

Unit 15: Amino Compounds

Syllabus	142
Some important terms, concepts and formulae	142
Subject Matter	143
15.1 Aliphatic amines	
Very Short Questions-Answers	
Q.1. Write down any two methods of preparation of aliphatic amines.	143
Q.2. Give the action of ethanamide with (a) LiAlH_4 and (b) Br_2/KOH .	143
Q.3. How does ethanamine reacts with (a) CHCl_3/KOH and (b) $\text{CH}_3\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-Cl}$?	144
Q.4. What happens when ethanamine is reacted with NaNO_2 in presence of HCl below 5°C ?	144
Q.5. Why is methylamine more basic than aniline?	144
Short Questions-Answers	
Q.6. Describe the method of separation of 1° , 2° and 3° amines from their mixture by using diethyloxalate.	145
Q.7. Discuss the following basicity order of different degree of amines: 2° amine $>$ 1° amine $>$ 3° amine.	145
Q.8. Carry out the following conversions: Methanamine to ethanamine and vice-versa.	146
15.2 Aromatic amine	
Very Short Questions-Answers	
Q.1. What happens when benzamide is heated with bromine in presence of NaOH ?	147
Q.2. What is carbylamine reaction?	147
Q.3. What happens when (a) Aniline is shaken well with aqueous bromine? (b) Aniline is reacted with acetaldehyde in acidic medium?	147
Q.4. Give an example of diazotization reaction.	147
Q.5. What is Schotten-Baumann reaction?	148
Short Questions-Answers	
Q.6. What are the products obtained when aniline reacts with (a) Conc. H_2SO_4 (b) acidified $\text{K}_2\text{Cr}_2\text{O}_7$ (c) NaNO_2/HCl . How will you convert aniline into phenol?	148
Q.7. Starting from aniline how would you obtain (i) O-nitroaniline and (ii) Picric acid?	149
Long Questions-Answers	
Q.8. Describe laboratory preparation of aniline. Starting from aniline how would you obtain (i) O-nitro aniline (ii) N-methyl aniline.	149

Unit 15: Amino Compounds

Syllabus

15.1 Aliphatic Amines:

- ☐ Introduction, nomenclature and classification
- ☐ Separation of primary, secondary and tertiary amines by Hoffmann's method
- ☐ Preparation of primary amines from haloalkane, nitriles, nitroalkanes and amides
- ☐ Physical properties
- ☐ Chemical Properties: basicity of amines, comparative study of basic nature of 1°, 2° and 3° amines. Reaction of Primary amines with chloroform, conc. HCl, R-X, RCOX and nitrous acid (NaNO₂ / HCl)
- ☐ Test of 1°, 2° and 3° amines. (nitrous acid test)

15.2 Aromatic Amine (Aniline):

- ☐ Laboratory preparation of aniline
- ☐ Physical properties
- ☐ Chemical properties: basicity of aniline, comparison of basic nature of aniline with aliphatic amines; alkylation, acylation, diazotization, carbylamine and coupling reaction
- ☐ Electrophilic substitution : Nitration, sulphonation and bromination
- ☐ Uses of amine

Some important terms, concepts and formulae

1. Amines are alkyl or aryl derivatives of ammonia.
2. Amines can be prepared by (i) ammonolysis of alkyl halides, (ii) reduction of nitrocompounds (iii) reduction of cyanide, amide and oximes, (iv) Reduction amination of aldehydes/Ketones.
3. Reaction of an amide with Br₂ in presence of NaOH to give a primary amine which has one C-atom less than parent amide is called Hoffmann's bromamide reaction.
4. Aliphatic amines are soluble in water but aromatic amines are insoluble.
5. Boiling point of amines are higher than alkanes but lower than carboxylic acids.
6. The basic strength of different degree of amines is :
 $2^\circ > 1^\circ > 3^\circ$ in aqueous medium and
 $3^\circ > 2^\circ > 1^\circ$ in non-aqueous medium.
7. Aromatic amines are weaker base than aliphatic amines.
8. Electron releasing groups like -CH₃, -OCH₃, -NH₂ etc. increase the basic strength while electron withdrawing groups like -NO₂, -CN etc. decreases the basic strength of aniline. The effect of these substituents is more at p-position and less at o-position.
9. Ortho substituted aniline are weaker bases than aniline irrespective of electron releasing or attracting effect of the substituent. This is referred so as ortho effect.
10. Aniline reacts with HNO₂ at 0-5°C to give benzene diazonium chloride.
11. -NH₂ group in aniline is ring activating and ortho-, para-directing group.
12. 1°, 2° and 3° amines can be distinguished by Hoffmann's method.

Read the above mentioned various definitions, explanations and formulae carefully. Then go through the following solved examples. After doing the solved examples, try to solve the other similar questions independently.

Subject Matter

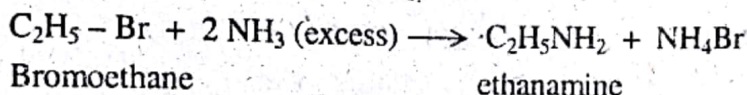
15.1 Aliphatic amines

Very Short Questions-Answers

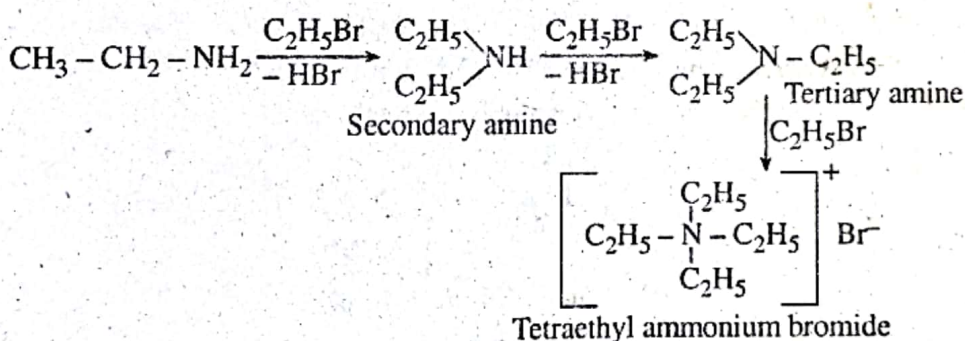
Q.1. Write down any two methods of preparation of aliphatic amines.

Ans: Aliphatic amines can be prepared as:

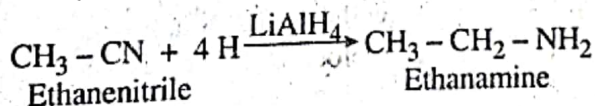
- (a) **By ammonolysis:** Alkyl halide reacts with ammonia to form primary, secondary and tertiary amines. If ammonia is used in excess, primary amine is the major product.



If alkyl halide is in excess, the primary amine formed further reacts with alkyl halide to form secondary amine, tertiary amine and finally quaternary ammonium salt.

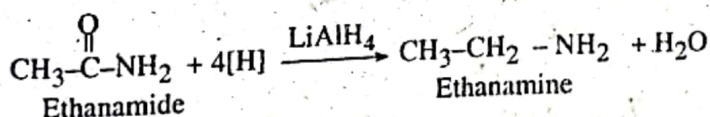


- (b) **By reduction of alkyl cyanides:** The alkyl cyanides on reduction with H_2/Ni , LiAlH_4 or $\text{Na}/\text{C}_2\text{H}_5\text{OH}$ give primary amines.

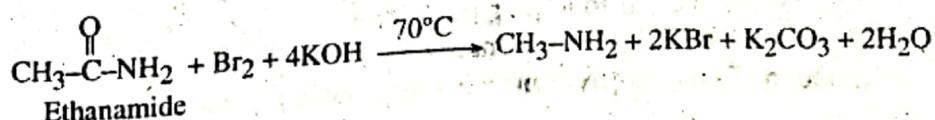


Q.2. Give the action of ethanamide with (a) LiAlH_4 and (b) Br_2/KOH .

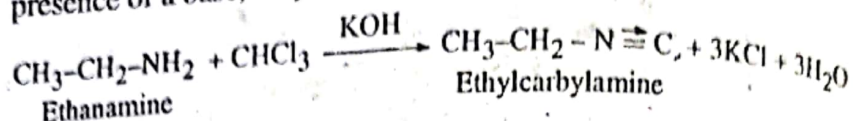
Ans: (a) LiAlH_4 : Ethanamide is reduced by LiAlH_4 into ethanamine.



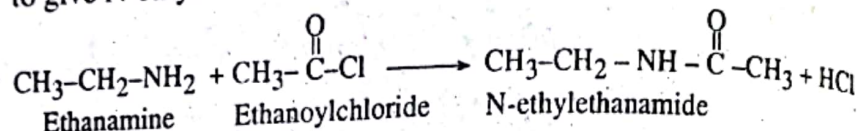
- (b) Br_2/KOH : Ethanamide gives methanamine when heated with bromine in the presence of alkali at about 70°C . This reaction is also known as **Hoffmann's -bromamide reaction**.



Q.3. How does ethanamine reacts with (a) CHCl_3/KOH and (b) CH_3COCl ?
Ans: (a) CHCl_3/KOH : When ethanamine is reacted with chloroform (CHCl_3) in presence of a base, ethylcarbylamine is obtained.

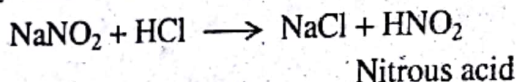


(b) CH_3COCl : On the otherhand, ethanamine reacts with ethanoylchloride to give N-ethylethanamide.

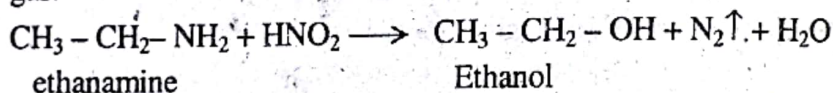


Q.4. What happens when ethanamine is reacted with NaNO_2 in presence of HCl below 5°C ?

Ans: NaNO_2 reacts with HCl below 5°C to give nitrous acid.

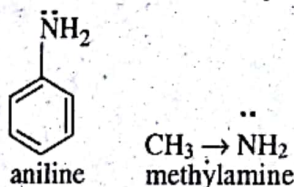


The nitrous acid thus obtained reacts with ethanamine to give ethanol and N_2 gas.



Q.5. Why is methylamine more basic than aniline?

Ans: Let us see the structures of aniline and methylamine.



Both in aniline and methylamine, N-atoms have a lone-pair of electrons as shown above.

Aromatic ring in aniline is electron-withdrawing. The lone-pair on N-atom in aniline is less available for donation to H^+ (i.e. for protonation) because the lone-pair is delocalised mostly into the benzene ring by resonance. Thus, aniline is less basic.

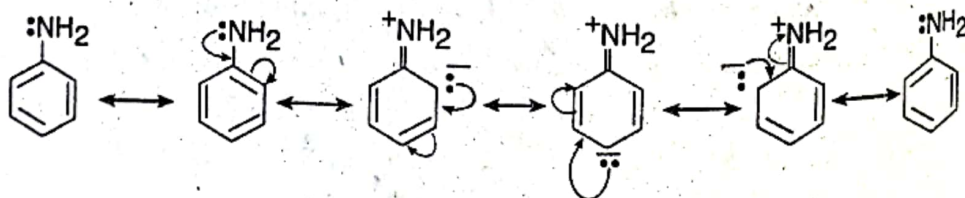


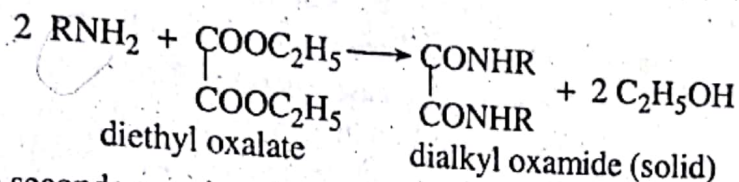
Fig.: resonance structures of aniline

In methylamine, the lone-pair of electrons does not participate in resonance. Furthermore, $-\text{CH}_3$ group in methylamine releases electron on N-atom and it consequently increases the electron density on N-atom by +I effect. Therefore, the lone-pair on N-atom is more available for protonation. The greater the tendency to donate the lone-pair, the more basic would be the compound. **Thus, methylamine is more basic than aniline.**

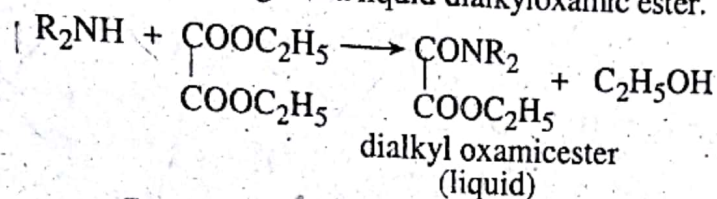
Q.6. Describe the method of separation of 1°, 2° and 3° amines from their mixture by using diethyloxalate.

Ans: To separate 1°, 2° and 3° amines from its mixture by Hoffmann's method, diethyl oxalate is added to the mixture, where different degree of amines react differently with diethyl oxalate to give different products.

(i) The primary amine reacts with diethyl oxalate to give solid dialkyl oxamide.

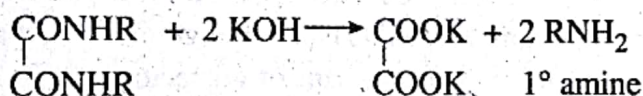


(ii) The secondary amine gives a liquid dialkyl oxamic ester.

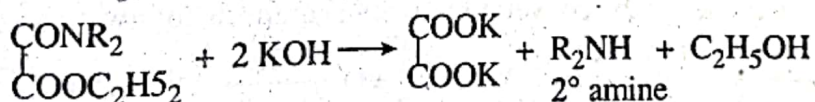


(iii) The tertiary amine does not react with diethyloxalate.

After this, the mixture containing all the products diethyl oxamide, dialkyl oxamic ester, alcohol and the reagents tertiary amine is first filtered to separate out the solid oxamide. It is obtained as residue, which is then heated with KOH to recover primary amine.



The filtrate is then subjected to fractional distillation when the tertiary amine distills over first followed by alcohol. At last, the residual oxamic ester is treated with aqueous KOH and distilled fractionally to get secondary amine and alcohol in different fractions.

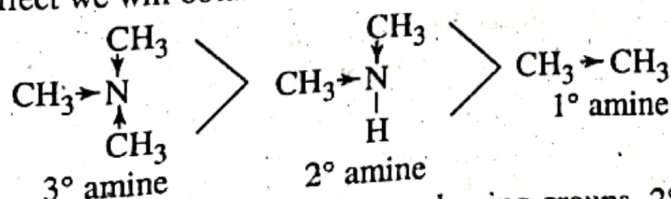


This method of separation of 1°, 2° and 3° amine is known as Hoffmann's method.

Q.7. Discuss the following basicity order of different degree of amines:

2° amine > 1° amine > 3° amine.

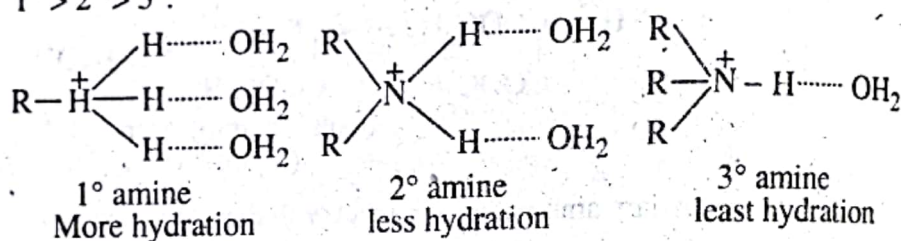
Ans: We know that alkyl amines are more basic than ammonia because alkyl groups are electron releasing groups which increases the electron density on nitrogen atom by +I effect. This effect makes the lone pair more easily available on N-atom and hence makes it more basic. If we treat the basicity on this sole effect we will obtain the following order.



As 3° amine has three electron releasing groups, 2° has only two and 1° has only one.

However it is not so. In fact the basic strength in aqueous solution depends not only upon electron releasing effect but also upon steric effect and hydration effect.

- (a) Steric effect refers to the crowding of alkyl groups around N-atom which hinders the attack of proton on the amine molecule and thus, decreases its basic strength. Since, crowding of alkyl groups around N-atom increased from primary to tertiary amines, consequently the basic strength of amine should decrease, in the order $1^\circ > 2^\circ > 3^\circ$.
- (b) Hydration effect refers to the stabilization of the protonated amine by the water molecules. The water molecules form H-bonds with protonated amine and release energy called hydration energy. Now greater the extent of H-bonding in protonated amine more will be its strength of the corresponding amine. The order of hydration is $1^\circ > 2^\circ > 3^\circ$.

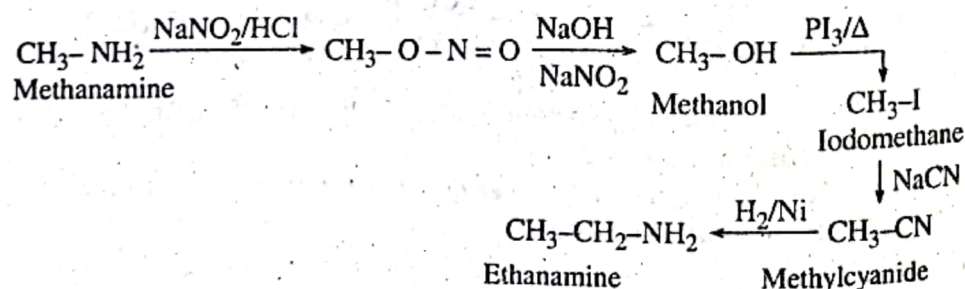


Therefore, basic strength should decrease from $1^\circ > 2^\circ > 3^\circ$. But, we find that in 3° amine hydration is least and steric hindrance is maximum. Thus, it is least basic in spite of maximum +I effect. In 1° amine steric hindrance is least hydration is maximum and +I effect is also minimum. Hence, its basic strength is more than 3° amine but less than 2° amine. The resultant of all factors cause 2° amine to be still more basic than 1° amine. Thus, over all basic strength varies as: $2^\circ > 1^\circ > 3^\circ$.

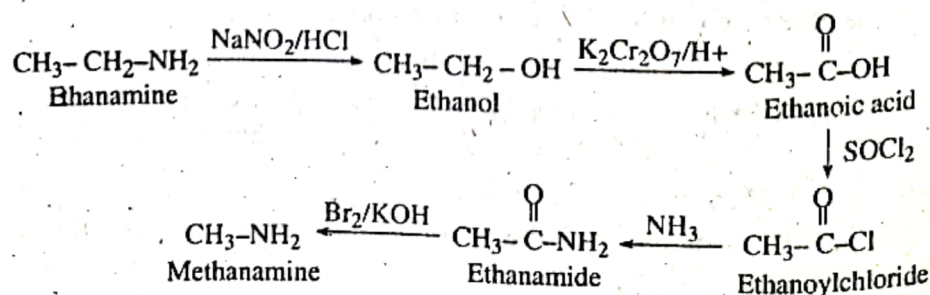
Q.8. Carry out the following conversions:

Methanamine to ethanamine and vice-versa.

Ans: Methanamine can be converted into ethanamine as follows:



Similarly, ethanamine can be converted into methanamine by the following reaction sequence given below:

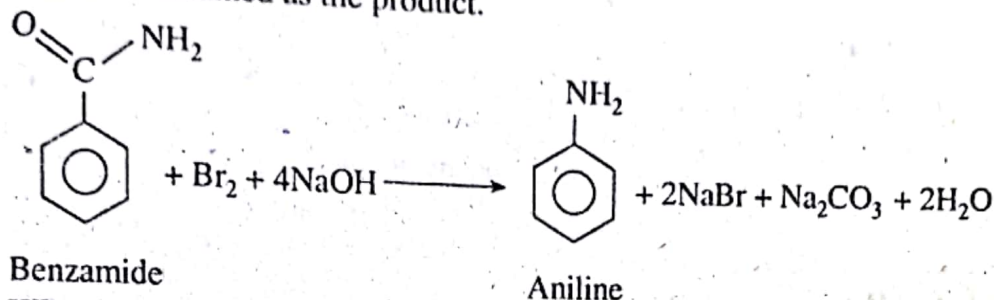


15.2 Aromatic amine

Very Short Questions-Answers

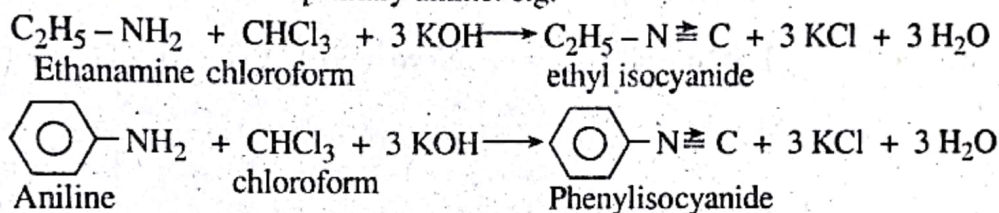
Q.1. What happens when benzamide is heated with bromine in presence of NaOH?

Ans: Aniline is obtained as the product.



Q.2. What is carbylamine reaction?

Ans: It is a method to detect primary amine in laboratory. When a primary amine is warmed with chloroform and alcoholic potassium hydroxide solution, an alkyl isocyanide or carbylamine with offensive smell is obtained. The generation of offensive smell confirms primary amine. e.g.

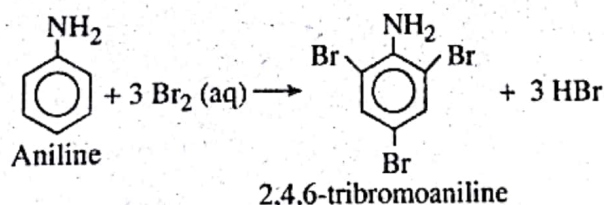


Q.3. What happens when

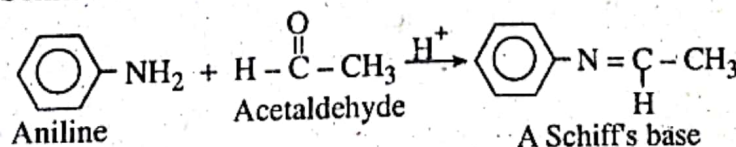
(a) Aniline is shaken well with aqueous bromine?

(b) Aniline is reacted with acetaldehyde in acidic medium?

Ans: (a) Benzene ring in aniline is highly activated due to presence of electron donating amine group. So, when it is reacted with aqueous bromine, 2,4,6-tribromo aniline is obtained.

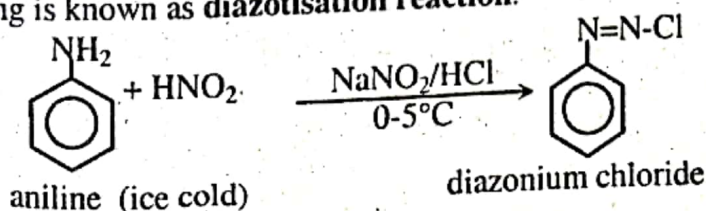


(b) When aniline is reacted with acetaldehyde in slightly acidic medium, a Schiff's base is obtained.



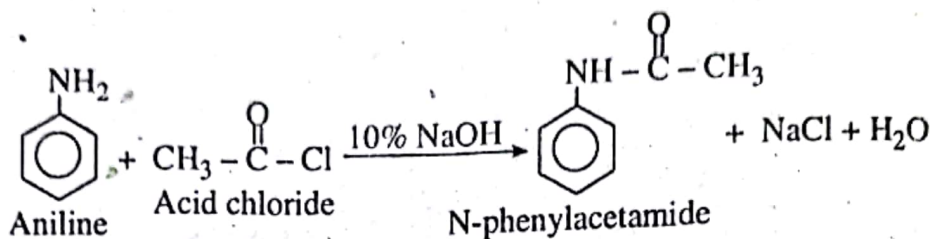
Q.4. Give an example of diazotization reaction.

Ans: When primary amine such as aniline is treated with ice cold solution of NaNO_2 in the presence of ice cold solution of dil. HCl (i.e., at $0-5^\circ\text{C}$), diazonium salt is produced. Thus, introduction of N_2^+Cl^- group in benzene ring is known as **diazotisation reaction**.



Q.5. What is Schotten-Baumann reaction?

Ans: Acylation of alcohol or amine by the action of acid chloride in the aqueous alkaline solution is known as **Schotten-Baumann reaction**. i.e.

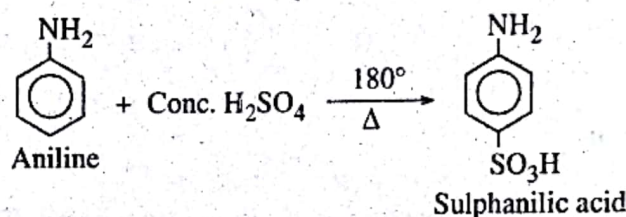


Short Questions-Answers

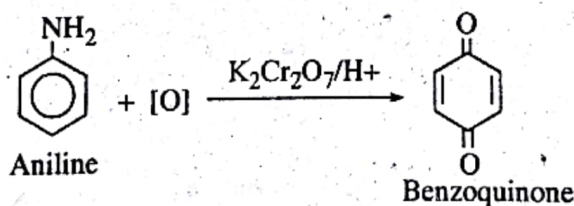
Q.6. What are the products obtained when aniline reacts with (a) Conc. H_2SO_4 , (b) acidified $\text{K}_2\text{Cr}_2\text{O}_7$ (c) NaNO_2/HCl .

How will you convert aniline into phenol?

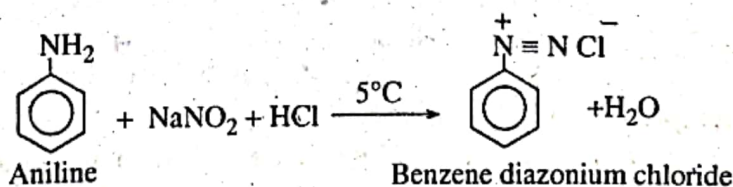
Ans: (a) **Conc. H_2SO_4 :** Aniline reacts with conc. H_2SO_4 to give sulphanilic acid



(b) **acidified $\text{K}_2\text{Cr}_2\text{O}_7$:** Aniline is oxidized by acidified $\text{K}_2\text{Cr}_2\text{O}_7$ into benzoquinone



(c) **NaNO_2/HCl :** aniline reacts with NaNO_2 in presence of HCl below 5°C to give benzene diazonium chloride.



Aniline can be converted into phenol as follows:

