

CHEMISTRY STUDY MATERIALS FOR CLASS 12

(NCERT BASED NOTES OF CHAPTER - 10)

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Haloalkanes and Haloarenes

Reaction with metals

- (i) Alkyl halides react with Mg metal in ether medium to form alkyl magnesium halide (an organometallic compound) commonly called Grignard reagent.



Alkyl halides alkyl magnesium halide



Ethyl bromide Ethyl magnesium bromide

Grignard reagent is an example for organometallic compound. These are compounds in which carbon atom of an organic compound is directly bonded to metal atom. Other examples are tetraethyl lead, trimethyl aluminium etc.

In the Grignard reagent, the carbon-magnesium bond is covalent but highly polar and the magnesium halogen bond is ionic.

Grignard reagents are highly reactive and react with any source of proton (water, alcohols, amines etc) to give hydrocarbons (alkanes). It is therefore necessary to avoid even traces of moisture from a Grignard reagent.



(ii) Wurtz reaction:

Alkyl halides react with sodium in dry ether to give alkanes with double the number of carbon atoms. This reaction is known as **Wurtz reaction**.



Alkyl halides Alkane



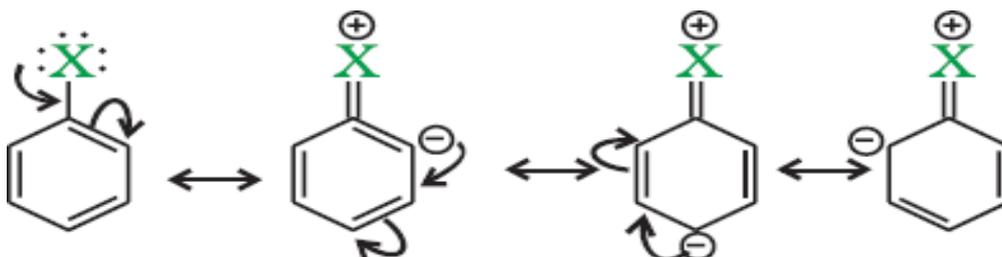
Methyl bromide Ethane

Reactions of Haloarenes

1. Nucleophilic Substitution Reaction:

Aryl halides are less reactive towards Nucleophilic substitution reactions due to the following reasons:

- i) **Resonance effect:** In haloarenes, the electron pairs on halogen atom are in conjugation with π -electrons of the ring and the following resonating structures are possible.



So the C—X bond acquires a partial double bond character.

Since it is difficult to break a C=C bond, the replacement of halogen atom by other atoms is not easy. So haloarenes are less reactive towards nucleophilic substitution reactions.

- ii) **Difference in hybridisation of carbon atom in C—X bond:**

In haloalkane, the halogen atom is attached to an sp^3 hybridised carbon while in haloarene, it is attached to an sp^2 hybridised carbon. Due to the greater s-character of sp^2 hybridised carbon, it is more electronegative and can hold the electron pair of C—X bond more tightly than sp^3 -hybridised carbon in haloalkane. So the C—X bond in haloarene is shorter than that in haloalkane. Since it is difficult to break a shorter bond than a longer bond, haloarenes are less reactive than haloalkanes towards Nucleophilic substitution reaction.

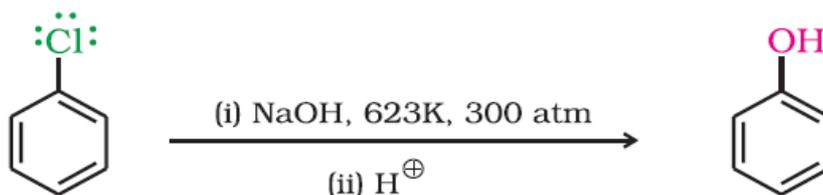
- iii) **Instability of phenyl cation:** In haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilized by resonance and therefore, S_N1 mechanism does not occur.

- iv) **Repulsion between nucleophile and electron rich benzene ring:**

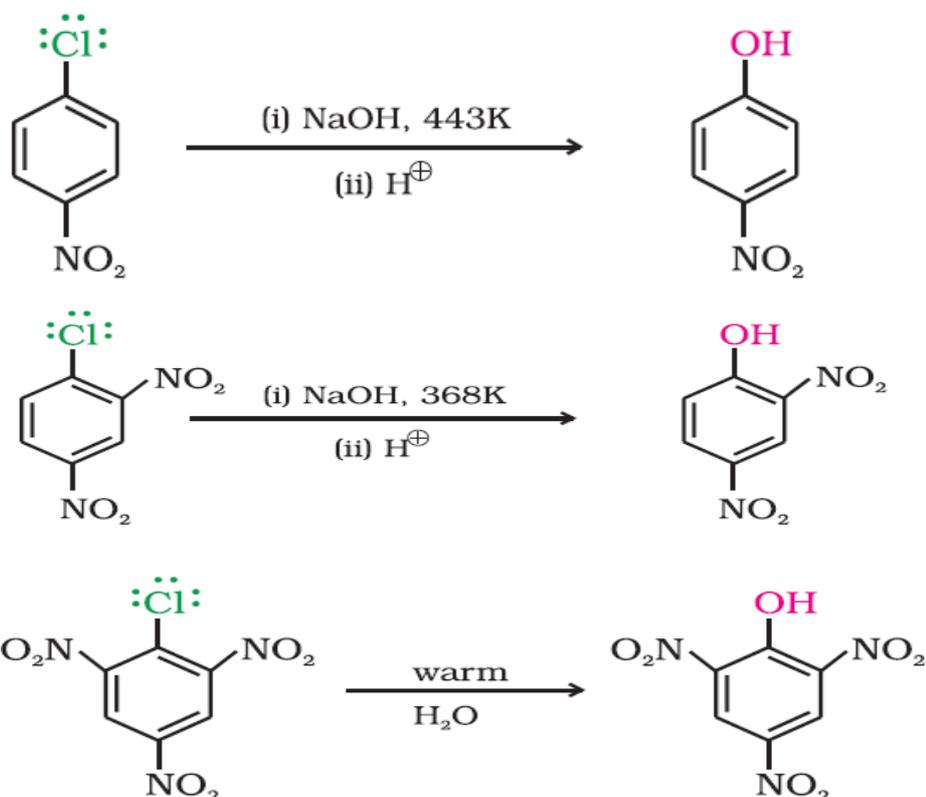
Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.

Replacement by hydroxyl group (Conversion to phenol)

Chlorobenzene when heated with aqueous sodium hydroxide solution at a temperature of 623K and a pressure of 300 atmospheres followed by acidification, we get phenol.



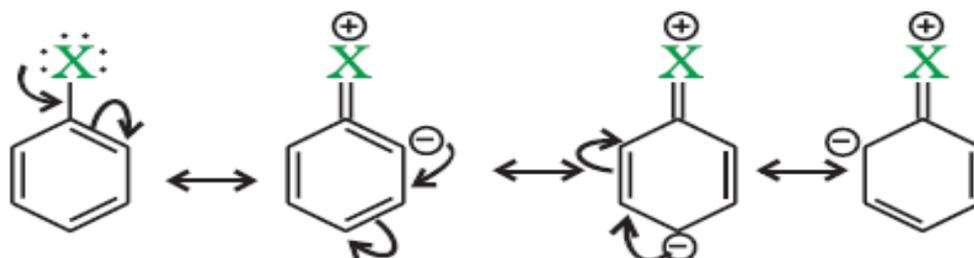
The presence of an electron withdrawing group (-NO₂) at ortho- and para-positions increases the reactivity of haloarenes.



The effect is more when -NO₂ group are present at ortho and para- positions. However, no effect on reactivity is observed by the presence of electron withdrawing group at meta-position.

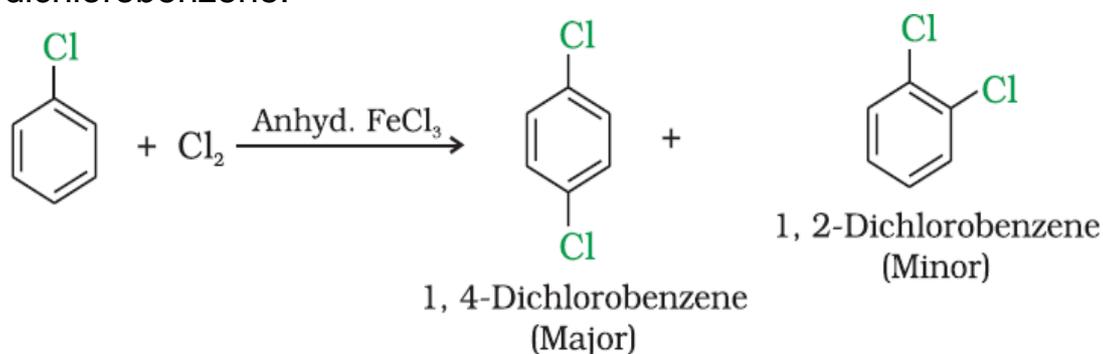
Electrophilic substitution reactions:

Haloalkanes are resonance stabilized as follows:

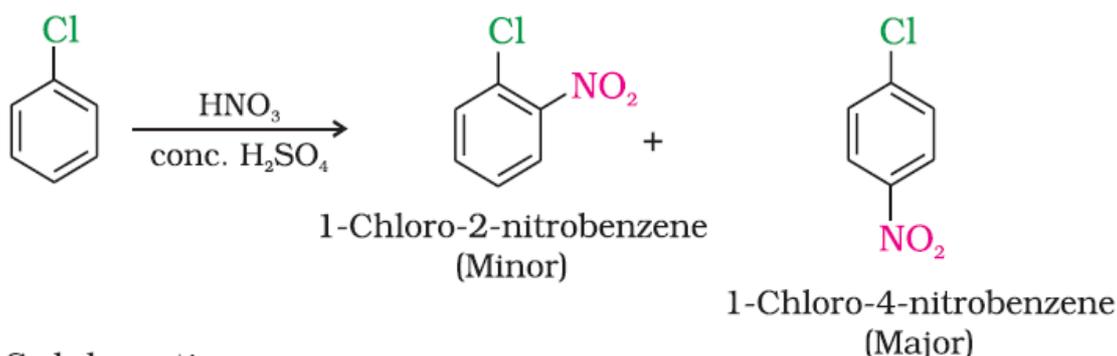


In the resonating structures, the electron density is greater on ortho-para positions. So the electrophile enters at these positions and hence halo group is an *ortho-para directing group*. Also because of its $-I$ effect, the halogen atom has a tendency to withdraw electrons from the benzene ring. So it is a *deactivating group*. Hence the electrophilic substitution reactions in haloarenes occur slowly and require more vigorous conditions.

v) **Halogenation**: Haloalkanes react with halogen (Chlorine or bromine) in presence of anhydrous ferric chloride to form o-dichlorobenzene and p-dichlorobenzene.

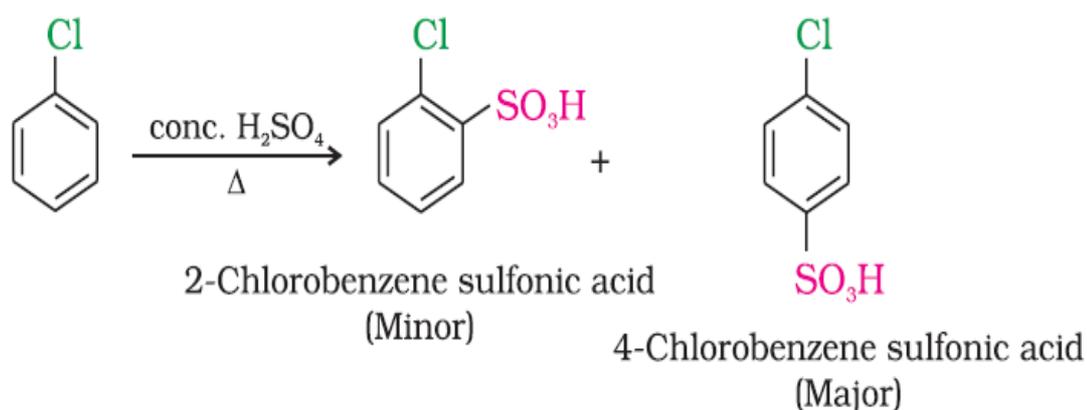


vi) **Nitration**: On nitration using Conc. HNO_3 and Conc. H_2SO_4 , chlorobenzene gives p-nitro chlorobenzene as the major product.

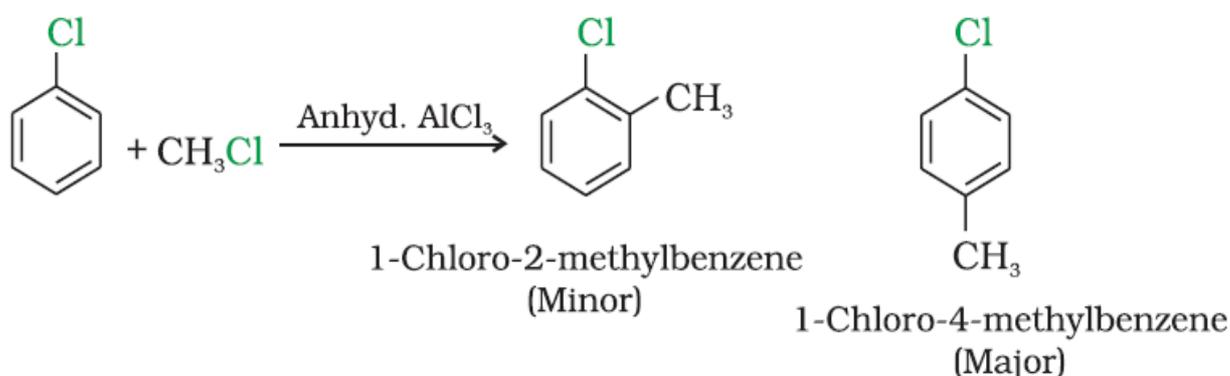


Electrophilic substitution reactions:

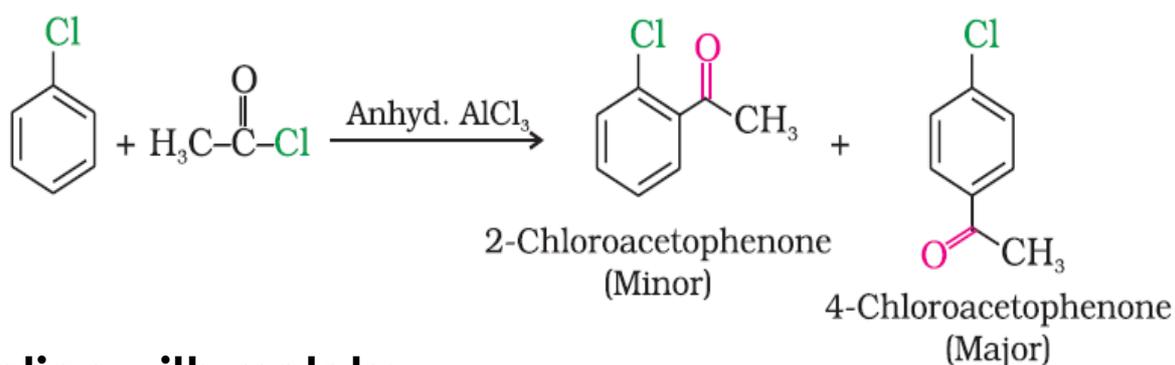
(iii) **Sulphonation**: On sulphonation using Conc. H_2SO_4 , chlorobenzene gives p-chloro benzenesulphonic acid as the major product.



(iv) Friedel – Crafts Alkylation: Chlorobenzene when treated with methyl chloride ($\text{CH}_3\text{-Cl}$) in presence of anhydrous AlCl_3 , we get p-chlorotoluene as the major product.

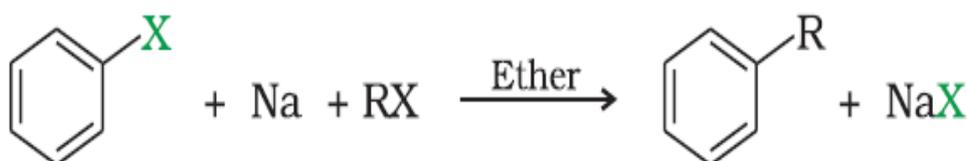


(v) Friedel – Crafts Acylation: Chlorobenzene when treated with acetyl chloride ($\text{CH}_3\text{-CO-Cl}$) in presence of anhydrous AlCl_3 , we get p-chloroacetophenone as the major product.



Reaction with metals:

- a) **Wurtz-Fittig reaction:** When a mixture of alkyl halide and aryl halide is treated with sodium in dry ether, an alkyl arene is formed and this reaction is called Wurtz-Fittig reaction.



For e.g. when Chlorobenzene is treated with methyl chloride in presence of metallic sodium in ether medium, we get toluene.

