

# **BOOKS**

- 1) Organic Chemistry Structure and Function, K. Peter C. Vollhardt, Neil Schore, 6th Edition
- 2) Organic Chemistry, T. W. Graham Solomons, Craig B. Fryhle
- 3) Organic Chemistry: A Short Course, H. Hart, L. E. Craine, D. J. Hart, C. M. Hadad,
- 4) Organic Chemistry: A Brief Course, R. C. Atkins, F.A. Carey

## 5. ALKYL HALIDES

### 5.1 Physical Properties of Alkyl halides

### 5.2 Synthesis of Alkyl halides

#### 5.2.1 Alkyl halides from Alkanes

#### 5.2.2 Hydrogen halide Addition to an Alkene

#### 5.2.3 Halogen Addition to an Alkene

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### 5.3 Reactions of Haloalkanes

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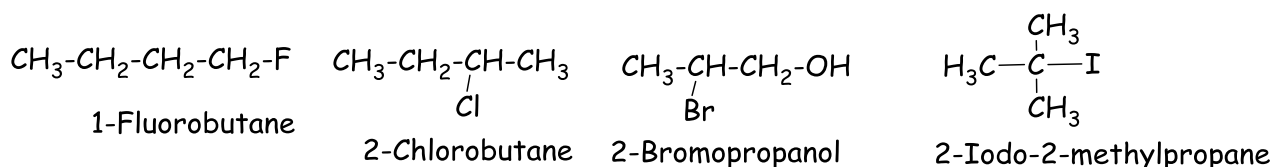
#### 5.3.4 Nitrile Formation

#### 5.3.5 Amine Formation

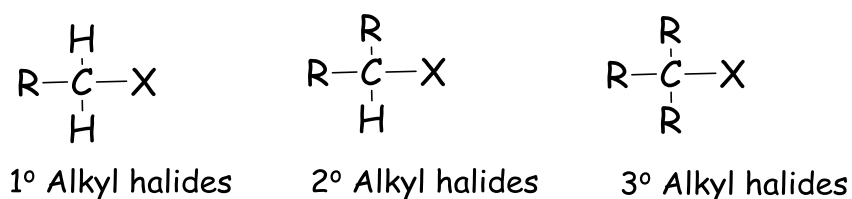
#### 5.3.6 Alkene Formation

#### 5.3.7 Reactions of Organo-metallic Reagents with Alkyl halides

Alkyl halides known as halo alkanes are compounds in which one or more hydrogen atoms in an alkane have been replaced by halogen atoms (fluorine, chlorine, bromine or iodine).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



Alcohols are classified as primary ( $1^\circ$ ), secondary ( $2^\circ$ ) or tertiary ( $3^\circ$ ), which refers to the carbon bearing the halogen group.



There is electronegativity differences between the carbon and halogen atoms, therefore the  $\sigma$  covalent bond between these atoms is polarized, with the carbon atom becoming slightly positive and the halogen atom partially negative. The bond length between carbon and halogen becomes longer and less polar as the halogen atom changes from fluorine to iodine.

## 5.1 Physical Properties of Alkyl halides

Iodomethane is a liquid and other methyl halides are the gas. The boiling points of different alkyl halides containing the same halogen increase with increasing chain length. For a given chain length, the boiling point increases as the halogen is changed from fluorine to iodine. The compound with the more highly-branched alkyl group normally has the lowest boiling point than the straight -chain analogues.

R	X=	H	F	Cl	Br	I
CH <sub>3</sub>		-161.7	-78.4	-24.2	3.6	42.4
CH <sub>3</sub> CH <sub>2</sub>		-88.6	-37.7	12.3	38.4	72.3
H <sub>3</sub> C-CH <sub>2</sub> -CH <sub>2</sub>		-42.1	-2.5	46.6	71.0	102.5
H <sub>3</sub> C-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub>		-0.5	32.5	78.4	101.6	130.5
H <sub>3</sub> C-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub>		36.1	62.8	107.8	129.6	157.0
Isopropyl		-	-9.4	34	59.4	89.4
Sec-butyl		-	-	68	91.2	120
Tert-butyl		-	-	51	73.3	100

Alkyl halides have little solubility in water but good solubility with nonpolar solvents, such as hexane, carbon tetrachloride. Many of the low molecular weight alkyl halides are used as solvents in reactions that involve nonpolar reactants, such as bromine.

## 5.2 Synthesis of Alkyl halides

There are some methods commonly used to prepare alkyl halides.

### 5.2.1 Alkyl halides from Alkanes

See "Alkanes" for details.

### 5.2.2 Hydrogen halide Addition to an Alkene

See "Alkenes" for details.

### 5.2.3 Halogen Addition to an Alkene

See "Alkenes" for details

## 5.2.4 Hydrogen halide Addition to an Alkyne

See "Alkynes" for details.

## 5.2.5 Halogen Addition to an Alkyne

See "Alkynes" for details.

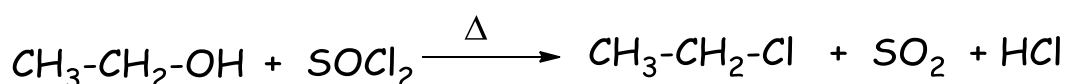
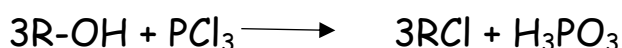
## 5.2.6 Alkyl Halides from Alcohols

### 5.2.6.1 Reaction with Halogen Acids

Alcohols are converted to alkyl halides by nucleophilic substitution ( $S_N$ ) reactions with halogen acids.

### 5.2.6.2 Reaction of Alcohols with Sulphur and Phosphorous Halides

A more efficient method of preparing alkyl halides from alcohols involves reactions with phosphorus trihalide ( $PX_3$ ), phosphorus pentahalide ( $PX_5$ ), or thionyl chloride ( $SOCl_2$ ).

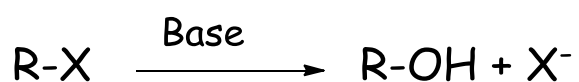


## 5.3 Reactions of Haloalkanes

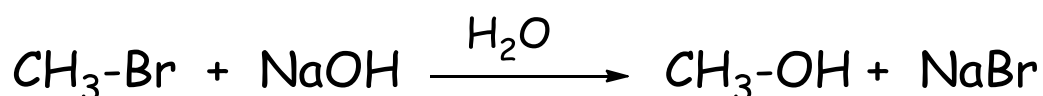
Here are some examples for the reactions of alkyl halides. The nucleophilic substitution ( $S_N$ ) is an extremely versatile reaction from a synthetic standpoint. Elimination reactions (E) are very useful for producing alkenes from alkyl halides.

### 5.3.1 Hydrolysis

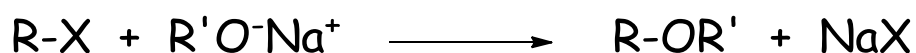
Hydrolysis of alkyl-halides give alcohols.



This is a nucleophilic substitution reaction and NaOH, KOH or  $H_2O$  can be used as a base.



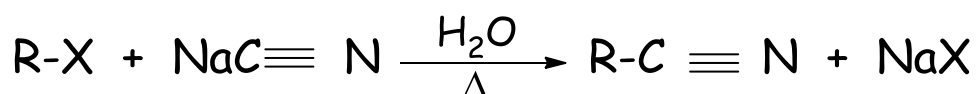
### 5.3.2 Williamson Ether Synthesis



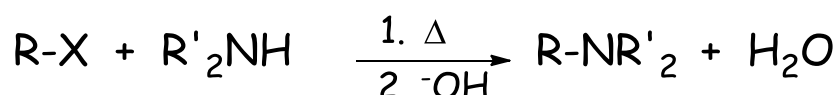
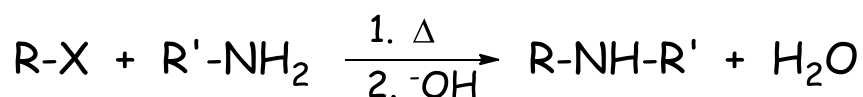
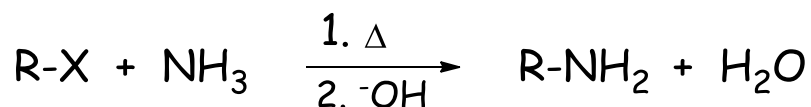
### 5.3.3 Grignard Reagent Formation



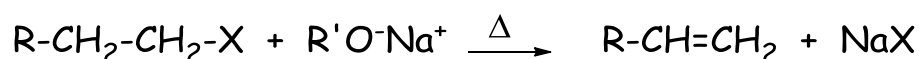
### 5.3.4 Nitrile Formation



### 5.3.5 Amine Formation

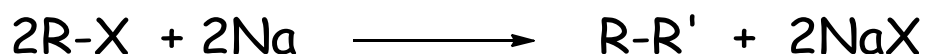


### 5.3.6 Alkene Formation



### 5.3.7 Reactions of Organo-metallic Reagents with Alkyl halides

The alkali metals (Li, Na, K etc.) are good reducing agents. Sodium and potassium reduce the carbon-halogen bonds of alkyl halides. The halogen is converted to halide anion, and the carbon bonds to the metal. Halide reactivity increases in the order:  $\text{Cl} < \text{Br} < \text{I}$ .



Lithium and magnesium are the commonly used metals and their reactions with alkyl halides give the organometallic compounds.

