CHEMISTRY STUDY MATERIALS FOR CLASS 12 (NCERT BASED NOTES OF CHAPTER - 10) GANESH KUMAR DATE:- 23/08/2021

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 (-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.

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



ii)*Nitration*: On nitration using Conc. HNO₃ and Conc. H₂SO₄, chlorobenzene gives p-nitro chlorobenzene as the major product.



Electrophilic substitution reactions:

(iii) Sulphonation: On sulphonation using Conc. H₂SO₄, chlorobenzene gives

p-chloro benzenesulphonic acid as the major product.



(iv) Friedel - Crafts Alkylation: Chlorobenzene when treated with methyl

chloride (CH₃-Cl) in presence of anhydrous AlCl₃, we get p-chlorotoluene as the major product.



(v)Friedel - Crafts Acylation: Chlorobenzene when treated with acetyl

chloride (CH₃-CO-Cl) in presence of anhydrous AlCl₃,

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.

 $\begin{array}{ccc} C_{6}H_{5}\text{-}CI + 2Na + CH_{3}\text{-}CI & \xrightarrow{ether} & C_{6}H_{5}\text{-}CH_{3} + 2NaCI \\ Chloro & Sodium Chloro & Toluene \\ Benzene & methane \end{array}$

b) Fittig reaction: Aryl halides when treated with sodium in dry ether,

we get diaryls (diphenyls). This reaction is called Fittig reaction.

