

Chapter 7: Halogenated and Organometallics Compounds

7.1. Halogenated Compounds

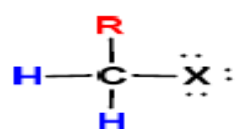
7.1.1. Definition:

Halogenated derivatives or alkyl halides result from the substitution of a halogen atom for a hydrogen atom in a hydrocarbon.

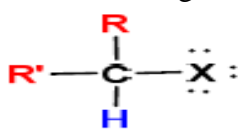
Each family of hydrocarbons corresponds to a family of halogenated derivatives:

- **R-X**: Saturated halogenated derivative (saturated R), $C_nH_{2n+1}X$.
- **R-CH=CH-X**: Ethylenic halogenated derivative.
- **Ar-X**: Aromatic halogenated derivative.

Saturated halogenated derivatives are classified into three categories based on the number of hydrogen atoms bonded to the carbon atom bearing the halogen atom.



Primary halogenated derivative

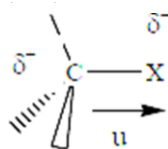


Secondary halogenated



Tertiary halogenated derivative

The C-X bond is polarized as follows:



7.1.2. Physical Properties of Halogenated Compounds:

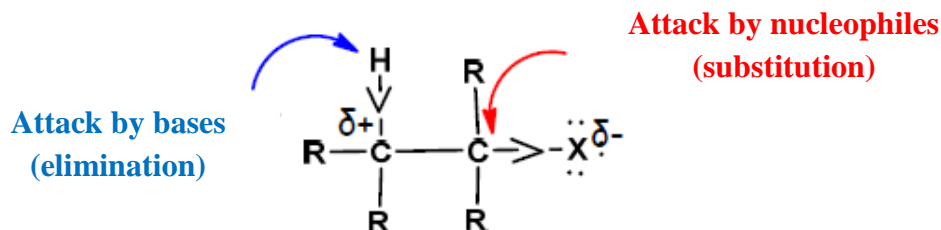
- ✓ The presence of one or more polar covalent Carbon-Halogen (C-X) bonds enables the formation of van der Waals intermolecular interactions, which increases the boiling point of the molecule.
- ✓ The boiling point increases with the size of the halogen, as attractive van der Waals interactions become stronger with bulkier halogens.

Table 7.1: Boiling points of Halogenated methanes

Molecular Formula	Molecular Weight (g/mol)	Boiling Point (°C)
CH ₄	16.04	-161.7
CH ₃ F	34.03	-78.4
CH ₃ Cl	50.49	-24.2
CH ₃ Br	94.94	3.6
CH ₃ I	141.94	42.4

- ✓ Halogenated alkanes are insoluble in water but miscible with organic solvents, such as alcohols, ethers, benzene, etc.
- ✓ The polarization of the bond increases with:
 - The electronegativity of the halogen (from I to F);

- The number of electron-donating groups (alkyls) attached to the carbon atom bonded to the halogen;
 - ✓ The polarizability of C-X bonds varies inversely, such that from fluorine to iodine the polarization decreases while polarizability increases: reactivity varies in the same direction as the latter.

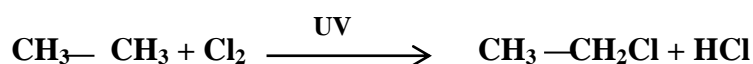


- Electrophilic Additions to Alkenes: H-X, X₂
- Double Electrophilic Additions to Alkynes: H-X, X₂
- Nucleophilic Substitution Reactions from Alcohols
- Electrophilic Aromatic Substitution: Halogenation

7.1.3. Preparation of Halogenated Compounds:

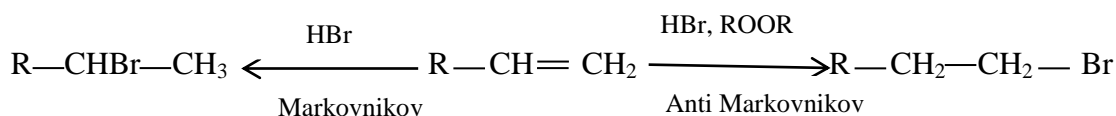
7.1.3.1. Monohalogenated derivatives

a. Radical Halogenation of Alkanes:



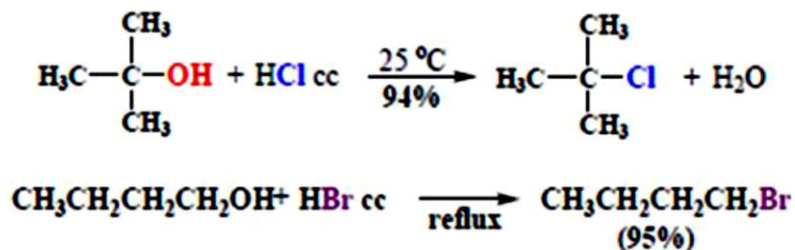
b. Electrophilic Additions to Alkenes: H-X:

The addition of a hydrohalic acid (H-X) to a double bond yields halogenated derivatives (see Chapter 5).

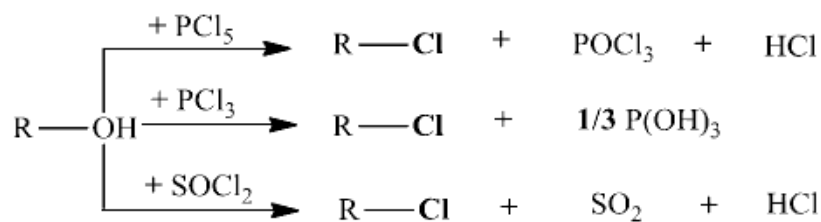


c. Nucleophilic Substitution reactions from alcohols:

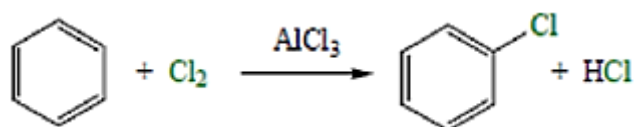
By the action of hydrohalic acid HX:



The formation of halogenated compounds is also possible through the action of halogenating agents, such as phosphorus pentachloride (PCl₅), phosphorus trichloride (PCl₃), or thionyl chloride (SOCl₂), on alcohols.

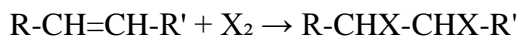


d. Halogenation of Benzene:



7.1.3.2. Dihalogenated Derivatives :

a. Synthesis from Alkenes:



Product: Vicinal dihalide (1,2-dihalogenated compound)

Notes: This electrophilic addition proceeds via halonium ion intermediate.

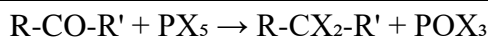
b. Synthesis from Alkynes:



Product: Geminal dihalide (1,1-dihalogenated compound)

Mechanism: Markovnikov addition occurring twice

c. Synthesis from Ketones using Phosphorus Halides



7.1.4. Reactivity of Halogenated Compounds:

Most reactions specific to halogenated derivatives were covered in the study of reaction mechanisms.

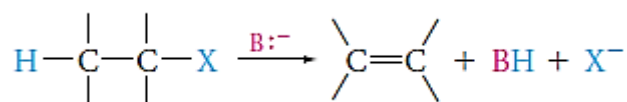
7.1.4.1. Nucleophilic Substitutions (SN1 and SN2):

Alkyl halides react with a variety of nucleophiles to give alcohols, ethers, alkyl halides.



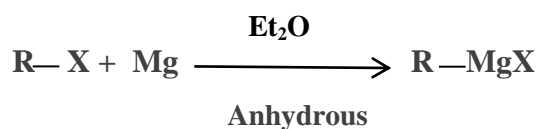
7.1.4.2. Elimination Reactions (E1 and E2):

Alkyl halides react with bases to give alkenes



7.1.4.3. Reaction with Metals:

Magnesium enables the preparation of organomagnesium compounds.



7.1.4.5. Condensation Reaction (Wurtz Reaction):



7.2. Organometallic Compounds:

7.2.1. Definition:

Organometallic compounds are organic compounds in which a metal is directly bonded to a carbon atom.

Example: methylmagnesium bromide (CH_3MgBr)

Two groups are distinguished in organometallic compounds:

True organometallics: where all metal bonds are saturated by hydrocarbon groups. For a divalent metal, their formula can be written as R-M-R' .

Examples: $\text{C}_2\text{H}_5\text{-Zn-C}_3\text{H}_7$; $\text{Al (C}_2\text{H}_5)_3$

Mixed Organometallic Compounds:

Mixed organometallics are compounds in which the metal center (M) is simultaneously bonded to both hydrocarbon groups and halogen atoms. Their general formulas are:

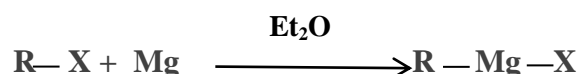
- For a **divalent metal**: R-M-X
- For a **tetravalent metal**: RR'-MX_2

Examples:

- $\text{C}_2\text{H}_5\text{-Mg-Cl}$ (Ethylmagnesium chloride)
- $(\text{C}_2\text{H}_5)_2\text{-Sn-I}_2$ (Diethyldiiodotin)

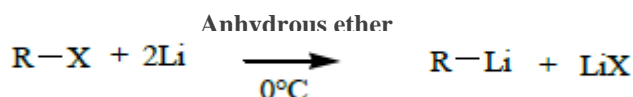
7.2.2. Preparation of Organometallic Compounds

- Formation of organomagnesium Compounds (Grignard Reagents)



7.2.3. Formation of organolithium Compounds:

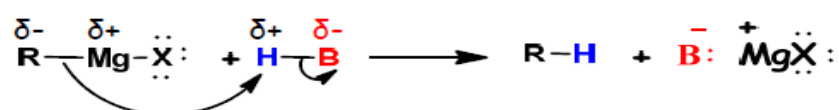
Organolithium compounds can be synthesized through the reaction between the metal (lithium) and a halogenated derivative. Various solvents may be employed, including ethers, pentane, and cyclohexane. It is essential to use rigorously anhydrous solvents and to carry out the reaction under an oxygen-free atmosphere.



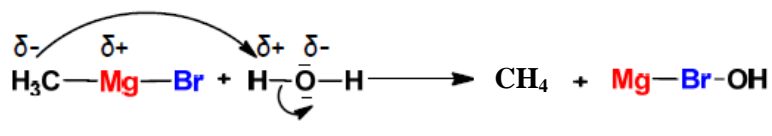
7.3. Reactivity of Organometallic Compounds (Grignard Reagents):

7.3. 1. Acid-Base Reactions with Compounds Containing Acidic Protons:

For compounds containing acidic hydrogen H-B: H-OH; H-OR; H-SR, H-NH₂; H-NHR; H-NR₃; H-C≡C-R; H-C≡N; H-X; H-OOC-R.

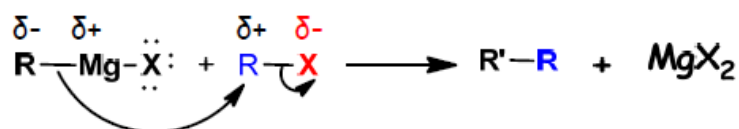


7.3. 2. Reaction with Water:



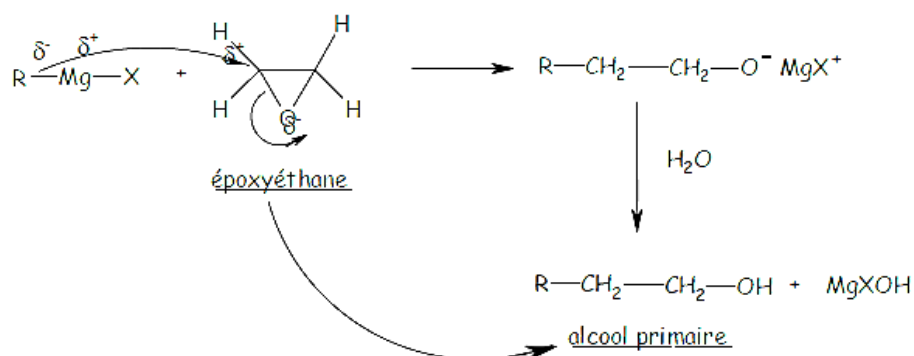
7.3.3. Nucleophilic Substitution Reaction:

On Halogenated Compounds R'-X:



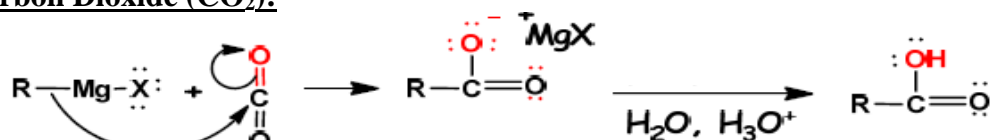
7.3.4. Nucleophilic Additions to:

7.3.4.1. Epoxides:



7.3.4.2. Carbonyl Groups :

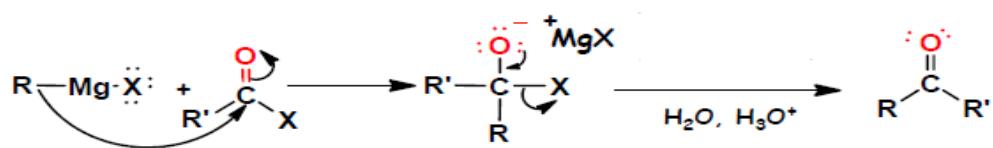
a. Carbon Dioxide (CO₂):



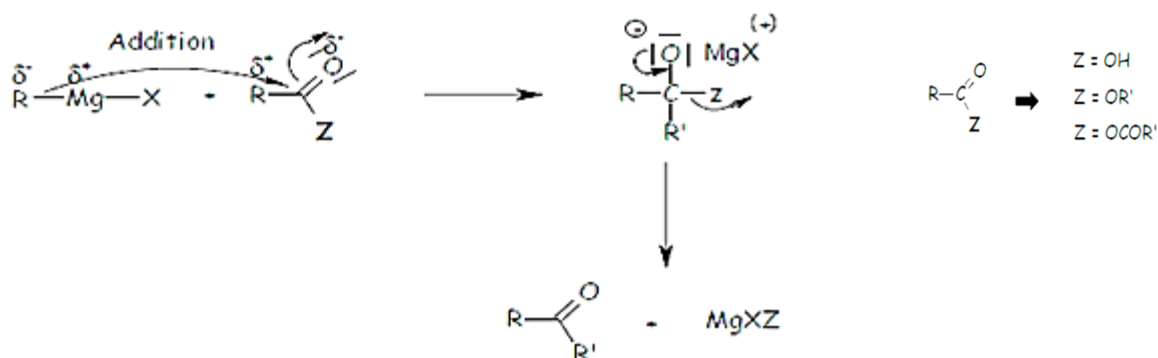
b. Aldehydes and Ketones:



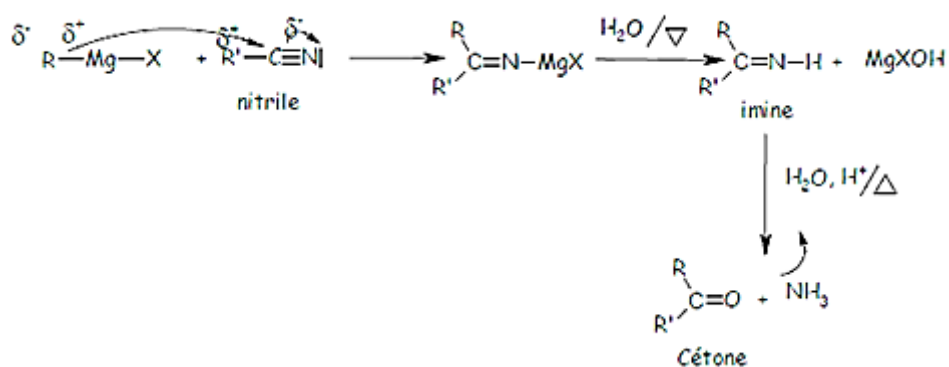
c. Acid Halides :



In general



7.3.5. Addition on nitrogen compounds:



7.3.6. Addition of oxygen:

