CHEMISTRY STUDY MATERIALS FOR CLASS 12 (NCERT BASED NOTES OF CHAPTER - 10) DATE: 15/09/2020 **GANESH KUMAR**

Haloalkanes and Haloarenes

Elimination Reactions

Alkyl halides having β -hydrogen atom when treated with alcoholic solution of KOH, they undergo elimination of one hydrogen halide molecule (dehydrohalogenation) to form alkenes. Since β -hydrogen atom is eliminated, the reaction is also called β -elimination.

e.g. : CH_3 - CH_2 -Br + KOH (alc) \longrightarrow CH_2 = CH_2 + KBr + H_2O

If there is possibility of formation of more than one alkene during dehydrohalogenation reaction, the major product is selected by Zaitsev (Saytzeff) rule. The rule states that "in dehydrohalogenation reactions, if there is possibility of formation of more than one alkene the preferred product is that alkene which contains greater number of alkyl groups attached to the doubly bonded carbon atoms."

So if 2-bromobutane is treated with alcoholic KOH, 2-butene is formed as the major product.

 CH_3 - CH_2 -CHBr- CH_3 + KOH (alc) \longrightarrow CH_3 - CH_2 - $CH=CH_2$ + CH_3 - $CH=CH-CH_3$ 2-Bromobutane

1-butene (minor) 2-butene (major)

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.

R-X + Mg	► RMg>	K [Grignard reagent]
Alkyl halides	alkyl magnesium halide	
CH ₃ -CH ₂ -Br + Mg	Dry ether	CH ₃ -CH ₂ MgBr
Ethyl bromide	Ethy	I 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.

 $R-MgX + H_2O \longrightarrow R-H + MgX(OH)$ $R-MgX + R-OH \longrightarrow R-H + MgX(OR)$ $R-MgX + NH_3 \longrightarrow R-H + MgX(NH_2)$

(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*.

2R-X + 2 Na	R-R + 2NaX
Alkyl halides	Alkane
2CH ₃ -Br + 2Na	CH ₃ -CH ₃ + 2NaBr
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 sp³ hybridised carbon while in haloarene, it is attached to an sp² hybridised carbon. Due to the greater s- character of sp² hybridised carbon, it is more electronegative and can hold the electron pair of C—X bond more tightly than sp³-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.
