Organic Chemistry
CHEM 145

2 Credit hrs

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Organic Halogen Compounds

Classes and Names of Halogen Compounds

Halogen compounds are classified according to the halogen, as *fluoro, chloro, bromo, and iodo compounds.*

Alkyl halides, R—X (X may be F, Cl, Br, or I).

Depending on the type of carbon to which the halogen is attached, ***Alkyl halides*** are subdivided into;

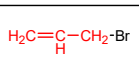
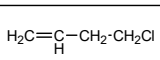
primary (1°), secondary (2°), or tertiary (3°).

	CH_3Cl	$CH_3CH_2CH_2Br$	$CH_3\underset{\displaystyle F}{\underset{\vert}{C}}HCH_3$
Common name:	Methyl chloride	*n*-Propyl bromide	Isopropyl fluoride
IUPAC name:	Chloromethane	1-Bromopropane	2-Fluoropropane
Class:	1°	1°	2°

			
Common name:	Cyclohexyl iodide	*t*-Butyl bromide	Methylcyclopentyl chloride
IUPAC name:	Iodocyclohexane	2-Bromo-2-methylpropane	1-Chloro-1-methylcyclopentane
Class:	2°	3°	3°

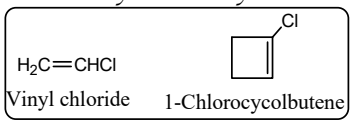
Allylic halides.

The halogen attached to a carbon next to a doubly bonded carbon.

			
Common name:	Allyl bromide		
IUPAC name:	3-Bromo-1-propene	4-Chloro-1-butene	3-Chlorocyclopentene

Vinylic halides.

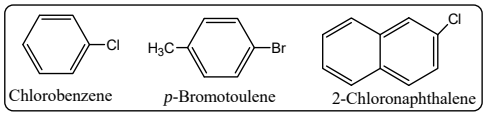
A halogen attached directly to a doubly bonded carbon.



Vinyl chloride — 1-Chlorocycolbutene

Aryl halides, Ar-X.

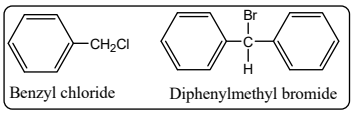
The halogen is directly attached to an aromatic ring.



Chlorobenzene — *p*-Bromotoulene — 2-Chloronaphthalene

- *Benzylic halides, Ar-C-X.*

  The halogen *one carbon away* from an aromatic ring.



- *Polyhalogen Compounds .*
  - CH_2X_2 = methylene halides, as in *methylene chloride, CH_2Cl_2*
  - CHX_3 = haloforms, as in *chloroform, $CHCl_3$*
  - CX_4 = carbon tetrahalides, as in *carbon tetrachloride, CCl_4*

Physical Properties of Organic Halides

- *Solubility*
  - All organic halides are insoluble in water.
  - All organic halides are soluble in common organic solvents (benzene, ether, etc.).
- *Density*
  - The simple monofluoro and monochloro compounds are less dense than water,
  - The monobromo and monoiodo derivatives have densities greater than water.
  - As the number of halogen atoms increases, the density increases.
- They are good solvents for fats and oils.
- Polychloro compounds, such as trichloroethylene and tetrachloroethylene, are widely used as solvents for dry cleaning.

Boiling points

- **Within a series of halides, the boiling points increase with increasing molecular weights.**

  Therefore, the boiling points increase in the order F <Cl <Br < I.

CH_3F (mol wt = 34; bp = -78°C)	CH_3Cl (mol wt = 50.5; bp = -24°C)
CH_3Br (mol wt = 95; bp = 4°C)	CH_3I (mol wt = 142; bp = 42°C)

- **Within a homologous series, the boiling points also increase regularly with molecular weights.**

CH_3Cl (bp = -24°C)	CH_3CH_2Cl (bp = 12°C)	$CH_3CH_2CH_2Cl$ (bp = 47°C)

- **Within a series of isomers, the straight-chain compound has the highest boiling point, and the most branched isomer the lowest boiling point.**

$CH_3CH_2CH_2CH_2Br$ (bp = 101°C)	$H_3C-C(CH_3)_2-CH_2Br$ (bp = 73°C)

Preparation of Halogen Compounds

Chloro, Bromo, and Iodo Compounds

Direct halogenation of hydrocarbons.

a) Halogenation of alkanes: Alkyl halides

$$RH + X_2 \xrightarrow{\text{uv or heat}} RX + HX \quad (X = Cl, Br)$$

b) Halogenation of alkenes: Allyl halides

$$H_2C{=}CHCH_2R + X_2 \xrightarrow{\text{uv or heat}} H_2C{=}CHCHXR + HX$$

c) Halogenation of alkyl benzenes: Benzyl halides

$$ArCH_2R + X_2 \xrightarrow{\text{uv or heat}} ArCH_2XR + HX \quad (X = Cl, Br)$$

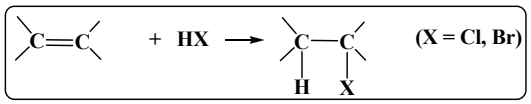
d) Halogenation of aromatic ring: Aryl halides

$$ArH + X_2 \xrightarrow{FeX_3} ArX + HX \quad (X = Cl, Br)$$

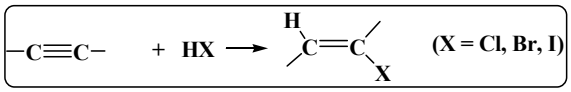
Conversion of alcohols: Alkyl halides

$$ROH + HX \text{ (or } PX_3 \text{ or } SOX_2) \xrightarrow{\text{heat}} RX \quad (X = Cl, Br, I)$$

- Addition of HX to unsaturated hydrocarbons
  - a) Addition of HX to alkenes: Alkyl halides



  - b) Addition of HX to alkynes: Vinyl halides



- Halogen Exchange: A Way to Alkyl Fluorides
  - An alkyl chloride or bromide is heated in the presence of a metallic fluoride such as AgF, Hg_2F_2, or SbF_3.

$$CH_3Br + AgF \xrightarrow{heat} CH_3F + AgBr$$

  - The manufacture of chlorofluoro compounds, known as Freons.

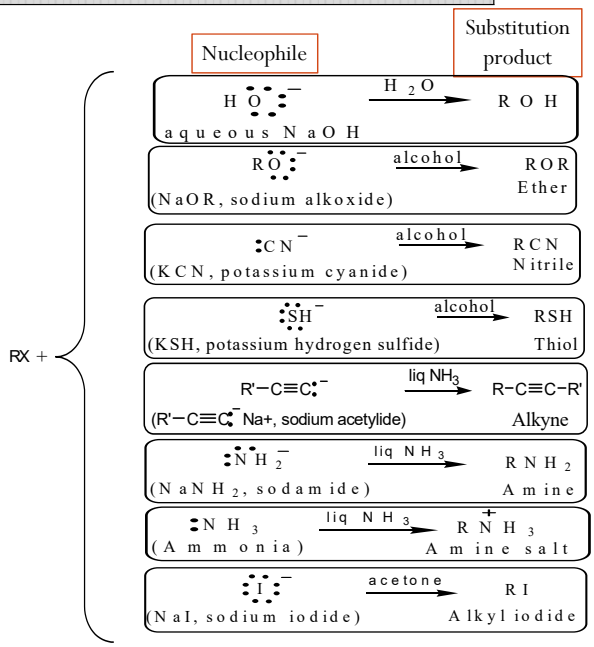
The simplest Freon, $CC1_2F_2$, is made as follows.

$$3CCl_4 + 2SbF_3 \xrightarrow{heat} 3CCl_2F_2 + 2SbCl_3$$

Reactions of Halogen Compounds

- The reactions of organic halides fall into three categories
  - Nucleophiic substitution, or S_N, reactions.
    Those in which the halogen is replaced by some other atom or group.
  - Elimination, or E, reactions.
    Those that involve the loss of HX from the halide.
  - Formation of organometallic compounds.
    Those that involve reaction with certain metals.

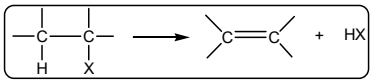
Nucleophilic substitution (S_N) Reactions



Elimination Reactions

- *General consideration*

  Alkyl halides can lose H and X from adjacent carbons to form alkenes by an elimination process.

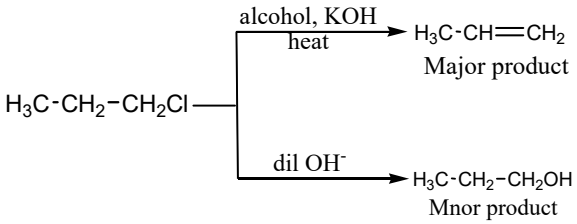


- **Mechanism of Eliminations are of two types:**
  - **The El (elimination unimolecular) reaction.**
  - **The E2 (elimination bimolecular) reaction.**
- *Generally*
  - **The El process accompanies the S_N1 reaction.**
  - **The E2 reaction accompanies the S_N2 reaction.**

Elimination versus Substitution

In general

Elimination is favored over substitution when strongly basic solutions and high temperatures are used.

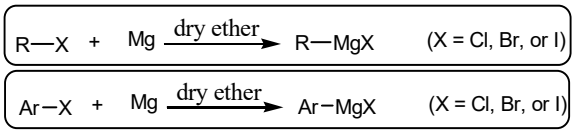


Formation Uses of Organometallic Compounds

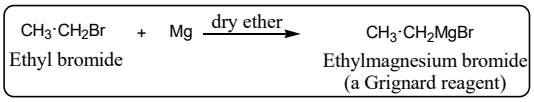
Most organic chlorides, bromides, and iodides react with certain metals to give organometallic compounds, molecules with carbon-metal bonds.

***Grignard reagents* are obtained by the reaction of alkyl or aryl halides with metallic magnesium in dry ether as the solvent.**

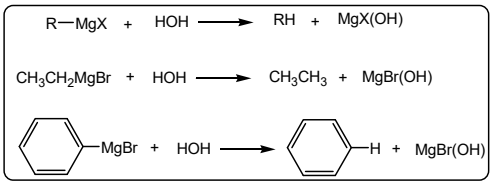
General reaction



Specific example



- ***Grignard reagents*** **react readily with any source of protons to give hydrocarbons.**



- **Organic halides form organometallic compounds when treated with metals other than magnesium.**
- ***Organometallic compounds*** **that are made by the reaction of halides with group IA metals (Li, Na, or K).**