



E – CONTENT

TOPIC – NITROBENZENE

B.Sc – HONOURS

PART – 2C

By

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DEPARTMENT OF CHEMISTRY

SUBJECT – ORGANIC CHEMISTRY

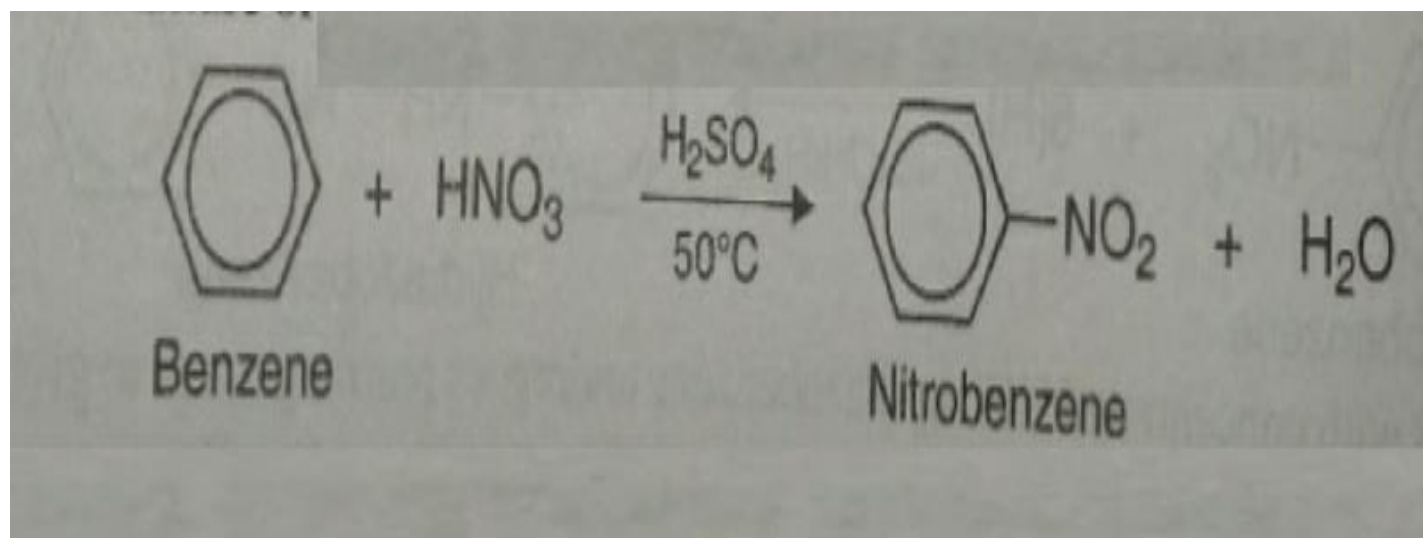
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Nitrobenzene, C₆H₅NO₂

It is the most important aromatic nitro compound.

Preparation. Both in the laboratory as well as in industry, nitrobenzene is prepared by heating benzene with a mixture of concentrated nitric acid and sulfuric acid at 50°C.



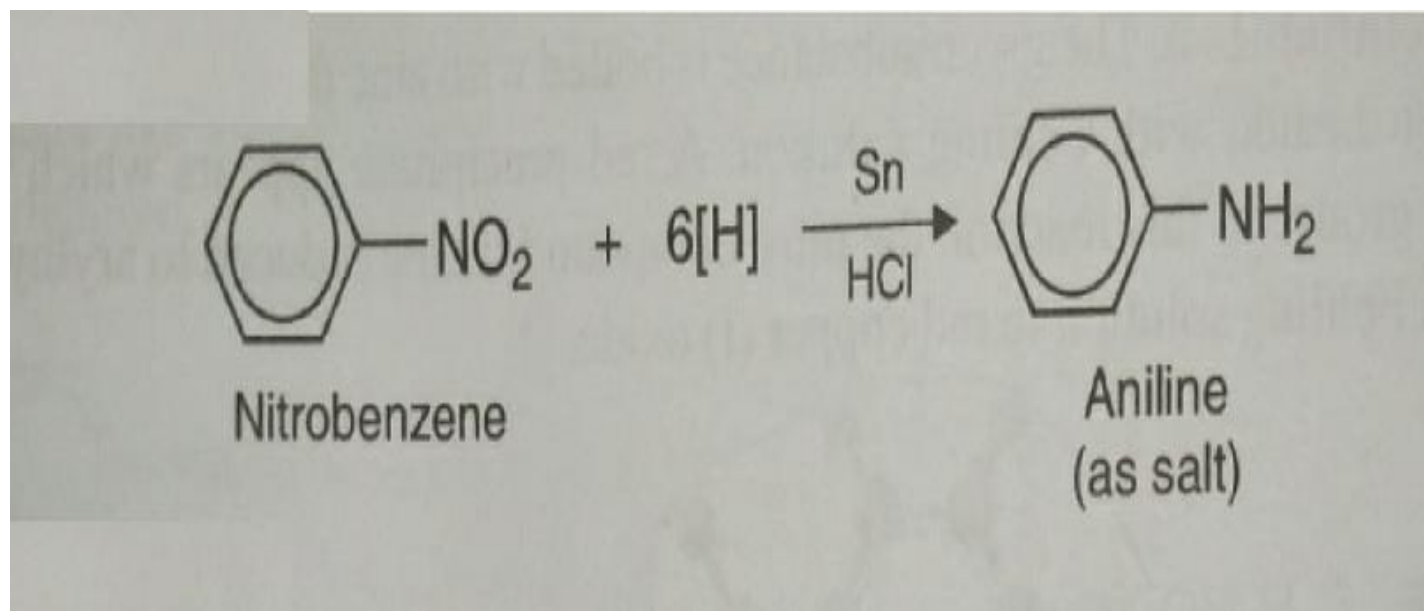
The resulting nitrobenzene is separated, washed with sodium carbonate solution to remove any acid, and purified by distillation using an air condenser. The laboratory procedure and the one used on a large scale differ only in working details.

Properties. (Physical) Nitrobenzene is a pale yellow liquid (bp 211°C ; sp. gr. 1.087) having odor of

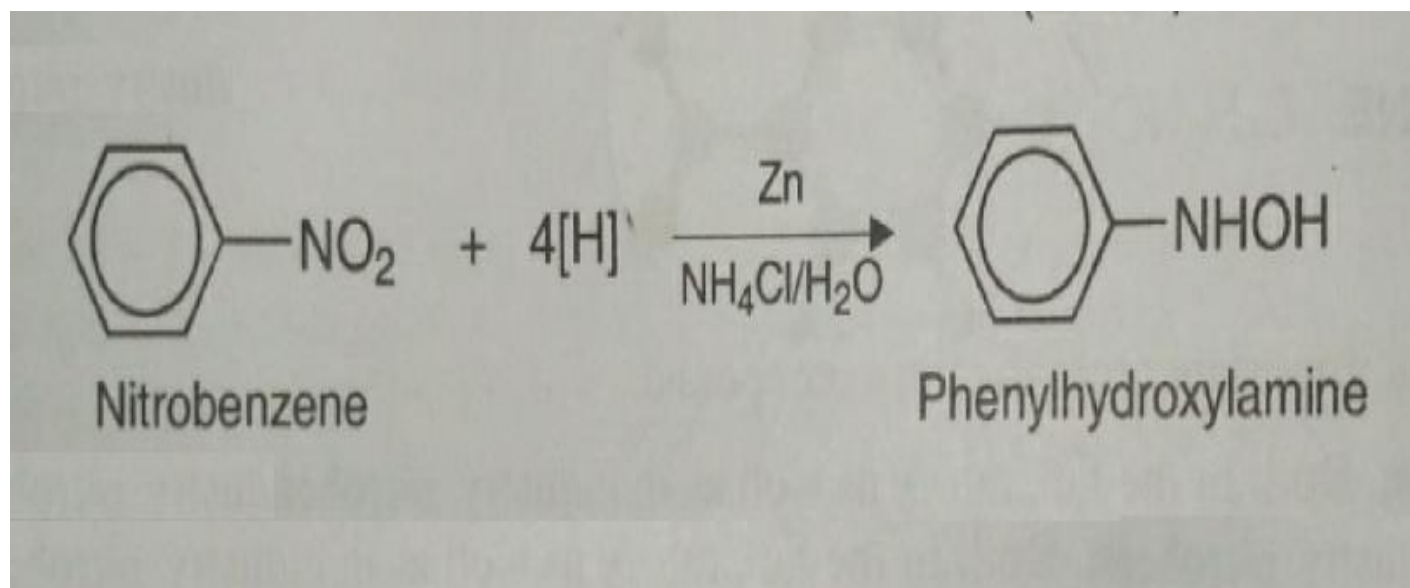
bitter almonds. It is insoluble in water but dissolves readily in most organic solvents. It is steam-volatile. Nitrobenzene is highly toxic.

(Chemical) The chemical reactions of nitrobenzene are those of the nitro group and the phenyl group. These have already been discussed. The only important reaction of $-NO_2$ group is that of reduction in acid medium, neutral medium or alkaline medium.

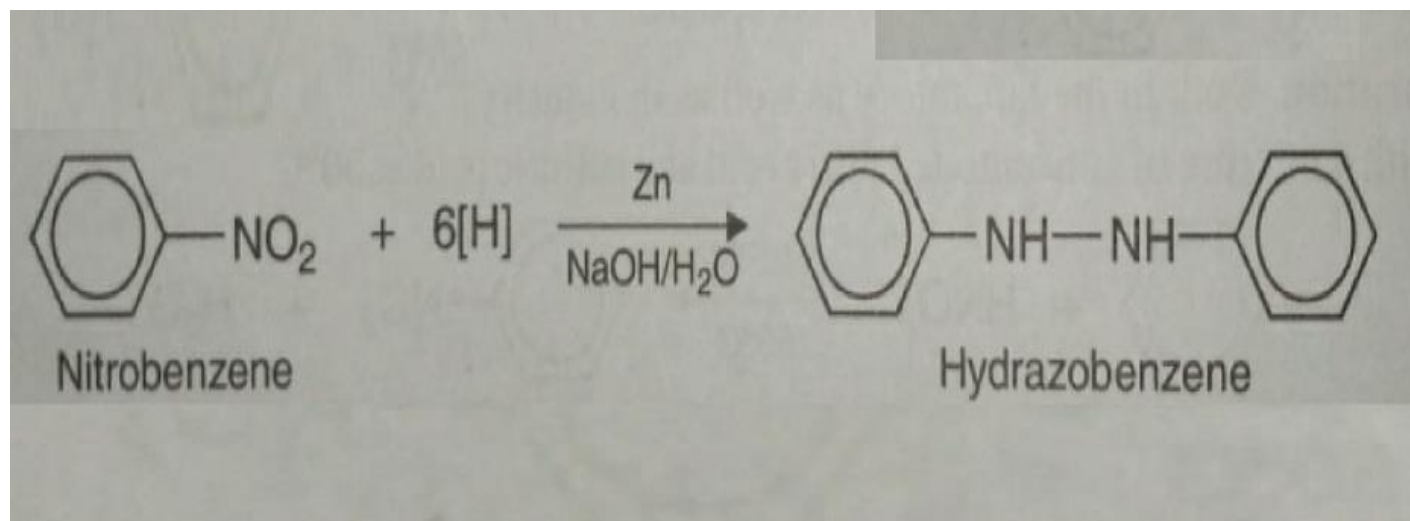
(a) Acid medium



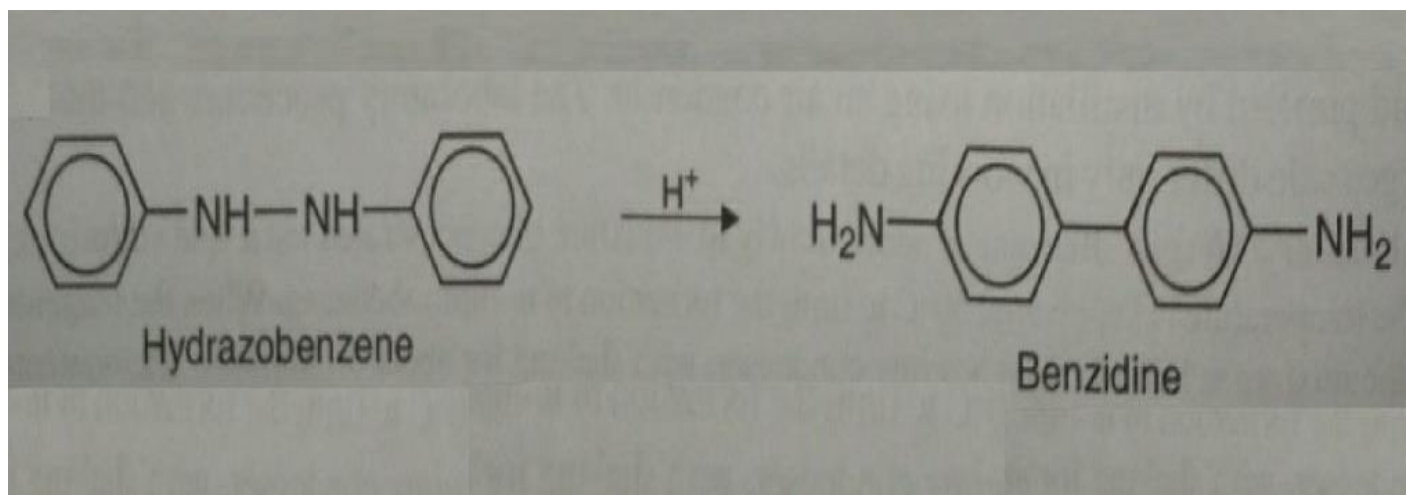
(b) Neutral medium



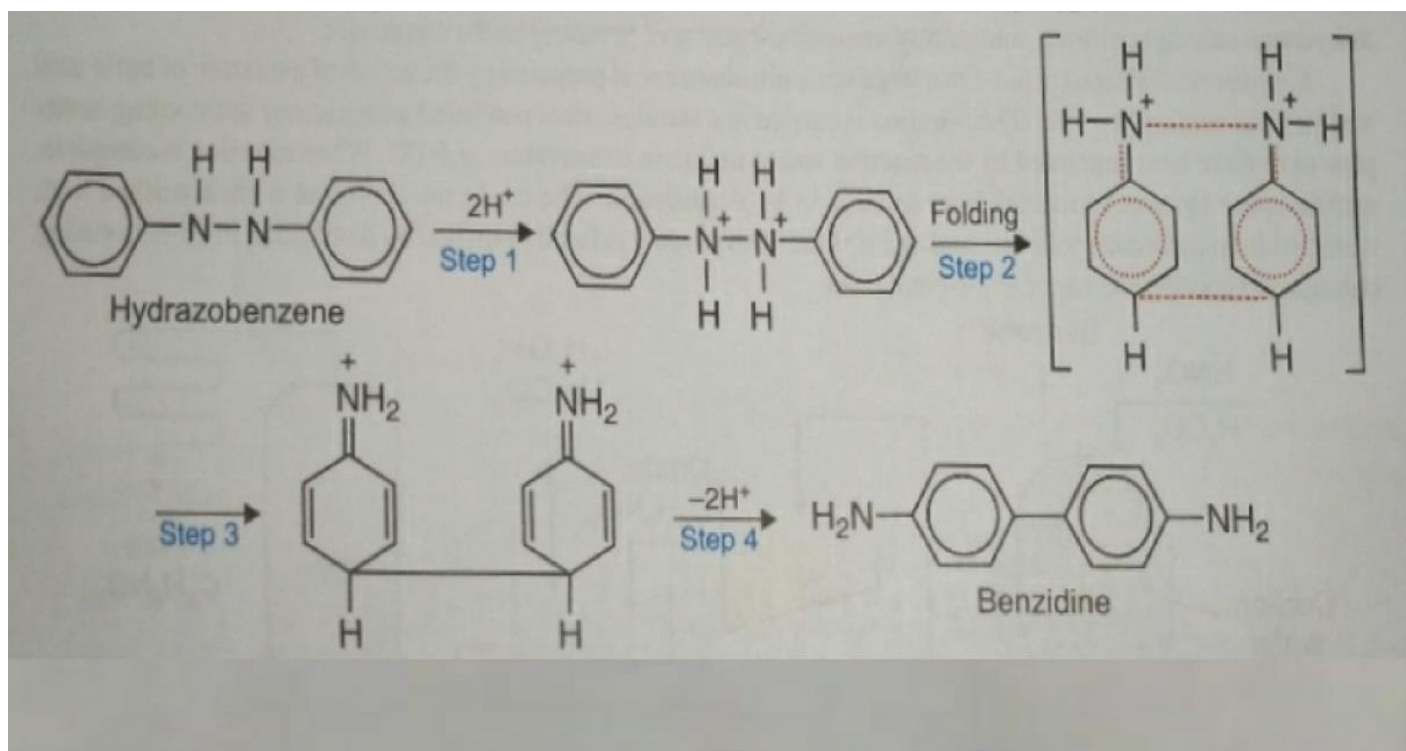
(c) Alkaline medium



When treated with concentrated HCl, hydrazobenzene undergoes rearrangement to give benzidine. The acid-catalyzed rearrangement of hydrazo compounds is called **Benzidine Rearrangement**. For example,

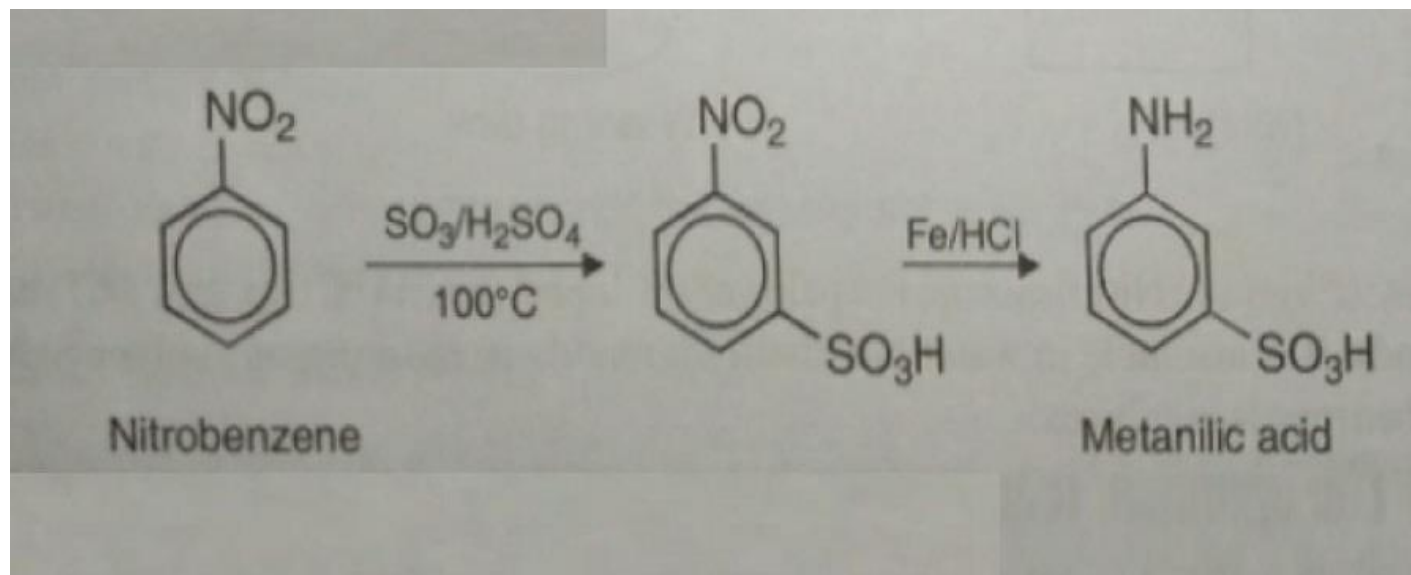


MECHANISM. It involves the formation of a bond between the para positions of the two rings, and cleavage of the nitrogen-nitrogen bond. Following four steps are involved :



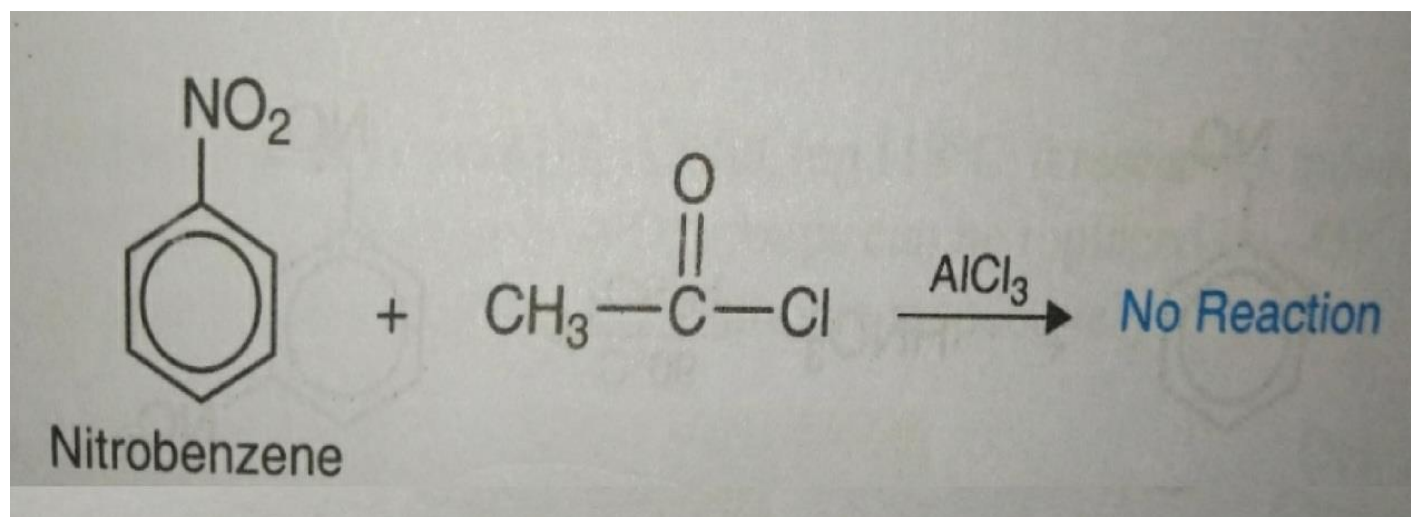
Nitrobenzene undergoes electrophilic substitution in

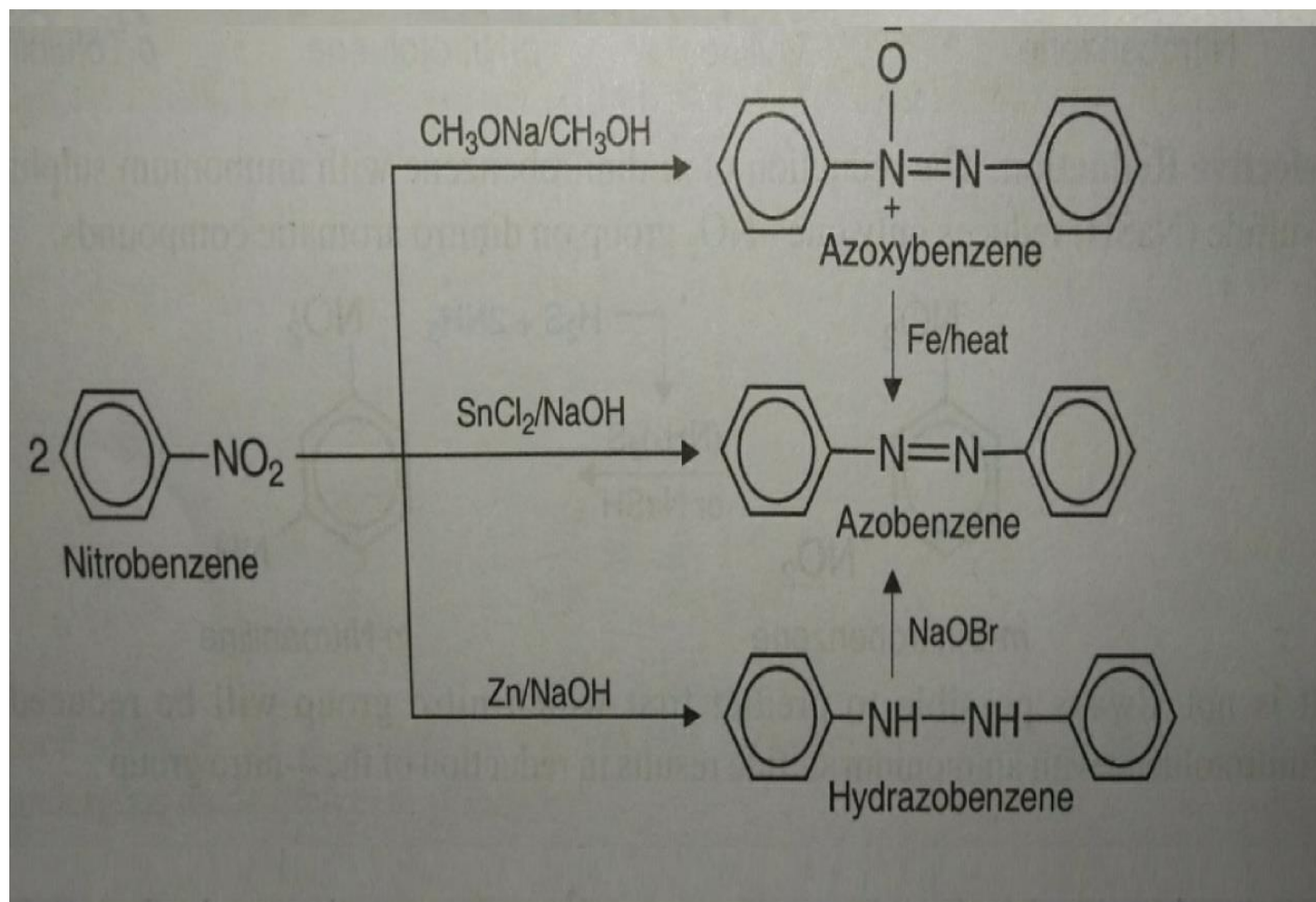
meta position. Thus it can be converted to metanilic acid by the following procedure.



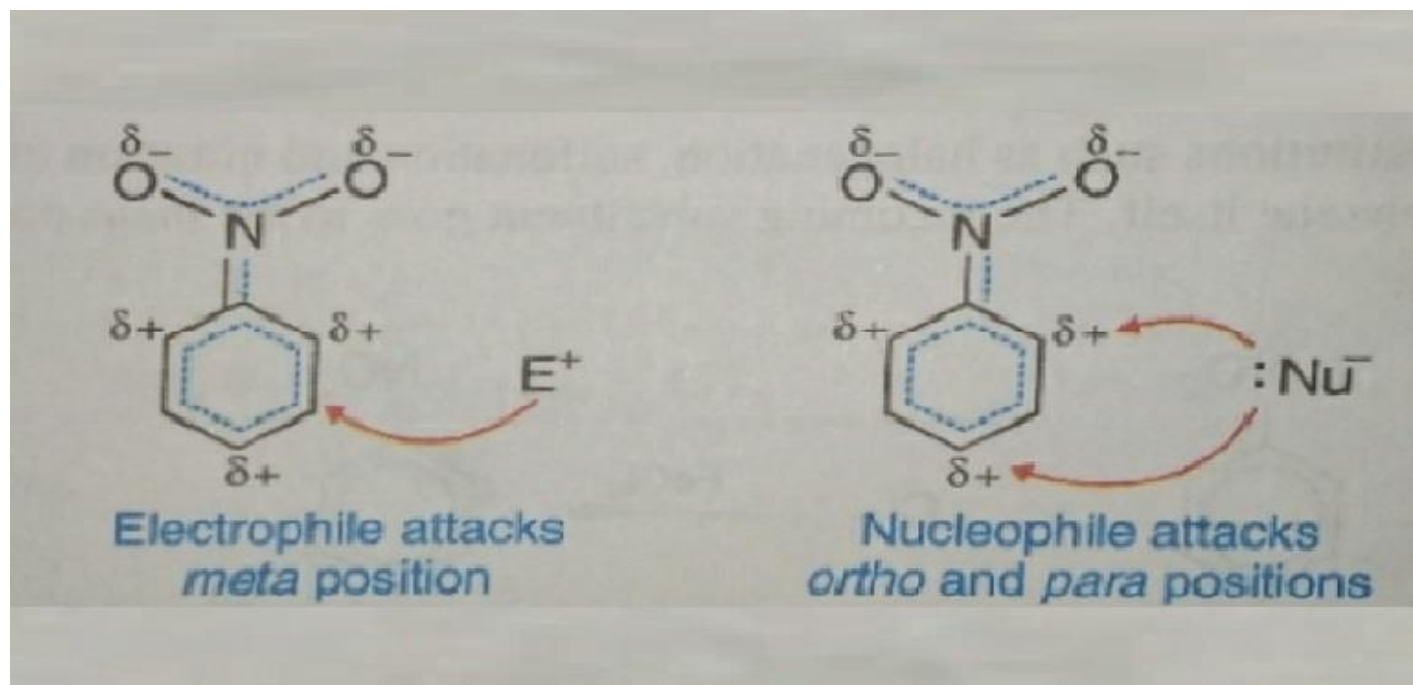
Both benzidine and metanilic acid are dye intermediates.

Remember that the nitro group is a deactivating group. As a result, nitrobenzene does not undergo Friedel-Crafts reactions.

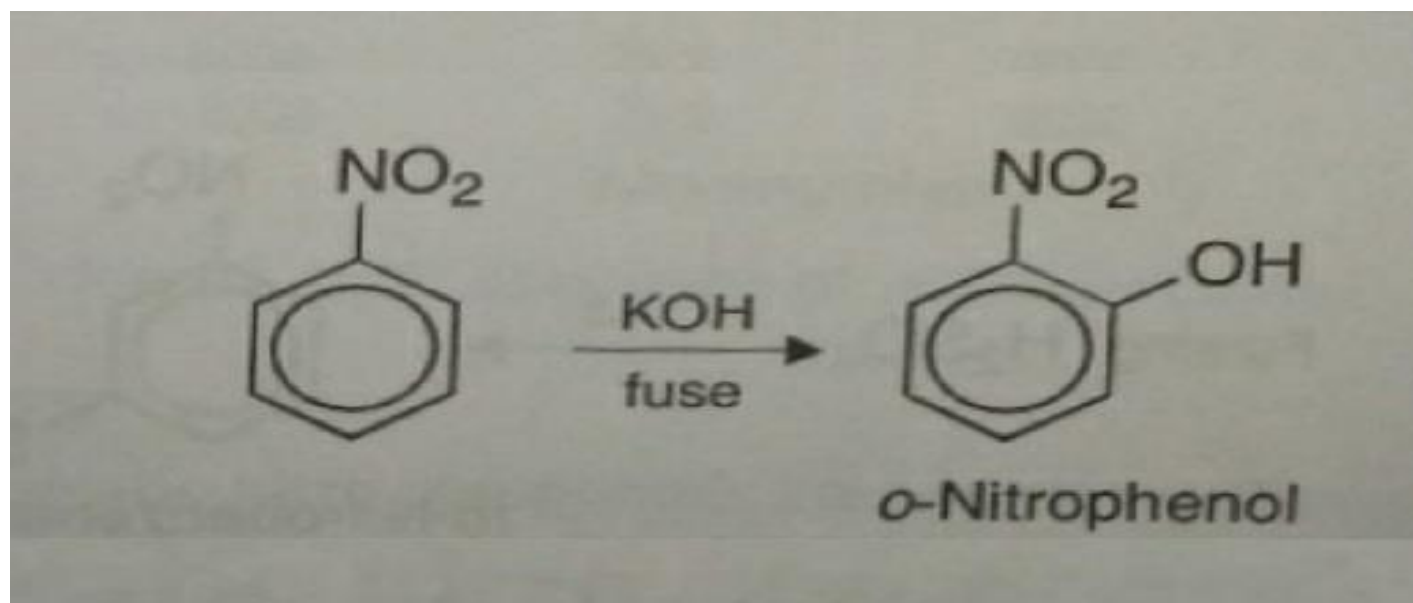




Nucleophilic Substitution Reactions. The benzene ring is deactivated to electrophiles (E^+) and activated to nucleophiles (Nu^-) due to withdrawal of electrons from it by inductive and resonance effects. As evident from the hybrid structure, the ring will undergo electrophilic substitution with difficulty at relatively electron-rich meta positions, and nucleophilic substitution at the ortho and para positions bearing positive charge.

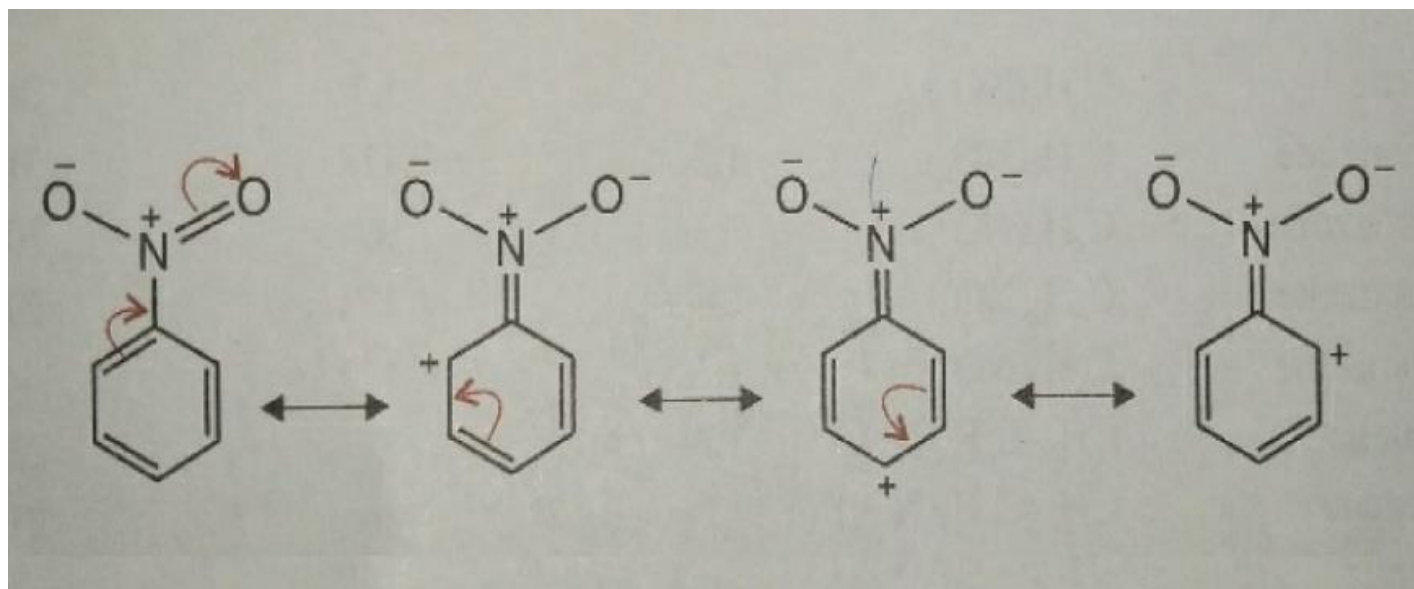


The ortho and para positions of nitrobenzene are attacked by nucleophiles relatively easily. Thus when fused with KOH, nitrobenzene gives o-nitrophenol through nucleophilic attack of OH on the ring.

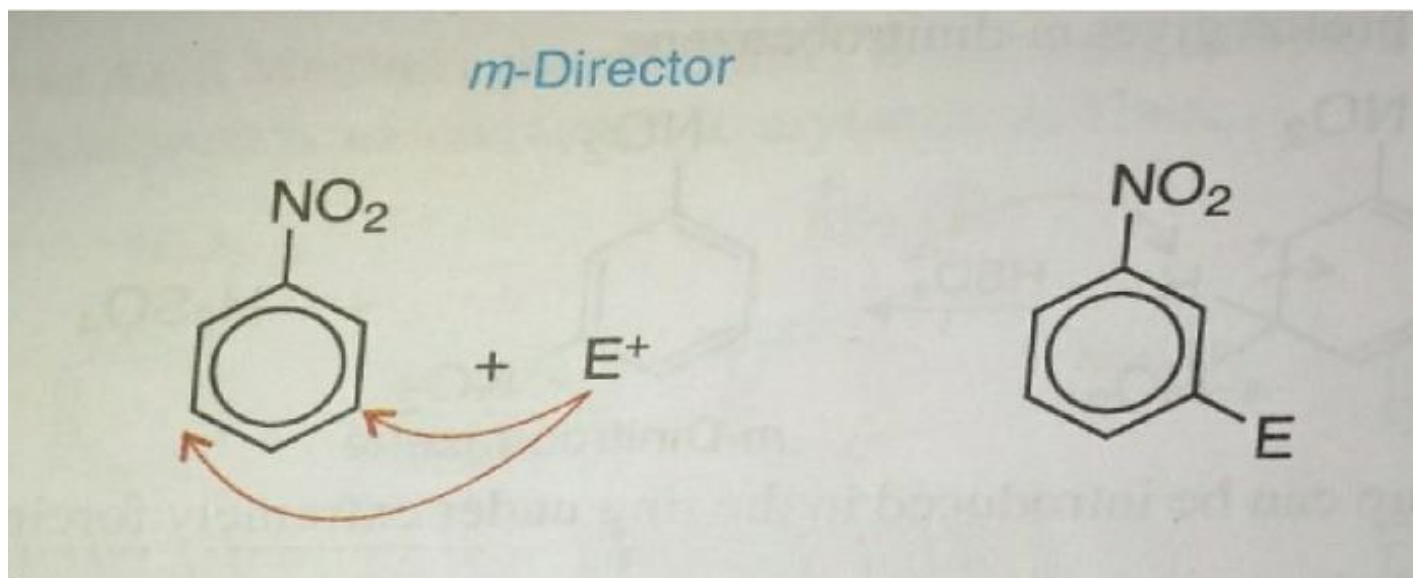


Electrophilic Substitution Reactions. The nitro group ($-\text{NO}_2$) acts as a meta director and deactivating when it is present on a benzene ring undergoing electrophilic substitution.

EXPLANATION. Nitrobenzene can be represented as a hybrid of the following resonance structures :



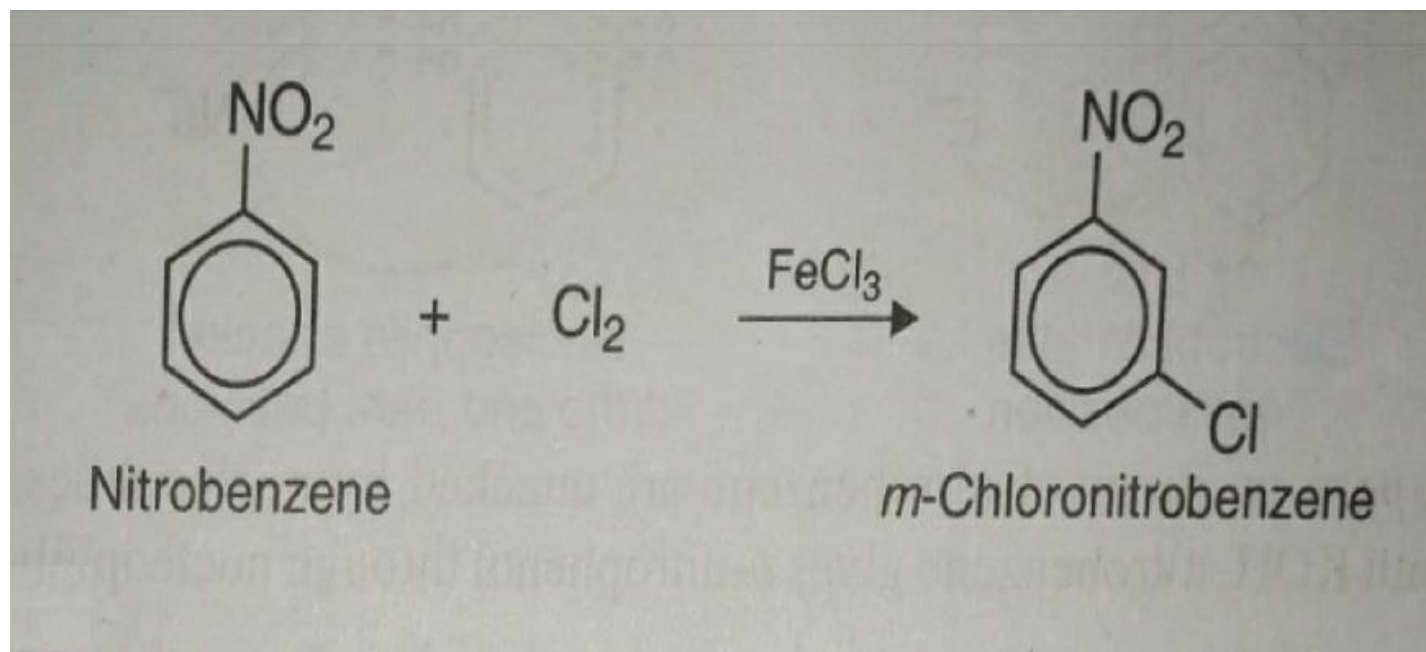
Notice that the ortho and para positions in the above resonance structures carry a positive charge. An electrophile (E^+) cannot attack these positions (like charges repel). It will attack the meta positions which are relatively electron-rich. Thus, the nitro group directs all electrophiles to the meta positions.



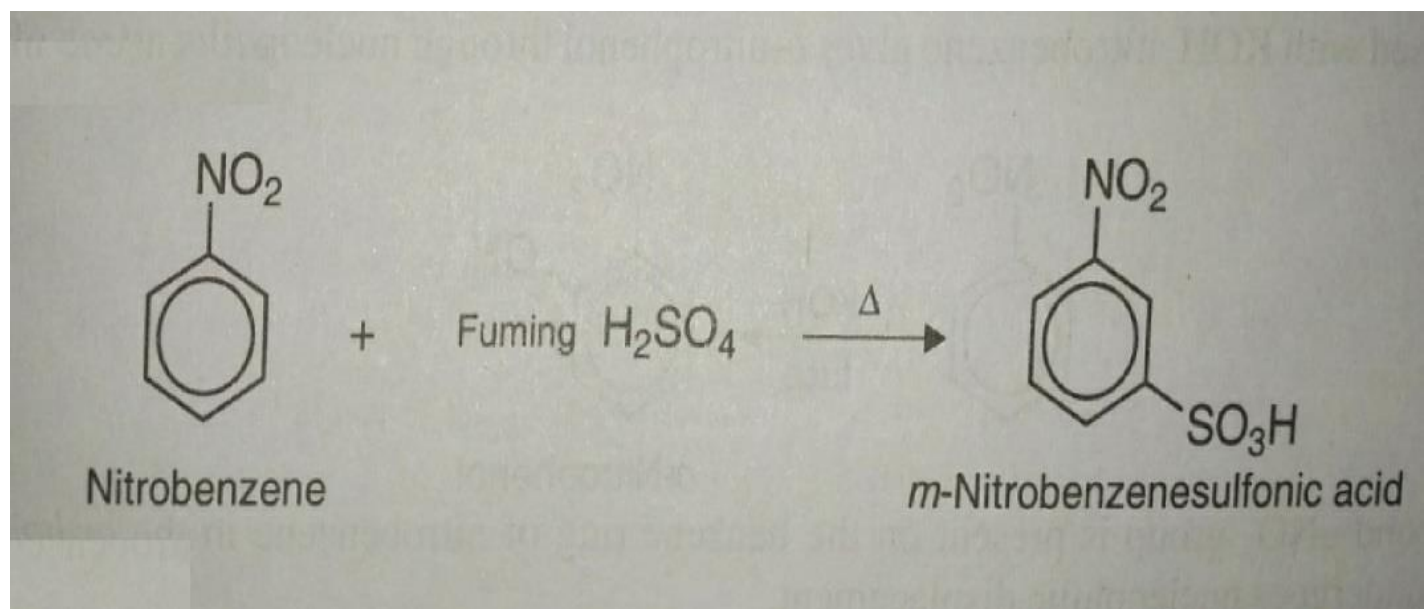
The $-\text{NO}_2$ group is deactivating. This means that nitrobenzene undergoes electrophilic substitution more slowly than benzene. Notice that the nitro group withdraws electrons from the ring by resonance. It decreases electron density of the ring and makes it less attractive to an incoming electrophile. Thus, the electrophilic substitution is slow, and requires vigorous reagents and conditions.

The $-\text{NO}_2$ group is deactivating and meta director. Therefore, the aromatic nitro compounds undergo the usual substitutions such as halogenation, sulfonation and nitration under more drastic conditions than for benzene itself. The incoming substituent goes to the meta position

(a) Halogenation



(c) Sulfonation



(c) Nitration

