

CHEMISTRY STUDY MATERIALS FOR CLASS 12 (NCERT BASED NOTES OF CHAPTER - 10) GANESH KUMAR DATE:- 04/09/2021

Haloalkanes and Haloarenes

These are compounds containing halogen atoms attached to an alkyl or aryl group. The general representation of **haloalkanes** is **R-X** and that of **haloarenes** is **Ar-X** [where X = F, Cl, Br, I].

Classification

1. On the basis of number of halogen atoms:

Based on this, haloalkanes and haloarenes are classified as mono, di or polyhalogen compounds. Monohalogen compounds contain only one halogen atom, dihalocompounds contain 2 halogen atoms and polyhalogen compounds contain more than 2 halogen atoms.

2. Compounds containing sp^3 C-X bond: They include

➤ **Alkyl halides or haloalkanes (R-X)**: Here the halogen atom is directly bonded to a sp^3 hybridized C atom of an alkyl group. They are further classified as primary, secondary or tertiary according to the nature of carbon to which halogen atom is attached. Their general formula may be:

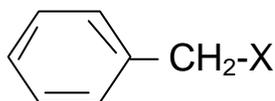
Primary haloalkane: $R-CH_2-X$

Secondary haloalkane: R_2CH-X

Tertiary haloalkane: R_3C-X

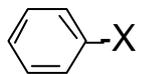
➤ **Allylic halides**: Here the halogen atom is bonded to a sp^3 hybridized carbon atom next to a C = C bond. e.g.: $CH_2=CH-CH_2X$

➤ **Benzylic halides**: These are compounds in which the halogen atom is bonded to a sp^3 hybridized carbon atom next to an aromatic ring. e.g.: $C_6H_5-CH_2-X$



3. Compounds having sp^2 C-X bond: They include

➤ **Vinyl halides:** Here the halogen atom is directly bonded to a sp^2 hybridized carbon atom of a C=C bond. E.g.: $CH_2=CH-X$

➤ **Aryl halides:** Here the halogen atom is directly bonded to a sp^2 hybridized carbon atom of an aromatic ring. E.g. : C_6H_5-X / 

Nomenclature

Common name of alkyl halides is obtained by adding -yl halide to the word root (i.e. word root + yl halide) and the IUPAC name is obtained by adding the prefix 'halo' to the name of the parent alkane (i.e. halo + alkane).

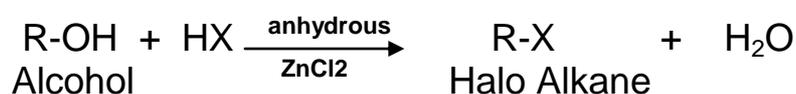
Some examples are:

Compound	Common Name	IUPAC Name
CH_3-Cl	Methyl chloride	Chloromethane
CH_3-CH_2-Br	Ethyl bromide	Bromoethane
$CH_3-CH_2-CH_2-Cl$	n-Propyl chloride	1-Chloropropane
$CH_3-CHCl-CH_3$	Isopropyl chloride	2-Chloropropane
$CH_3-CH_2-CH_2-CH_2-Br$	N-Butyl bromide	1-Bromopropane
$(CH_3)_3C-Cl$	tert-butyl chloride	2-Chloro-2-methyl propane
C_6H_5-Cl	Chlorobenzene	Chlorobenzene
$C_6H_5-CH_2-I$	Benzyl iodide	Iodo phenyl methane

Methods of preparation:

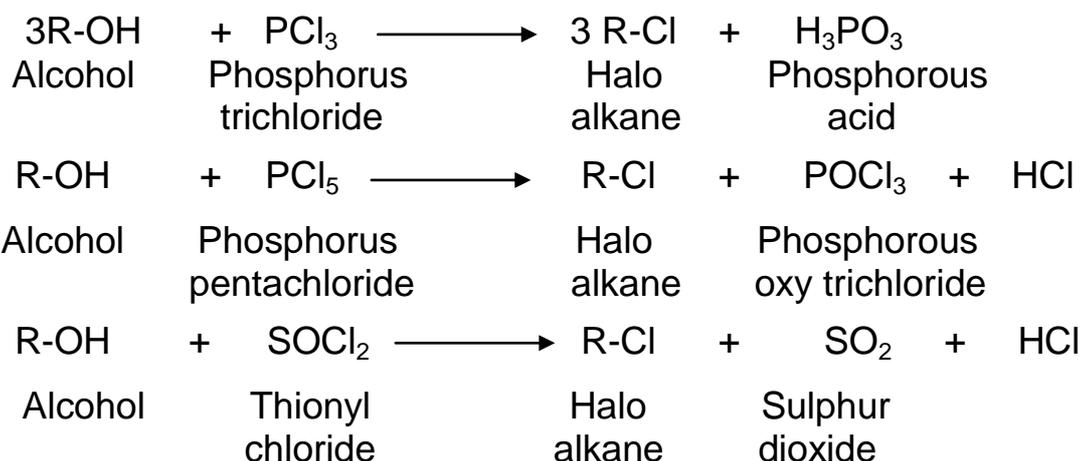
From alcohols:

a) By the action of concentrated halogen acids on alcohols in presence of anhydrous $ZnCl_2$ as catalyst.



Reactions of primary and secondary alcohols with HI require the presence of anhydrous $ZnCl_2$, while tertiary alcohols do not require the catalyst.

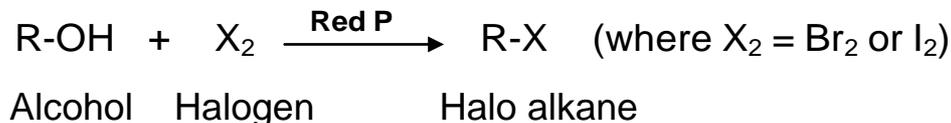
b) Alkyl chlorides are obtained by the action of PCl_3 , PCl_5 or SOCl_2 with alcohols.



$\text{R} \rightarrow$ Alkyl group such as $-\text{CH}_3$ (methyl group), $-\text{CH}_2\text{CH}_3$ (ethyl group)

Among these methods, the reaction with thionyl chloride (SOCl_2) is preferred, since the byproducts are gases and are easily escaped from the reaction medium.

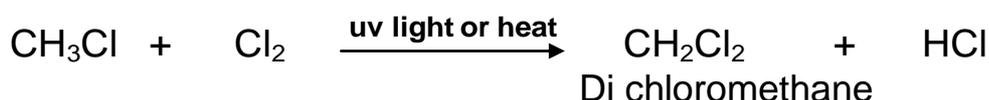
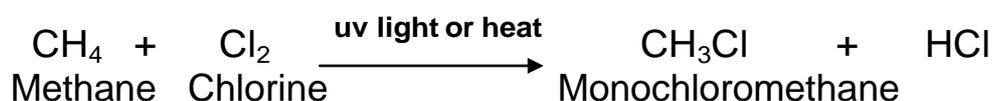
For the preparation of alkyl bromides and iodides, alcohols are treated with bromine or iodine in presence of red phosphorus, since PBr_3 and PI_3 are unstable.

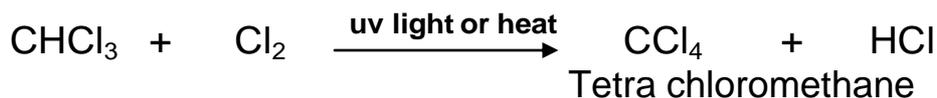


From Hydrocarbons

a) Free radical halogenation:

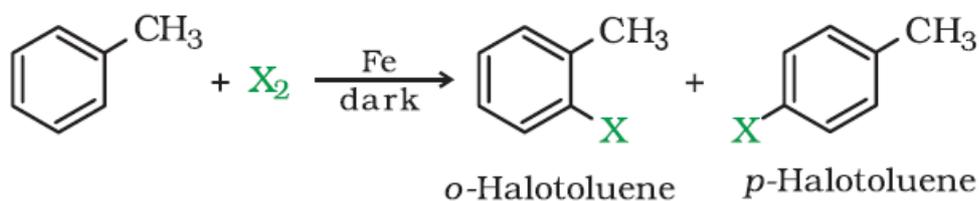
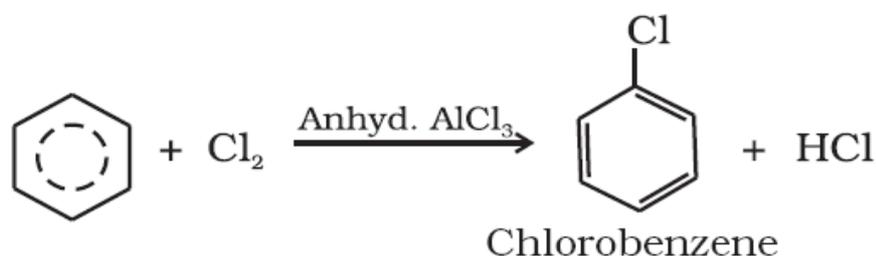
Alkanes react with chlorine or bromine in presence of sunlight; we get a mixture of mono, di and polyhaloalkanes. **For e.g.** when methane is chlorinated in presence of sunlight (uv light), we get a mixture of 4 products namely monochloromethane (methyl chloride, $\text{CH}_3\text{-Cl}$), dichloromethane (methylene chloride, CH_2Cl_2), trichloromethane (chloroform, CHCl_3) and tetra chloromethane (carbon tetrachloride, CCl_4).





b) Electrophilic substitution:

Benzene or its derivatives when heated with Cl_2 or Br_2 in presence of iron or Lewis acids like anhydrous FeCl_3 (ferric chloride) or AlCl_3 , we get aryl chlorides or bromides.

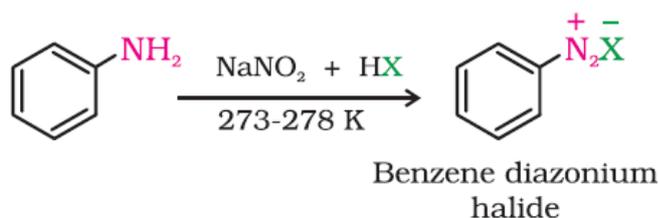


The ortho and meta isomers can be easily separated due to their large difference in melting point.

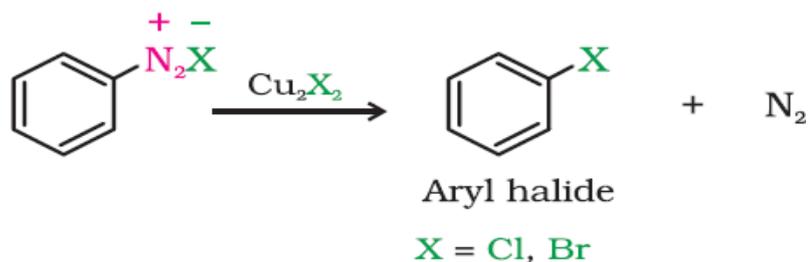
For the preparation of aryl iodides, arenes are treated with I_2 in presence of an oxidising agent like HNO_3 or HIO_4 (per Iodic acid) to oxidize the HI formed during the reaction.

c) Sandmeyer's reaction:

Aromatic primary amines when treated with mineral acids like HCl and sodium nitrite (NaNO_2) at cold condition ($0 - 5^\circ\text{C}$), an aromatic diazonium salt is formed. This reaction is called *Diazotisation*.



When a diazonium salt is treated with HX in presence of cuprous halide (Cu_2X_2), we get halo benzene. This reaction is called Sandmeyer's reaction.



Note: If the cuprous halide is replaced by copper powder, the reaction is called **Gattermann's reaction**.

For the preparation of iodobenzene, the diazonium salt is treated with potassium iodide (KI).

