## **Alkyl Halides**

Nucleophilic Aliphatic Substitution and Elimination

Dr. huda saleh abood For 1<sup>st</sup> Stage Students

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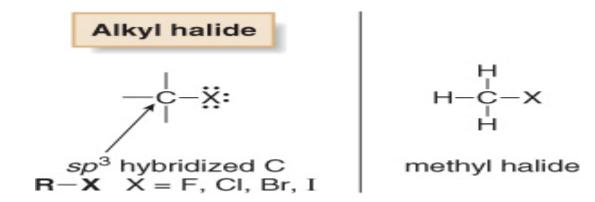
Alkyl halides are organic molecules containing a halogen atom bonded to an sp3 hybridized carbon atom.

- Alkyl halides are classified as primary (1°), secondary (2°), or tertiary (3°), depending on the number of carbons bonded to the carbon with the halogen atom.
- The halogen atom in halides is often denoted by the symbol "X"

## **General structure of alkyl halides**

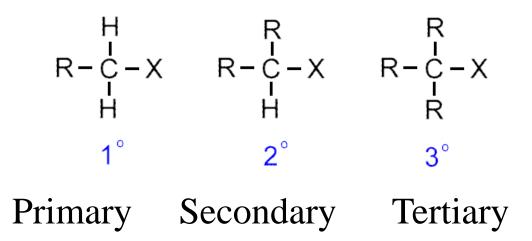
R-X (X = F, Cl, Br, I)

## **R** is any simple alkyl or substituted alkyl group



## **Classification**

Alkyl halides can be classified according to the class of the carbon that the halogen is attached to.



There are other types of organic halides, These include:

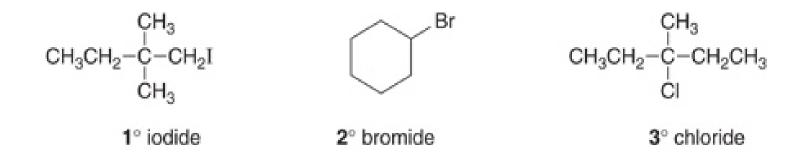
• Vinyl halides have a halogen atom (X) bonded to a C=C double bond.

• Aryl halides have a halogen atom bonded to a benzene ring.

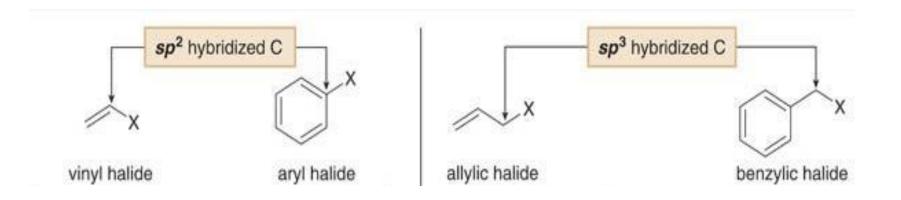
• Allylic halides have X bonded to the carbon atom adjacent to a C=C double bond.

• Benzylic halides have X bonded to the carbon atom adjacent to a benzene ring.

#### Examples of 1°, 2°, and 3° alkyl halides



Four types of organic halides (RX) having X near a  $\pi$  bond



## **Nomenclature**

**Common name:** replacing **—ane** of alkane by **—yl** and follow by **halide** for longest chain.

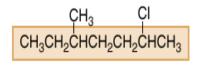
**IUPAC name:** prefixing **Halo-** followed by **alkane**, as in alkanes.

#### *How To* Name an Alkyl Halide Using the IUPAC System

Example Give the IUPAC name of the following alkyl halide:

 $\begin{array}{ccc} \mathsf{CH}_3 & \mathsf{CI} \\ \mathsf{I} \\ \mathsf{CH}_3\mathsf{CH}_2\mathsf{CHCH}_2\mathsf{CH}_2\mathsf{CHCH}_3 \end{array}$ 

Step [1] Find the parent carbon chain containing the halogen.

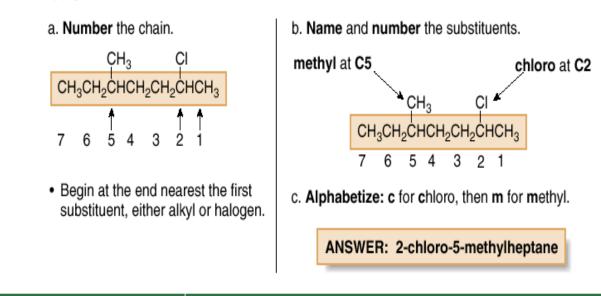


 Name the parent chain as an *alkane*, with the halogen as a substituent bonded to the longest chain.

7 C's in the longest chain

7 C's ---→ heptane

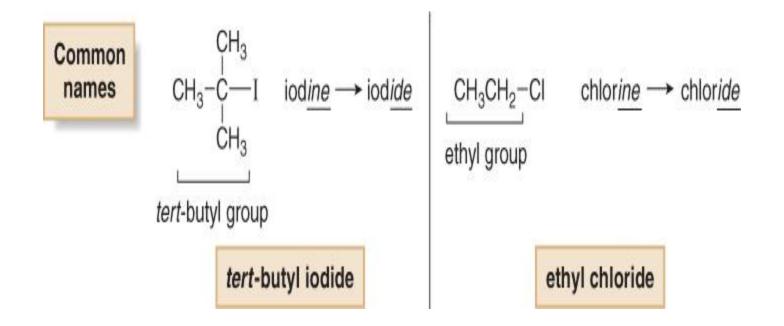
Step [2] Apply all other rules of nomenclature.

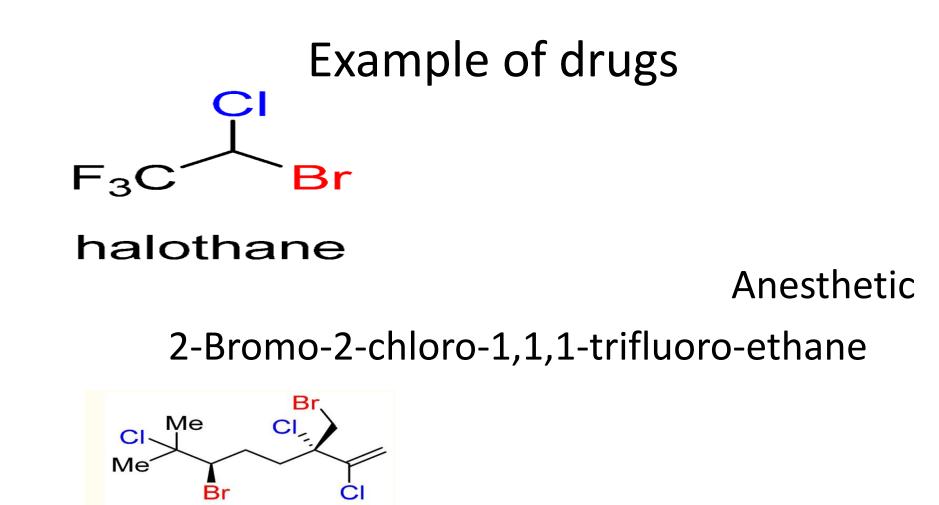


## **Common names**

Common names are often used for simple alkyl halides. To give a common name: 1-Name all the carbon atoms for longest chain of the molecule as a separate alkyl group by replacing –ane of alkane by –yl. 2-Name the halogen (replace to halide) that bonded to the alkyl group .

Combine the names of the alkyl group and halide, separating the words with a space.





6-Bromo-3-(bromomethyl)-2,3,7trichloro-7-methyl-1-octene

(+)-halomon

Common name	Structure	IUPAC name	No. of C atom
Methyl bromide	H <sub>3</sub> C Br	Bromomethane	1
Ethyl bromide	Br	Bromoethane	2
n-Propyl bromide	Br	1-Bromopropane	2
lsopropyl bromide	Br	2-Bromopropane	3

n-Butyl bromide	Br	1-Bromobutane
sec-Butyl bromide	Br	2-Bromobutane
Isobutyl bromide	Br	1-Bromo-2-methylpropane
tert-Butyl bromide	Br	2-Bromo-2-methylpropane

Q/ Give the structure and IUPAC name of n-, iso-, sec-, tertand neo-pentyl chloride.

Q/ Give the common and IUPAC name of the following:

 $\begin{array}{c} \mathsf{CH}_3 & \mathsf{Br}\\ {}_{|} \\ \mathsf{CH}_3\mathsf{CHCH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_3\end{array}$ 

CI $H_3CHCH_2CH_3$ 

 $CH_2CH_2F \\ \overset{|}{C}H_3CH_2CH_2CH_2CH_2CH_3$ 

# Physical properties of alkyl halide

• Because of greater molecular weight, haloalkanes have considerably higher boiling points than alkanes of the same number of carbons.

n-Pentane (36 °C) n-Pentyl chloride (108 °C)

- For a given alkyl group, the boiling point increases with increasing atomic weight of the halogen, so that a fluoride is the lowest boiling, an iodide the highest boiling.
- For a given halogen, b.p. rises with increasing number of carbon atoms.

n-Propyl chloride (47) n-Butyl chloride (78.5)

- The branching lowers the b.p. n-Butyl bromide (102) sec-Butyl bromide (91)
- In spite of their polarity, alkyl halides are insoluble in water, probably because of their inability to form hydrogen bonds. They are soluble in the typical organic solvents.
- Iodo, bromo, and polychloro compounds are more dense than water.

## **Preparation**

## **1- From alcohols**

Alcohols react with hydrogen halides or phosphorus halides.

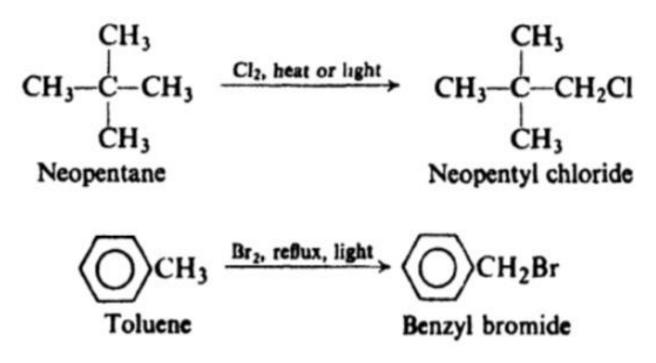
 $R-OH \longrightarrow R-X R-X$ 

conc. HBr CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br or n-Propyl alcohol NaBr, H2SO4. n-Propyl bromide heat CH-CH<sub>3</sub> CH CH-ÓН Br 1-Phenylethanol 1-Bromo-1-phenylethane a-Phenylethyl alcohol a -Phenylethyl bromide

## 2- Halogenation of certain hydrocarbons.

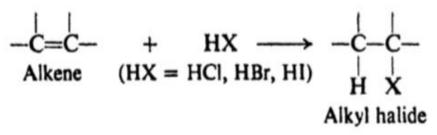
Under the influence of ultraviolet light, or at 250-400, chlorine or bromine converts alkanes into chloroalkanes (alkyl chlorides) or bromoalkanes (alkyl bromides.

$$R-H \xrightarrow{X_2} R-X + HX$$



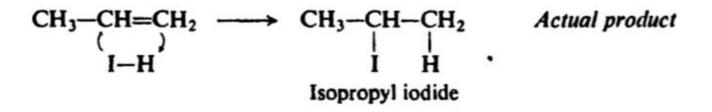
## **3- Addition of hydrogen halides to alkenes.** Markovnikov's rule

An alkene is converted by hydrogen chloride, hydrogen bromide, or hydrogen iodide into the corresponding alkyl halide.



$$CH_3 - CH = CH_2 \xrightarrow{} CH_3 - CH - CH_2$$

n-Propyl iodide



### 4- Addition of halogens to alkenes and alkynes

Alkenes are readily converted by chlorine or bromine into saturated compounds that contain two atoms of halogen attached to adjacent carbons.

> $\begin{array}{cccc} -C = C - & + & X_2 & \longrightarrow & -C - C - \\ Alkene & (X_2 = Cl_2, Br_2) & & \downarrow & \downarrow \\ \end{array}$ Vicinal dihalide  $\begin{array}{cccccc} CH_2 = CH_2 + Br_2 & \xrightarrow{CCl_4} & CH_2 - CH_2 \\ Ethene & & & & & \\ \end{array}$ (Ethylene) 1,2-Dibromoethane (Ethylene bromide)  $CH_3CH=CH_2 + Br_2 \xrightarrow{CCl_4} CH_3-CH--CH_2$ Propene Br (Propylene) 1,2-Dibromopropane (Propylene bromide)

**5- Halide exchange (Finkelstein reaction).** 

$$R - X + I^{-} \xrightarrow{acetone} R - I + X^{-}$$

An alkyl iodide is prepared from the corresponding bromide or chloride by treatment with a solution of sodium iodide in acetone, the less soluble bromide or chloride precipitates from solution and can be removed by filtration.

 $CH_3CH_2Br_{(acetone)} + Nal_{(acetone)} \rightarrow CH_3CH_2I_{(acetone)} + NaBr_{(s)}$