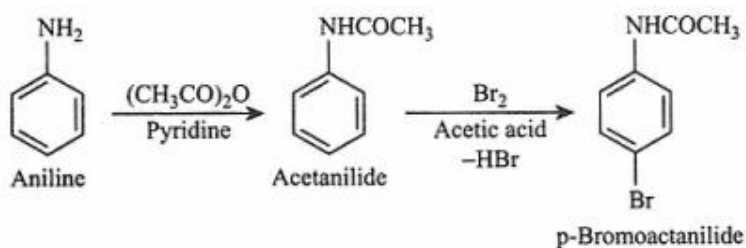
(5) Give the conversions: Acetanilide from nitrobenzene.

**Sol:**



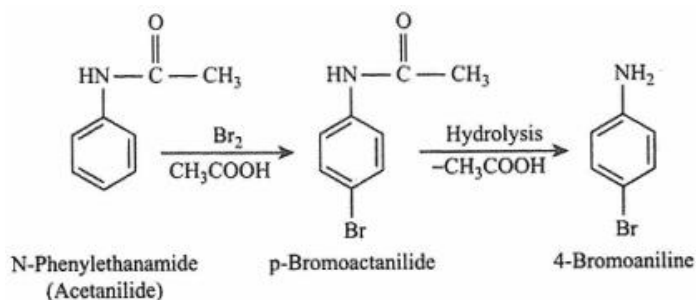
(6) Give the conversions: p-Bromoacetanilide from aniline.

Sol:



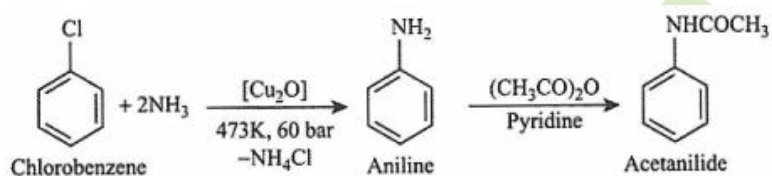
(7) Give the conversions: p-Bromoaniline from acetanilide.

Sol:



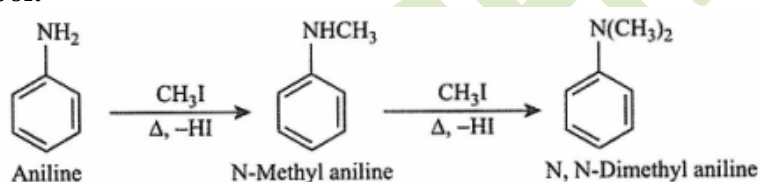
(8) Give the conversions: Acetanilide from chlorobenzene.

Sol:



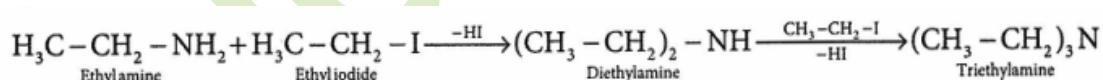
(9) Give the conversions: N, N-Dimethyl aniline from aniline.

Sol:



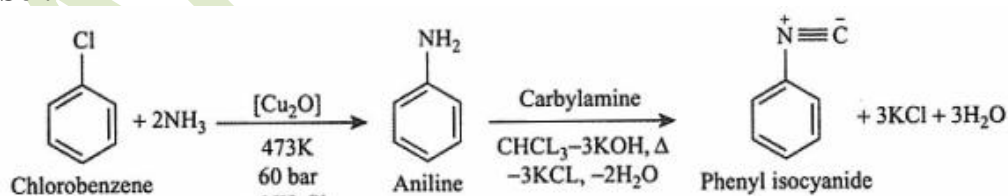
(10) Give the conversions: Triethylamine from ethylamine

Sol:



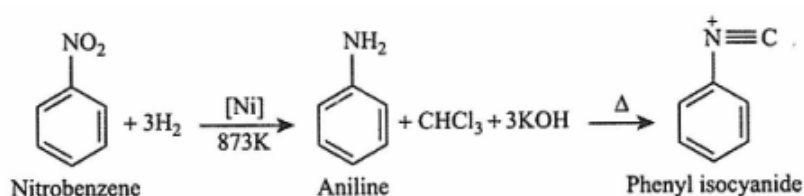
(11) Give the conversions: Phenyl isocyanide from chlorobenzene

Sol:

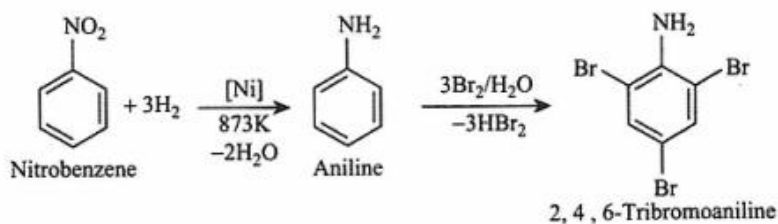


(12) Give the conversions: Phenyl isocyanide from nitrobenzene

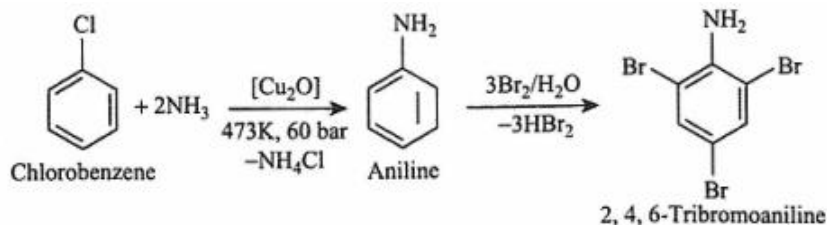
Sol:



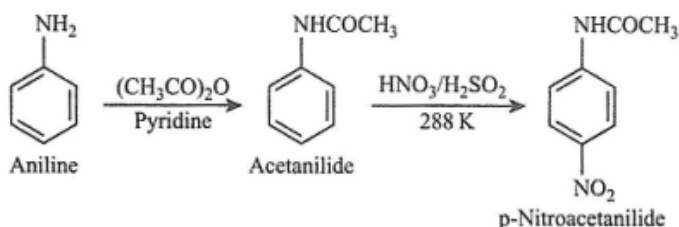
- (13) Give the conversions: 2,4,6-Tribromoaniline from nitrobenzene  
Sol:



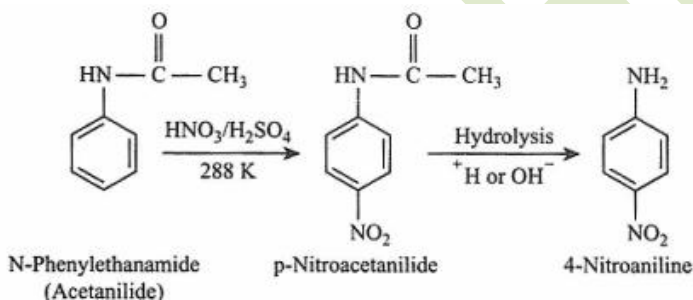
- (14) Give the conversions: 2,4,6-Tribromoaniline from Chlorobenzene  
Sol:



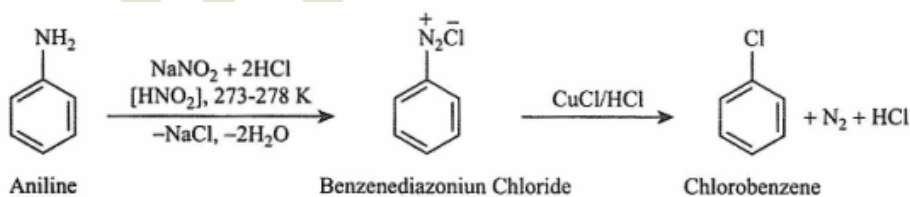
- (15) Give the conversions: p-Nitroacetanilide from aniline.  
Sol:



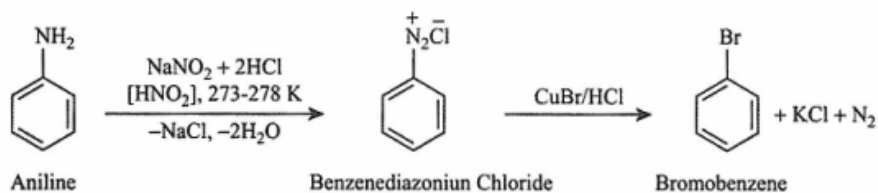
- (16) Give the conversions: 4-Nitroaniline from acetanilide.  
Sol:



- (17) Give the conversions: Chlorobenzene from aniline  
Sol:



- (18) Give the conversions: Bromobenzene from aniline  
Sol:



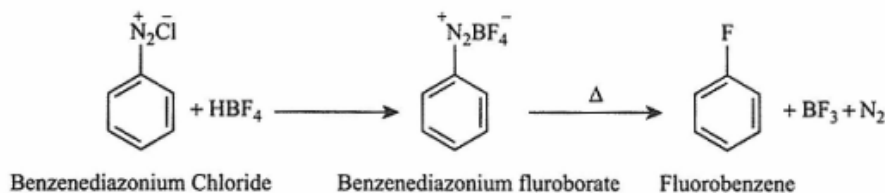
(19) Give the conversions: Benzonitrile from aniline

Sol:



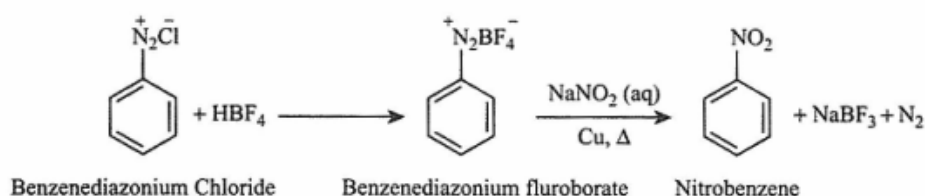
(20) Give the conversions: Fluorobenzene from benzenediazonium chloride.

Sol:



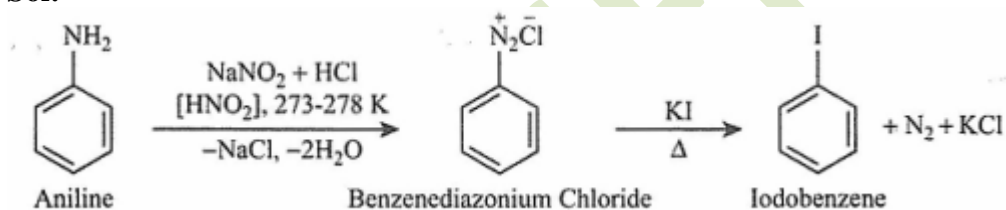
(21) Give the conversions: Nitrobenzene from benzenediazonium chloride.

Sol:



(22) Give the conversions: Iodobenzene from aniline.

Sol:



(23) Give the conversions: Benzene from aniline.

Sol:



(24) Give the conversions: Phenyl hydrazine from aniline.

Sol:



(25) Give the conversions: Phenol from aniline.

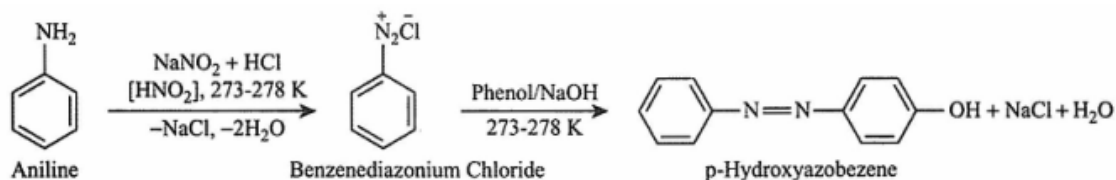
Sol:





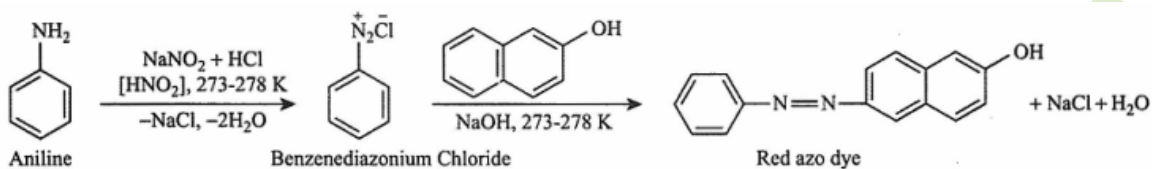
(26) Give the conversions: p-Hydroxyazobenzene from aniline.

**Sol:**



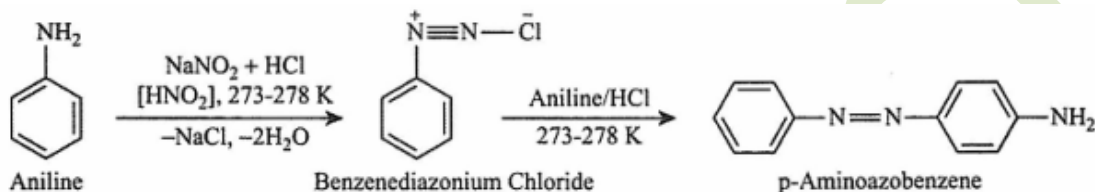
(27) Give the conversions: β-Naphthylazobenzene from aniline.

**Sol:**



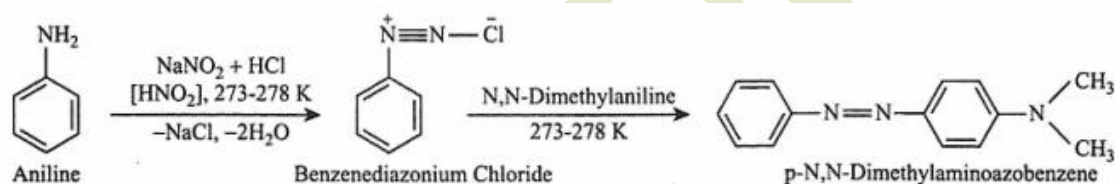
(28) Give the conversions: p-Aminoazobenzene from aniline

**Sol:**



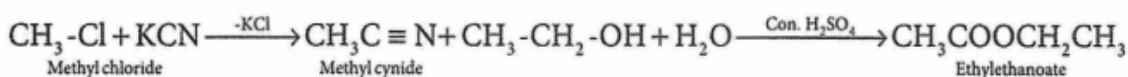
(29) Give the conversions: p-N,N-Dimethylaminobenzene from aniline.

**Sol:**



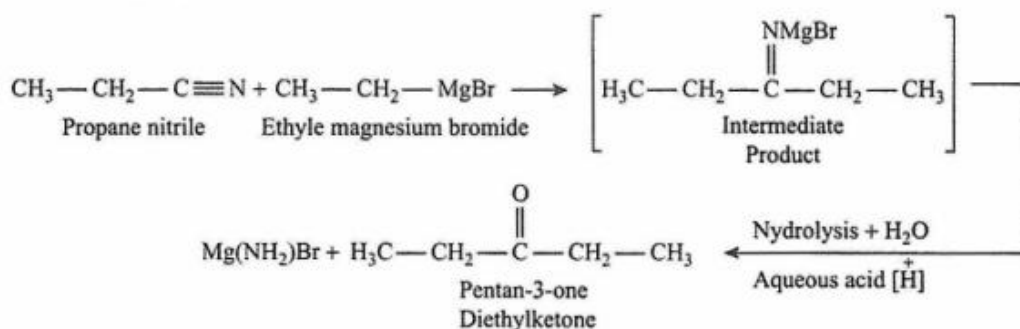
(30) Give the conversions: Ethylethanoate from methyl chloride.

**Sol:**



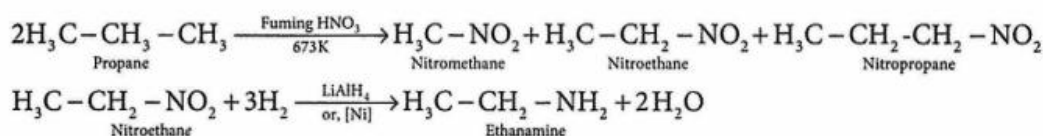
(31) Give the conversions: Pentane-3-one from propane nitrile.

**Sol:**



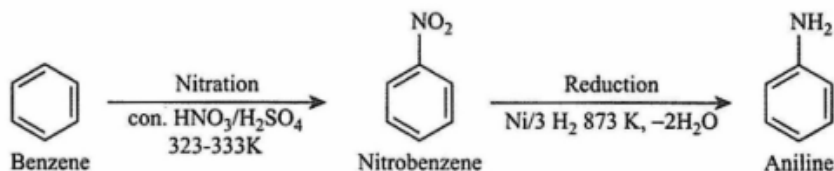
(32) Ethanamine from propane.

**Sol:**

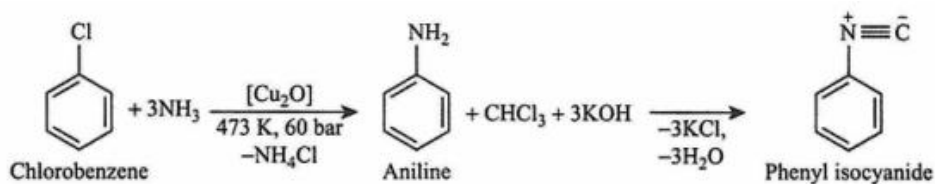


(33) Give the conversions: Aniline from benzene

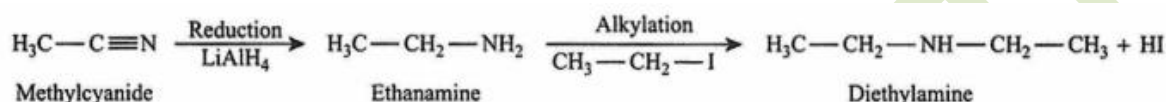
**Sol:**



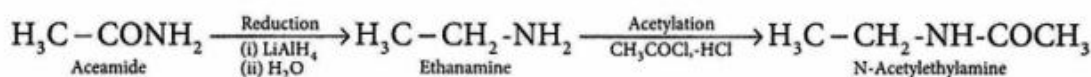
- (34) Give the conversions: Phenyl isocyanide from chlorobenzene  
Sol:



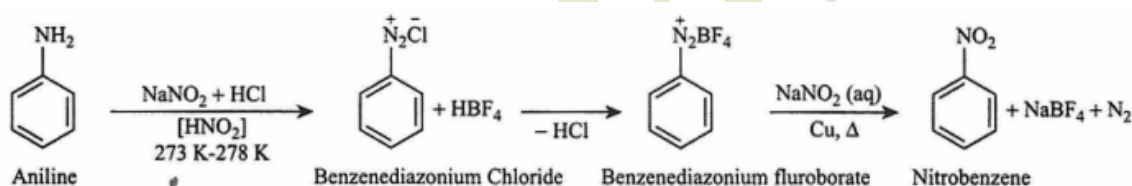
- (35) Give the conversions: Diethylamine from methylcyanide  
Sol:



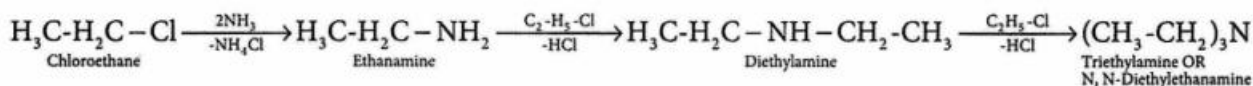
- (36) Give the conversions: N-acetyl ethylamine from acetamide  
Sol:



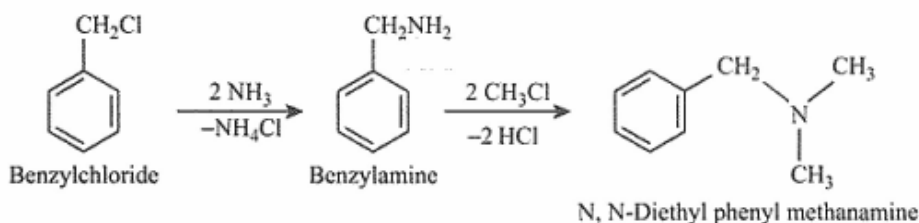
- (37) Give the conversions: Nitrobenzene from aniline  
Sol:



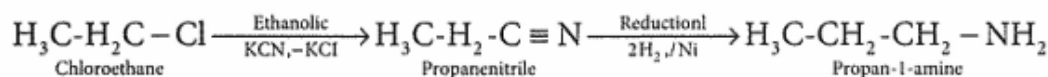
- (38) Give the conversions: N, N-Diethylethanamine from chloroethane  
Sol:



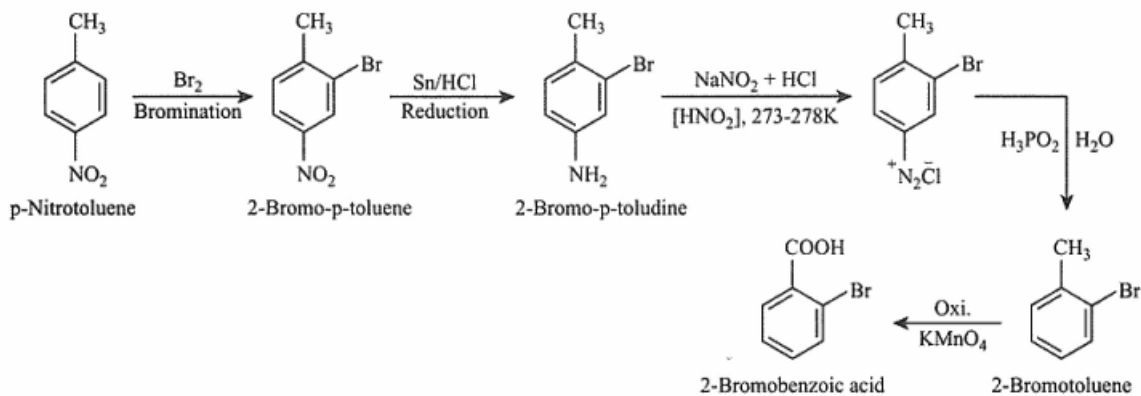
- (39) Give the conversions: N, N-Dimethylphenylmethanamine from benzyl chloride  
Sol:



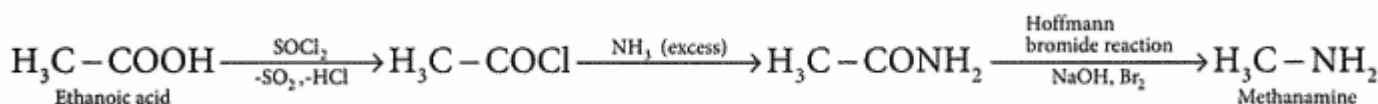
- (40) Give the conversions: Propan-1-amine from chloroethane  
Sol:



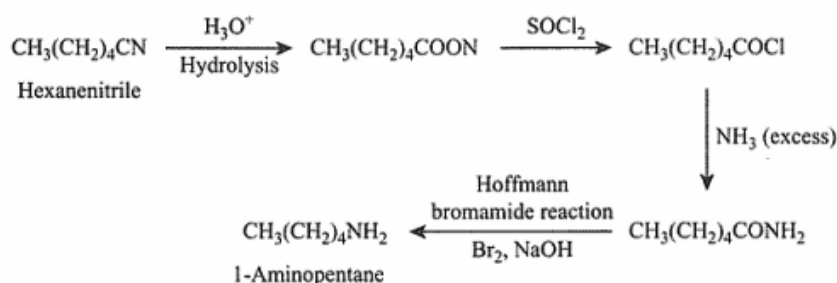
- (41) Give the conversions: 2-Bromobenzoic acid from p-nitrotoluene.  
Sol:



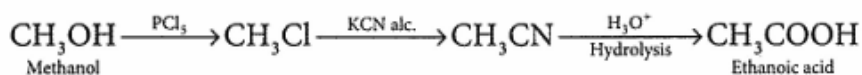
- (42) Give the conversions: Ethanoic acid into Methanamine  
Sol:



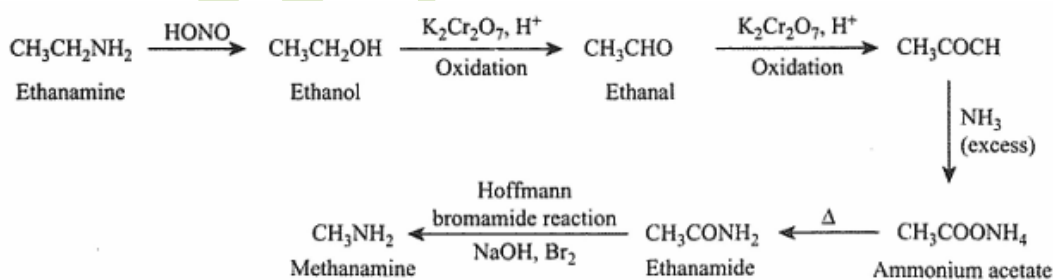
- (43) Give the conversions: Hexanenitrile into 1 aminopentane  
Sol:



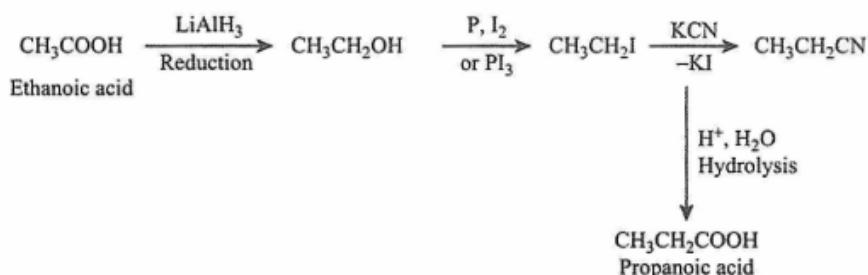
- (44) Give the conversions: Methanol to ethanoic acid  
Sol:



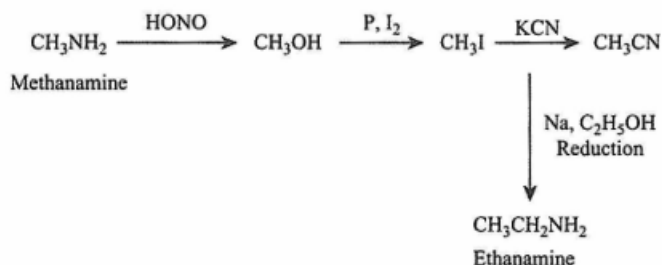
- (45) Give the conversions: Ethanamine into Methanamine  
Sol:



- (46) Give the conversions: Ethanoic acid into propanoic acid  
Sol:

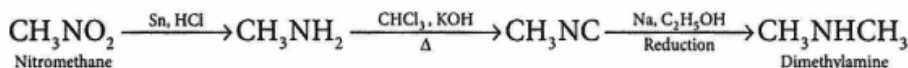


- (47) Give the conversions: Methanamine into ethanamine  
Sol:



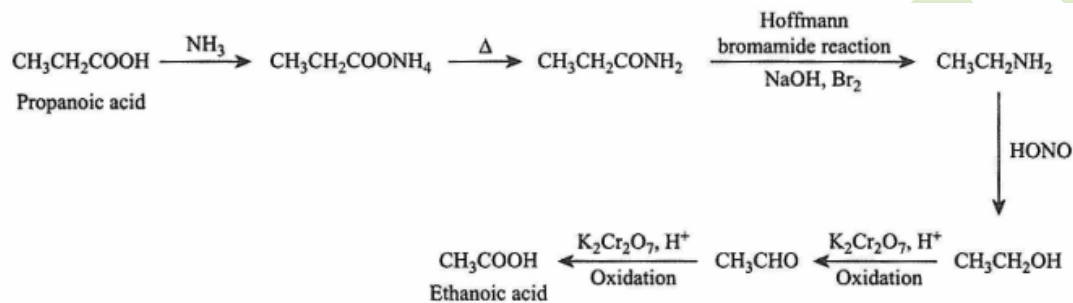
(48) Give the conversions: Nitromethane into dimethylamine

Sol:



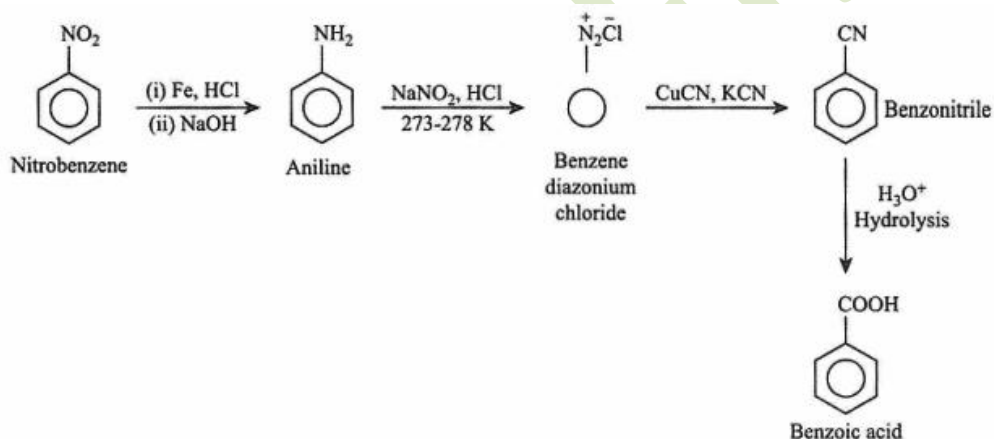
(49) Give the conversions: Propanoic acid into ethanoic acid

Sol:



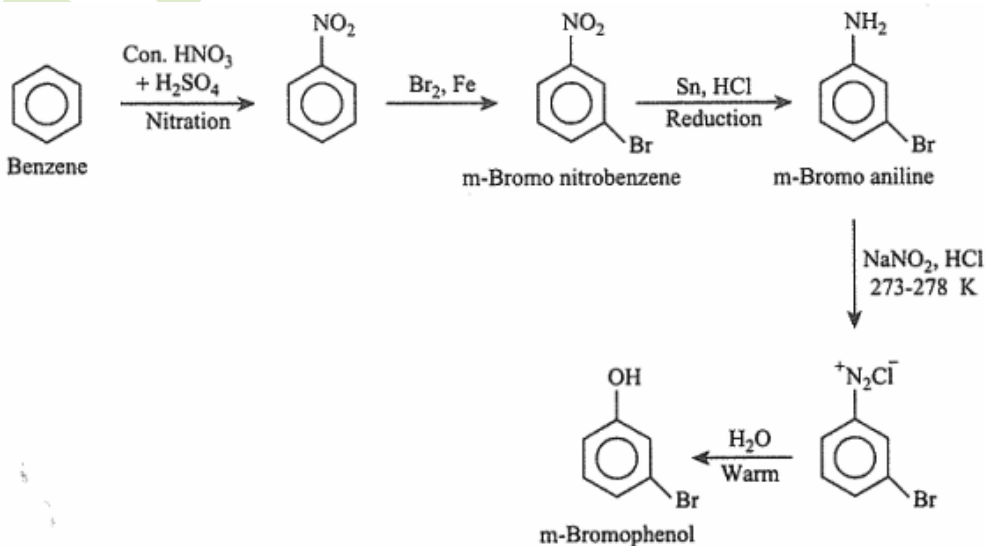
(50) Give the conversions: Nitrobenzene to benzoic acid.

Sol:



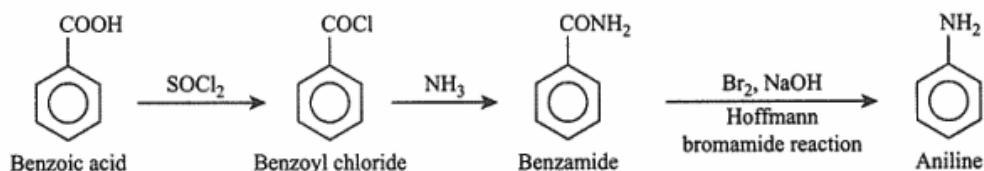
(51) Give the conversions: Benzene to m-bromophenol

Sol:



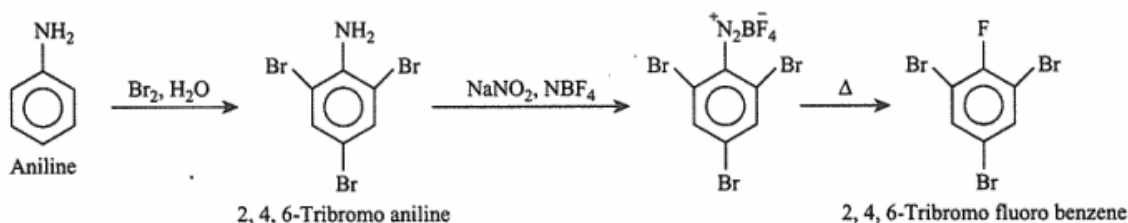
(52) Give the conversions: Benzoic acid to aniline

Sol:



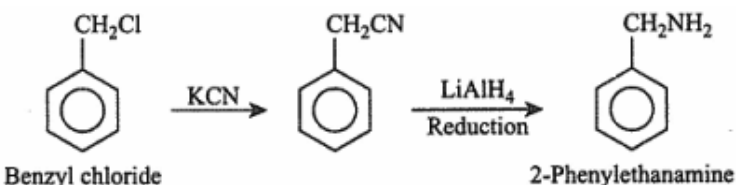
(53) Give the conversions: Aniline to 2,4,6 tribromofluorobenzene

Sol:



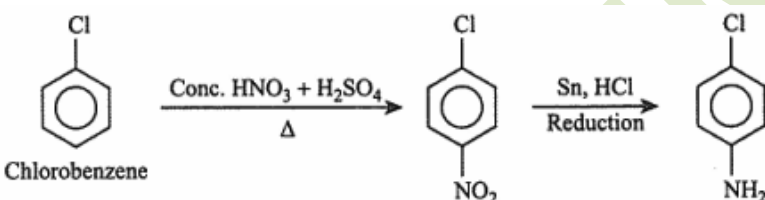
(54) Give the conversions: Benzyl chloride to 2-phenylethanamine

Sol:



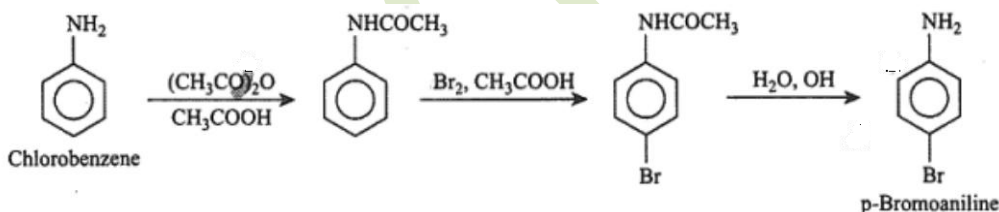
(55) Give the conversions: Chlorobenzene to p-chloroaniline

Sol:



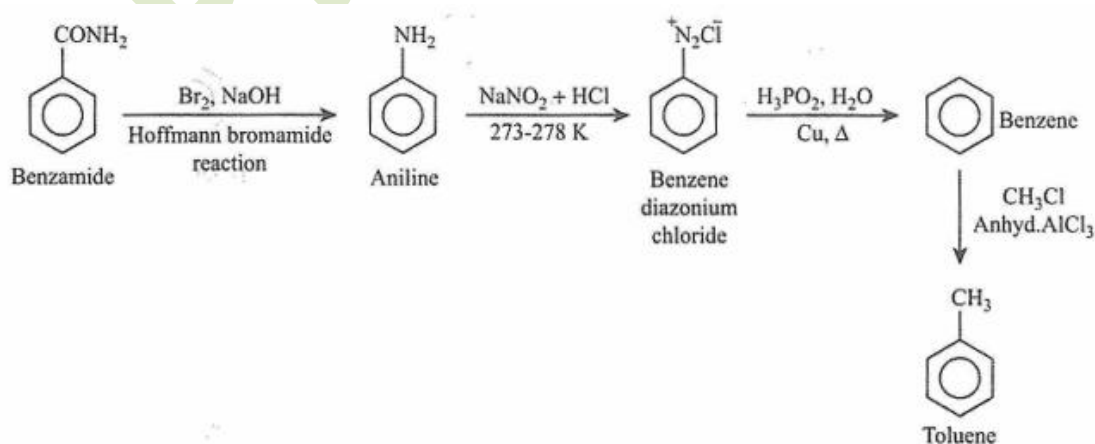
(56) Give the conversions: Aniline to p-bromoaniline

Sol:



(57) Give the conversions: Benzamide to toluene

Sol:

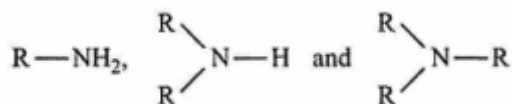


(58) Write classification of amines giving examples.

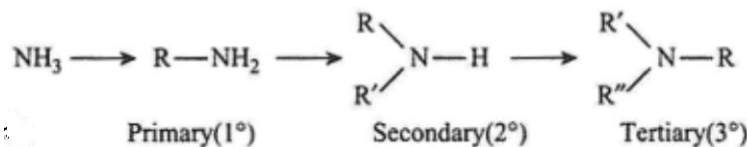
Sol: The classification of amine compounds is made on the basis of alkyl or aryl groups combined with nitrogen of amino group. If alkyl group is attached it is called alkyl amine and if the aryl group is attached it is called aryl amine.

On replacement of hydrogen present in ammonia, if one alkyl group or aryl group is attached with

nitrogen, it is called primary ( $1^\circ$ ) amine, if two groups are attached then secondary ( $2^\circ$ ) and if three groups are joined, then tertiary ( $3^\circ$ ) amine. The general formula of compounds in amino class is shown as:

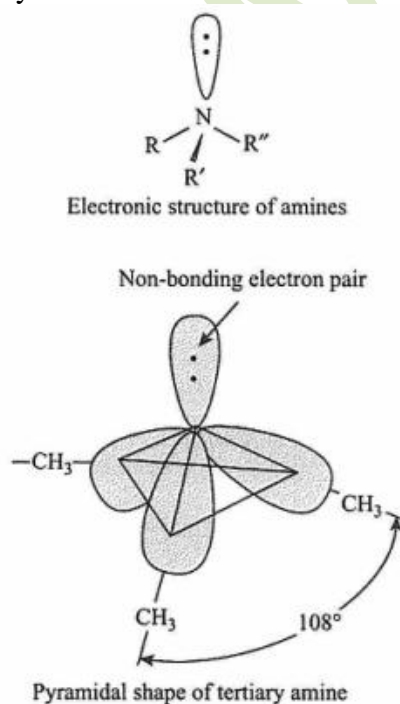


Where R = alkyl or aryl group. If the alkyl or aryl groups in amine compounds are same they are called simple amines and if different groups are there, then they are called mixed amines. Alkyl amines are called aliphatic amines and aryl amines are called aromatic amines.



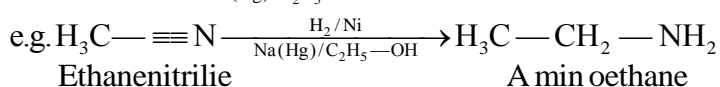
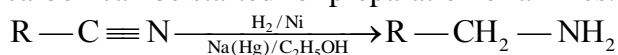
**(59) Write electron configuration of amine (with figure).**

**Sol:** Like ammonia, in amine compounds, nitrogen atom is trivalent and possesses one nonbonding electron pair. Therefore the atomic orbital of nitrogen atom in ammonia compounds possess  $sp^3$  hybridization and the compounds possess pyramidal structure. Each  $sp^3$  hybrid orbit of nitrogen gets overlapped with atomic orbital of carbon and forms amine compounds. The fourth orbital of nitrogen possesses nonbonding electron pair. Because of the presence of nonbonding electron pairs, C–N–R (Where R is H or C) bond angle decreases slightly from  $109^\circ 28'$ . As shown in the fig. 6.1 the bond angle in trimethyl amine is  $108^\circ$ .



**(60) Explain reduction of nitrile compounds.**

**Sol:** Reduction of nitrile: By reaction of nitrile with lithium aluminium hydride ( $\text{LiAlH}_4$ ) or by catalytic hydrogenation reaction, reduction takes place and primary amine is obtained. This reaction is useful in increasing the number of carbons in the amine series i.e. reaction of amine with one carbon can be started for preparation of amines.

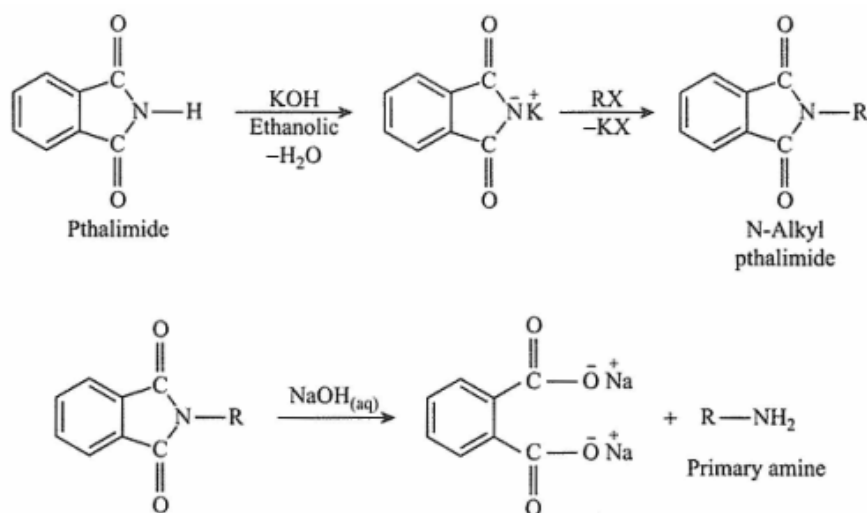


**(61) Write Gabriel Phthalimide synthesis.**

**Sol:** Reaction for the Gabriel Phthalimide synthesis is as under:

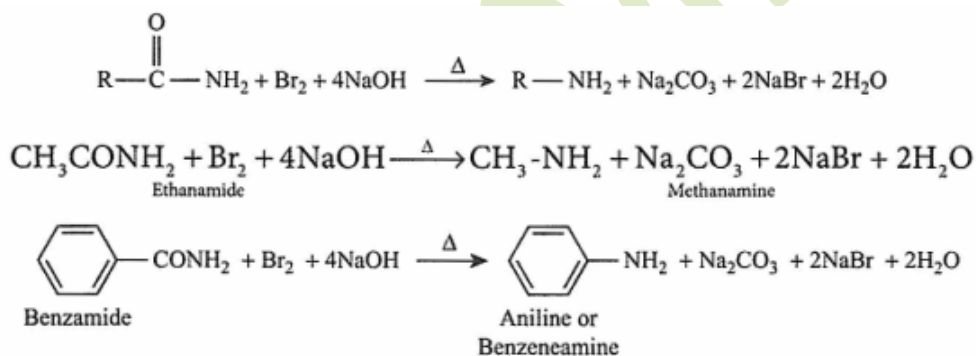
**Gabriel synthesis is used in the preparation of primary amines:** By reaction of phthalimide with ethanolic potassium hydroxide, potassium salts of phthalimide are obtained which are when heated alkyl halide primary amines are obtained by alkaline aromatic hydrolysis. Primary aromatic amine

cannot be prepared by this method because nucleophilic aryl halide, does not become favorable anion for phthalimide.



**(62) Explain Hoffmann reaction with example.**

**Sol:** In Hoffmann reaction to prepare primary amine, the amide is heated with ethanolic solution of sodium hydroxide so that during the decomposition reaction, in place of carbonyl carbon in amide the nitrogen atom migrates to alkyl or aryl group. Primary amine having one carbon less than amide is thus obtained.

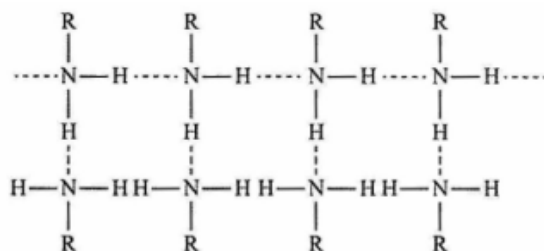


**(63) Explain physical properties of amines.**

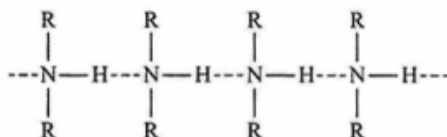
**Sol:** The boiling points of primary amines having same number of carbon atoms containing alkane are higher; also the boiling points increases successively with the increase in number of carbon atoms in primary amine viz, in Methanamine (boiling point 280 K), ethanamine (boiling point 290 K), propanamine (boiling point 322 K) increases successively with the increase in number of carbon atoms. In the isomeric alkyl amines having same molecular formula, the boiling point decrease from primary amine to tertiary amine, viz. (1°) propanamine (boiling point 322 K), (2°) ethylmethyl amine (boiling point 309 K) and (3°) trimethyl amine (boiling point 276 K) boiling points are decreasing.

As the electronegativity of nitrogen is less than that of oxygen, the  $\text{N}^{\delta-} - \text{H}^{\delta+}$  bond in amines is less polar than the  $\text{O}^{\delta-} - \text{H}^{\delta+}$  bond in alcohol. Hence, amine compounds are more polar than alkane but less polar than alcohol. Also, the intermolecular attraction in amine is less than that in alcohol. Hence, the boiling points of amine are higher than those of their corresponding alkanes and lower than those of their corresponding alcohols, viz ethanamine (boiling point 290 K) is more than ethane (boiling point 184 K) but lower than ethanol (boiling point 351 K).

There are intermolecular hydrogen bonds in primary and secondary amines while they are not there in tertiary amine. Hence, in isomeric primary alkyl amines having same molecular formula, it is highest, in secondary amine it is comparatively less and it is least in tertiary amine. Viz. in (1°) propanamine, (2°) ethylmethylamine and (3°) trimethylamine there is decrease in boiling point which is shown in following figure.

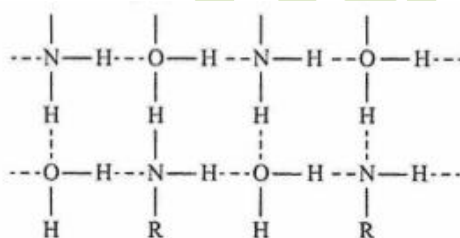


**Intermolecular hydrogen bond between molecules of primary amine**

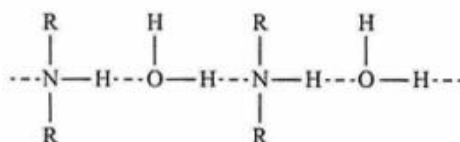


**Intermolecular hydrogen bond between molecules of secondary amine**

In the aqueous solutions of primary and secondary amine compounds, water and amine molecules form hydrogen bonds so the intermolecular attraction increases. In primary amines, there are two hydrogen atoms on nitrogen and in secondary amine one hydrogen atom on nitrogen so the number of hydrogen bonds in primary amine becomes double. Hence, secondary amines corresponding to their primary amines having less molecular mass are less soluble in water as shown in the following figure.



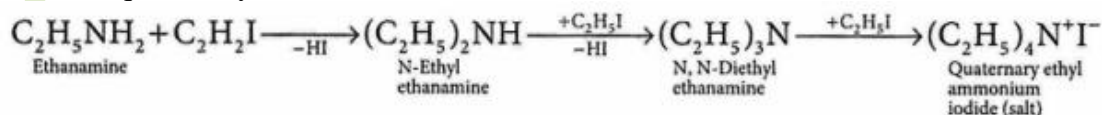
**Intermolecular hydrogen bond between molecules of primary amine and water**



**Intermolecular hydrogen bond between molecules of secondary amine and water**

**(64) Explain alleviation of methanamine and aniline.**

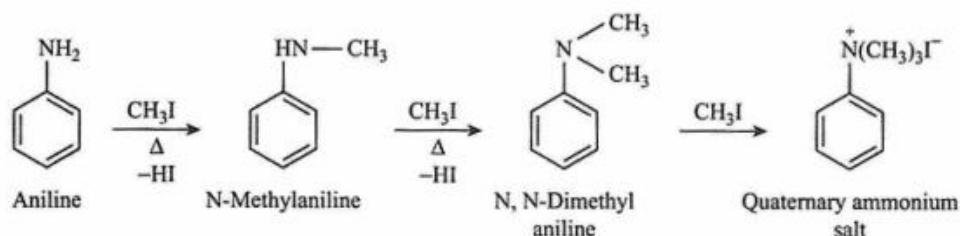
**Sol: Alkylation:** By reaction of aliphatic and aromatic primary ( $1^\circ$ ) amines with alkyl halide, secondary ( $2^\circ$ ) amine is obtained. If it reacts with more amount of alkyl halide, then successively tertiary and then quaternary ammonium salt is obtained.



On reacting ethanamine with ethyl iodide, N-ethylethanamine is obtained. By reacting this product with more amount of ethyl iodide, first N, N-diethylethanamine and then tetramethyl ammonium iodide salt is obtained.

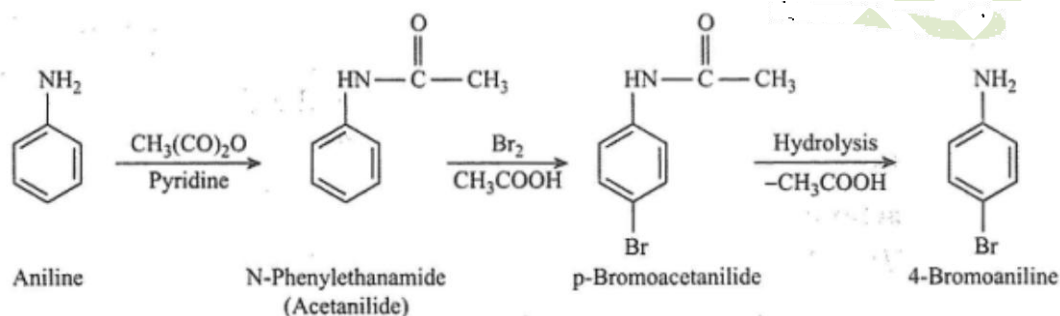
(b) Similarly, on heating aniline with methyl iodide N-Methylaniline is obtained. If methyl iodide is taken in excess proportion then tertiary amine and then quaternary ammonium salt is obtained.





(65) **Explain giving example the reaction to obtain monosubstituted aniline.**

**Sol:** Following two reactions are possible on monosubstituted aniline derivatives i.e. bromination and nitration. If only monosubstituted aniline derivative is desired then first, acetylation of  $-\text{NH}_2$  group with acetic anhydride, (electrophilic substitution) is carried out. At the end of this reaction the amide product is hydrolysed so that monosubstituted aromatic amine is obtained.

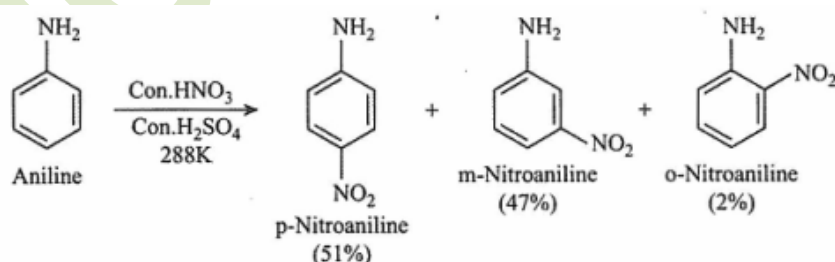


Here also, to obtain monosubstituted derivative, first acetylation of  $-\text{NH}_2$  group with acetic anhydride is carried out and then nitration is carried out.



(66) **Explain nitration of aniline.**

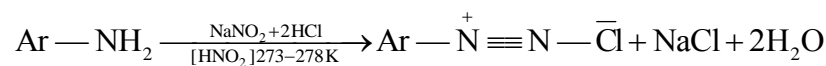
**Sol: Nitration:** Aniline in presence of con.  $\text{H}_2\text{SO}_4$  reacts with con.  $\text{HNO}_3$  at 288 K temperature and mixture of p- and o-nitroaniline with m-nitroaniline are obtained by nitration because the anilinium ion  $-\text{NH}_3^+$  formed in acidic medium is m-directing group.



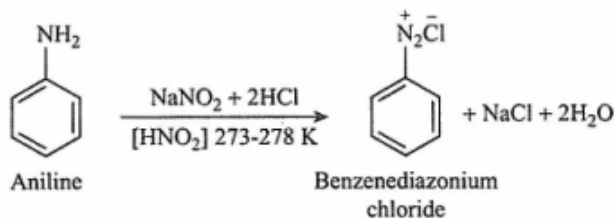
(67) **Give the preparation of benzenediazonium chloride and explain.**

**Sol:** Preparation of benzenediazonium chloride salt: in the reaction between primary aromatic amine and nitrous acid carried out at low temperature, diazonium salt is formed. This reaction is called diazotization.

A solution of aniline in dilute hydrochloric acid is prepared and, it is cooled 273–278K temperature; on adding sodium nitrite, nitrous acid is formed and benzene diazonium chloride (salt) is obtained. As benzenediazonium salt is unstable at higher temperature, it is necessary to keep the temperature 273–278 K.

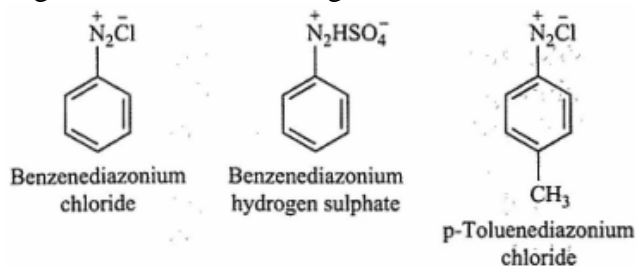


As diazonium salt is unstable, it is used immediately.



Diazonium salt is shown by general formula as  $\text{ArN}_2^+\bar{\text{X}}$  where  $\bar{\text{X}} = \text{Cl}^-, \text{Br}^-, \text{HSO}_4^-, \text{BF}_4^-$  etc.  $\text{N}_2^+$  ( $-\text{N}^+ \equiv \text{N}$  group is called diazonium group).

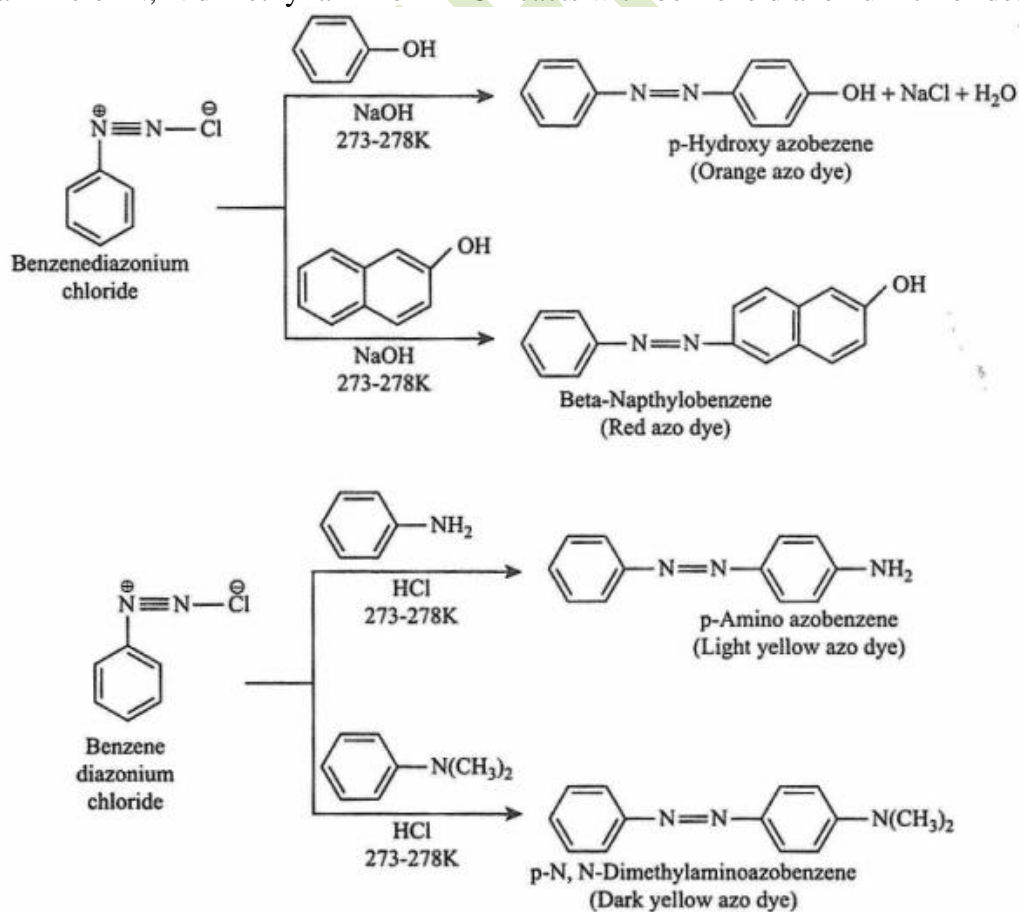
In their nomenclature diazonium suffix is applied to original hydrocarbon and then the name of negative ion is written, e.g.,



**(68) Explain azo coupling reactions.**

**Sol:** Reaction for azo coupling is as under:

**Azo coupling reaction:** Solution of phenol or beta naphthol ( $\beta$ -naphthol) in sodium hydroxide when reacts with benzene diazonium chloride at 273–278K temperature, orange and red color azo dyes are obtained. Also, light yellow and dark yellow colored azo dyes are respectively obtained when solutions of aniline or N, N dimethyl aniline in HCl reacts with benzene diazonium chloride.



(69) Write electronic properties of cyanide.

**Sol:** Electronic structure of cyanide:

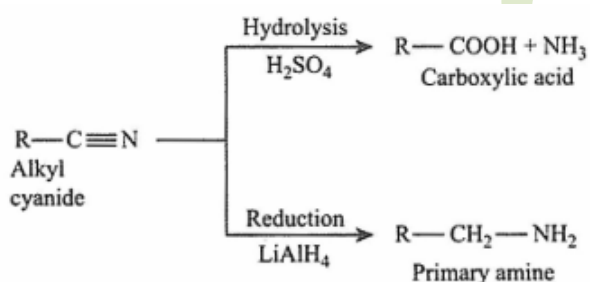
**Physical properties of cyanides:**

In alkyl cyanide compounds  $C^{+\delta} \equiv N^{-\delta}$  bond being polar and absence of intermolecular hydrogen bond, the boiling points of alkyl cyanides are less than their corresponding carboxylic acid, viz. the boiling points of ethane nitrile (boiling point 355K) and propane nitrile are lower than the boiling points of ethanoic acid (boiling point 370K) and propanoic acid (boiling point 414K) respectively.

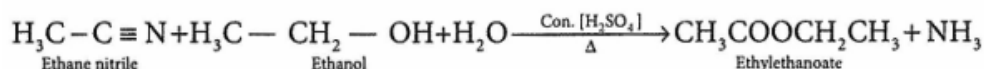
Alkyl cyanides are very weak basic compounds, having fine fragrant smell are non-poisonous compounds. The alkyl cyanides having less molecular masses are soluble in water as well as in many other organic solvents. Ethane nitrile (acetonitrile) is the most dipolar and so it makes many types of organic reagents soluble in it. Its boiling point being normal, it can be easily removed so that it can be used again and it being inert it is useful as solvent in many most of the organic reactions.

(70) Write chemical reactions of cyanide compounds.

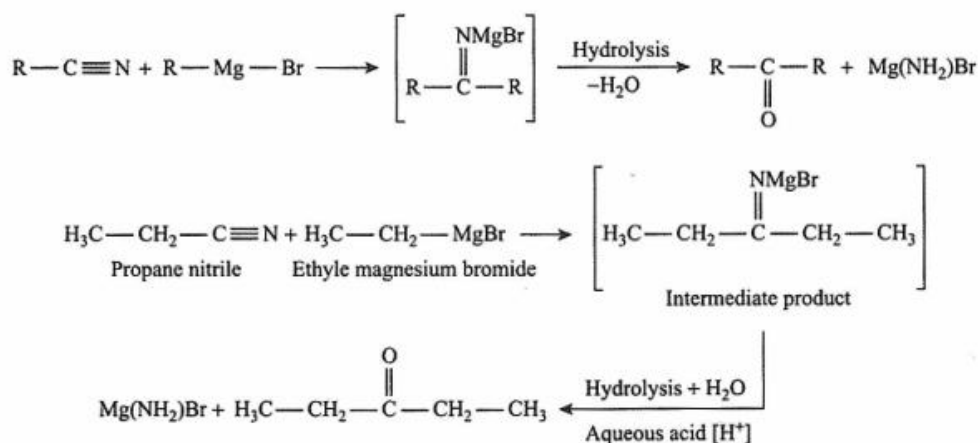
**Sol:** **Chemical properties of cyanides:** Carboxylic acids are obtained by hydrolysis of cyanide compounds in presence of sulphuric acid and ammonia is liberated. Primary amide is obtained by reduction with  $LiAlH_4$ .



Ethylethanoate (ethyl acetate) is formed when ethane nitrile and ethanol are heated in presence of concentrated sulphuric acid.

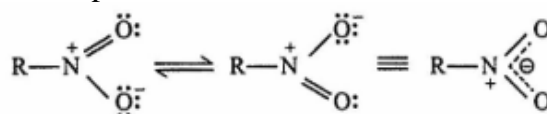


Ketone is obtained by hydrolysis of the intermediate product in presence of aqueous acid the intermediate product is obtained by addition reaction of cyanide compound with Grignard reagent ( $R-Mg-X$ ) ( $X = Br, I$ ),



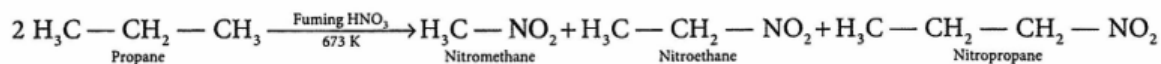
(71) Mention the physical properties and resonance structures of nitro compounds.

**Sol:** Nitro compounds are colorless, having odour, neutral and sparingly soluble in water. The resonance forms of alkyl nitro compounds:

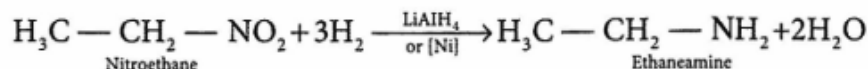


(72) Explain preparation of nitro compounds and their reduction.

**Sol:** The mixture of alkyl nitro compounds is obtained by nitration reaction of alkane hydrocarbon and heating with fuming nitric acid in vapour state at 673 K temperature, viz. by nitration of propane, nitro methane, nitro ethane and nitro propane are obtained. The industrial production of alkyl nitro compounds is carried out by this method.



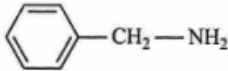
Primary alkyl amines are obtained by carrying out reduction of nitro alkane with lithium aluminium hydride (LiAlH<sub>4</sub>) or with hydrogen in presence of nickel catalyst.



(73) Give structural formula and IUPAC names:

Isopropyl amine, Benzylamine

Sol:

Sr.	Common name	IUPAC name	Structural formula
1.	Isopropyl amine	Propan-2-amine	$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_3 \\   \\ \text{NH}_2 \end{array}$
2.	Benzylamine	1-Phenylmethanamine	

(74) Give structural formula and IUPAC names:

Propyl amine, Dimethyl amine

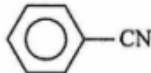
Sol:

Sr.	Common name	IUPAC name	Structural formula
1.	Propyl amine	Propan-1-amine	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -NH <sub>2</sub>
2.	Dimethyl amine	N-methylmethanamine	CH <sub>3</sub> -NH-CH <sub>3</sub>

(75) Give structural formula and IUPAC names:

Ethyl methyl amine, Phenylcyanide


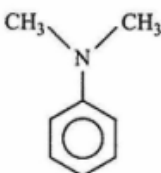
Sol:

Sr.	Common name	IUPAC name	Structural formula
1.	Ethyl methyl amine	N-Methylethanamine	CH <sub>3</sub> -NH-CH <sub>2</sub> -CH <sub>3</sub>
2.	Phenylcyanide	Benzene carbonitrile or Benzonitrile	

(76) Give structural formula and IUPAC names:

p-Nitroaniline, N, N-Dimethyl aniline

Sol:

Sr.	Common name	IUPAC name	Structural formula
1.	p-Nitroaniline	4-Nitrophenylamine	
2.	N, N-Dimethyl aniline	N, N-Dimethyl benzenamine	

(77) Give structural formula and IUPAC names:

Methylpropyl amine, Diethyl methyl amine

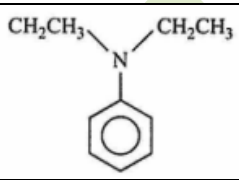
Sol:

Sr.	Common name	IUPAC name	Structural formula
1	Methylpropyl amine	N-Methylpropan-1-amine	$\text{CH}_3 - \text{NH} - \text{CH}_2\text{CH}_2\text{CH}_3$
2	Diethyl methyl amine	N-Ethyl-N-methyl ethanamine	$\begin{array}{c} \text{CH}_3 - \text{N} - \text{CH}_2\text{CH}_3 \\   \\ \text{CH}_2\text{CH}_3 \end{array}$

(78) Give structural formula and IUPAC names:

N,N-Diethyl aminobenzene, Methyl isocyanide

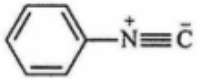
Sol:

Sr.	Common name	IUPAC name	Structural formula
1.	N,N-Diethyl aminobenzene	N, N-Diethyl benzenamine	
2.	Methyl isocyanide	Isocyanomethane	$\text{CH}_3 - \text{NC}$

(79) Give structural formula and IUPAC names:

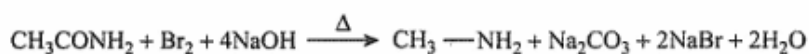
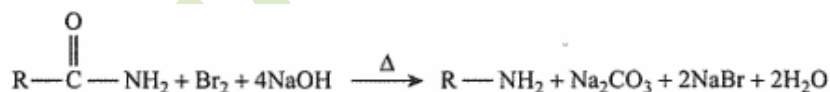
Phenyl isocyanide, Isopropyl cyanide

Sol:

Sr.	Common name	IUPAC name	Structural formula
1.	Phenyl isocyanide	Phenyl isocyanide	
2.	Isopropyl cyanide	2-Methyl propane nitrile	$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CN} \\   \\ \text{CH}_3 \end{array}$

(80) Write Hoffmann reaction.

Sol: Reaction is as under:



Ethanamide

Methanamine

(81) Write reaction of nitrous acid with alkyl amine.

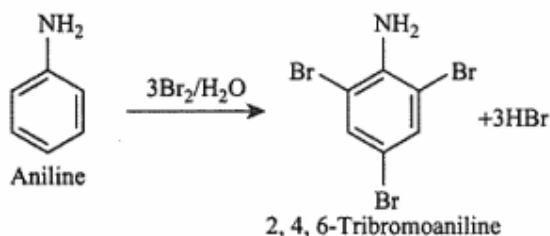
Sol: Reaction of nitrous acid with alkyl amine is as under:



(82) Write bromination of aniline.

Sol: Bromination of aniline is as under:

At room temperature aniline reacts with bromine water and gives white precipitates of 2, 4, 6 – tribromoaniline.



(83) **Explain: The boiling points of primary amines are higher than those of alkanes.**

**Sol:** The boiling points of primary amines having same number of carbon atoms containing alkane are higher; because electronegativity of nitrogen is higher than that of carbon and due to this reason, intermolecular attraction in amine is higher than that of corresponding alkanes. Therefore, boiling points of primary amines are higher than those of alkanes.

(84) **Explain: The boiling points of primary amines are less than those of their corresponding alcohols.**

**Sol:** As the electronegativity of nitrogen is less than that of oxygen, the  $N^{\delta-} - H^{\delta+}$  bond in amines is less polar than the  $O^{\delta-} - H^{\delta+}$  bond in alcohol. Hence, amine compounds are less polar than alcohol. Also, the intermolecular attraction in amine is less than that in alcohol. Hence, the boiling points of primary amines are less than those of their corresponding alcohols viz ethanamine (boiling point 290 K) is lower than ethanol (boiling point 351 K).

(85) **Explain: The boiling point of isomeric secondary amine is more than that of tertiary amine and that of primary amine is the highest.**

**Sol:** There are intermolecular hydrogen bonds in primary and secondary amines while they are not there in tertiary amine. Hence, in isomeric primary alkyl amines having same molecular formula, it is highest, in secondary amine it is comparatively less and it is least in tertiary amine. Viz. in ( $1^\circ$ ) propanamine, ( $2^\circ$ ) ethylmethylamine and ( $3^\circ$ ) trimethylamine there is decrease in boiling point

(86) **Explain: Aniline is less basic than methylamine.**

**Sol:** The resonance structures are not available in methylamine, like aniline, so the electron pair on their N atom is localized. Hence, these compounds can easily donate electron pairs so that their basicity is more than that of aniline. The order of basicity of amine compounds can be written as follows:

Tertiary amine > secondary amine > primary amine > ammonia > aniline

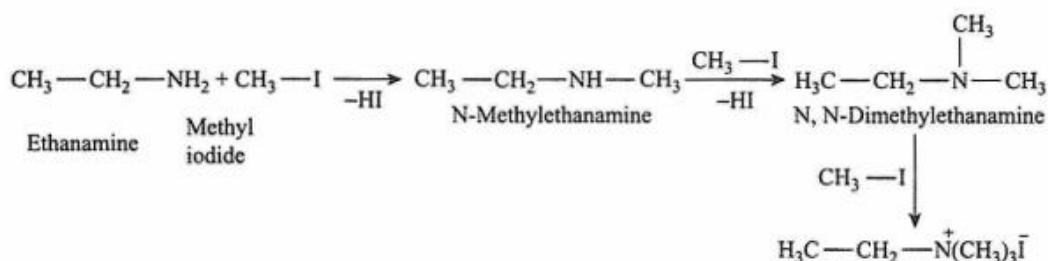
(87) **Explain: The boiling points of alkyl cyanides are lower than their corresponding carboxylic acids.**

**Sol:** In alkyl cyanide compounds  $C^{\delta+} \equiv N^{\delta-}$  bond being polar and absence of intermolecular hydrogen bond, the boiling points of alkyl cyanides are less than their corresponding carboxylic acid, viz. the boiling points of ethane nitrile (boiling point 355K) and propane nitrile are lower than the boiling points of ethanoic acid (boiling point 370K) and propanoic acid (boiling point 414K) respectively.

(88) **Explain: Secondary amines corresponding to their primary amines having less molecular mass are less soluble in water. OR The aqueous solubility of primary amine is more than that of secondary amine.**

**Sol:** In the aqueous solutions of primary and secondary amine compounds, water and amine molecules form hydrogen bond so the intermolecular attraction increases. In primary amines, there are two hydrogen atoms on nitrogen and in secondary amine one hydrogen atom on nitrogen so the number of hydrogen bonds in primary amine becomes double. Hence, secondary amines corresponding to their primary amines having less molecular mass are less soluble in water.

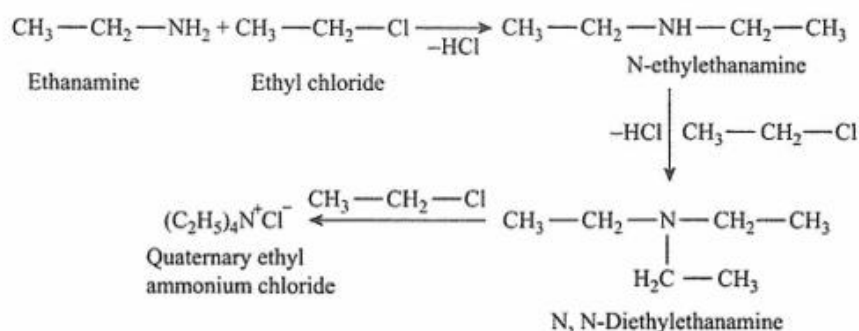
(89) **Explain: Methyl iodide**



**Sol:**

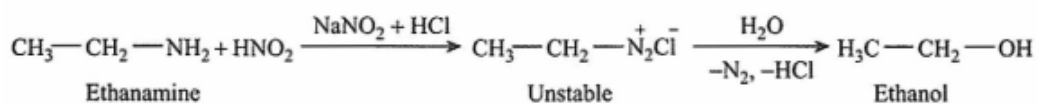
Reason: The carbon-halogen bond which is present in alkyl or aryl halide is easily broken by nucleophilic reagent. Hence by reaction of ethylamine on alkyl halide (methyl iodide), the nucleophilic reagent ( $\text{NH}_2$ ) substitutes the halogen and secondary amine is formed. Then it reacts with alkyl halide by chain reaction and tertiary amines are formed. In the end quaternary ammonium salt is formed.

- (90) **Explain: Ethyl chloride:**  
**Sol:**



Reason: The carbon– halogen bond which is present in alkyl or aryl halide is easily broken by nucleophilic reagent. Hence by reaction of ethylamine on alkyl halide (ethyl chloride), the nucleophilic reagent (NH<sub>2</sub>) substitutes the halogen and secondary amine is formed. Then it reacts with alkyl halide by chain reaction and tertiary amines are formed. In the end quaternary ammonium salt is formed.

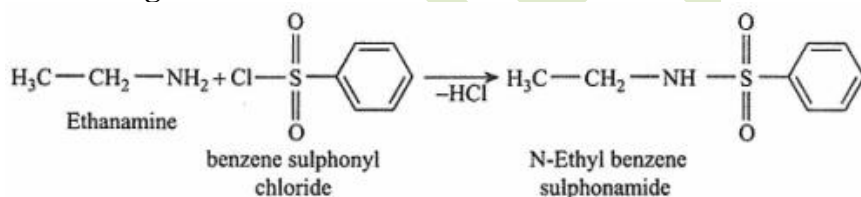
- (91) **Explain: Nitrous acid**



**Sol:**

Reason: Primary alkyl amine (ethanamine) reacts with nitrous acid [which is prepared by the reaction of sodium nitrite (NaNO<sub>2</sub>) and hydrochloric acid (HCl)] and gives ethyldiazonium chloride which is unstable and so this salt releases nitrogen and changes to ethanol.

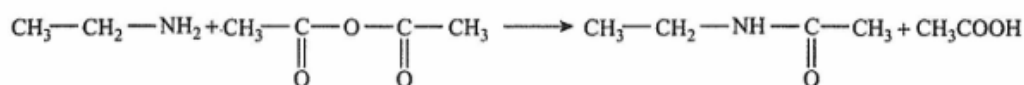
- (92) **Explain: Hinsberg reaction**



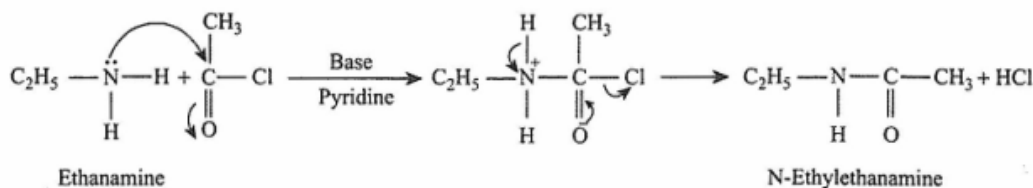
**Sol:**

Reason: Primary amine (ethanamine) reacts with benzene sulphonyl chloride (Hinsberg reagent) and gives sulphonide product N–ethyl benzene sulphonamide (2°).

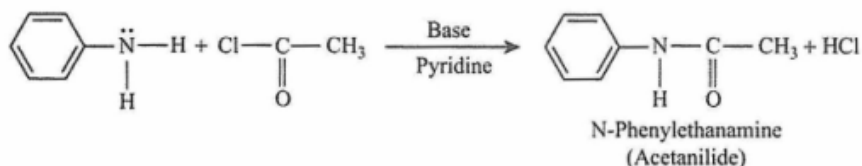
- (93) **Explain: Acetic anhydride**  
**Sol:**



Reason: When aliphatic and aromatic primary and secondary amines react with acid chloride or acid anhydride, nucleophilic substitution reaction takes place and amide product is obtained. This reaction is known as acylation. This reaction is carried out in pyridine which is a stronger base than amine. When ethylamine reacts with acetyl chloride in presence of strong base like pyridine, it gives N–acetyl ethylamine. Mechanism of the reaction is as under:



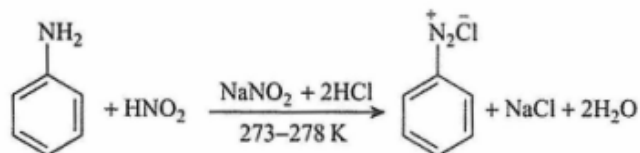
- (94) **Explain: Acetyl chloride**



**Sol:**

Reason: When primary aromatic amine aniline reacts with acetyl chloride, nucleophilic substitution reaction takes place and amide product N-phenylethanamine (acetanilide) is obtained. This reaction is known as acylation. This reaction is carried out in pyridine which is a stronger base than amine.

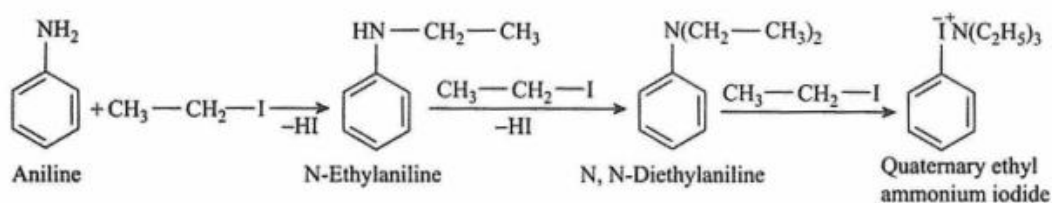
(95) **Explain: Nitrous acid**



**Sol:**

Reason: Primary aromatic amine aniline reacts with nitrous acid [which is prepared by the reaction of sodium nitrite (NaNO<sub>2</sub>) and hydrochloric acid (HCl)] at low temperature (273–278 K) and gives phenyldiazonium chloride. As benzenediazonium salt is unstable at higher temperature, it is necessary to keep the temperature 273–278 K.

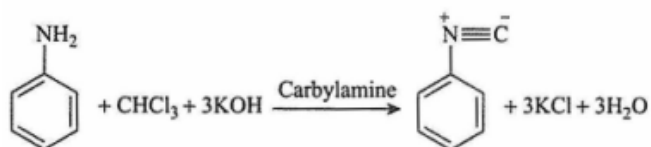
(96) **Explain: Ethyl iodide**



**Sol:**

Reason: The carbon halogen bond which is present in alkyl halide is easily broken by nucleophilic reagent. Hence by reaction of aniline on alkyl halide (ethyl chloride), the nucleophilic reagent (NH<sub>2</sub>) substitutes the halogen and secondary amine is formed. Then it reacts with alkyl halide by chain reaction and tertiary amines are formed. In the end quaternary ammonium salt is formed.

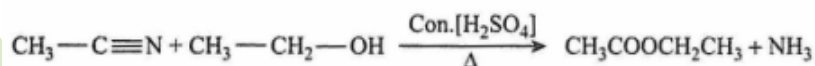
(97) **Explain: CHCl<sub>3</sub>/KOH**



**Sol:**

Reason: On heating aromatic primary amine aniline with chloroform (CHCl<sub>3</sub>) and alcoholic potassium hydroxide (KOH) foul smell possessing poisonous isocyanide (carbylamine) phenylisocyanide is formed. This reaction is called carbylamine test or isocyanide identification. Secondary and tertiary amines do not give this test.

(98) **Explain: Reaction of methyl cyanide with ethanol.**



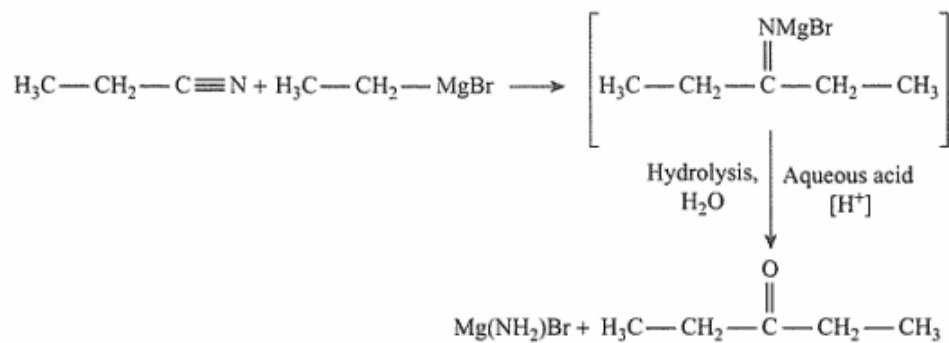
**Sol:**

Reason: Carboxylic acids are obtained by hydrolysis of cyanide compounds in presence of sulphuric acid and ammonia is liberated. Here, ethanoic acid is obtained by hydrolysis of methyl cyanide and former compound reacts with ethanol to produce ethylethanoate (ethyl acetate).

(99) **Explain: Ethyl cyanide with ethyl magnesium bromide.**

**Sol:**





Reason: Here, ketone pentane-3-one (diethylketone) is obtained by hydrolysis of the intermediate product in presence of aqueous acid; the intermediate is obtained by addition reaction of ethyl cyanide with Grignard reagent ethyl magnesium bromide.