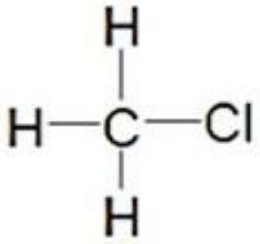
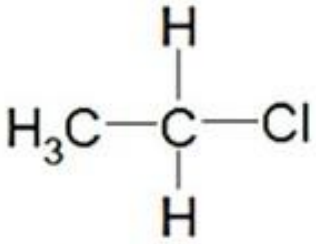
# *Alkyl halides*

Alkyl halides (haloalkanes) are a class of compounds where a halogen atom or atoms are attached to a tetrahedral carbon ($sp^3$) atom. The functional group is __ X, where __ X may be __ F, __ Cl, __ Br or __I.

Two simple members of this class are methyl chloride ($CH_3Cl$) and ethyl chloride ($CH_3CH_2Cl$).

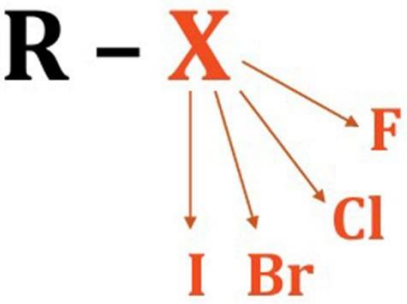


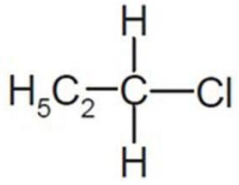

Chloromethane
Methyl chloride



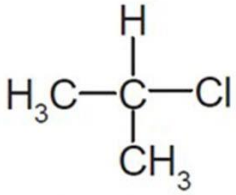

Chloroethane
Ethyl chloride

Based on the number of alkyl groups attached to the C–X unit, alkyl halides are classed as primary (1º), secondary (2º) or tertiary (3º).

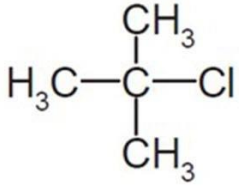



Chloropropane
(Propyl chloride)
(1º halide)




2-Chloropropane
(Isopropyl chloride)
(2º halide)




2-Chloro-2-methyl propane
(*tert*-Butyl chloride)
(3º halide)

## PHYSICAL PROPERTIES OF ALKYL HALIDES

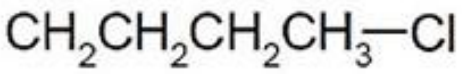
A. Polarity: Electronegativity

B. Boiling Point: Interaction and forces

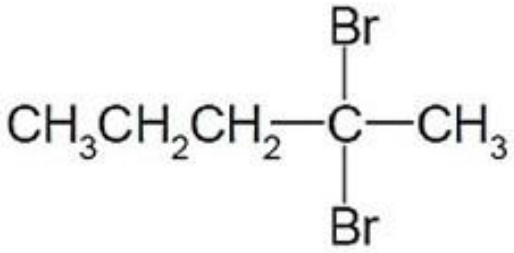
C. Density: larger mass; denser

# Nomenclature of alkyl halides

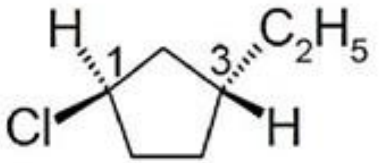
According to the IUPAC system, alkyl halides are treated as alkanes with a halogen substituent. The halogen prefixes are fluoro-, chloro-, bromo- and iodo-. An alkyl halide is named as a haloalkane with an alkane as the parent structure.



Chlorobutane



2,2-Dibromopentane



*trans*-1-Chloro-3-ethylcyclopentane

Often compounds of $CH_2X_2$ type are called methylene halides, e.g. methylene chloride ($CH_2Cl_2$), $CHX_3$ type compounds are called haloforms, e.g. chloroform ($CHCl_3$), and $CX_4$ type compounds are called carbon tetrahalides, e.g. carbon tetrachloride ($CCl_4$). Methylene chloride (dichloromethane, DCM), chloroform and carbon tetrachloride are extensively used in organic synthesis as nonpolar solvents.

# Preparation of Alkyl Halides

## 1. Preparation of Alkyl Halides from Alkenes

**General Reaction**

$$\underset{\text{Alkene}}{R-CH=CH_2} + H-X \rightarrow \underset{\text{Hydrogen halide}}{R-CH_2-CH_2X} \text{ OR } \underset{\text{Alkyl halide}}{R-CH_2X-CH_2}$$

Conversion of $-C=C-$ (Alkenes) into $-X$ (Alkyl halides)

$$\underset{\text{Symmetric alkene}}{R-CH=CH-R} + \underset{\text{Hydrogen halide}}{H-X} \rightarrow \underset{\text{Alkyl halide}}{R-CH_2-CHX-R}$$

**Preparation of Alkyl Chloride / Alkyl Bromides / Alkyl Iodides:**

$$\underset{\text{Symmetric alkene}}{R-CH=CH-R} + \underset{\text{Hydrogen chloride}}{H-Cl} \rightarrow \underset{\text{Alkyl chloride}}{R-CH_2-CHCl-R}$$

$$\underset{\text{Unsymmetric alkene}}{R-CH=CH-R'} + H-X \rightarrow R-CH_2-CHX-R' \rightarrow \underset{\text{Alkyl halide}}{R-CHX-CH_2-R'}$$

(Hydrogen chloride)

## 2. Preparation of Alkyl Halides by Free Radical Halogenation

$$CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2/UVlight} CH_3CH_2CHClCH_3 + CH_3CH_2CH_2CH_2Cl$$

## 3. Preparation of Alkyl Halides from Alcohols

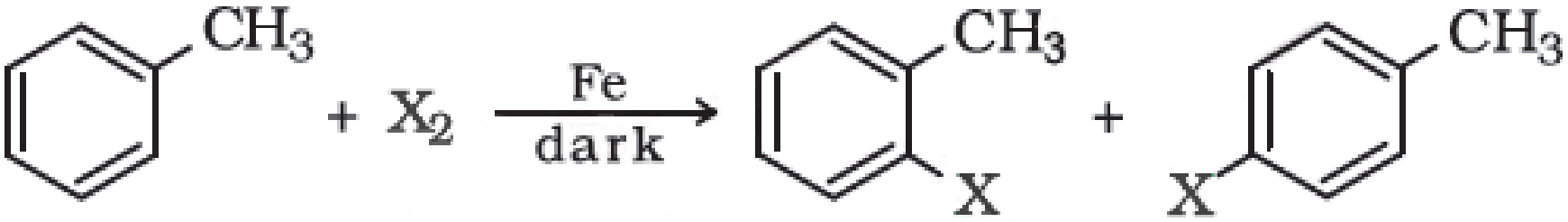
$$CH_3CH_2OH + SOCl_2 \xrightarrow{\Delta} CH_3CH_2Cl + SO_2 + HCl$$

$$CH_3CH_2OH + PCl_2 \xrightarrow{\Delta} CH_3CH_2Cl + P(OH)_3 + HCl$$

$$CH_3CH_2OH + PCl_5 \xrightarrow{\Delta} CH_3CH_2Cl + P(OH)_3 + HCl$$

$$CH_3CH_2OH + PBr_3 \xrightarrow{\Delta} CH_3CH_2Br + P(OH)_3 + HBr$$

# 4. Preparation of Aryl Halides by Electrophilic Substitution Reactions




# 5. Preparation of Aryl Halides through Sandmeyer's Reaction

**Sandmeyer Reaction :**