

1. AROMATIC ELECTROPHILIC SUBSTITUTION REACTIONS

Electrophilic substitution :

Substitution reactions which involve electrophilic reagents and are called electrophilic substitutions.

Electrophilic reagents are called electrophiles. They are electron deficient species. So they attack centres which are electron rich. So they are called electrophiles (electron loving species). They may be positively charged or neutral species.

Some examples of electrophiles : (i) NO_2^+ (Positively charged nitronium ion) ii. SO_3 (Neutral) iii. RCO^+ (acyl cation) (v). Cl^+ (vi). Br^+ etc.

Examples of electrophiles substitution reactions of benzene :

- i. Nitration
- ii. Sulphonation
- iii. Friedel Craft's acylation and alkylation etc.

General mechanism of aromatic electrophilic substitution

The general mechanism of aromatic electrophilic substitution consists of three steps.

- (i) Generation of the electrophile
- (ii) Formation of carbonium ion and
- (iii) Proton transfer to yield the final product,

Illustration :

Refer Nitration, Sulphonation etc reactions which appear in subsequent pages.

Effect of Substituents

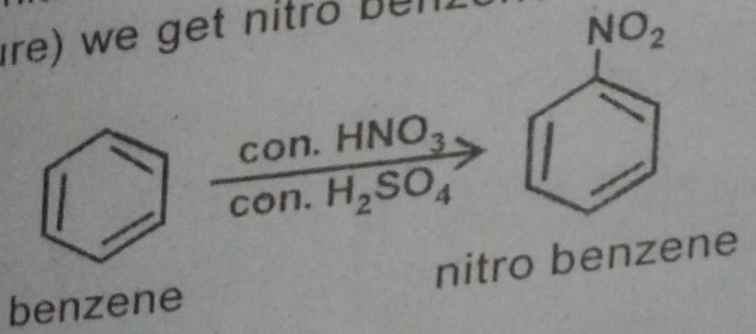
When one group is introduced into the benzene ring, only one product is possible, when a second group is introduced three isomers are possible, depending upon whether the incoming group goes to the ortho, meta or para position with respect to the existing group.

bond breaking
reaction.

1. NITRATION

Reaction :

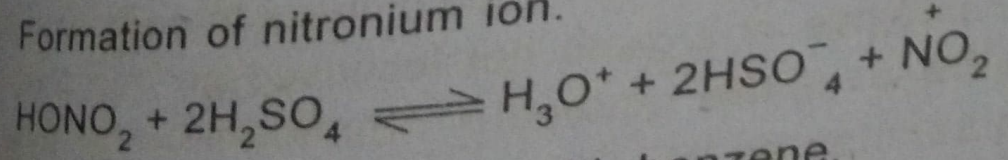
When benzene is nitrated with concentrated nitric acid and concentrated nitric acid and concentrated sulphuric acid mixture (called nitrating mixture) we get nitro benzene.



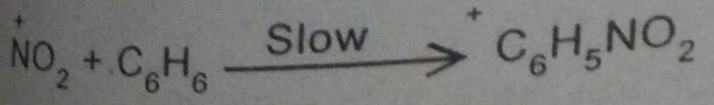
Mechanism :

The commonly accepted mechanism for nitration involves the following steps.

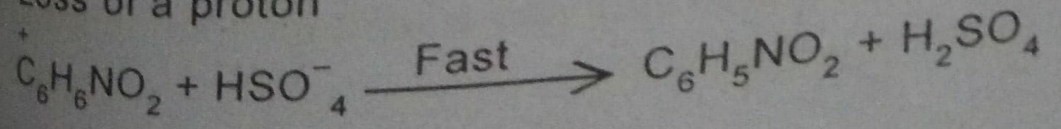
1. Formation of nitronium ion.



2. Reaction of nitronium ion with benzene.

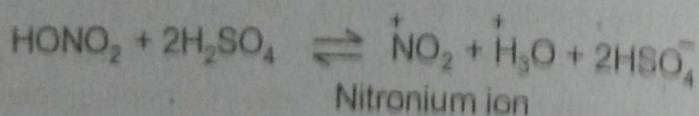


3. Loss of a proton



1. Formation of nitronium ion :

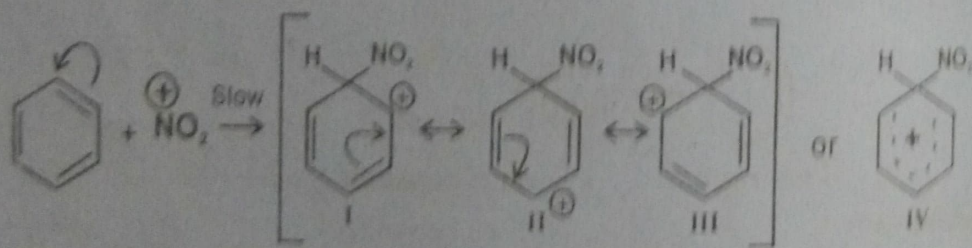
When only nitric acid is used the nitration is very slow. It suggests that H_2SO_4 is reacting with nitric acid rather than with benzene. The reaction of HNO_3 and H_2SO_4 can be written as



The nitronium ion is well known, existing in salts such as nitronium perchlorate NO_2^+ , ClO_4^- and nitronium fluorate NO_2^+ , BF_4^- . Solutions of those nitronium salts (in solvents like nitromethane or acetic acid) have been found to nitrate aromatic compounds smoothly. The yield was also good at room temperature. This confirms that nitronium ion is responsible for nitration. Instead of H_2SO_4 other strong acids like HClO_4 , HF and FB_3 have also been found to liberate NO_2^+ ion from nitric acid.

2. Reaction of nitronium ion with benzene :

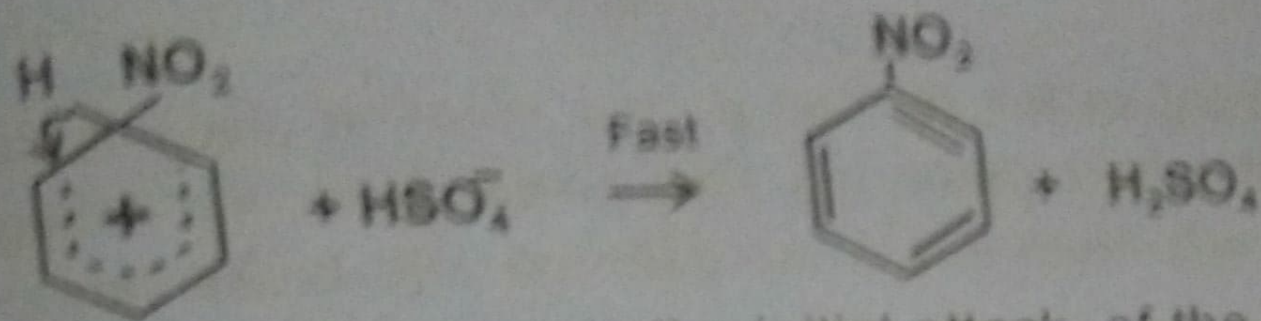
NO_2^+ ion, which is the electrophilic particle actually attacks the benzene ring. This reaction is simply an acid-base reaction. A σ complex is formed. It is a carbonium ion. We find that the carbonium ion can be represented by three resonating structures I, II and III. These differ only in the position of double bonds and positive charge.



The actual ion must then be a resonance hybrid of these three structures. This means that the positive charge is not localised on one carbon atom. It is distributed over the molecule. Sometimes the hybrid carbonium ion is represented as IV.

3. Loss of a proton :

The formation of the carbonium ion (step 2) is more difficult a step. Once the carbonium ion is formed, it loses a hydrogen ion (proton) to form the products. This is a fast step.

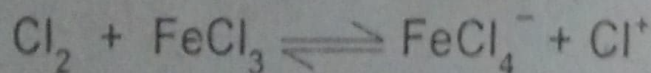


The rate determining step is the initial attack, of the nitronium ion (NO_2^+). The removal of proton is very fast and does not affect the rate. This has been confirmed by the fact that the rate of nitration remains unaffected when the hydrogens of the benzene ring are replaced by the heavier isotope, deuterium.

3. HALOGENATION

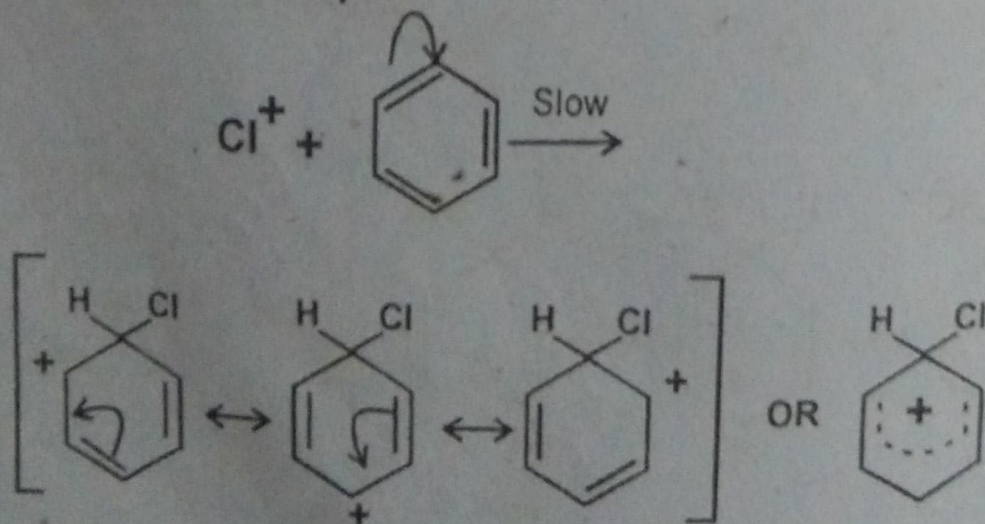
Halogenation (chlorination and bromination) takes place in the presence of Lewis acids such as ZnCl_2 , FeCl_3 , FeBr_3 , AlCl_3 , AlBr_3 , etc. Chlorination can be taken as an illustration for halogenation. The usual practise is to add to the reaction mixture some iron filings which are converted by chlorine into ferric chloride. Ferric chloride acts as catalyst. The function of the catalyst is to induce a small degree of polarization in the halogen molecule. The sequence of reaction is illustrated below:

1. Generation of electrophile

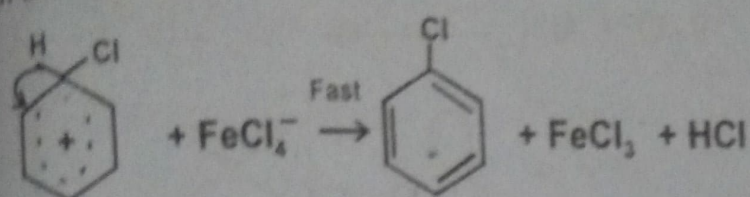


This step is an acid-base equilibrium. The ferric chloride (or any other catalyst) attaches itself to a chlorine molecule to form the FeCl_4^- ion and a positive chlorine ion.

2. Formation of σ - complex



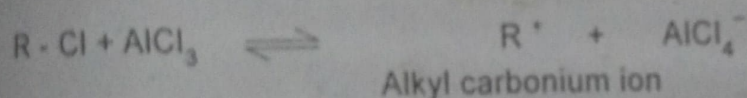
Proton transfer to yield the final product



FRIEDEL - CRAFT'S ALKYLATION

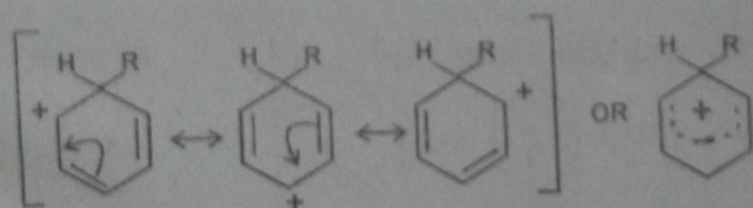
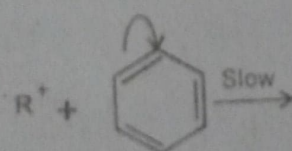
This reaction involves the introduction of an alkyl group (R^+) into the benzene ring by using an alkyl chloride (RCl) and a Lewis acid as catalyst. The usual catalyst is anhydrous aluminium chloride. The Friedel-Crafts' alkylation is a complicated affair. It can proceed by two mechanisms. We shall discuss the mechanism which will fit into the pattern of electrophilic aromatic substitution.

1. Generation of electrophile

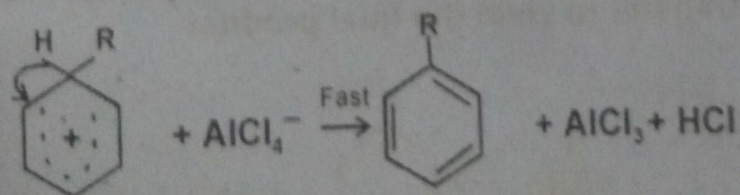


Alkyl halides, alcohols, esters, olefins, aldehydes and ketones may be used as alkylating agents.

2. Formation of carbonium ion (σ - complex)



3. Transfer of proton to yield the final product



Alternate mechanism :

In certain cases, the actual attacking reagent may not be a free alkyl carbonium ion. On the other hand, the attack may be brought