Organic Halogen compounds II year Bsc Paper- III ( Module-III)

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## Definition.

- Classes of Halogen compounds.
- □ Nomenclature of Halogen compounds.
- Physical properties.
- Preparation of Halogen compounds.
  - A. Direct halogenation of hydrocarbons
  - B. Conversion of alcohols: alkyl halides
- Reactions of Organic Halides.
  - A. Nucleophilic substitution Reactions
  - B. Elimination Reactions.
  - C. Reduction Reactions.

Most of the material presented in this section has been introduced in previous chapters. Here we shall review, correlate, and amplify the topics.

## Definition

**Organic halogen compounds** are a large class of natural and synthetic chemicals that contain one or more halogens (fluorine, chlorine, bromine, or iodine) combined with carbon and other elements.

# Classes of Halogen compounds:

## 1. Alkyl Halides, R-X.

• Alkyl halides: Halogen, X, [X may be F, Cl, Br or I.] is directly bonded to *sp*<sup>3</sup> carbon.

• Alkyl Halides are **subdivided** into primary (1°), secondary (2°) or tertiary (3°), depending on **the type of carbon** to which **halogen** attached.

#### Examples

Alkyl Halides Classification

**1. Methyl halides**: halide is attached to a methyl group.

CH<sub>3</sub>Cl CH<sub>3</sub>Br

Common name: IUPAC name: MethylChloride Chloromethane MethylBromide Bromomethane **2. Primary alkyl halide**: Carbon to which halogen is bonded is attached to *only one* other **carbon**.



**Secondary alkyl halide** : Carbon to which halogen is bonded is attached *to two* other carbons.



**Tertiary alkyl halide** : Carbon to which halogen is bonded is attached *to three* other carbon.



**Examples** 



• Geminal dihalide: two halogen atoms are bonded to the same carbon.



geminal dihalide

• Vicinal dihalide: two halogen atoms are bonded to adjacent carbons.

## $\frac{Br-CH_2CH_2-Br}{Br}$

vicinal dihalide

#### Write the structure of the following:

(a) Bromoform

(b) Hexafluoroethane

(c) *p*-Nitrobenzylbromide

(d) Vinylbromide

(e) Cis-2-Methylcyclohexyl bromids

(f) Triphenylmethyl chloride

## Classify the following organic Halides



## Nomenclature of Organic Halides:

#### A. Haloalkane style: (IUPAC system)

The IUPAC names of alkyl halides are obtained by using the following:

- (a) Select the longest carbon chain containing the halogen atom and name the alkyl halide.
- (b) Number the chain so as to give *the carbon carrying the halogen* atom the *lowest* possible number.

(c) Indicate the position of the halogen atom by a number and by the *fluoro*-, *chloro*-, *bromo*-, or *iodo*-.

(d) Name other *substituents* and indicate their positions by numbers.

2-chlorobutane

6-bromo-2-methylnonane

#### **B.** Alkyl halide style: (Common)

- The alkyl group is attached to the halogen atom is named first.
- -The alkyl groups is a substituent on halide, then follow by an appropriate word *fluoride*, *chloride*, *bromide*, or *iodide*.
- <u>Useful</u> only for *small* alkyl groups.

## Examples

CH<sub>3</sub> CH<sub>3</sub>CHCH<sub>2</sub> Br

CH<sub>3</sub> CH<sub>3</sub>CH<sub>2</sub>CH-Br



iso-butyl bromide

sec-butyl bromide

tert-butyl bromide

#### • Solubility

All organic halides are insoluble in water and soluble in common organic solvents (benzene, ethers, etc.).

#### • The boiling point

The boiling point of <u>the organic halide</u> increase, as <u>the size of</u> the halogen increase (molecular wt). Therefore, the boiling points increases in the order F<Cl<Br<I

 $\begin{array}{c} CH_{3}F & CH_{3}Cl \\ (Mol \ wt= \ 34; \ bp = -78^{\circ}C) & (Mol \ wt= \ 50.5; \ bp = -24^{\circ}C) \\ CH_{3}Br & CH_{3}I \\ (Mol \ wt= \ 95; \ bp = 4^{\circ}C) & (Mol \ wt= \ 142; \ bp = \ 42^{\circ}C) \\ Within \ a \ homologous \ serious \ the \ boiling \ point \ also \ increase \ regularly \\ with \ molecular \ weight. \ For \ example, \end{array}$ 

CH <sub>3</sub> CI	CH <sub>2</sub> CH <sub>2</sub> Cl	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> C
$(bp = -24^{\circ}C)$	$(bp = 12^{\circ}C)$	$(bp = 74^{\circ}C)$

As expected, within a series of isomers, the straight-chain compounds has the highest boiling points, and the most branched isomer the lowest boiling p.



## Note that:

Alkyl halides have higher melting points than alkanes, alkenes & alkynes because of:

Polarity
 Molecular weight



a- alkanes

b- alkenes @ Anti-Makownikkoff's

c- alkynes

$$R \longrightarrow R \longrightarrow X$$

d- aromatic ring & alkyl benzenes.

$$Ar \longrightarrow Ar \longrightarrow X$$

to alkyl halides  $R \longrightarrow R \longrightarrow X$ 

2-

Conversion of alcohols

By using either

a-conc halogen acid HX b-phosphorus halides; PX<sub>3</sub> or PX<sub>5</sub> c-thionylchlorid; SOCl<sub>2</sub>

$$Ar - CH_2 - H \longrightarrow Ar - CH_2 - X$$

The main methods for preparing organic chlorides, bromides and Iodides are Summarized here. All these reactions have been discussed in previous chapters.

## **1- Direct halogenation of hydrocarbons**

## a- Halogenation of alkanes

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

## **b-Halogenation of alkenes**

1. 
$$H_2C = CHCH_2R + X_2 \xrightarrow{UV \text{ or heat}} H_2C = CHCHR + HX$$
  
2.  $H_2C = CHCH_2R + X_2 \xrightarrow{CCl_4} H_2C = CHCH_2R$   
 $X \xrightarrow{X}$ 

3. The addition of hydrogen halides (HX) to unsymmetrical alkenes or alkynes obeys the Markownikkoff's rule



The addition of HBr ( but **not** HCl or HI) in **the presence** of *peroxide* occurs in the *contrary to* Markownikkoff's rule

$$\begin{array}{cccc} \text{RCH} & = \text{CH}_2 + \text{HBr} & \xrightarrow{\text{Peroxide}} & \text{RCH} - \text{CH}_2 \\ \hline \text{H}_2\text{O}_2 & \text{H} & \text{Br} \\ \end{array}$$

$$\begin{array}{cccc} \text{CH}_3\text{CH}_2\text{CH}_2 + \text{HBr} & \xrightarrow{\text{Peroxide}} & \text{CH}_3\text{CH}_2\text{CH}_2 - \text{CH}_2 \\ \hline \text{H}_2\text{O}_2 & \text{CH}_3\text{CH}_2\text{CH} - \text{CH}_2 \\ \hline \text{CH}_3 & \text{Br} \end{array}$$

## c- Halogenation of alkynes



## d- Halogenation of aromatic ring and alkyl benzenes



## 2- Conversion of alcohols: alkyl halides

•Alkyl Halides are best prepared from alcohols, which are easily accessible.

$$R \longrightarrow R \longrightarrow X$$

•The hydroxyl group of an alcohol is **replaced by** halogen on reaction with either:

- Concentrated halogen acid; HX

or

- Phosphorus halides; PX<sub>3</sub> or PX<sub>5</sub>

or

- Thionylchlorid ;SOCl<sub>2</sub>

## a- Preparation using concentrated halogen acid HX:

#### **General Reaction**



Alcohols react with HBr or HI to give alkyl bromide or alkyl iodide. They react with HCl in presence of  $(ZnCl_2)$  zinc chloride catalyst.

## **b- Preparation using phosphorus halides; PX**<sub>3</sub>**or PX**<sub>5</sub>**:** *General Reaction*



c- Preparation using thionylchlorid; SOCl<sub>2</sub>:

#### **General Reaction**



**Examples** 







is replaced by some other atom or group

of HX from the halide.

to form organometalic compounds.

## 1- Nucleophilic Substitution Reactions: The general equation describing *nucleophilic substitution* of alkyl halides is:



The alkyl halide undergo nucleophilic substitution reactions in which a stronger nucleophile replace a weaker nucleophile.

•Due to the electronegativity differences between carbon and the halide, the C-X bond is polar with a partial positive charge ( $\delta^+$ ) on the carbon atom and a partial negative charge ( $\delta^-$ ) on the halogen.

•Halogens are good leaving groups and can be replaced by an incoming nucleophile as in the general reaction shown above.

#### Figure 8.2 Some nucleophlilic reaction of alkyl halides *Elements of organic Chemistry*; Zimmerman, page 223



## **Examples of common nucleophiles:**

-ÖH	-X	Θ -CN
-ÖR	-NH <sub>2</sub>	нс≡с
-SH Or -SR	-NHR	RC <u></u> — C <sup>Θ</sup>

**Reaction Examples** 



#### Note that;

the reaction always involves *breakage* of Carbon—Halogen bond.



## 2- Elimination Reactions Alkyl Halides can undergo elimination reaction *E* producing an alkene.

**General Elimination Reaction** 



Elimination of HX

The most common bases used in elimination reactions are *negatively charged oxygen* compounds, such as HO<sup>-</sup> and its alkyl derivatives, RO<sup>-</sup>, called alkoxides.



3- Reactions of Organometalic Compounds (Reduction): The alkali metals (Li, Na, K etc.) and the alkaline earth metals (Mg and Ca, together with Zn) are good reducing agents

I-Reduction with alkaline earth metals

(a) Formation of Grignard reagent (X = Cl, Br, I) R - X + Mg - Dry ether RMgXAr - X + Mg - Dry ether ArMgX

(b) Reaction of Grignard reagent



#### II-Reduction with alkali metals

a) Reduction by Zinc metal and acids or by metal hydrides

$$CH_{3}CH_{2}CH_{2}Br + Zn \xrightarrow{H^{+}} CH_{3}CH_{2}CH_{3} + ZnBr_{2}$$

$$CH_{3}CH_{2}CH_{2}CH_{2}Br \xrightarrow{+} CH_{3}CH_{2}CH_{2}CH_{3}$$

b) Reduction by sodium metal (coupling reaction)

 $2CH_3 - Br + 2Na \longrightarrow H_3C - CH_3 + 2NaBr$ 

c) Reduction using lithium dialkyl cuprate (Gilman reagent)

 $(CH_3CH_2)_2CuLi + CH_3Br \longrightarrow CH_3CH_2CH_3$ 

## Thankyou

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