

Unit 14: Nitro Compounds

Syllabus

14.1 Aliphatic Nitrocompounds (Nitroalkane):

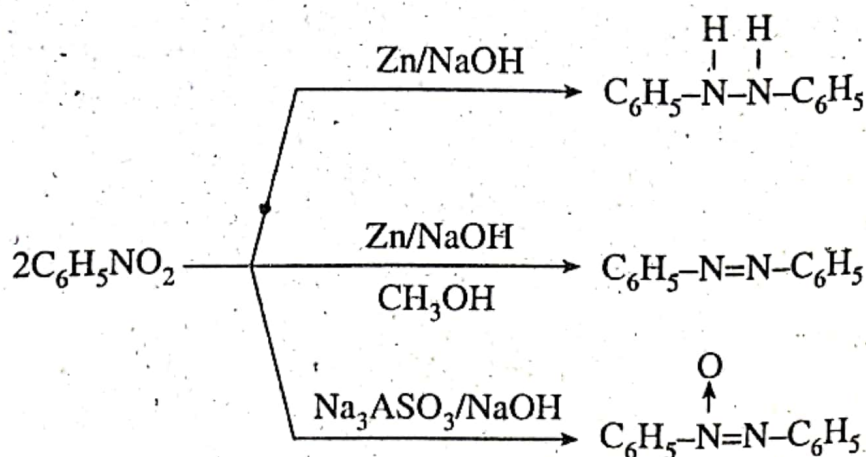
- ☐ Introduction and nomenclature
- ☐ Preparation from haloalkane and alkane
- ☐ Physical properties
- ☐ Reduction of nitroalkane
- ☐ Uses

14.2 Aromatic Nitrocompounds:

- ☐ Laboratory preparation of nitrobenzene
- ☐ Physical properties
- ☐ Chemical properties
 - Reduction in different media
 - Electrophilic substitution reactions
 - Uses of nitrobenzene

Some important terms, concepts and formulae

1. Nitrobenzene is prepared by direct nitration of benzene.
2. Nitrocompounds have relatively high boiling point due to their polar nature.
3. Reduction of nitro group gives different products in different medium.
 - (a) In acidic medium (Using Zn/HCl), $-\text{NO}_2$ group is changed into $-\text{NH}_2$ group.
 - (b) In neutral medium (Using Zn/ NH_4Cl), $-\text{NO}_2$ group is reduced to $-\text{NH}-\text{OH}$.
 - (c) Reduction with LiAlH_4 converts aliphatic nitro compounds into amine and aromatic nitro compound into $\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_5$.
 - (d) Electrolytic reduction of $\text{C}_6\text{H}_5\text{NO}_2$ produces aniline in weakly acidic medium and p-hydroxyaniline in strongly acidic medium.
 - (e) In alkaline medium,



4. $-\text{NO}_2$ group in nitrobenzene is ring deactivating and meta-directing group.
5. Nitrobenzene does not show Friedel-Craft's reaction.

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.

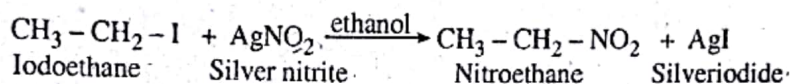
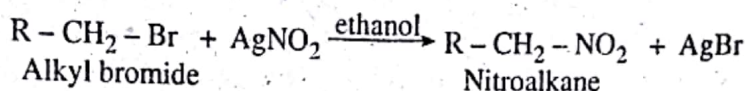
Subject Matter

14.1 Aliphatic Nitro-compounds

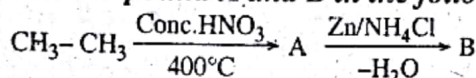
Very Short Questions-Answers

Q.1. Give an example of preparation of nitroalkane.

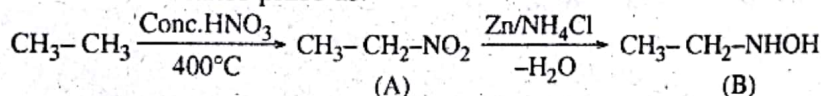
Ans: Nitroalkane: Nitroalkane can be prepared by reacting alkylhalide with silver nitrite in ethanolic solution.



Q.2. Identify the compound A and B in the following reaction:



Ans: The reaction takes place as:

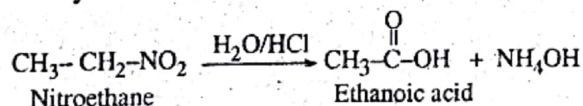


\therefore A = $\text{CH}_3-\text{CH}_2-\text{NO}_2$ (Nitroethane)

B = $\text{CH}_3-\text{CH}_2-\text{NHOH}$ (N-ethylhydroxylamine)

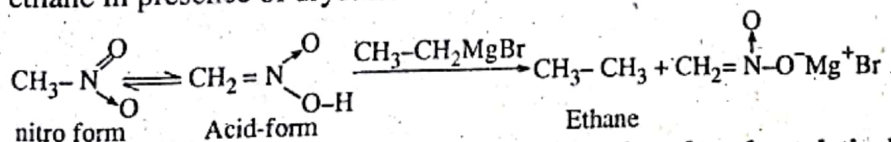
Q.3. How can we get ethanoic acid from nitroethane?

Ans: Nitroethane can be converted into ethanoic acid by hydrolysis of nitroethane with dilute hydrochloric acid.



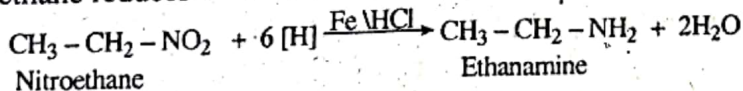
Q.4. What is the main product obtained when nitromethane is reacted with ethylmagnesium bromide in presence of dry ether?

Ans: Acidic form of nitromethane reacts with ethylmagnesium bromide to give ethane in presence of dry ether.



Q.5. Name the product obtained when nitroethane is reduced catalytically.

Ans: Nitro ethane reduces in acidic medium to give Ethanamine as:



14.2 Aromatic Nitro-compounds

Very Short Questions-Answers

Q.1. Explain, why $-\text{NO}_2$ group in nitrobenzene is meta-directing?

Ans: A substituent or group that directs an incoming group to the meta position in aromatic ring is known as **meta-director**.

Nitrobenzene can be represented by the following resonating structures.

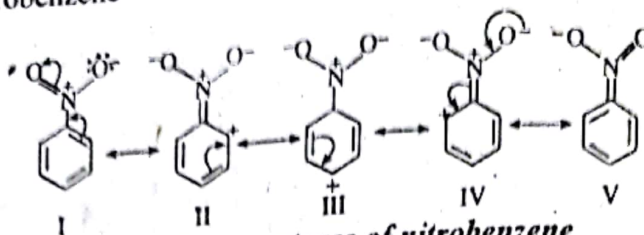
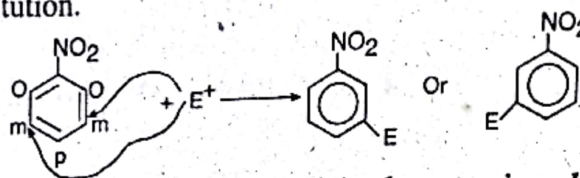


Fig: resonating structures of nitrobenzene

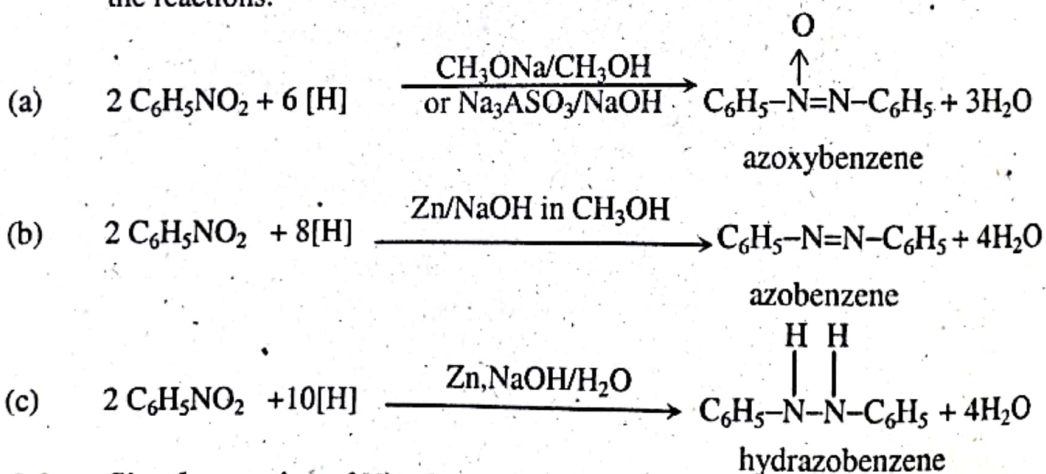
In nitrobenzene, $-\text{NO}_2$ group is linked to the benzene ring and acts as electron withdrawing group. The $-\text{NO}_2$ group withdraws the electron from the benzene ring by resonance especially from ortho and para positions. Therefore, positive charge is developed in benzene ring especially at o-and p-position where electron density becomes relatively lower than meta position. An incoming electrophile (E^+) cannot attack the ring at o and p-positions (like (+) charges repel each other). So, it can attack the meta position relative to $-\text{NO}_2$ group which has relatively higher electron density than o-and p-positions. Thus, NO_2 group is meta director in electrophilic aromatic substitution.



Q.2. What are the products obtained when nitrobenzene is reduced in alkaline medium under different conditions?

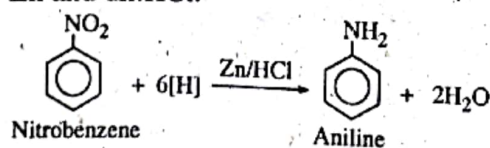
Ans: When nitrobenzene is reduced in alkaline medium, varieties of products are obtained depending upon the nature of reducing agents used.

The reduction of nitrobenzene in alkaline medium is given below in the reactions.

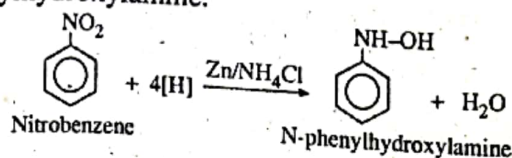


Q.3. Give the reaction of Nitrobenzene with (a) $\text{Zn}/\text{dil. HCl}$ and (b) $\text{Zn}/\text{NH}_4\text{Cl}$.

Ans: (a) $\text{Zn}/\text{dil. HCl}$: Nitrobenzene gets reduced into aniline when reacted with Zn and dil. HCl.

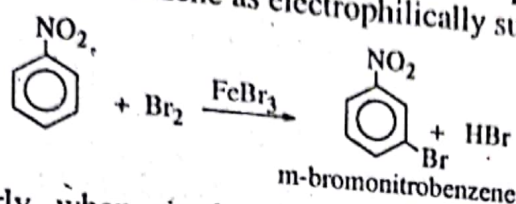


(b) $\text{Zn}/\text{NH}_4\text{Cl}$: In neutral medium, nitrobenzene is reduced into N-phenylhydroxylamine.

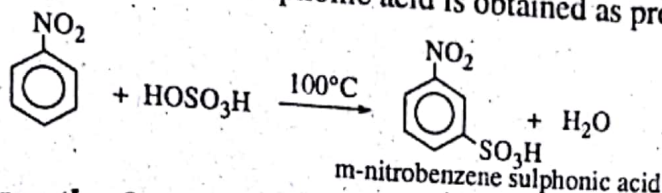


Q.4. Mention any two examples of electrophilic substitution in nitrobenzene.

Ans: Nitrobenzene reacts with Br_2 in presence of FeBr_3 to give m-bromonitrobenzene as electrophilically substituted product.

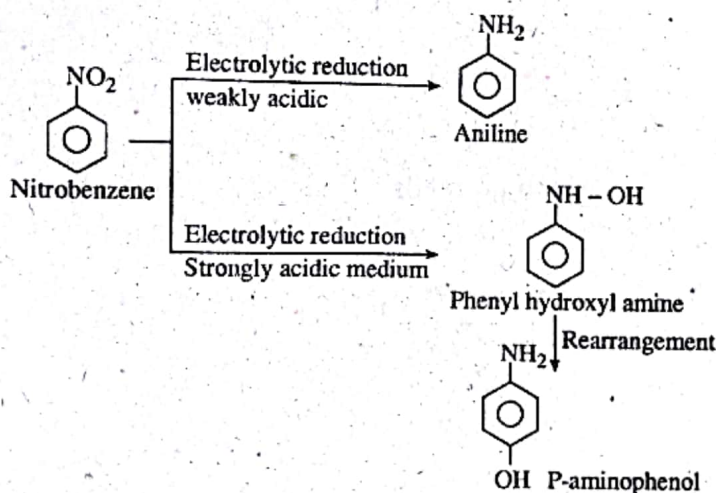


Similarly, when nitrobenzene is sulphonated with fuming sulphuric acid at 100°C , m-nitrobenzene sulphonic acid is obtained as product.



Q.5. What are the factor that governs the product of electrolytic reduction of nitrobenzene?

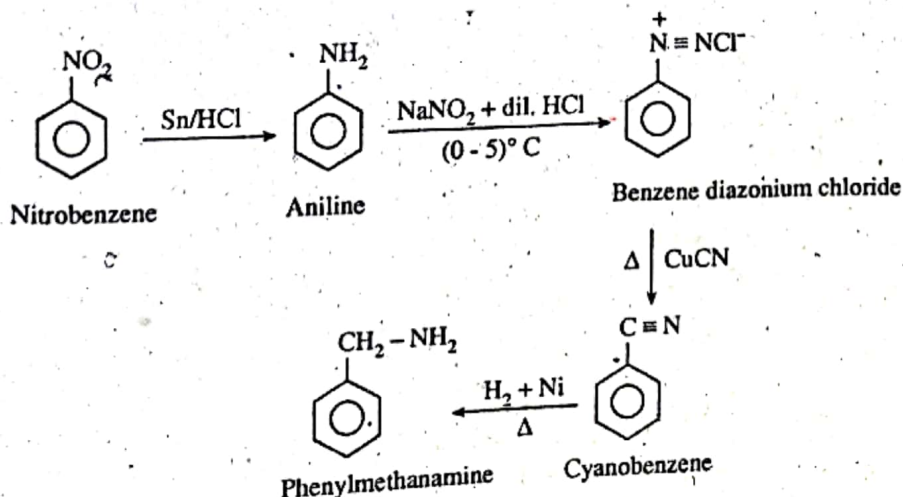
Ans: The products of electrolytic reduction of nitrobenzene depend upon the acidity of the medium. In weakly acidic medium aniline is obtained as major product while in strongly acidic medium p-amino phenol is the major product.



Short Questions-Answers

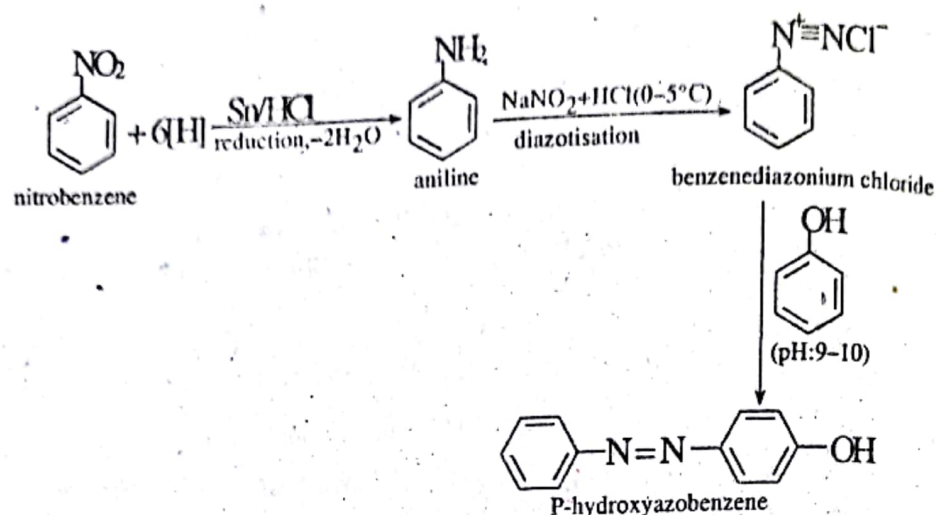
Q.6. How can you convert nitrobenzene into phenylmethanamine?

Ans: The conversion can be carried out as shown in the reaction sequence given below:

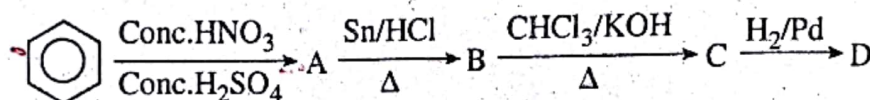


Q.7. How can we get *p*-hydroxy azobenzene from nitrobenzene?

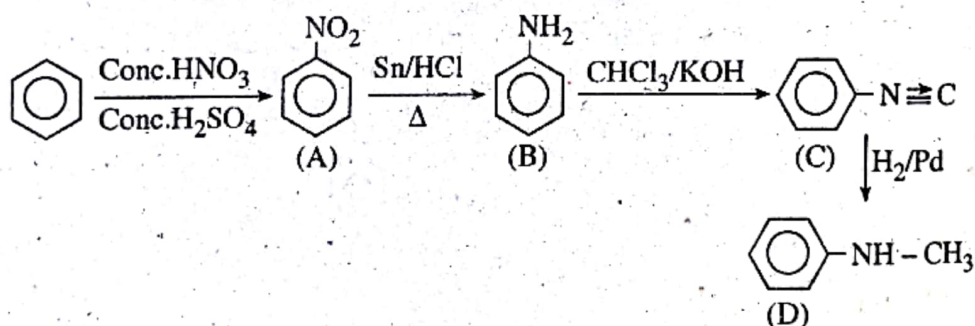
Ans: Nitrobenzene can be converted into *p*-hydroxyazobenzene as follows:



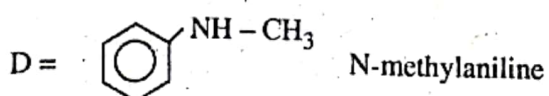
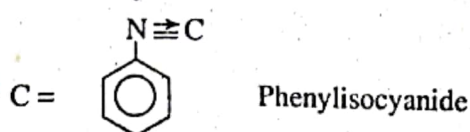
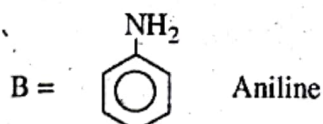
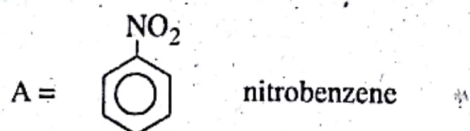
Q.8. Write down the structure of organic compounds A, B, C and D in the reaction sequence given below :



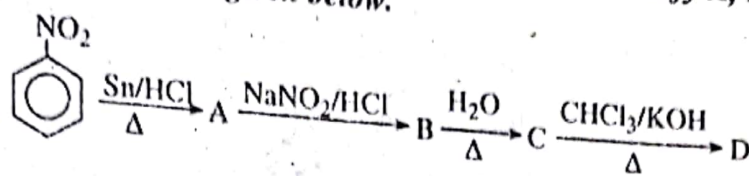
Ans: The above chain reaction proceeds as follows:



Hence, the products in the chain reaction are:



Q.9. Describe laboratory preparation of nitrobenzene. Identify A, B, C and D in the reaction sequence given below.

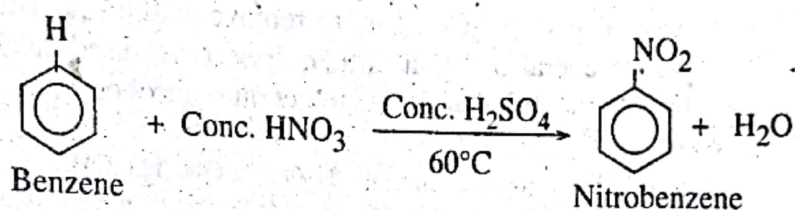


What happens when C is treated with aqueous Bromine?

Ans: Laboratory preparation of nitrobenzene

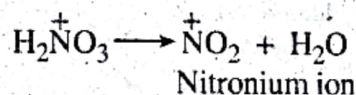
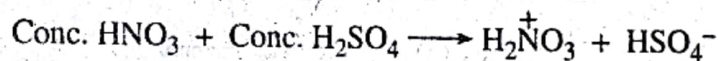
Pure and dry nitrobenzene is prepared as:

(a) **Theory / Principle:** Nitrobenzene is prepared in laboratory by directly nitrating benzene with nitrating mixture (Conc. H_2SO_4 + Conc. HNO_3) at 60°C .

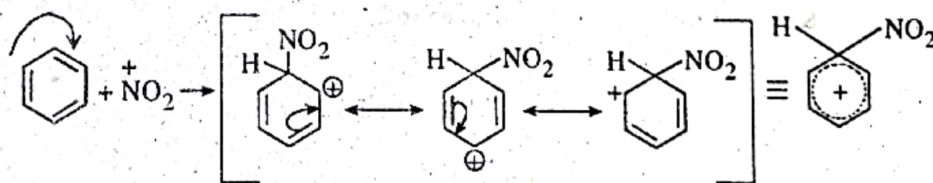


Mechanism: Nitration of benzene is an electrophilic substitution reaction and it takes place by the attack of nitronium (NO_2^+) ion as:

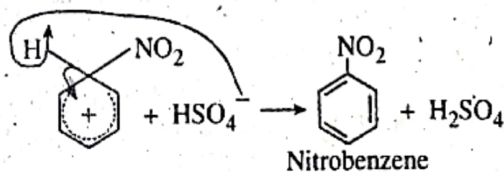
Formation of nitronium ion



Attack of nitronium ion on benzene ring



Loss of proton to give nitro benzene



[Note: H_2SO_4 is used up initially and regenerated ultimately. Hence it is acting like a catalyst.]

(b) **Procedure:** 50 mL of Conc. HNO_3 and 50 mL of Conc. H_2SO_4 is taken in a round bottom flask fitted with a reflux condenser and the mixture is shaken well and cooled under tap water. Then, nearly 50mL of benzene is added to the flask slowly and a little at a time with continuous cooling of the flask. After, the whole benzene has been added, the flask is refluxed at 60°C for one and half hour till the yellow oily layer appears on the surface.

(c) Instrumentation:

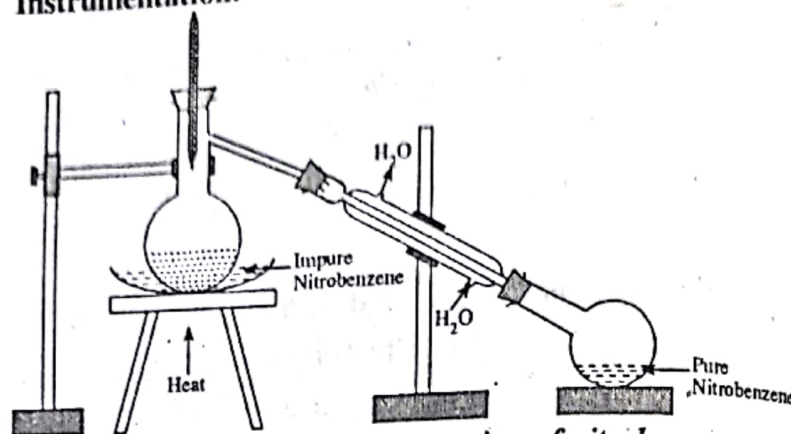
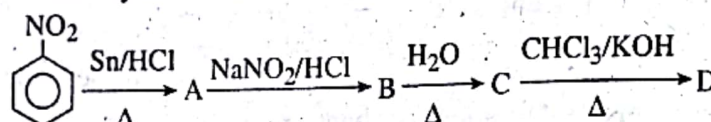
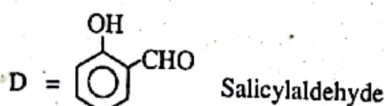
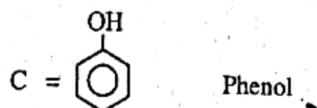
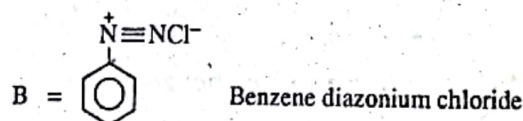
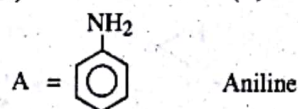
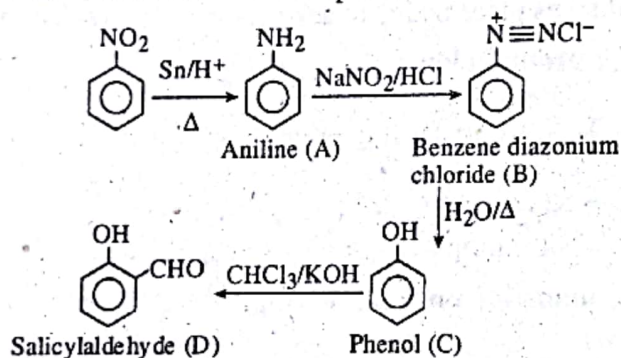


Fig: Laboratory preparation of nitrobenzene

- (d) **Purification:** The refluxed mixture is then taken in a separating funnel and the upper layer of nitrobenzene is separated. It is then washed with Na_2CO_3 first to remove acidic impurities and then with water several times. It is then dried over fused calcium chloride and finally redistilled at 211°C to get pure nitrobenzene.



The above chain reaction proceeds as



When the compound C is reacted with aqueous bromine, a white precipitate of 2, 4, 6-tribromophenol is obtained.

