



# Chem 145

## Organic Halogen Compounds

### Chapter 6

1434-14345  
2013-2014  
1<sup>st</sup> semester

Dr. Seham ALTERARY

# Chapter outlines

- ❑ 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  $sp^3$  carbon.
- Alkyl Halides are subdivided into primary ( $1^\circ$ ), secondary ( $2^\circ$ ) or tertiary ( $3^\circ$ ), depending on the type of carbon to which halogen attached.

### Alkyl Halides Classification

#### Examples

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



Common name:

MethylChloride

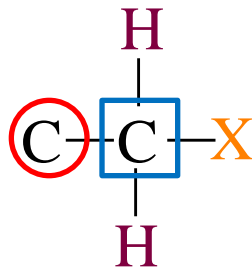
MethylBromide

IUPAC name:

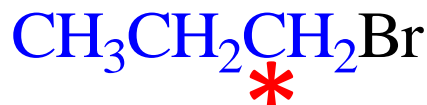
Chloromethane

Bromomethane

2. **Primary alkyl halide**: Carbon to which **halogen** is bonded is attached to *only one* other **carbon**.



## Examples



**Common name:**

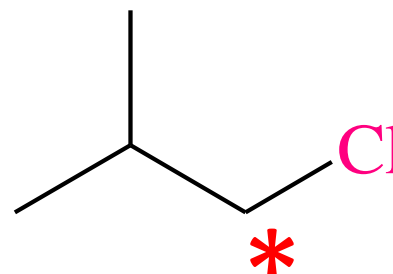
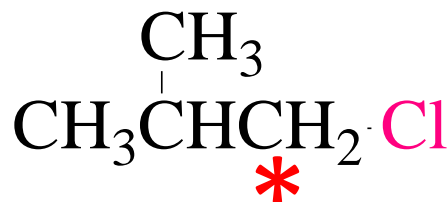
*n*-propylBromide

**IUPAC name:**

1-Bromopropane

**Class**

(1°)



**Common name:**

Isobutyl Chloride

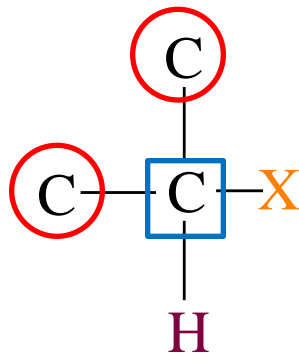
**IUPAC name:**

1-Chloro-2-methylpropane

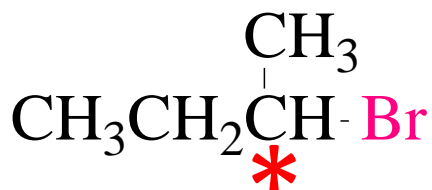
**Class**

(1°)

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



## Examples



**Common name:**

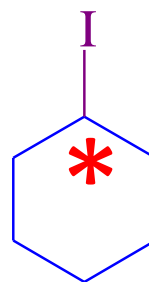
*sec*-Butyl bromide

**IUPAC name:**

2-Bromobutane

**Class**

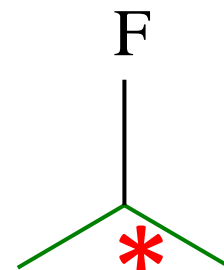
(2°)



Cyclohexyl iodide

Iodocyclohexane

(2°)

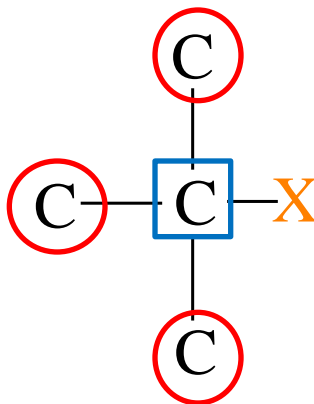


Isopropyl fluoride

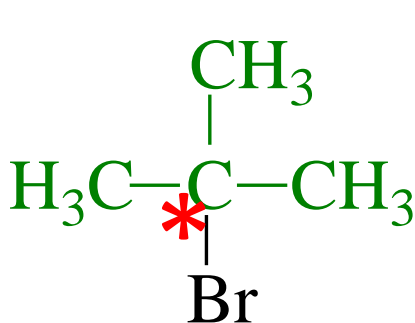
2-fluoropropane

(2°)

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



## Examples



Common name:

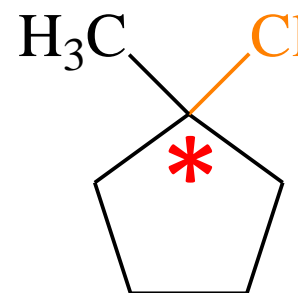
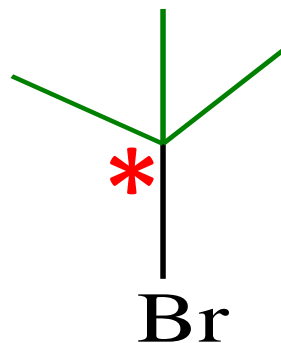
t-butyl bromide

IUPAC name:

2-bromo-2-methylpropane

Class

(3°)



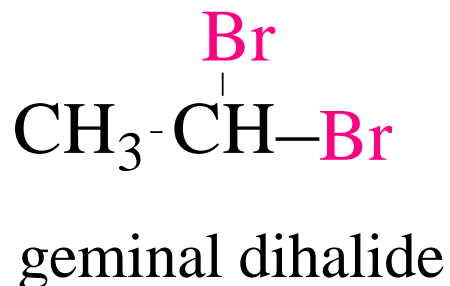
Methylcyclopentylchloride

1-chloro-1-methylcyclopentane

(3°)

# Types of Dihalides

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



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





## Practice

Write the structure of the following:

(a) Bromoform

(b) Hexafluoroethane

(c) *p*-Nitrobenzylbromide

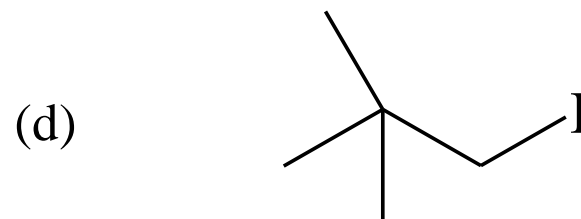
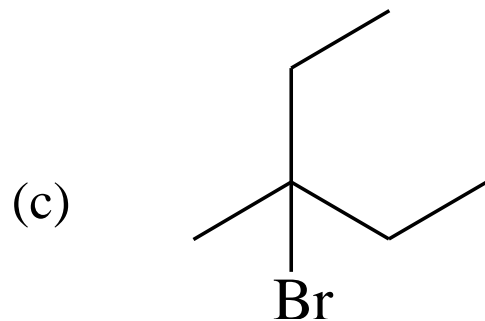
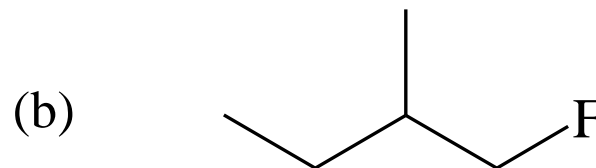
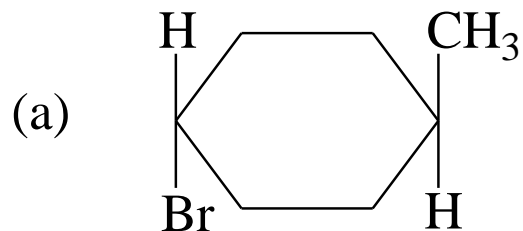
(d) Vinylbromide

(e) *Cis*-2-Methylcyclohexyl bromide

(f) Triphenylmethyl chloride

## Practice

## Classify the following organic Halides



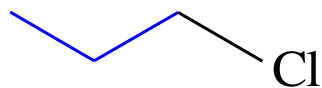
# Nomenclature of Organic Halides:

## A. Haloalkane style: (IUPAC system)

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

- Select the longest carbon chain containing the halogen atom and name the alkyl halide.
- Number the chain so as to give the carbon carrying the halogen atom the lowest possible number.
- Indicate the position of the halogen atom by a number and by the *fluoro-*, *chloro-*, *bromo-*, or *iodo-*.
- Name other *substituents* and indicate their positions by numbers.

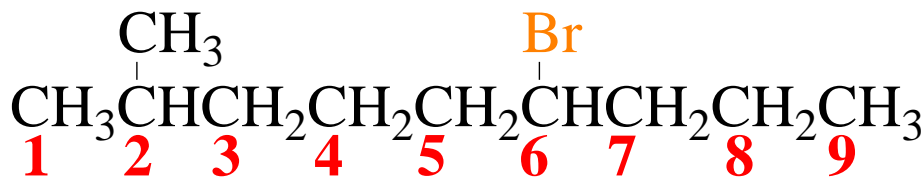
### Examples



1-chloropropane



2-chlorobutane

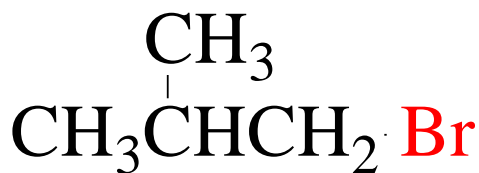


6-bromo-2-methylnonane

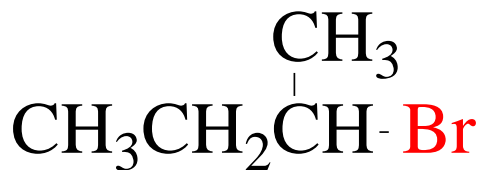
## B. Alkyl halide style: (Common)

- 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*.
- Useful only for *small* alkyl groups.

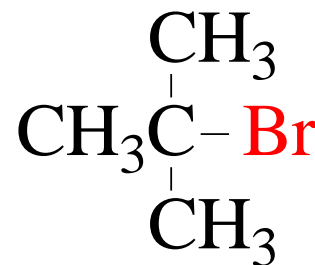
### Examples



*iso*-butyl bromide



*sec*-butyl bromide



*tert*-butyl bromide

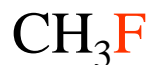
# Physical Properties of Organic Halides

- *Solubility*

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

- *The boiling point*

The boiling point of the organic halide **increase**, as the size of the **halogen increase** (molecular wt). Therefore, the boiling points increases in the order



(Mol wt= 34; bp = -78°C)



(Mol wt= 50.5; bp = -24°C)



(Mol wt= 95; bp = 4°C)



(Mol wt= 142; bp = 42°C)

Within a homologous series **the boiling point also increase** regularly with **molecular weight**. For example,



(bp = -24°C)



(bp = 12°C)

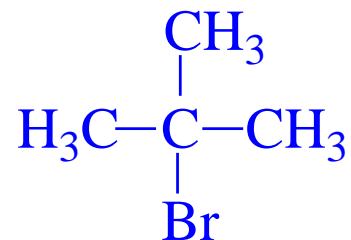


(bp = 74°C)

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.



(bp = 101°C)



(bp = 73°C)

### Note that:

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

**1. Polarity**

**2. Molecular weight**

# Preparation of Halogen Compounds

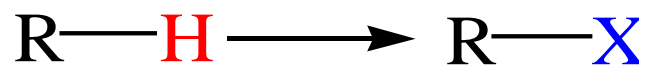
-1-

Direct halogenation  
of hydrocarbons

a- alkanes

b- alkenes     © Anti-Markovnikov's

c- alkynes



d- aromatic ring & alkyl benzenes.



2-

Conversion of alcohols  
to alkyl halides



By using either

a-conc halogen acid HX

b-phosphorus halides;  $\text{PX}_3$  or  $\text{PX}_5$

c-thionylchloride;  $\text{SOCl}_2$

# Preparation of Halogen Compounds

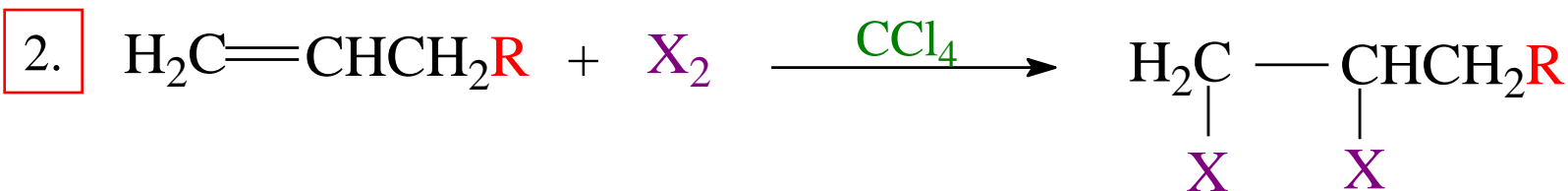
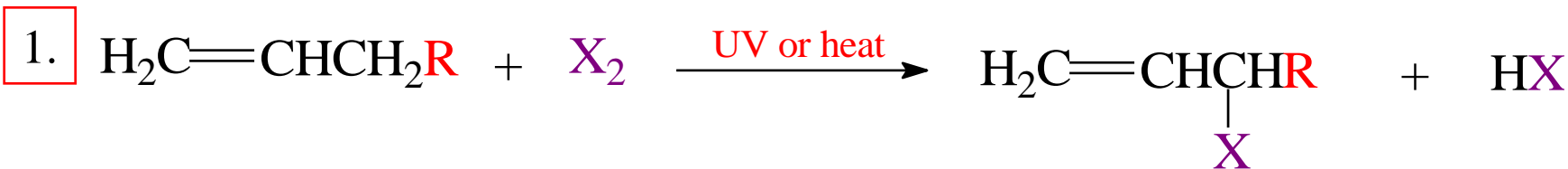
The main methods for preparing organic chlorides, bromides and Iodides are Summarized here. All these reactions have been discussed in previous chapters.

## 1- Direct halogenation of hydrocarbons

### a- Halogenation of alkanes

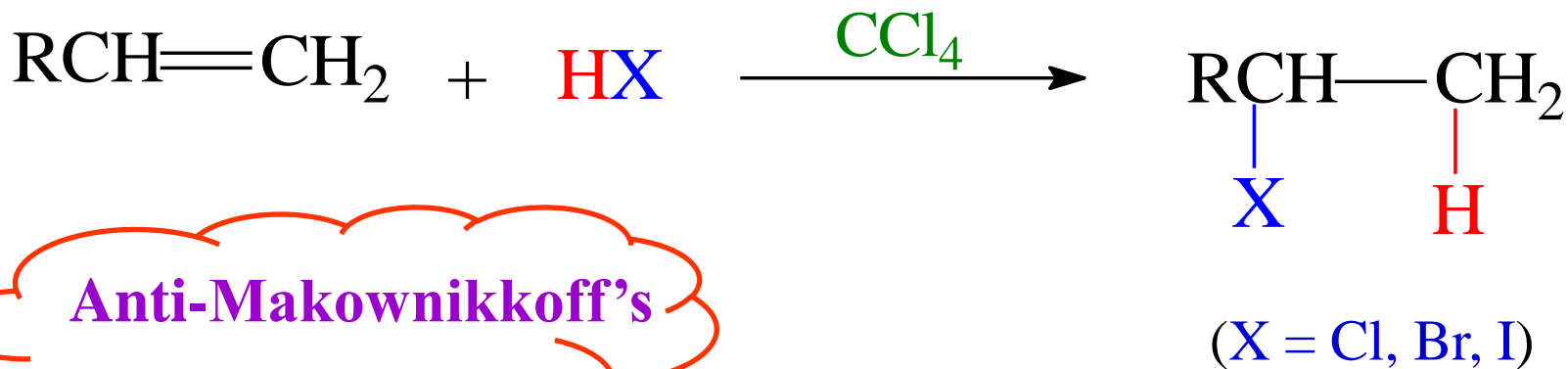


### b- Halogenation of alkenes



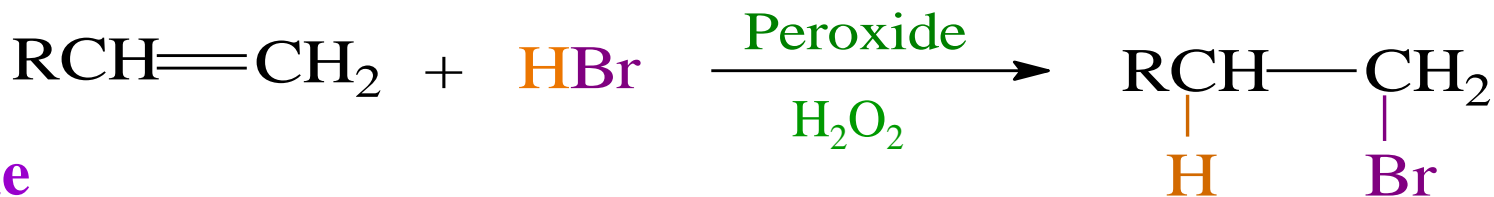


3. The addition of hydrogen halides (HX) to unsymmetrical alkenes or alkynes obeys the Markownikoff's rule

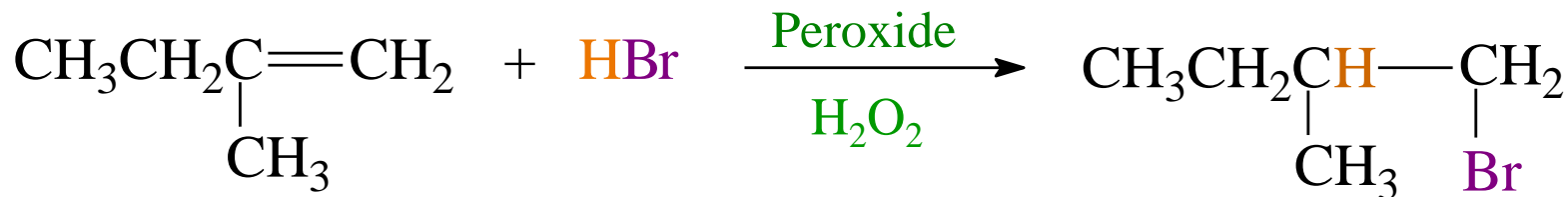


Anti-Markownikoff's

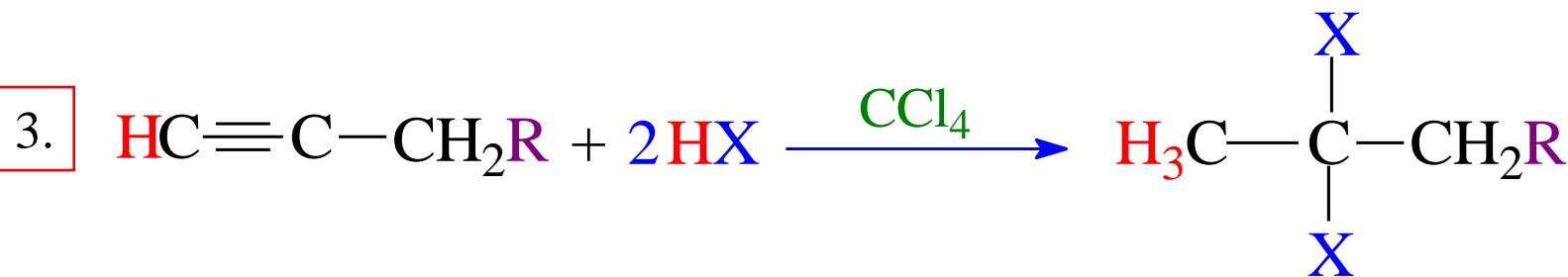
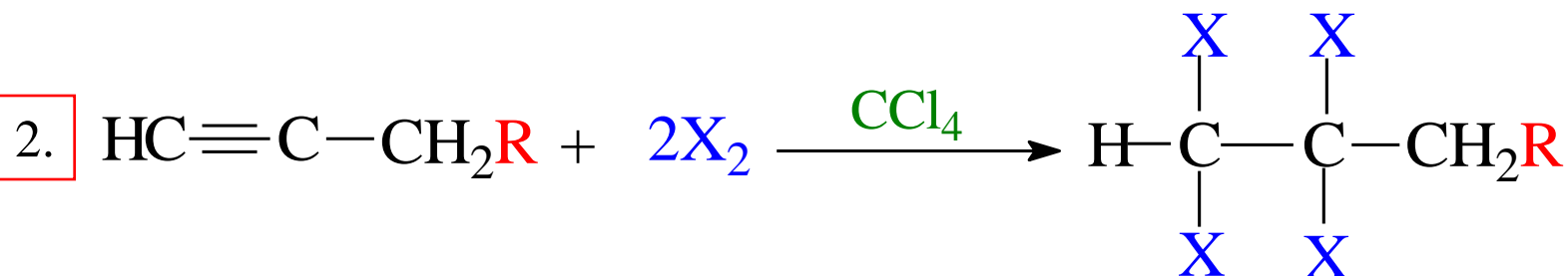
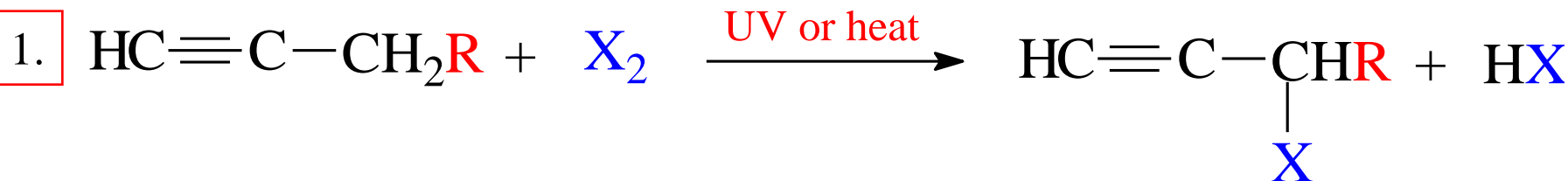
The addition of HBr ( but not HCl or HI) in the presence of *peroxide* occurs in the *contrary to* Markownikoff's rule



Example

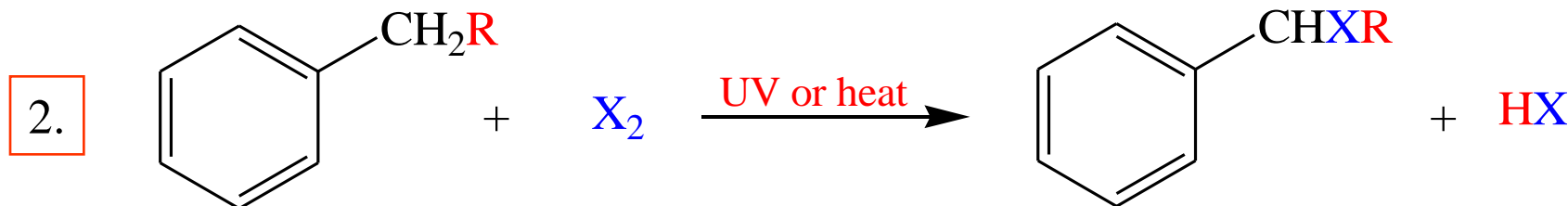
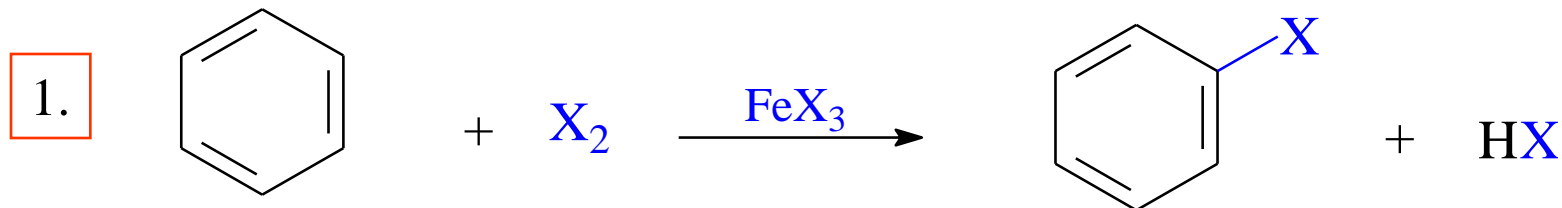


## c- Halogenation of alkynes



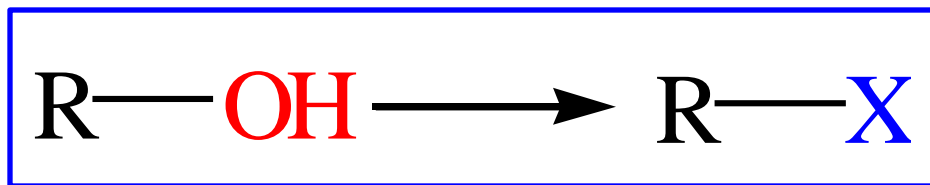
(X = Cl, Br, I)

## 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.



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

- Concentrated halogen acid;  $\text{HX}$

or

- Phosphorus halides;  $\text{PX}_3$  or  $\text{PX}_5$

or

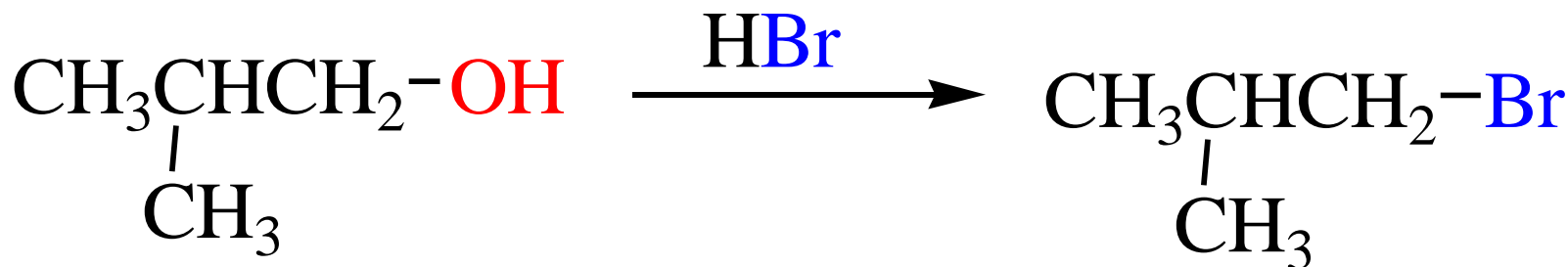
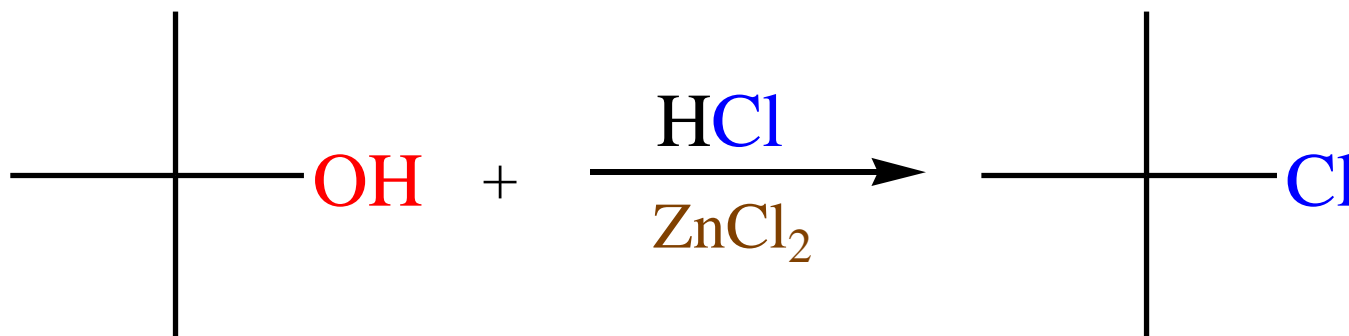
- Thionylchlorid ;  $\text{SOCl}_2$

## a- Preparation using concentrated halogen acid HX:

### General Reaction



### Example

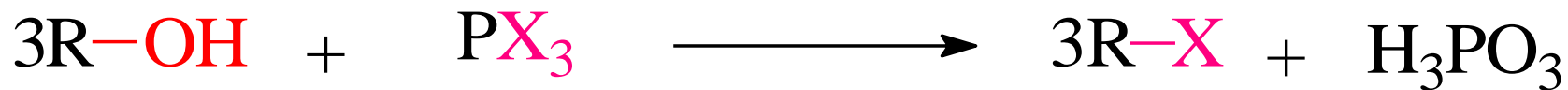


### Note That

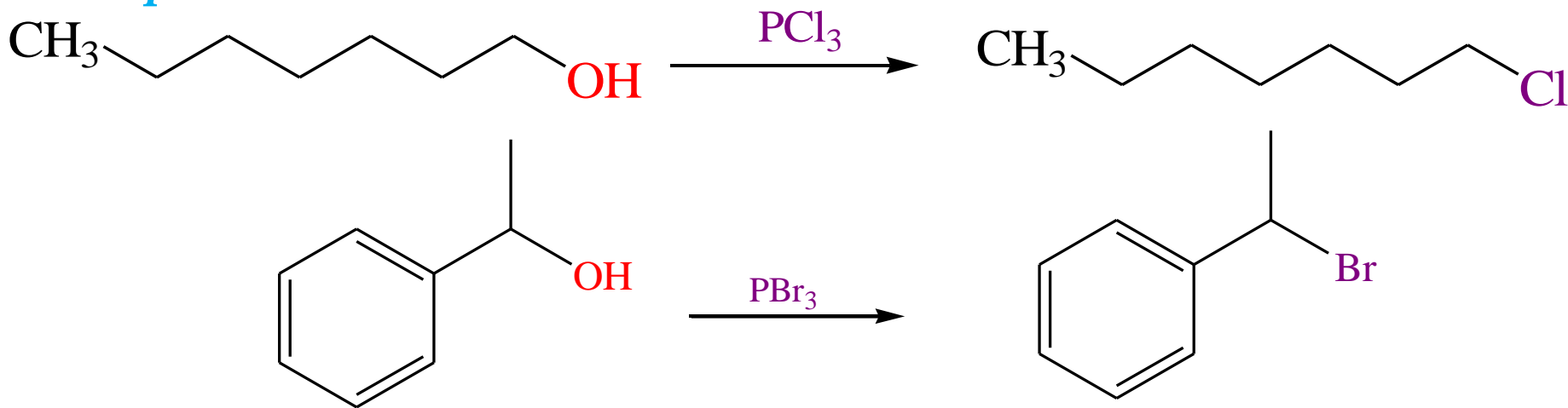
Alcohols react with HBr or HI to give alkyl bromide or alkyl iodide. They react with HCl in presence of (ZnCl<sub>2</sub>) zinc chloride catalyst.

## b- Preparation using phosphorus halides; $PX_3$ or $PX_5$ :

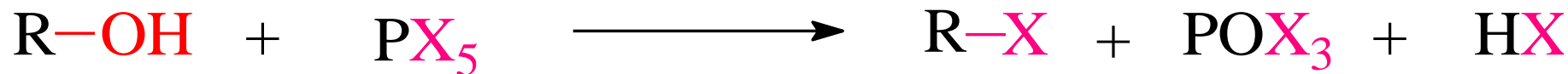
### *General Reaction*



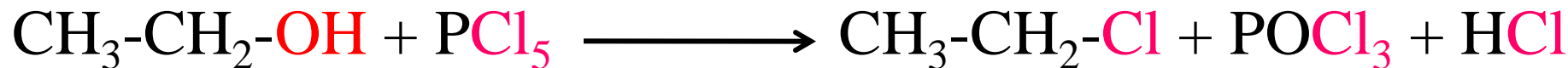
### *Example*



### *General Reaction*



### *Example*

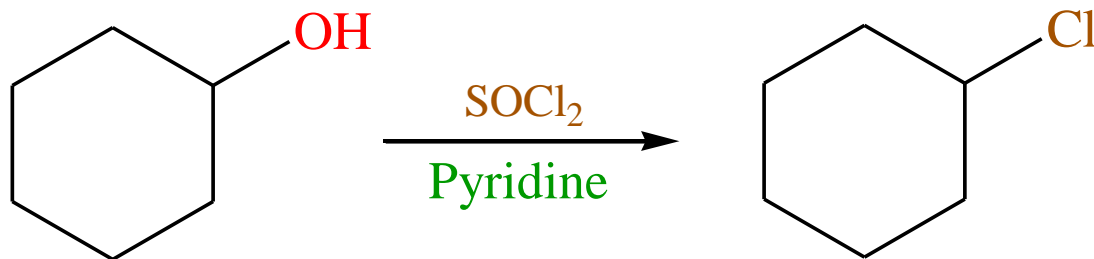


## c- Preparation using thionylchlorid; $\text{SOCl}_2$ :

### *General Reaction*

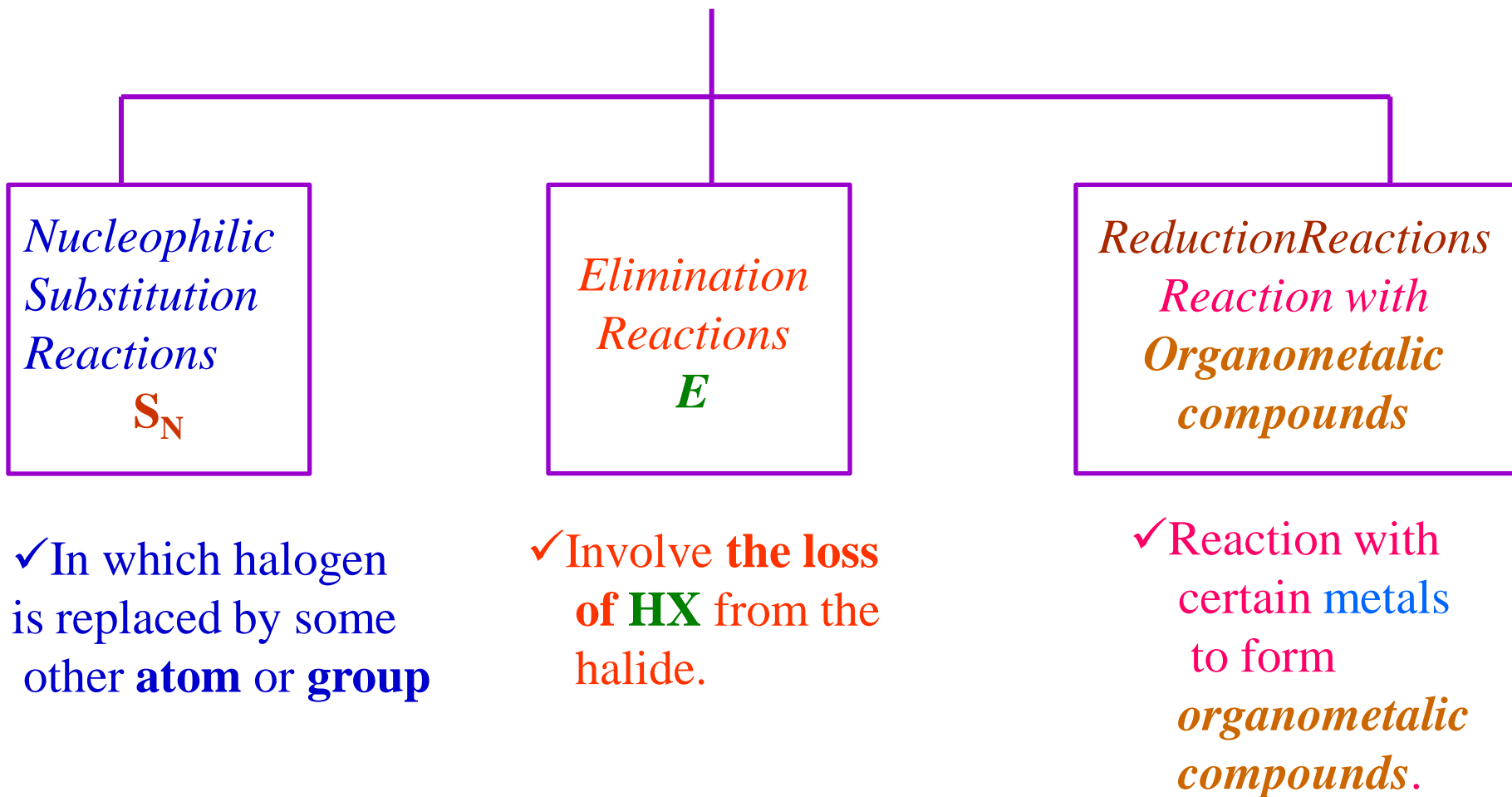


### *Examples*



# Reactions of Organic Halides

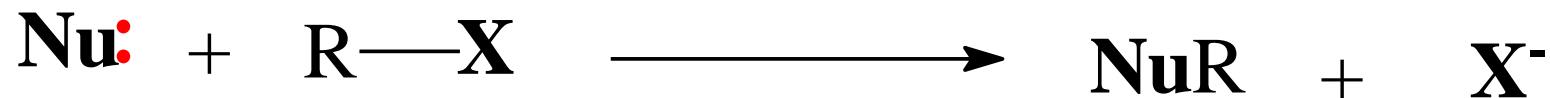
The reactions of organic halides are classified into three categories





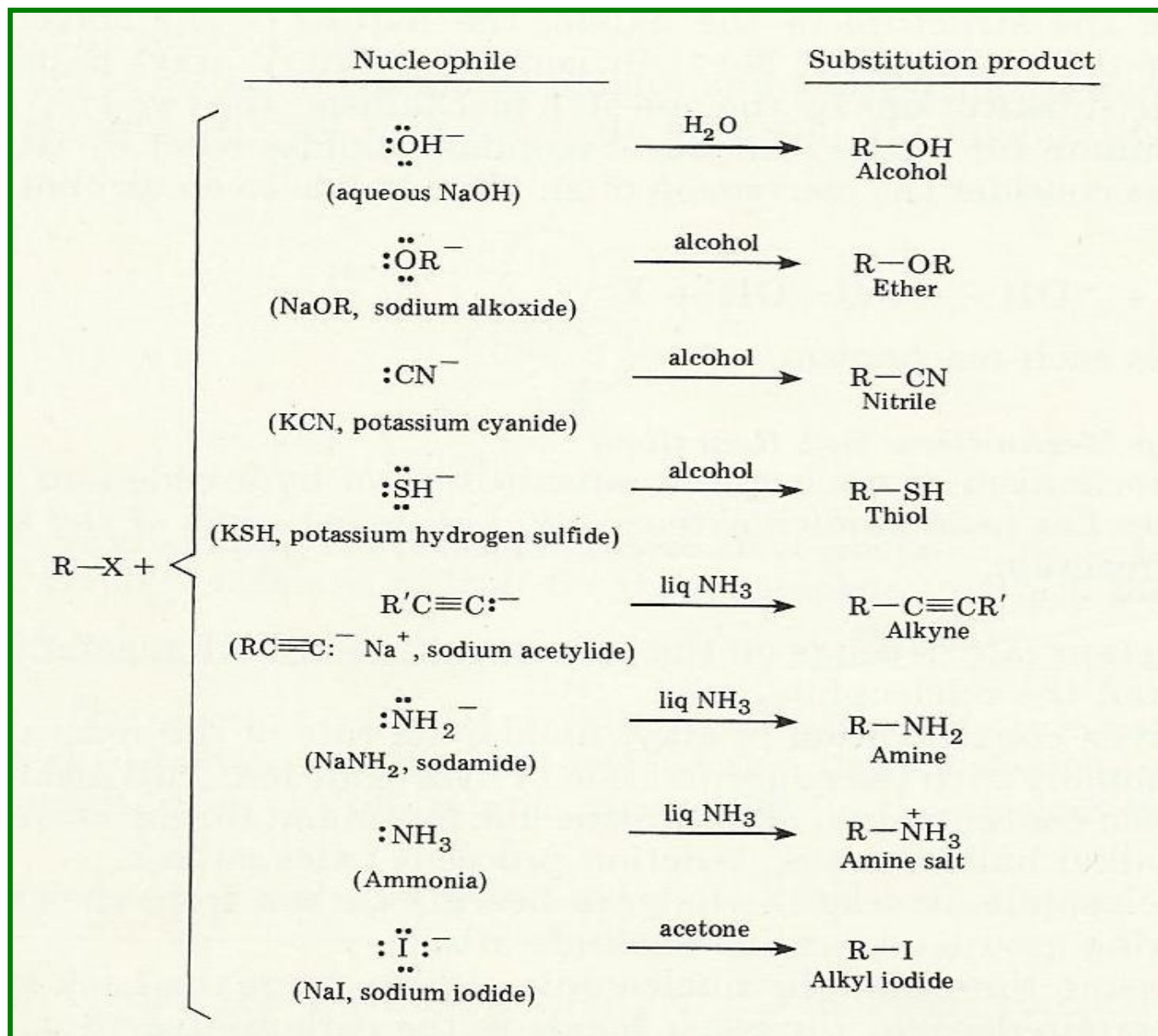
# 1- Nucleophilic Substitution Reactions:

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 nucleophilic reaction of alkyl halides  
*Elements of organic Chemistry; Zimmerman, page 223*



## Examples of common nucleophiles:

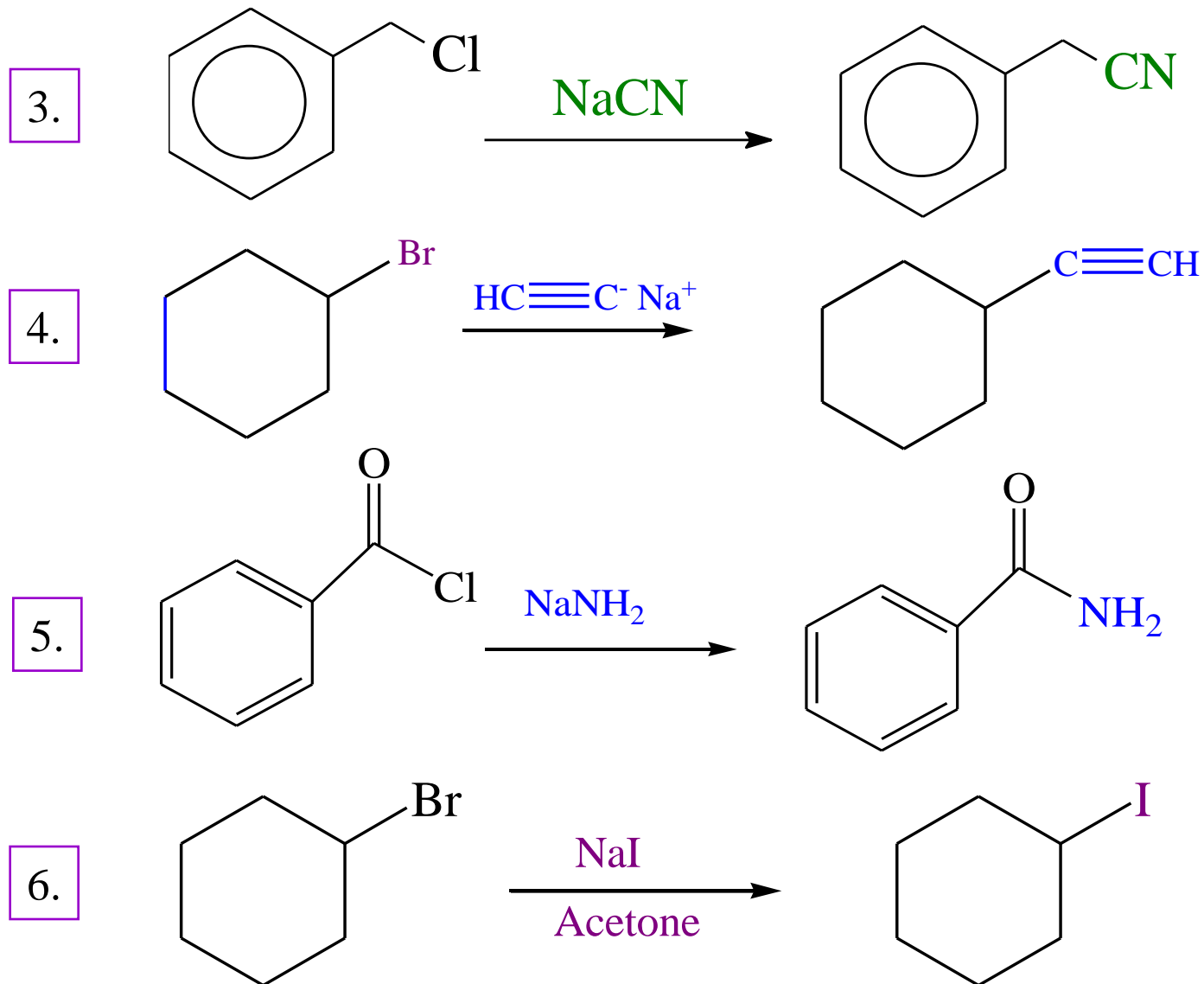
$\text{-}\ddot{\text{O}}\text{H}$	$\text{-}\overset{\ominus}{\text{X}}$	$\overset{\ominus}{\text{C}}\text{N}$
$\text{-}\ddot{\text{O}}\text{R}$	$\text{-}\ddot{\text{N}}\text{H}_2$	$\text{HC}\equiv\text{C}^\ominus$
$\text{-}\ddot{\text{S}}\text{H}$ Or $\text{-}\ddot{\text{S}}\text{R}$	$\text{-}\ddot{\text{N}}\text{HR}$	$\text{RC}\equiv\text{C}^\ominus$

### Reaction Examples



Note that;

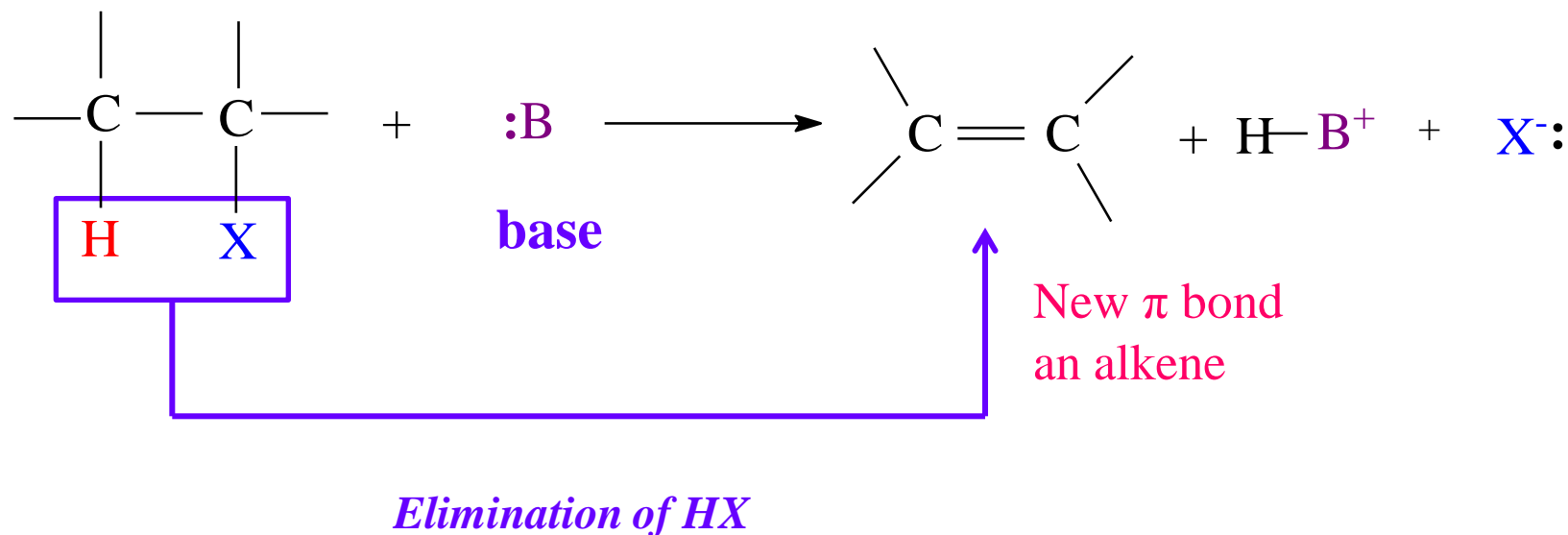
the reaction always involves *breakage* of **Carbon—Halogen** bond.



## 2- Elimination Reactions

Alkyl Halides can undergo **elimination reaction** *E* producing an **alkene**.

### General Elimination Reaction

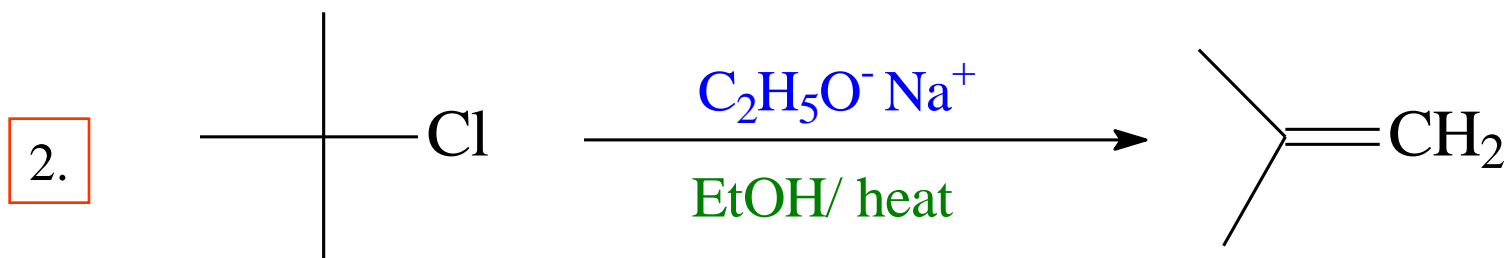
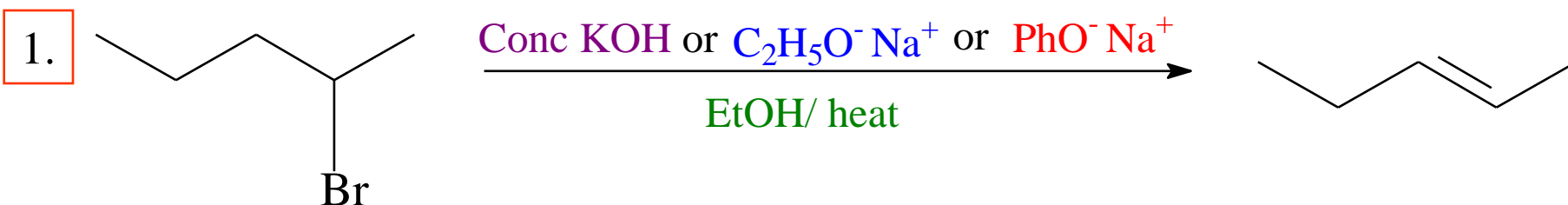


The most common bases used in **elimination reactions** are ***negatively charged oxygen*** compounds, such as  $\text{HO}^-$  and its alkyl derivatives,  $\text{RO}^-$ , called alkoxides.

**Common basis used in dehydrohalogenation**

$\text{Na}^+ \text{ } ^-\text{OH}$	sodium hydroxide
$\text{K}^+ \text{ } ^-\text{OH}$	potassium hydroxide
$\text{Na}^+ \text{ } ^-\text{OCH}_3$	sodium methoxide
$\text{Na}^+ \text{ } ^-\text{OCH}_2\text{CH}_3$	sodium ethoxide
$\text{K}^+ \text{ } ^-\text{OC}(\text{CH}_3)_3$	potassium <i>tert</i> -butoxide

***Examples***



### 3- Reactions of Organometallic Compounds (Reduction):

The **alkali metals** (Li, Na, K etc.) and the **alkaline earth metals** (Mg and Ca, together with Zn) are good reducing agents

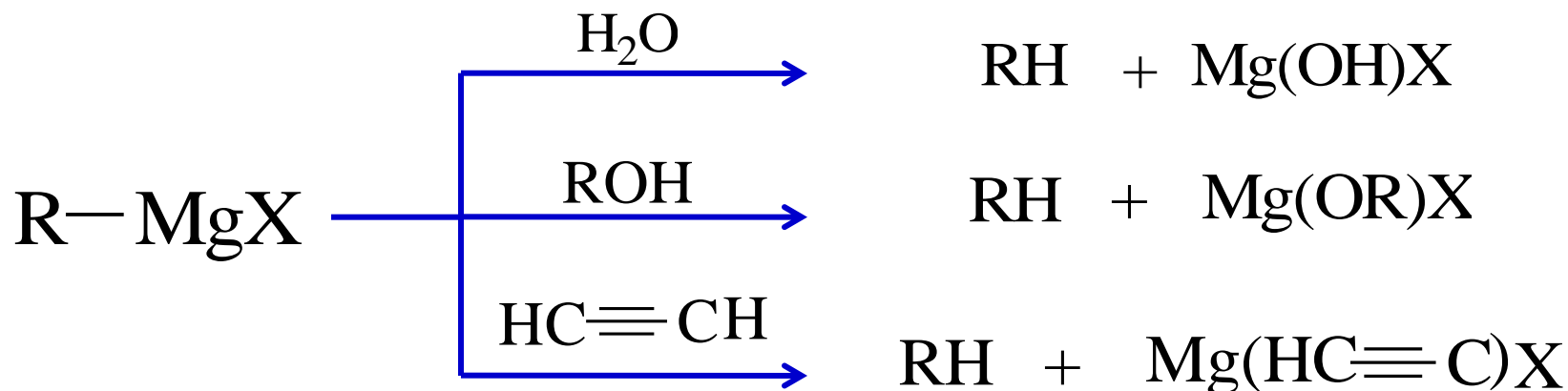
#### I- Reduction with alkaline earth metals

##### (a) Formation of Grignard reagent

(X = Cl, Br, I)

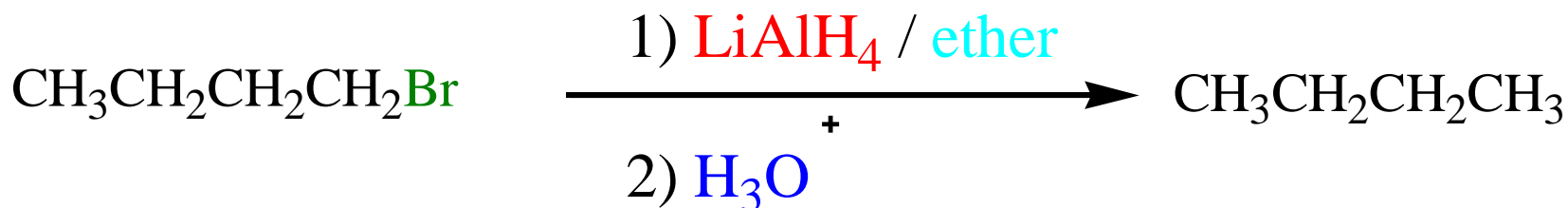
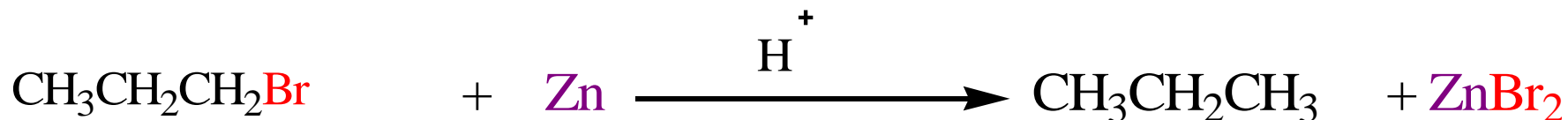


##### (b) Reaction of Grignard reagent

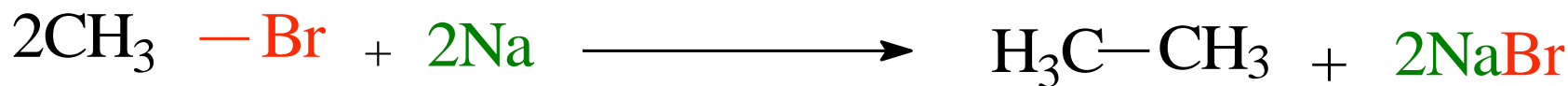


## II- Reduction with alkali metals

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



b) Reduction by sodium metal (coupling reaction)



c) Reduction using lithium dialkyl cuprate (Gilman reagent)





*Thank you  
For your attention*

