

241 Chem

CH-1

Organic Halides

# Learning objectives

By the end of this chapter the student will:

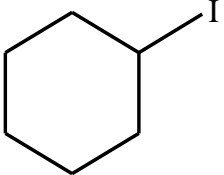
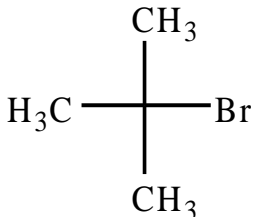
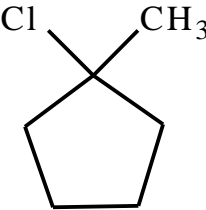
- Recognize the structure and classes of alkyl halides.
- Knowing the common names and understand the IUPAC rules for nomenclature of halo compounds.
- Understand the physical properties of halo compounds (solubility and boiling points).
- Knowing the different methods used in preparation of halo compounds.
- Knowing the reactions of halo compounds; nucleophilic substitution, elimination, reduction reactions of Grignard reagents and know the previously disused methods of reducing alkyl halides.
  - $S_N1$  and  $S_N2$  mechanisms
  - E1 and E2 mechanisms

# Organic Halides and their uses

- **Organic Halides** 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.
- Halogen compounds are very important for a number of reasons:
  - Simple alkyl and aryl halides (especially: Cl & Br) are versatile reagent in syntheses.
  - Halogen can be converted to unsaturated compounds through dehydrogenation (*Elimination reactions*).
  - Halogen can be replaced by many other functional groups (*substitution reactions*).
  - Some halogens have some uses for example: as solvent fire retardants, cleaning fluids, refrigerants, and in polymers such as Teflon

# Classification Alkyl Halides

1. **Alkyl Halides**, R- X: compounds which have a halogen atom bonded to one  $sp^3$  hybrid C atom. Alkyl halides are also called **haloalkanes**. (primary ( $1^\circ$ ), secondary ( $2^\circ$ ) or tertiary ( $3^\circ$ ))

Compound	$\text{CH}_3\text{-Cl}$	$\text{CH}_3\text{-CH}_2\text{-Br}$	$(\text{CH}_3)_2\text{-CHF}$
Common name	Methyl Chloride	Ethyl bromide	Isopropyl fluoride
IUPAC name	Chloromethane	Bromoethane	2-Fluoropropane
Class	$1^\circ$	$1^\circ$	$2^\circ$
Compound			
Common name	Cyclohexyl Iodide	t-Butyl bromide	Methylcyclopentyl chloride
IUPAC name	Iodocyclohexane	2-Bromo-2-methylpropane	1-Chloro-1-methylcyclopentane
Class	$2^\circ$	$3^\circ$	$3^\circ$

# Classification Alkyl Halides

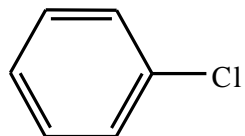
2. **Vinylic Halides**,  $C=C-X$  : has a halogen atom bonded to one  $sp^2$  hybrid C atom.



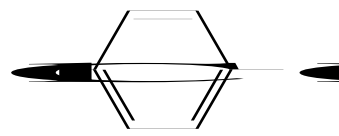
**Common name:** Vinyl bromide

**IUPAC name:** Bromoethene

3. **Aryl Halides**,  $Ar-X$  : has a halogen atom bonded directly to an aromatic ring.



Chlorobenzene



**Common name:** *p*-Bromo toluene

**IUPAC name:** 4-Bromo toluene

4. **Allylic Halides**,  $C=C-C-X$  : has a halogen atom bonded to one  $sp^3$  hybrid C atom.



**Common name:** Allyl chloride

**IUPAC name:** 3-Chloro-1-propene

5. **Benzylic halides**,  $Ar-C-X$  : has a halogen atom bonded to Carbon one away from aromatic ring.

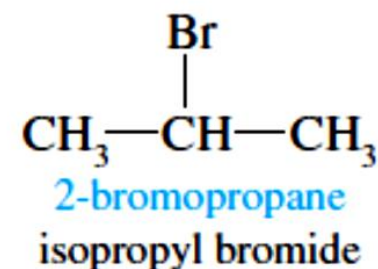
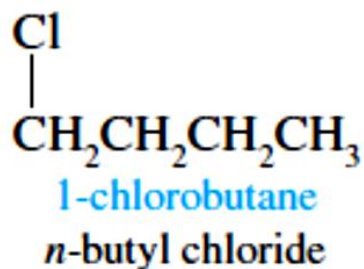
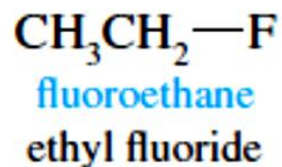
**Common name:** Benzyl Chloride

**IUPAC name:** Chloromethylbenzene

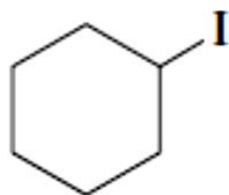
# Nomenclature OF Alkyl halides

- **IUPAC names** derived from the names of parent organic compound (alkane or alkene or alkyne or alcohol or aldehydes and so on) with a prefix indicating halogens and their positions.
- **Common names** derived from the corresponding alkyl group followed by the name of halogen atom.

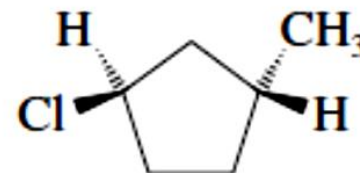
IUPAC name:  
common name:



IUPAC name:  
common name:

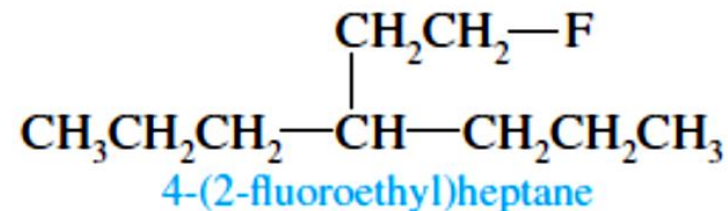
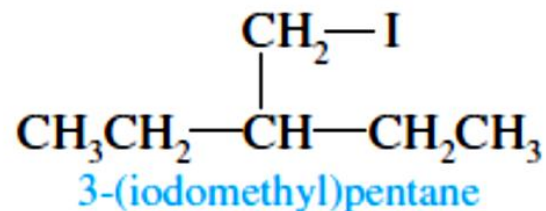


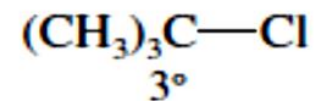
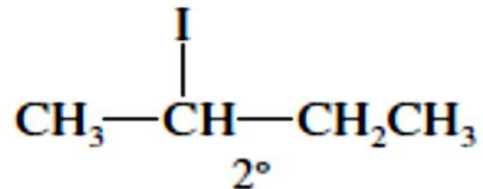
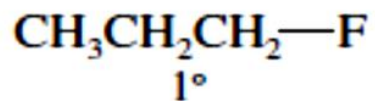
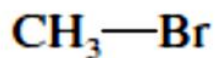
iodocyclohexane  
cyclohexyl iodide



*trans*-1-chloro-3-methylcyclopentane  
(none)

IUPAC name:



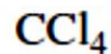
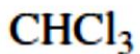
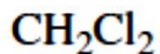


IUPAC name: bromomethane  
common name: methyl bromide

IUPAC name: 1-fluoropropane  
common name: *n*-propyl fluoride

IUPAC name: 2-iodobutane  
common name: *sec*-butyl iodide

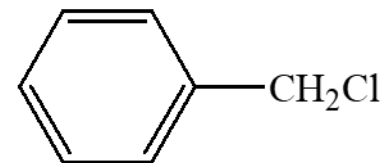
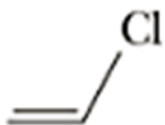
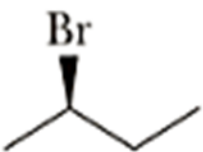
IUPAC name: 2-chloro-2-methylpropane  
common name: *tert*-butyl chloride



IUPAC name: dichloromethane  
common name: methylene chloride

IUPAC name: trichloromethane  
common name: chloroform

IUPAC name: tetrachloromethane  
common name: carbon tetrachloride

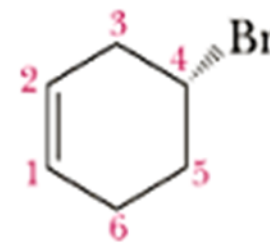
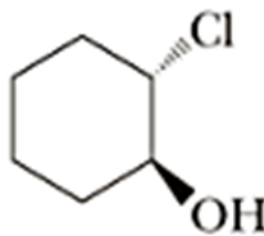
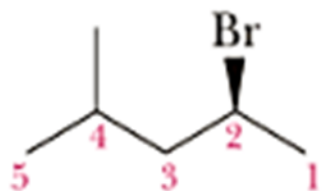


IUPAC name: (*R*)-2-Bromobutane  
common name: (*R*)-*sec*-Butyl bromide

IUPAC name: Chloroethene  
common name: Vinyl chloride

IUPAC name: 3-Chloropropene  
common name: Allyl chloride

IUPAC name: Chloromethylbenzene  
common name: Benzyl Chloride



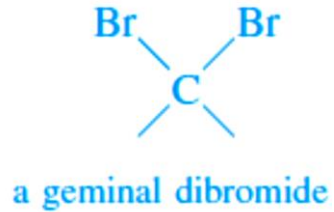
IUPAC name: (*S*)-2-Bromo-4-methylpentane

IUPAC name: (1*S*,2*S*)-2-Chlorocyclohexanol

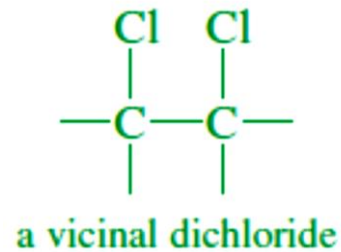
IUPAC name: (*R*)-4-Bromocyclohexene

# Types of Dihalides

- **Geminal dihalide** (Latin, *geminus*, “twin”) has the two halogen atoms bonded to the same carbon atom.



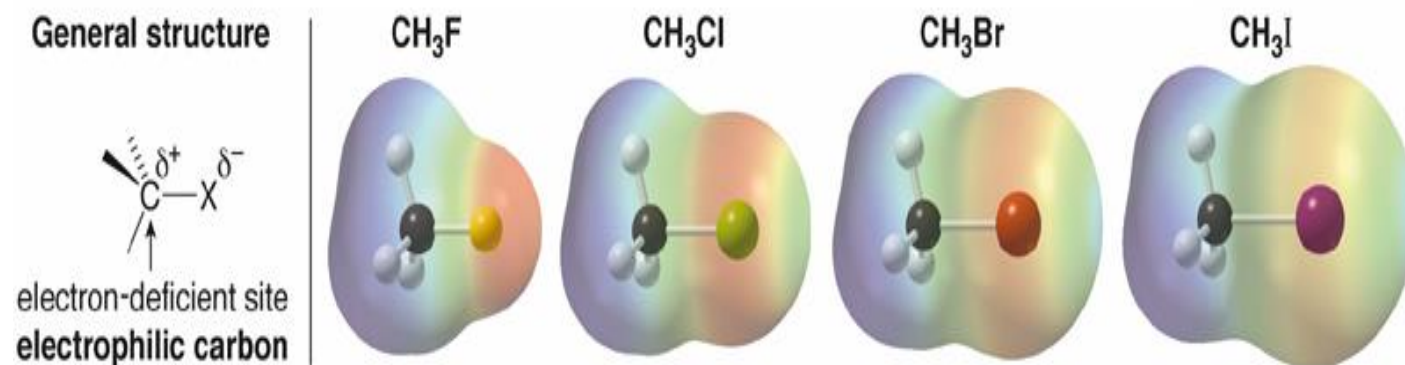
- **Vicinal dihalide** (Latin, *vicinus*, “neighboring”) has the two halogens bonded to adjacent carbon atoms.



# Physical Properties

## Polarity

- Fluorine, chlorine, and bromine are all more electronegative than carbon ; as a result, C-X bonds with these atoms are polarized with a partial negative charge on halogen and a partial positive charge on carbon.



- The polar C-X bond makes the carbon atom *electron deficient* in each CH<sub>3</sub>X molecule.

# Physical Properties

## Solubility

- Alkyl halides have some polar character, but only alkyl fluorides have an atom that can form a hydrogen bond with water. The other alkyl halides are less soluble in water
- In General, all organic halides **are insoluble in water** and soluble in common organic solvents.

## The boiling point

- The boiling points of alkyl halides increase with increasing molecular weight because of the increase in van der Waals forces.

$\text{CH}_3\text{CH}_2\text{CH}_2\text{F}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$
bp = 47°C	bp = 71°C	bp = 102°C
- Alkyl halides have higher boiling point than the corresponding alkanes, alkenes, and alkynes because:
  1. Polarity
  2. Molecular weight

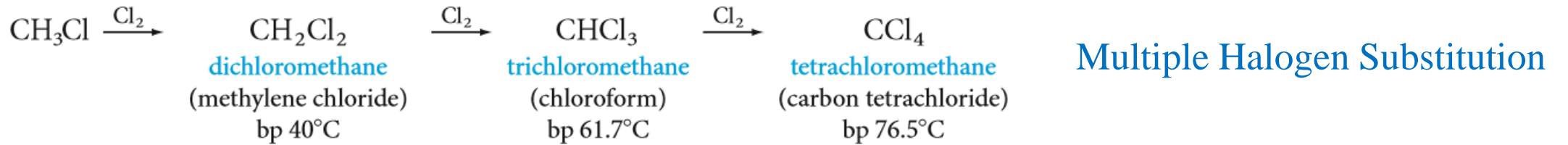
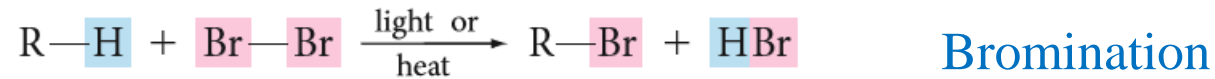
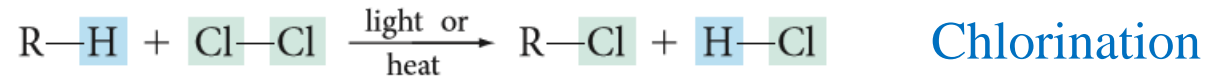
Ethane (bp = -89°C) & Bromoethane (bp = 38°C)

Butyl bromide (bp = 100°C) & *tert*-Butyl bromide (bp = 72°C)

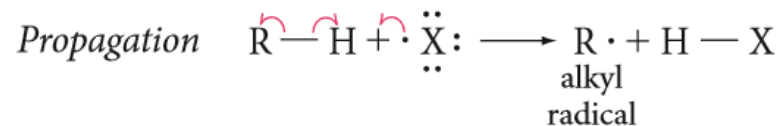
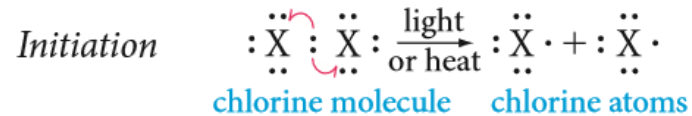
# Preparation Of Organic Halides

## 1- Direct halogenation of hydrocarbons

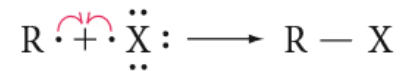
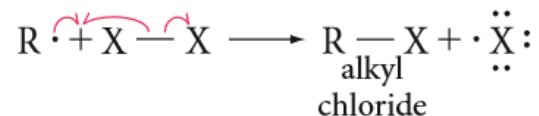
A. Halogenation of alkanes: Substitution reaction called Radical halogenation



### Mechanism:

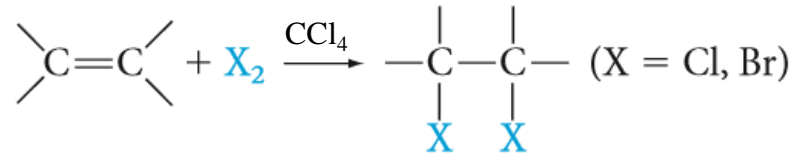


(X = Cl, Br)

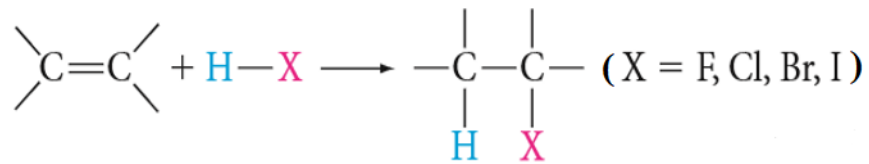


# Preparation Of Organic Halides

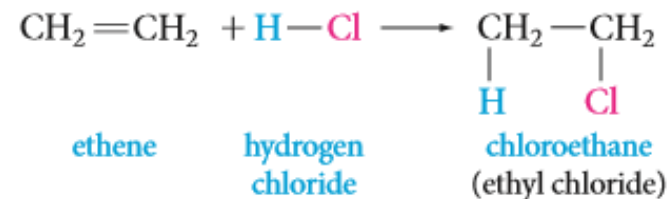
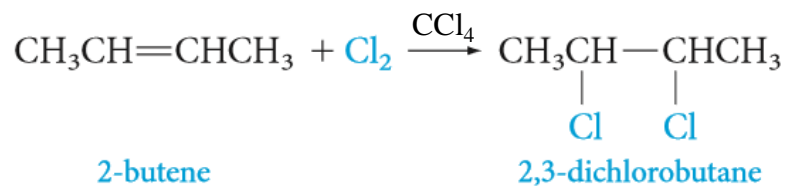
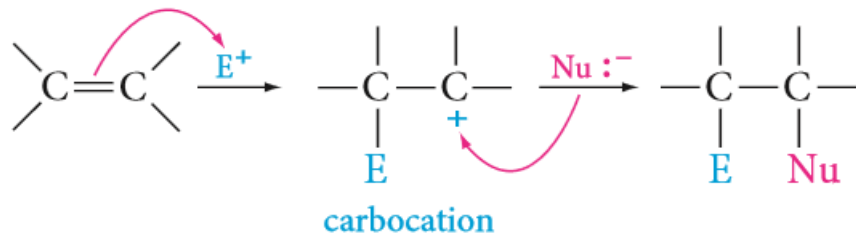
## B. Halogenation of alkenes: Electrophilic Addition



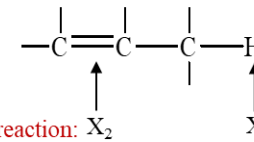
Markovnikov's Rule



Mechanism:



Hint:



Addition reaction:  
low temperature  
Absence of light

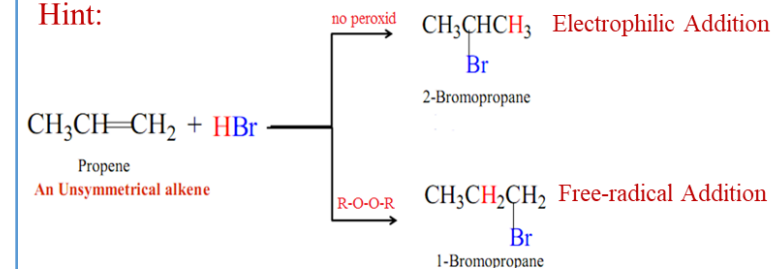
Substitution reaction:  
High temperature  
or Ultraviolet light  
Allylic Halogenation



cyclobutene

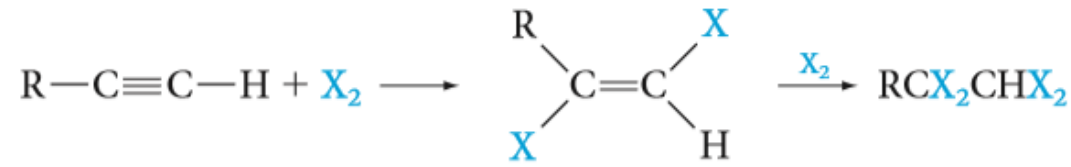
Trans-1,2-dibromocyclobutane

Hint:

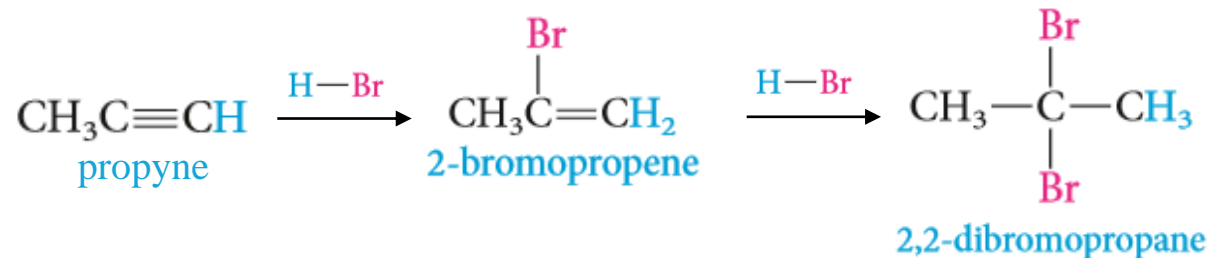
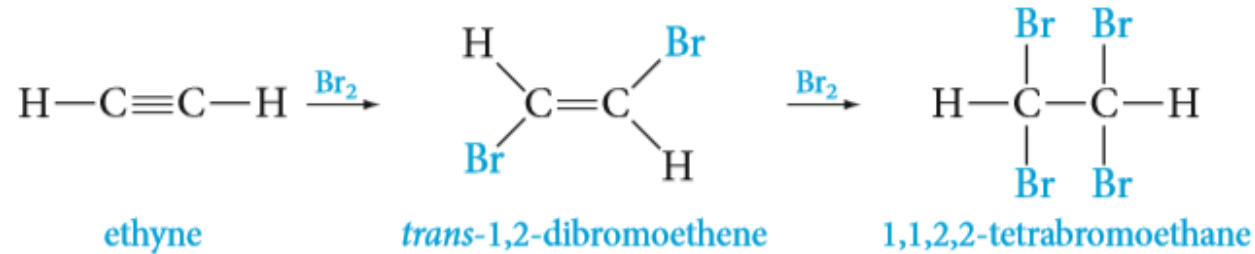


# Preparation Of Organic Halides

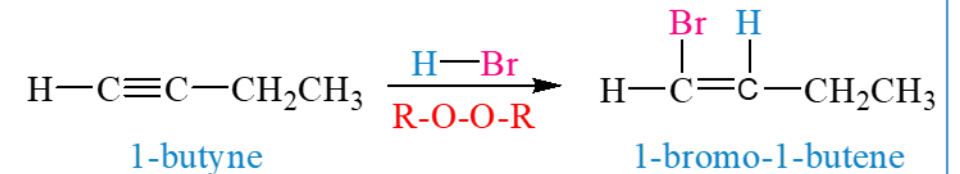
## C. Halogenation of alkynes : Electrophilic Addition



Markovnikov's Rule



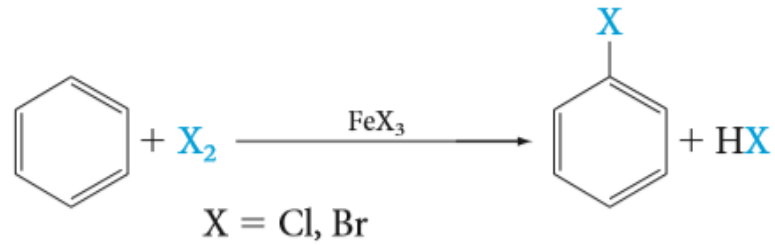
Hint:



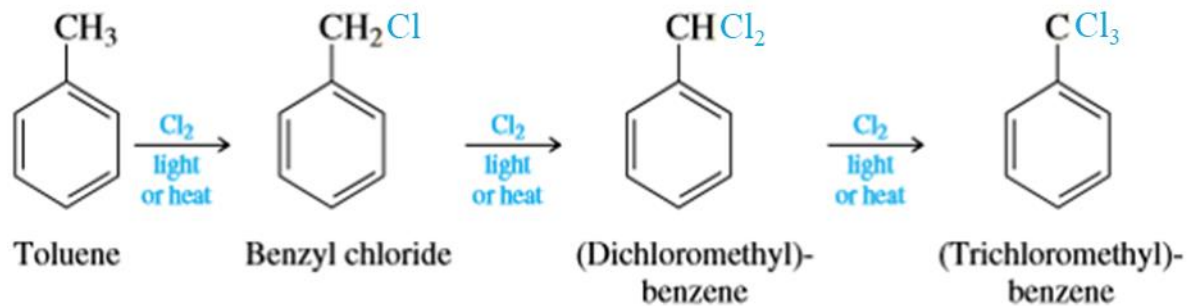
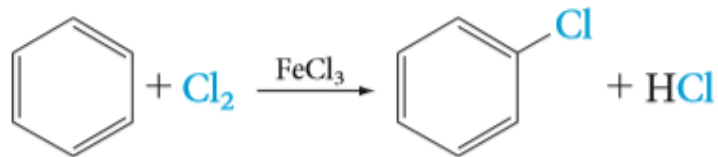
Free-radical Addition  
Anti Markovnikov addition

# Preparation Of Organic Halides

## D. Halogenation of aromatic ring and alkyl benzene:



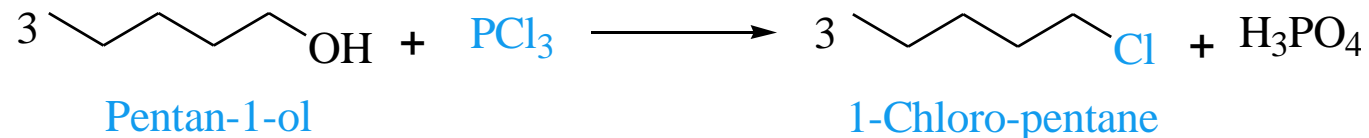
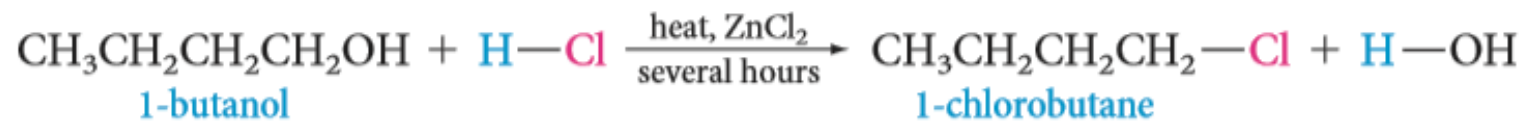
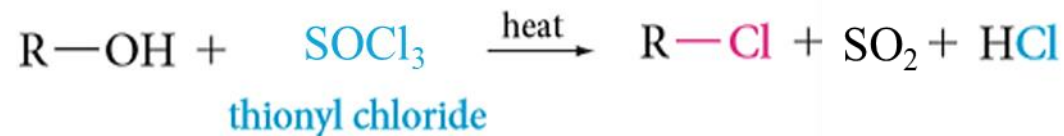
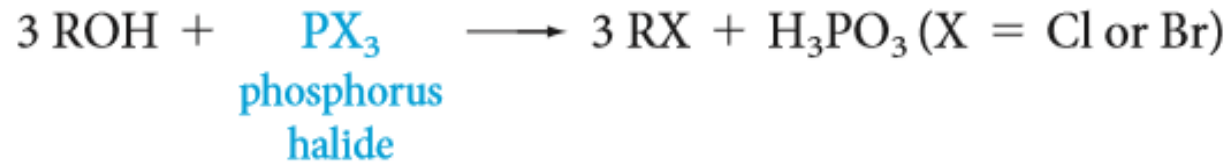
Electrophilic Aromatic Substitution: Halogenation



Radical halogenation

# Preparation Of Organic Halides

## 2-Conversion of alcohols into alkyl halides: Nucleophilic Substitution



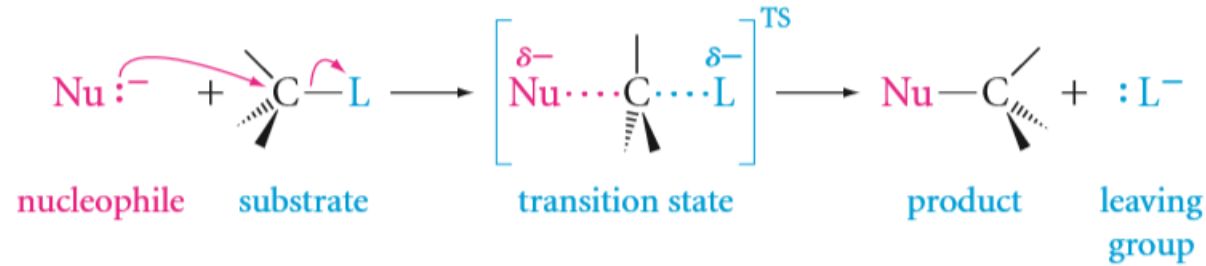
# Reactions Of Halocompounds

1. Nucleophilic Substitution Reactions
2. Elimination Reactions
3. Formation of Grignard reagent and its reactions
4. Reduction of alkyl halides:
  - Reduction by Zinc metal and acids or by metal hydrides
  - Reduction by sodium metal (coupling reaction)
  - Reduction using lithium dialkyl cuprate

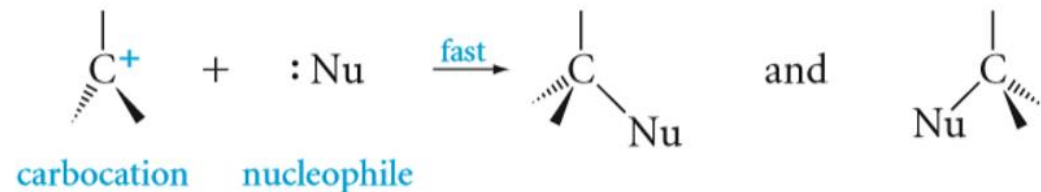
# Reactions Of Organic Halides

## 1- Nucleophilic Substitution Reactions ( $S_N1$ and $S_N2$ )

### $S_N2$ : Bimolecular Nucleophilic Substitution



### $S_N1$ : Unimolecular Nucleophilic Substitution



Hint: Rearrangement

## Factors Favoring S<sub>N</sub>1 versus S<sub>N</sub>2 Reaction:

Factor	S <sub>N</sub> 1	S <sub>N</sub> 2
Substrate	3° (requires formation of a relatively stable carbocation)	Methyl > 1° > 2° (requires unhindered substrate)
Nucleophile	Weak Lewis base, neutral molecule, nucleophile may be the solvent (solvolysis)	Strong Lewis base, rate increased by high concentration of nucleophile
Solvent	Polar protic (e.g., alcohols, water)	Polar aprotic (e.g., DMF, DMSO)
Leaving group	I > Br > Cl > F for both S <sub>N</sub> 1 and S <sub>N</sub> 2 (the weaker the base after the group departs, the better the leaving group)	

## Reactions of Common Nucleophiles with Alkyl Halides:

Nu		R—Nu		Comments
Formula	Name	Formula	Name	
<i>Oxygen nucleophiles</i>				
1. $\text{HO}^-$	hydroxide	$\text{R}-\ddot{\text{O}}\text{H}$	alcohol	These ions lose a proton and the products are alcohols and ethers. $\xrightarrow{-\text{H}^+} \text{R}\ddot{\text{O}}\text{H}$ (alcohol) $\xrightarrow{-\text{H}^+} \text{R}\ddot{\text{O}}\text{R}$ (ether)
2. $\text{RO}^-$	alkoxide	$\text{R}-\ddot{\text{O}}\text{R}$	ether	
3. $\text{HOH}$	water	$\text{R}-\overset{+}{\text{O}}\begin{matrix} \text{H} \\ \text{H} \end{matrix}$	alkyloxonium ion	
4. $\text{ROH}$	alcohol	$\text{R}-\overset{+}{\text{O}}\begin{matrix} \text{R} \\ \text{H} \end{matrix}$	dialkyloxonium ion	
5. $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\ominus}{\text{O}}$	carboxylate	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\ominus}{\text{O}}-\text{R}$	ester	

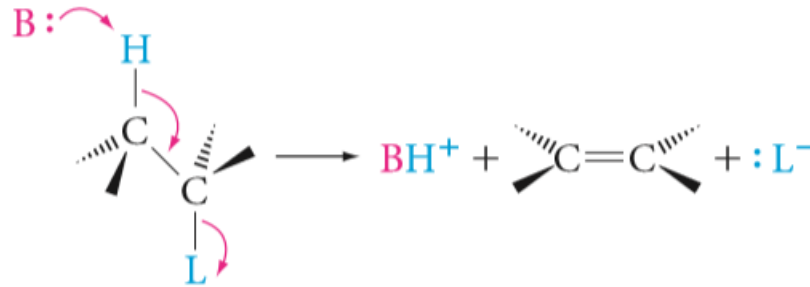
## Reactions of Common Nucleophiles with Alkyl Halides:

<b>Nitrogen nucleophiles</b>				
6.	$\ddot{\text{N}}\text{H}_3$	ammonia	$\text{R}-\overset{+}{\text{N}}\text{H}_3$	alkylammonium ion
7.	$\text{R}\ddot{\text{N}}\text{H}_2$	primary amine	$\text{R}-\overset{+}{\text{N}}\text{H}_2\text{R}$	dialkylammonium ion
8.	$\text{R}_2\ddot{\text{N}}\text{H}$	secondary amine	$\text{R}-\overset{+}{\text{N}}\text{HR}_2$	trialkylammonium ion
9.	$\text{R}_3\ddot{\text{N}}$	tertiary amine	$\text{R}-\overset{+}{\text{N}}\text{R}_3$	tetraalkylammonium ion
				} With a base, these ions readily lose a proton to give amines. $\begin{aligned} &\xrightarrow{-\text{H}^+} \ddot{\text{R}}\text{NH}_2 \\ &\xrightarrow{-\text{H}^+} \text{R}_2\ddot{\text{N}}\text{H} \\ &\xrightarrow{-\text{H}^+} \text{R}_3\ddot{\text{N}}: \end{aligned}$
<b>Sulfur nucleophiles</b>				
10.	$\text{H}\ddot{\text{S}}:^-$	hydrosulfide	$\text{R}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{S}}}\text{H}$	thiol
11.	$\text{R}\ddot{\text{S}}:^-$	mercaptide	$\text{R}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{S}}}\text{R}$	thioether (sulfide)
12.	$\text{R}_2\ddot{\text{S}}:$	thioether	$\text{R}-\overset{+}{\underset{\cdot\cdot}{\text{S}}}\text{R}_2$	trialkylsulfonium ion
<b>Halogen nucleophiles</b>				
13.	$:\ddot{\text{I}}:^-$	iodide	$\text{R}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{I}}}$	alkyl iodide
<b>Carbon nucleophiles</b>				
14.	$^-:\text{C}\equiv\text{N}:$	cyanide	$\text{R}-\text{C}\equiv\text{N}:$	alkyl cyanide (nitrile)
15.	$^-:\text{C}\equiv\text{CR}$	acetylide	$\text{R}-\text{C}\equiv\text{CR}$	alkyne

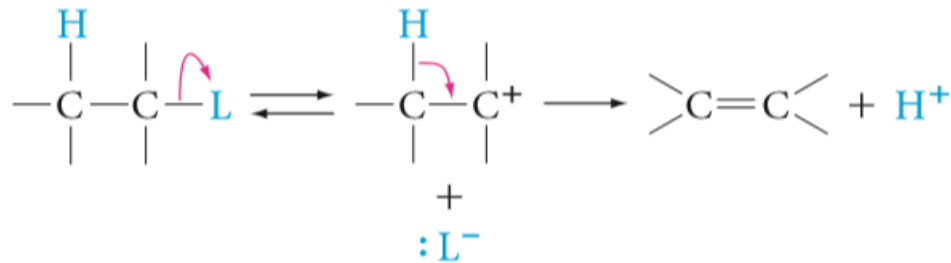
# Reactions Of Organic Halides

## 2- Elimination Reactions (E1 and E2 )

E2 : Bimolecular Elimination

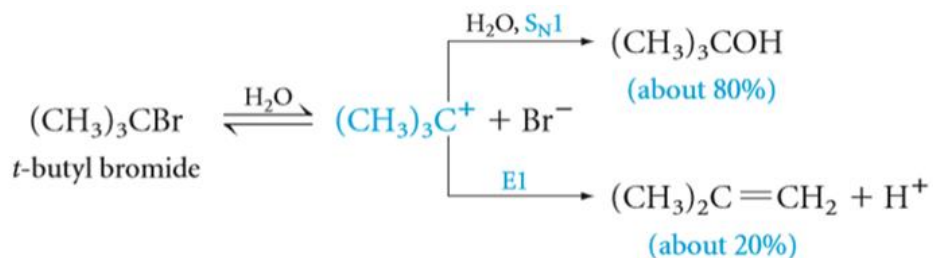
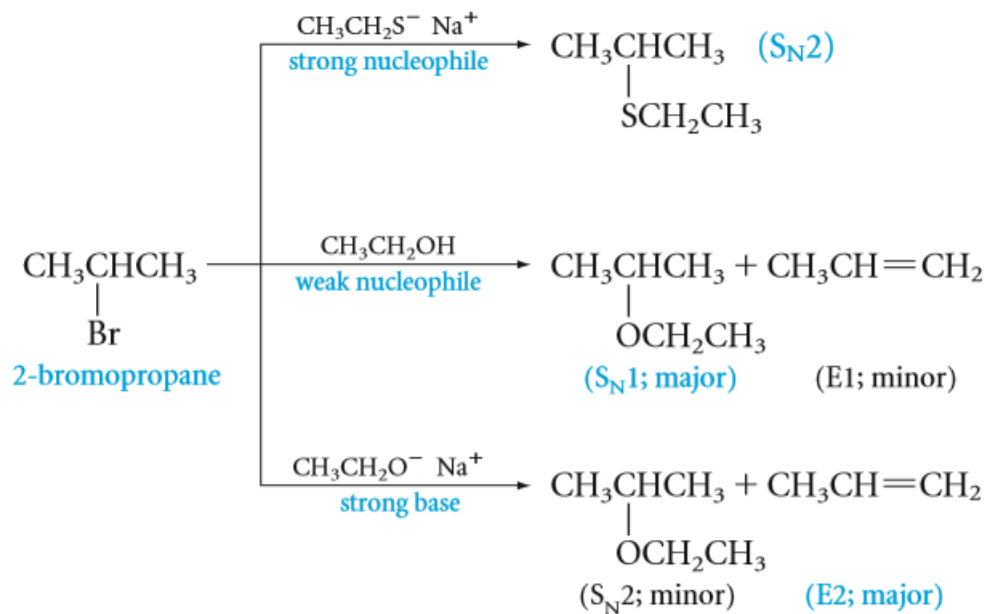
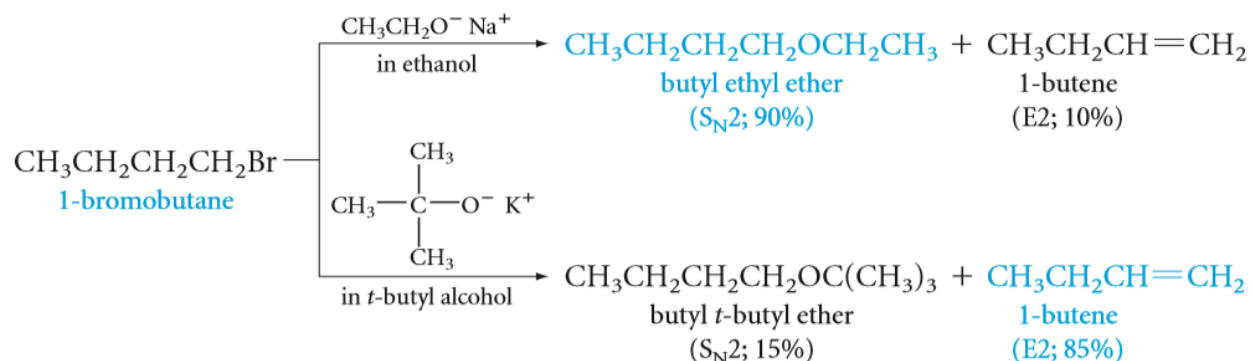


E1 : Unimolecular Elimination



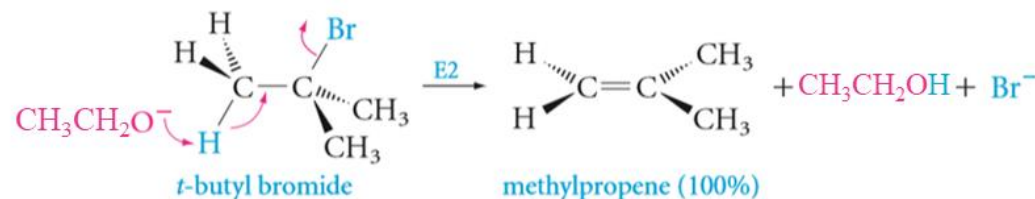
Hint: Rearrangement

# Substitution and Elimination in Competition:



## Zaitsev's Rule

Hint: Overall Summary of $\text{S}_{\text{N}}1$ , $\text{S}_{\text{N}}2$ , E1, and E2 Reactions			
$\text{CH}_3\text{X}$	$\begin{array}{c} \text{H} \\   \\ \text{R}-\text{C}-\text{X} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{R} \\   \\ \text{R}-\text{C}-\text{X} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{R} \\   \\ \text{R}-\text{C}-\text{X} \\   \\ \text{R} \end{array}$
<b>Methyl</b>	1°	2°	3°
<b>Bimolecular (<math>\text{S}_{\text{N}}2/\text{E2}</math>) Reactions Only</b>			<b><math>\text{S}_{\text{N}}1/\text{E1}</math> or E2</b>
Gives $\text{S}_{\text{N}}2$ reactions	Gives mainly $\text{S}_{\text{N}}2$ except with a hindered strong base [e.g., $(\text{CH}_3)_3\text{CO}^-$ ] and then gives mainly E2.	Gives mainly $\text{S}_{\text{N}}2$ with weak bases (e.g., $\text{I}^-$ , $\text{CN}^-$ , $\text{RCO}_2^-$ ) and mainly E2 with strong bases (e.g., $\text{RO}^-$ ).	No $\text{S}_{\text{N}}2$ reaction. In solvolysis gives $\text{S}_{\text{N}}1/\text{E1}$ , and at lower temperatures $\text{S}_{\text{N}}1$ is favored. When a strong base (e.g., $\text{RO}^-$ ) is used, E2 predominates.

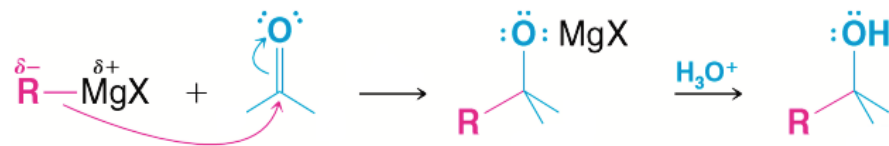
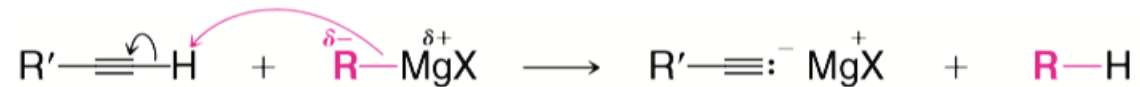
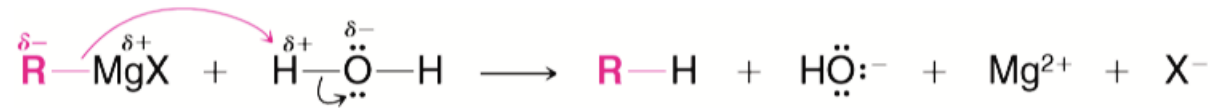


# Reactions Of Organic Halides

## 3- Formation of Grignard reagent and its reactions:



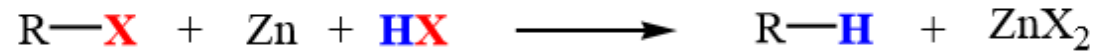
## Reactions of Grignard reagent



# Reactions Of Organic Halides

## 4- Reduction of alkyl halides:

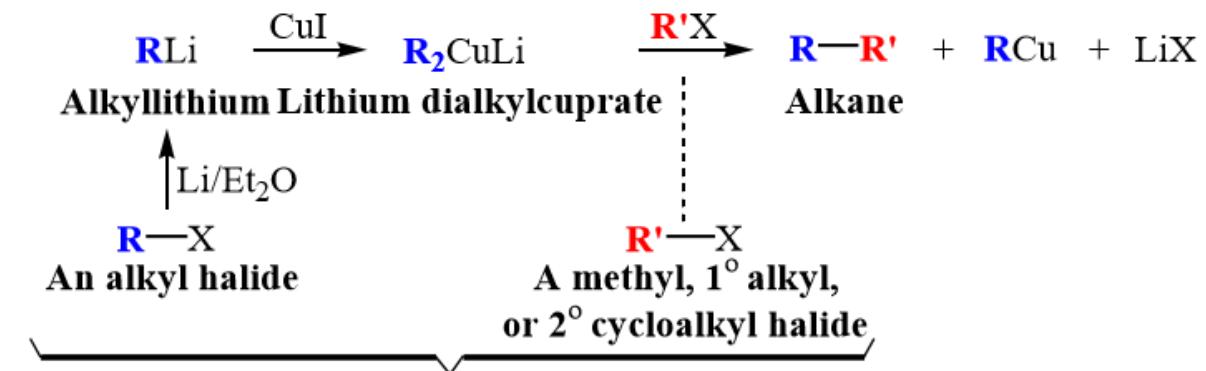
- Reduction by Zinc metal and acids or by metal hydrides



- Reduction by sodium metal (coupling reaction)



- Reduction using lithium dialkylcuprate



There are organic starting materials. The R- and R'- groups need not be different.