Haloalkanes and haloarenes

Haloalkenes and haloarenes can be classified as follows:

- Basis of number of halogen atoms:

    1) Mono
    2) Di
    3) Polyhalogen

Depends on whether they have 1,2 or more halogens associated with the element

- According to the hybridisation of carbon atom to which the halogen is bonded:
    - Alkyl halides or haloalkanes
        - Primary
        - Secondary
        - Tertiary
    - Allylic halides:
        - Bounded to sp^3 hybridised carbon atom next to carbon-carbon double bonds (C=C)
    - Benzyilic halides:

        - Halogen atom is bonded to an sp^3 hybridised carbon atom next to an aromatic ring.

- Compound containing sp^2C-X bond:
    - Vinylic halides:
        - There are the compounds in which the halogen atom is bonded to an sp^2 hybrid carbon atom.

    - Aryl halides:
        - Halogen atom is bonded to the sp^2 hybrid carbon atom of an aromatic ring.

Nomenclature:

- Common name: n-propyl bromide ; IUPAC name: 1-Bromo Propane
- Isopropyl chloride: 2-Chloro propane
- Isobutyl chloride: 1-chloro,2-methyl propane

Nature of C-X bond:

- The halogens being more electronegative than carbon, the carbon-halogen bond of alkyl halide is polarised.
    - Carbon- partial (+)ve charge
    - Halogen- partial (-)ve charge
- Carbon-halogen bond length also increases from C-F to C-I as size increases from F-I.

Preparation:

- From alcohols:
  - OH is replaced by halogen on reaction with concentrated halogen acids, phosphorous halides or thionyl chloride.
  - We prefer thionyl chloride as the residual products are all gasses.
  - Primary and secondary alcohols with HX need Zinc Chloride as a catalyst, while for tertiary alcohol, to form haloalkanes, shaking of a mixture of the alcohol with Hydrochloric acid at room temperature is sufficient.
  - The reactivity of alcohols is in the following order:
    - Tertiary>secondary>primary
  - This method is NOT used for Aryl halides.

- By free radical halogenations:

(c) **Sand Meyer's reaction**

- When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed.
- Mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by –Cl or –Br.

- Replacement of the diazonium group by iodine does not require the presence of cuprous halide and is done simply by shaking the diazonium salt with potassium iodide.

(d) from alkenes:

- Addition of hydrogen halides: An alkene is converted to corresponding alkyl halide by reaction with hydrogen chloride, hydrogen bromide or hydrogen iodide.
- Propene yields two products, however only one predominates as per Markovnikov's rule.
- Addition of halogens: In the laboratory, addition of bromine in CCl_4 to an alkene resulting in discharge of reddish brown colour of bromine constitutes an important method for the detection of double bond in a molecule. The addition results in the synthesis of vic-dibromides, which are colourless.

Halogen exchange:

- Alkyl iodides are often prepared by the reaction of alkyl chlorides/ bromides with NaI in dry acetone. This reaction is known as Finkelstein reaction.
- NaCl or NaBr thus formed is precipitated in dry acetone. It facilitates the forward reaction according to Le Chatelier's Principle.
- The synthesis of alkyl fluorides is best accomplished by heating an alkyl chloride/bromide in the presence of a metallic fluoride such as AgF, Hg_2F_2, CoF_2 or SbF_3. The reaction is termed as Swarts reaction.

Physical properties:

- Alkyl halides are colourless when pure. However, bromides and iodides develop colour when exposed to light. Many volatile halogen compounds have sweet smell.

- the boiling points of chlorides, bromides and iodides are considerably higher than those of the hydrocarbons of comparable molecular mass. (Due to greater polarity as well as higher molecular mass as compared to the parent hydrocarbon, the intermolecular forces of attraction (dipole-dipole and van der Waals) are stronger in the halogen derivatives.)
- The boiling points of isomeric haloalkanes decrease with increase in branching.
- Boiling points of isomeric dihalobenzenes are very nearly the same. However, the para-isomers are high melting as compared to their ortho and meta-isomers. It is due to symmetry of para-isomers that fits in crystal lattice better as compared to ortho- and meta-isomers.
- The density increases with increase in number of carbon atoms, halogen atoms and atomic mass of the halogen atoms.
- The haloalkanes are only very slightly soluble in water, However, haloalkanes tend to dissolve in organic solvents.

Chemical reactions:

- ***Nucleophilic substitution reactions***
    - a nucleophile reacts with haloalkane (the substrate) having a partial positive charge on the carbon atom bonded to halogen.
    - A substitution reaction takes place and halogen atom, called leaving group departs as halide ion.

- Groups like cyanides and nitrites possess two nucleophilic centres and are called ambident nucleophiles.
- the order of reactivity followed is:

Primary halide > Secondary halide > Tertiary halide.