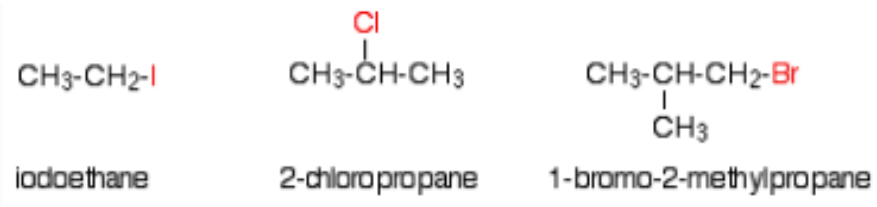
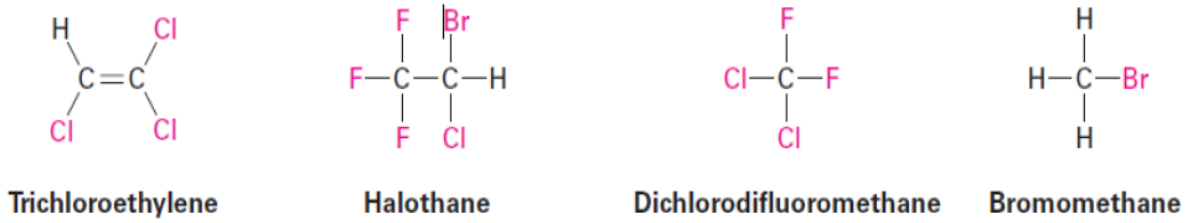
ALKYL HALIDES

Alkyl halides are also known as haloalkanes. Alkyl halides are compounds in which one or more hydrogen atoms in an alkane have been replaced by halogen atoms (fluorine, chlorine, bromine or iodine).

Some examples of Alkyl halide include:





Classification Of Alkyl Halide

A. Number of Halogen Atoms

1. Mono Haloalkane

Example: CH_3-CH_2-X [Where X can be Cl, F, Br or I]

2. Dihaloalkane

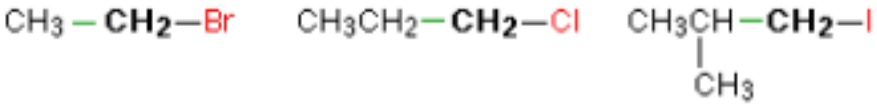
Example: X-CH_2-CH_2-X [Where X can be Cl, F, Br or I]

3. Trihaloalkane

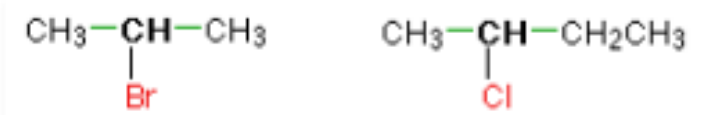
Example: X-CH_2-CHX-CH_2-X [Where X can be Cl, F, Br or I]

B. The Position of Halogen atom Along the Chain of Carbon Atom

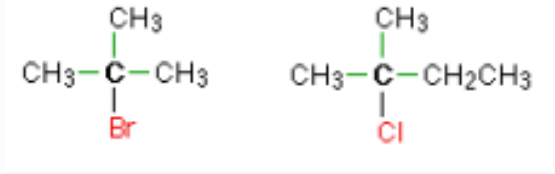
1. Primary alkyl halide



2. Secondary alkyl halide



3. Tertiary alkyl halide



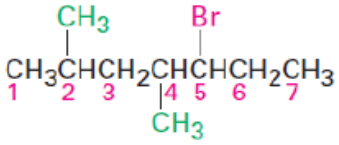
Names of Alkyl Halides

Step 1

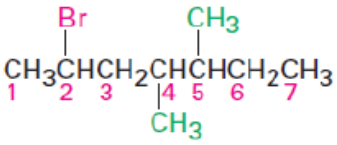
Find the longest chain, and name it as the parent. If a double or triple bond is present, the parent chain must contain it.

Step 2

Number the carbons of the parent chain beginning at the end nearer the first substituent, whether alkyl or halo. Assign each substituent a number according to its position on the chain.

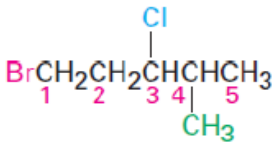


5-Bromo-2,4-dimethylheptane



2-Bromo-4,5-dimethylheptane

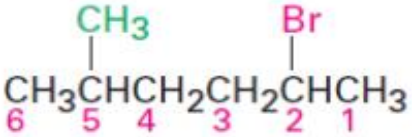
If different halogens are present, number all and list them in alphabetical order when writing the name.



1-Bromo-3-chloro-4-methylpentane

Step 3

If the parent chain can be properly numbered from either end by step 2, begin at the end nearer the substituent that has alphabetical precedence.

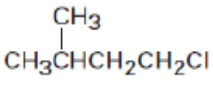


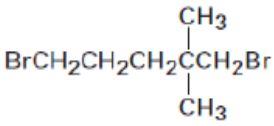
2-Bromo-5-methylhexane
(*Not* 5-bromo-2-methylhexane)

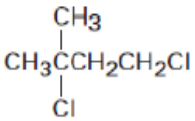
Exercise

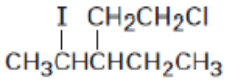
Give IUPAC names for the following alkyl halides:

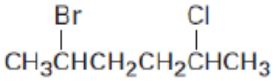
(a) $CH_3CH_2CH_2CH_2I$

(b) 

(c) 

(d) 

(e) 

(f) 

Problem 10.2

Draw structures corresponding to the following IUPAC names:

(a) 2-Chloro-3,3-dimethylhexane
(b) 3,3-Dichloro-2-methylhexane
(c) 3-Bromo-3-ethylpentane
(d) 1,1-Dibromo-4-isopropylcyclohexane
(e) 4-*sec*-Butyl-2-chlorononane
(f) 1,1-Dibromo-4-*tert*-butylcyclohexane

Alkyl Halide Properties

Alkyl halides are colourless when they exist in pure form. But, bromides and iodides develop colour when exposed to light. Many volatile halogen compounds have a sweet smell.

Boiling and Melting Points

- Methyl chloride, methyl bromide, ethyl chloride and some chlorofluoromethanes are in the form of gas at room temperature.
- Molecules of organic halogen compounds are polar in nature.
- Due to greater polarity and greater molar mass as compared to parent hydrocarbon, the intermolecular force of attraction is stronger in halogen derivatives.
- So, the boiling points of chlorides, bromides and iodides are considerably higher than that of the hydrocarbon with the same molecular mass.
- The boiling points of alkyl halides will decrease in the order RI > RBr > RCl > RF.

Density

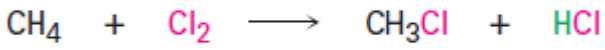
- Bromo-derivatives, iodo-derivatives and polychloro derivatives of hydrocarbons are heavier than water.
- The density increases with an increase in the number of carbon atoms, halogen atoms and atomic mass of halogen atoms.

Solubility

- The haloalkanes are less soluble in water.
- The haloalkanes will dissolve in the organic solvent than in the water.

Preparation Alkyl Halides

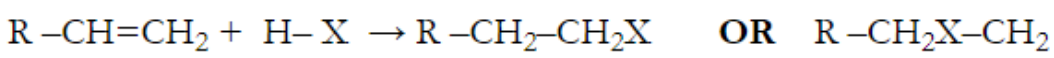
1. Preparing Alkyl Halides from Alkanes: Radical Halogenation



$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

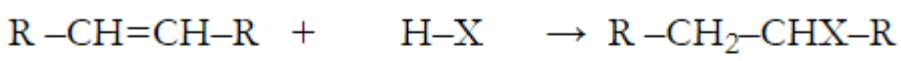
2. Preparing Alkyl Halides from alkenes

General Reaction



$$R\text{–}CH{=}CH_2 + H\text{–}X \rightarrow R\text{–}CH_2\text{–}CH_2X \quad \textbf{OR} \quad R\text{–}CH_2X\text{–}CH_2$$

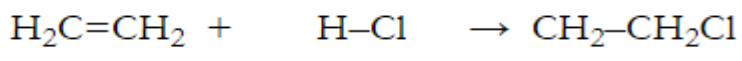
Alkene Hydrogen halide Alkyl halide



$$R\text{–}CH{=}CH\text{–}R + H\text{–}X \rightarrow R\text{–}CH_2\text{–}CHX\text{–}R$$

Symmetric alkene Hydrogen halide alkyl halide

Example – 1: Preparation of ethyl chloride (Chloroethane) from Ethylene (Ethene):



$$H_2C{=}CH_2 + H\text{–}Cl \rightarrow CH_2\text{–}CH_2Cl$$

Ethylene hydrogen chloride Ethyl chloride

Example 2 :

$CH_3–CH=CH–CH_3 + H–Br \rightarrow CH_3–CH_2–CH_2Br–CH_3$

butylene Hydrogen bromide sec-butyl bromide

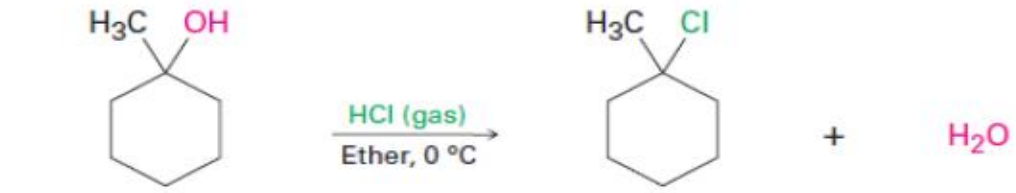
3. Preparing Alkyl Halides from alcohols

General Reaction:

$R–OH + HX \rightarrow R–X + H_2O$

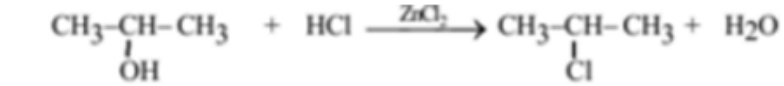
Alcohol Halogen acid alkyl halide

Example 1:-



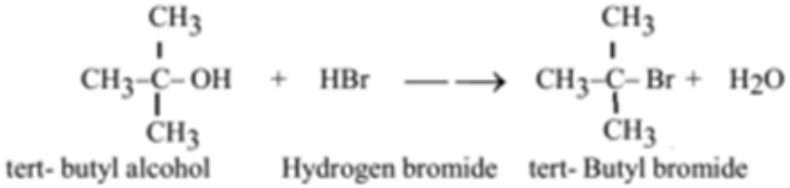
1-Methylcyclohexanol 1-Chloro-1-methylcyclohexane (90%)

Example – 2: (Preparation of isopropyl chloride (2-Chloropropane) from isopropyl alcohol (Propan-2-ol):

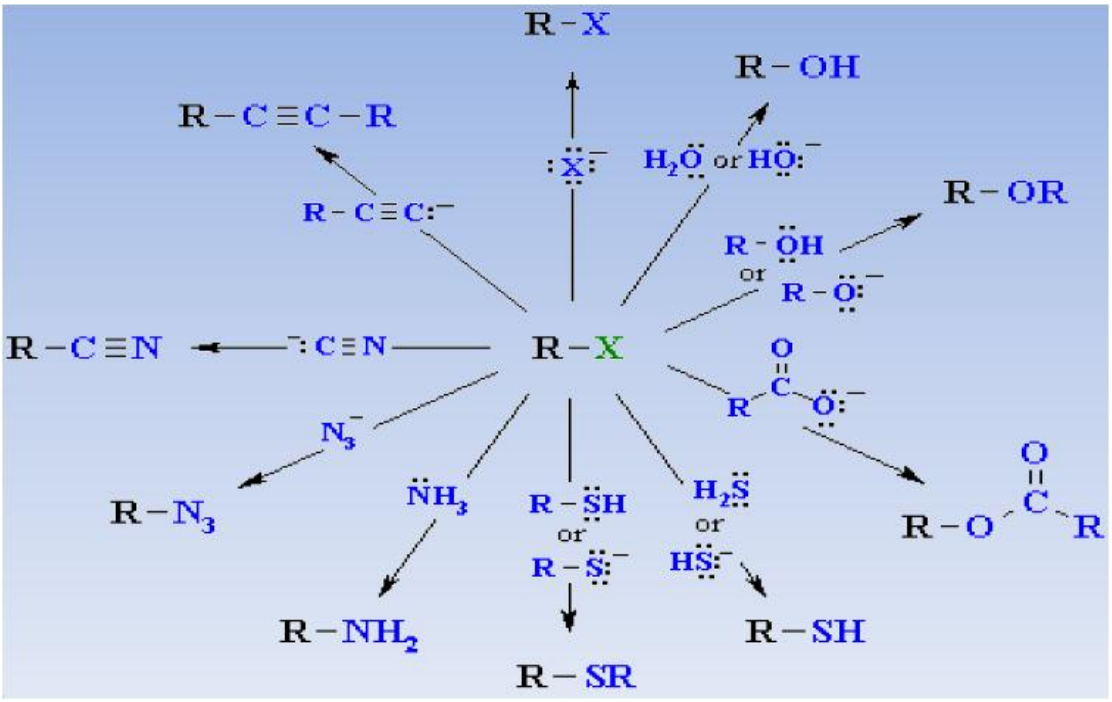


iso- Propyl alcohol Conc.Hydrochloric acid iso- Propyl chloride

Example – 3: (Preparation of tert- Butyl bromide (2-Bromo-2-methylpropane) from tert- Butyl alcohol (2-Methylpropan-2-ol):



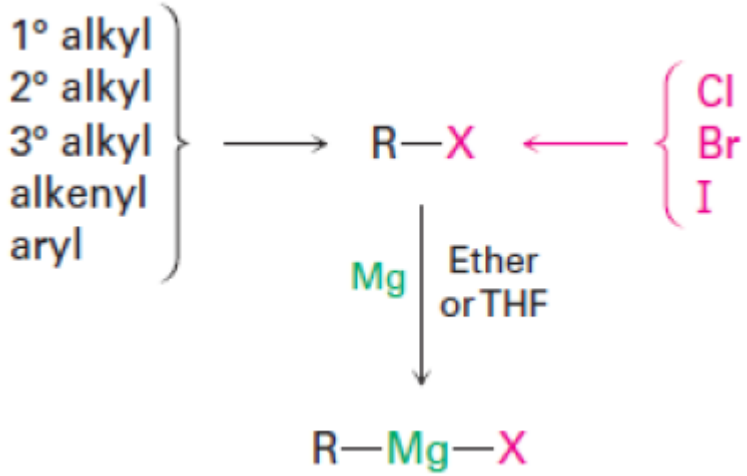
Reactions of Alkyl Halides



1. Grignard Reagents

Alkyl halides, RX, react with magnesium metal in ether or tetrahydrofuran (THF) solvent to yield alkylmagnesium halides, RMgX. The products, called Grignard reagents after their discoverer, Victor Grignard, are examples of *organometallic* compounds because they contain a carbon–metal bond. In addition to alkyl halides, Grignard reagents can also be made from alkenyl (vinylic) and aryl (aromatic) halides. The halogen can be Cl, Br, or I, although chlorides are less

reactive than bromides and iodides. Organofluorides rarely react with magnesium.



2. Organometallic Coupling Reactions