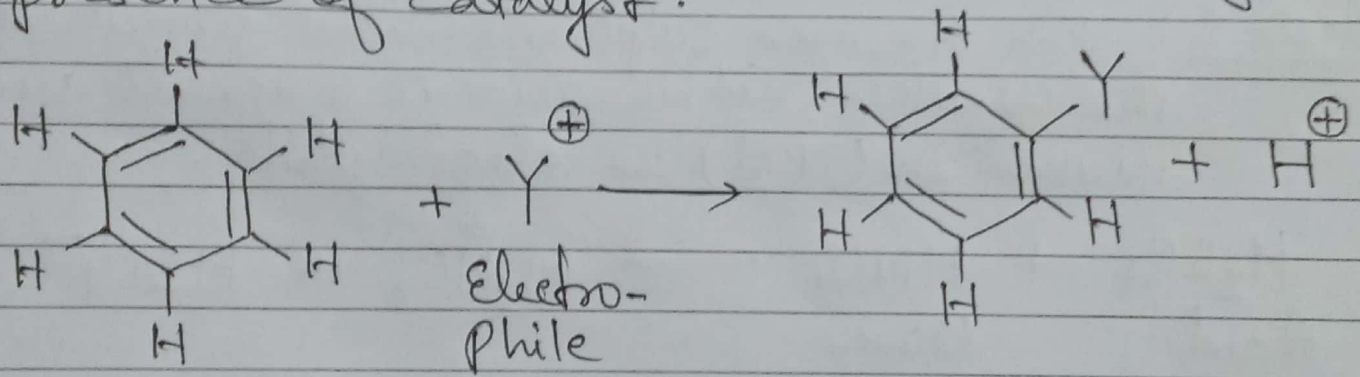
Expt. No. Chemical Properties of Aromatic Compounds Date .....

(A) Electrophilic Substitution Reaction

Electrophilic substitution reaction is the characteristic reaction of aromatic compounds due of π-electron cloud of the aromatic ring.

Aromatic compounds have high degree of unsaturation but they resist addition reactions, because they donot want to lose their aromatic character, which provides extr stability in terms of resonance energy

Electrophilic aromatic substion involves successive replacement of benzene ring hydrogens by reaction with an electrophile usually in presence of catalyst.



Common electrophilic substitution reactions of benzene and its derivatives are as follows:

(1) Nitration - When benzene is heated with mixture of concentrated sulphuric acid and nitric acid at 50 - 60°C for an hour, nitrobenzene is obtained.

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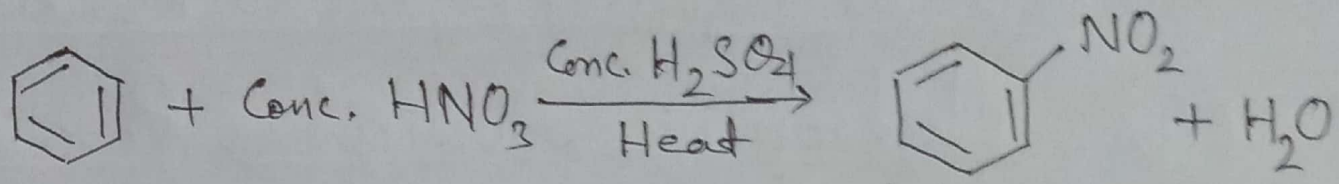

Benzene — Nitrobenzene

Concentrated sulphuric acid helps to produce nitronium ion (NO_2^+) as electrophile from nitric acid. This fact can be explained on the basis of mechanism of nitration reaction.

Mechanism of nitration of benzene

Following steps are involved in the mechanism of nitration of benzene.

Step-1: The stronger sulphuric acid protonates the weaker nitric acid to generate nitronium ion (NO_2^+) as electrophile.

$$\underset{\text{Acid}}{H_2SO_4} + \underset{\text{Base}}{HNO_3} \longrightarrow \overset{\oplus}{H_2}NO_3 + HSO_4^-$$

$$\overset{\oplus}{H}NO_3 \rightleftharpoons H_2O + \overset{\oplus}{N}O_2$$

Step-2: The nitroniu ion ($\overset{\oplus}{N}O_2$) attacks on benzene ring to form a ~~complex~~ sigma complex. A sigma complex is the resonance stabilised carbonium ion produced by attachment of electrophile on aromatic ring.

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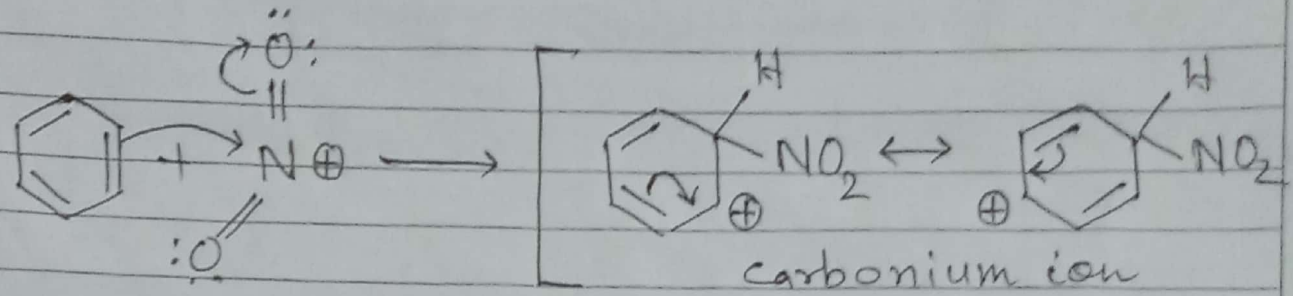
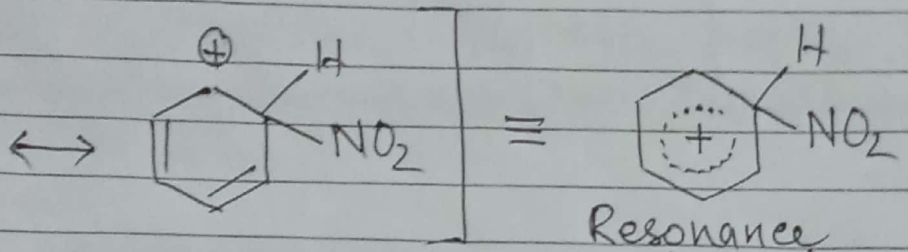
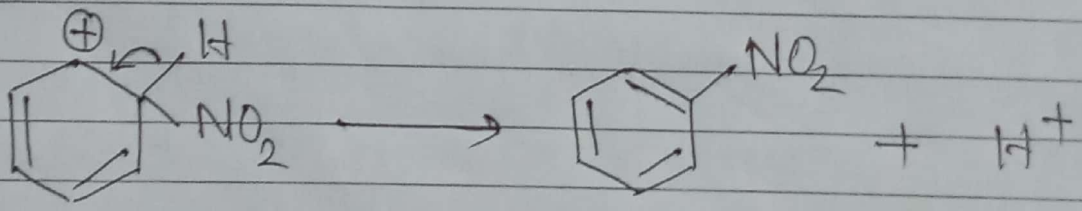




Step-3: The sigma complex loses a proton to form nitrobenzene and attain aromatic character.



$$H^+ + HSO_4^- \longrightarrow H_2SO_4.$$

* In the mechanism of nitration, step-1 is the acid base reaction in which weaker nitric acid behaves as a base
* In step-2, by formation of a sigma complex known as Wheland intermediate, aromatic character of the ring is destroyed, therefore it is slow and rate determining step.

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