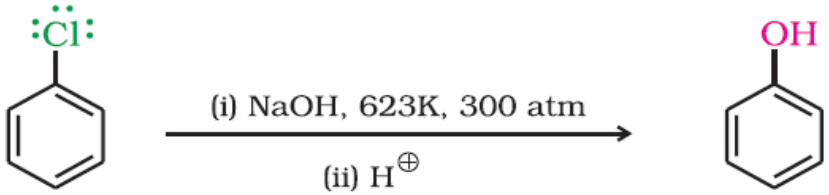
Chemistry Study Materials for Class 12
(NCERT Based Notes of Chapter - 10)
Ganesh Kumar Date:- 16/09/2020

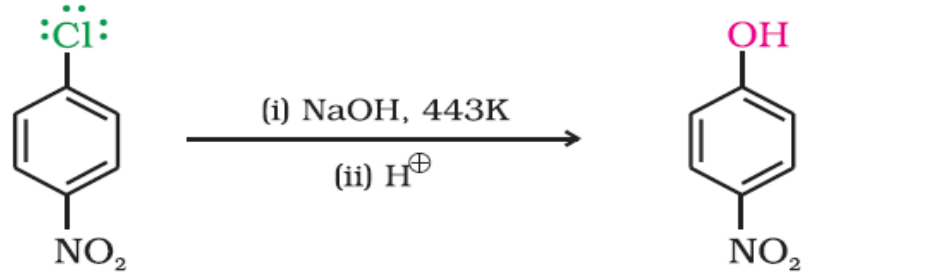
Haloalkanes and Haloarenes

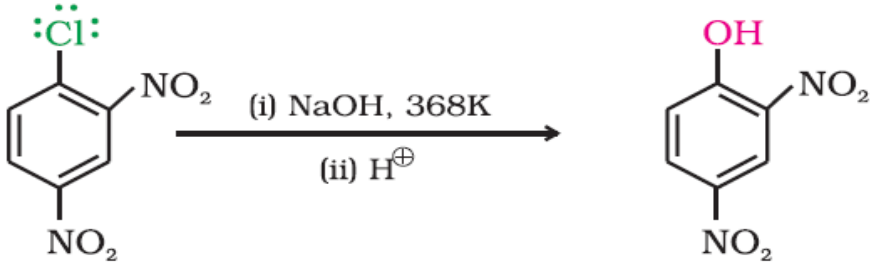
Replacement by hydroxyl group (Conversion to phenol)

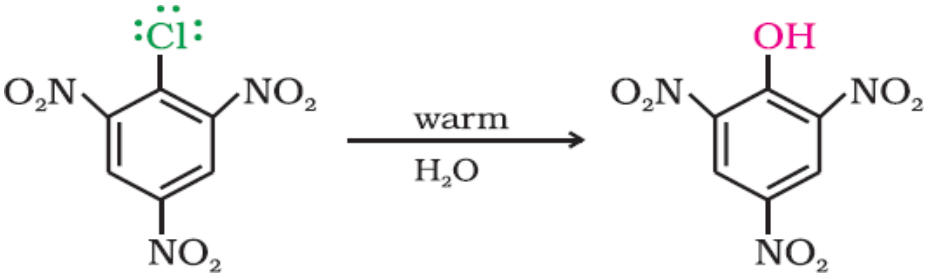
Chlorobenzene when heated with aqueous sodium hydroxide solution at a temperature of 623K and a pressure of 300 atmospheres followed by acidification, we get phenol.



The presence of an electron withdrawing group (-NO_2) at ortho- and para-positions increases the reactivity of haloarenes.



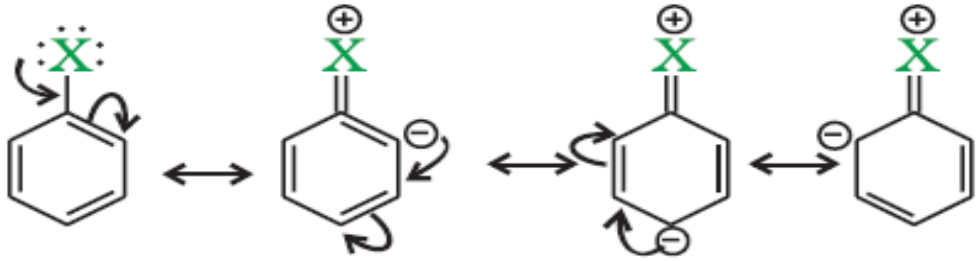




The effect is more when -NO_2 group are present at ortho and para- positions. However, no effect on reactivity is observed by the presence of electron withdrawing group at meta-position.

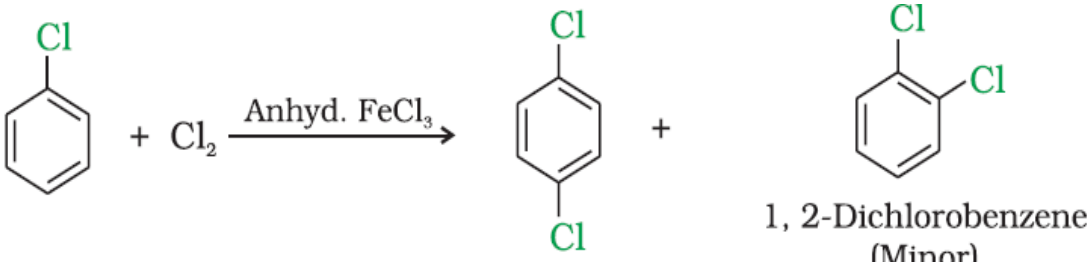
Electrophilic substitution reactions:

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.

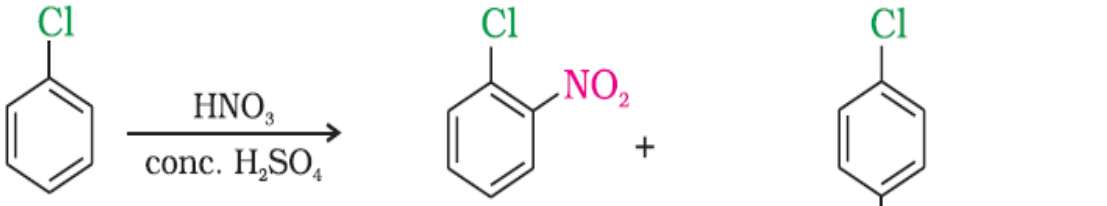
i) *Halogenation*: Haloalkanes react with halogen (Chlorine or bromine) in presence of anhydrous ferric chloride to form o-dichlorobenzene and p-dichlorobenzene.



1, 4-Dichlorobenzene (Major)

1, 2-Dichlorobenzene (Minor)

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



1-Chloro-2-nitrobenzene (Minor)

1-Chloro-4-nitrobenzene (Major)

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