Organic halides

Learning objectives

In this chapter will discusses the following topics and by the end of this chapter the students will:

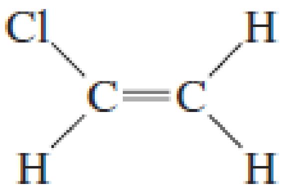
- Recognize the structure and classes of alkyl halides.
- Know the common names and understand the IUPAC rules for nomenclature of halo compounds.
- Understand the physical properties of halo compounds (solubility and boiling points).
- Know the different methods used in preparation of halo compounds.
- Know the reactions of halo compounds; nucleophilic substitution, elimination, reduction reactions of Grignard reagents and know the previously disused methods of reducing alkyl halides.
    - SN1 and SN2 mechanisms
    - E1 and E2 mechanisms

Organic halogen compounds and their uses

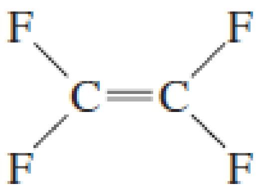
- **Organic halogen compounds** are a large class of natural and synthetic chemicals that contain one or more halogens (fluorine, chlorine, bromine, or iodine) combined with carbon and other elements.
- Halogen compounds are very important for a number of reasons:
  - Simple alkyl and aryl halides (especially: 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

Examples of some General Uses of Organic halogen compounds:

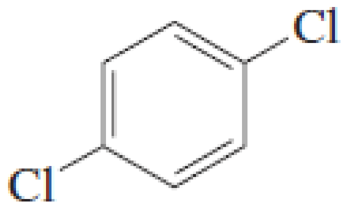
$CHCl_3$	$CHClF_2$	$CCl_3—CH_3$	$CF_3—CHClBr$
chloroform	Freon-22®	1,1,1-trichloroethane	Halothane
solvent	refrigerant	cleaning fluid	nonflammable anesthetic



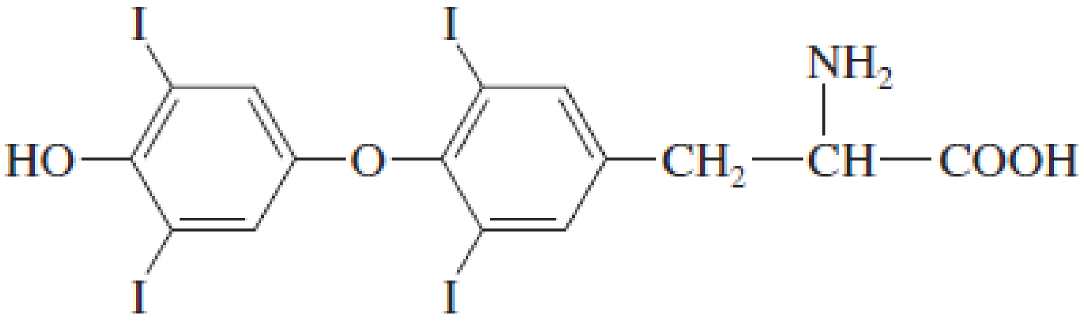
vinyl chloride
monomer for poly(vinyl chloride)



tetrafluoroethylene (TFE)
monomer for Teflon®



para-dichlorobenzene
mothballs



thyroxine
thyroid hormone

Classification Alkyl Halides

According to type of hydrocarbon attached to halide:

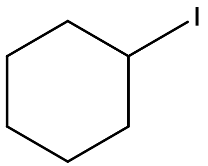
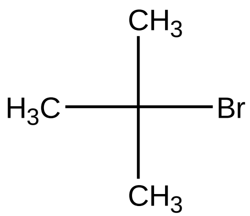
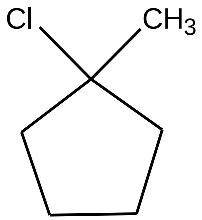
- **1.Alkyl Halides**, **R- X:**compounds which have a halogen atom bonded to one sp3 hybrid C atom. Alkyl halides are also called **haloalkanes.**

  primary (1°), secondary (2°) or tertiary (3°)….

(depending on the type of carbon to which halogen attached)

- **2. Vinylic Halides**: has a halogen atom bonded to one sp^2 hybrid C atom
- **3. Aryl Halides:** has a halogen atom bonded directly to an aromatic ring
- **4. Allylic Halides**: has a halogen atom bonded to one sp^3 hybrid C atom
- **5. Benzylic halides:** has a halogen atom bonded to Carbone one away from aromatic ring

Classification Alkyl Halides

1-Alkyl halides (R-X):	CH_3-Cl	CH_3-CH_2-Br	$(CH_3)_2$-CH-F
Common	Methyl Chloride	Ethyl bromide	Isopropyl fluoride
IUPAC	Chloromethane	Bromoethane	2-Fluoropropane
Class	1°	1°	2°
			
Common	Cyclohexyl Iodide	t.Butyl bromide	Methylcyclopentyl chloride
IUPAC	Iodocyclohexane	2-Bromo-2-methylpropane	1-Chloro-1-methylcyclopentane
Class	2°	3°	3°

Classification Alkyl Halides

2-Vinylic halides

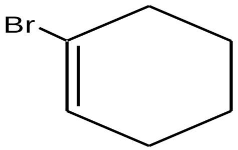
C=C-X

CH_2=CHBr
Vinyl bromide
Bromoethene

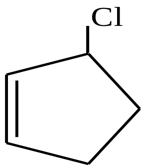
3-Allyl halides

C=C-C- X

CH_2=CHCH_2Cl
Allyl chloride
3-Chloro-1-propene

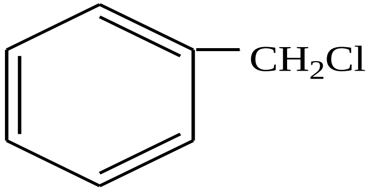


Bromocyclohexene



3-Chlorocyclopentene

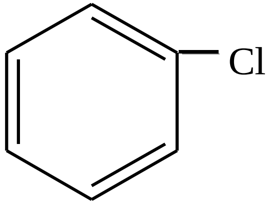
4-Benzylic halides: Ar-C-X



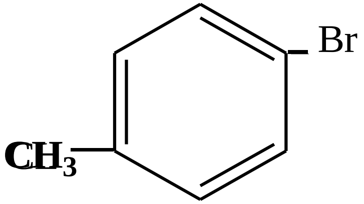
Benzyl Chloride

5-Aryl halides:

Ar-X (X directly attached to benzene ring)



Chlorobenzene



***p*-Bromo toluene**

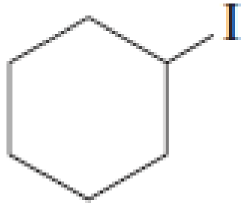
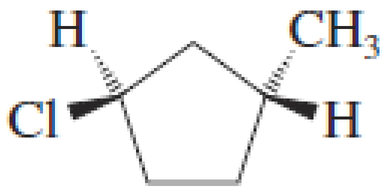
Nomenclature OF Alkyl halides

- **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.
- **Examples:**

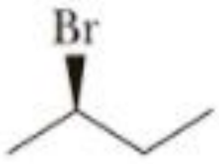
	CH_2X_2	CHX_3	CX_4
Common name	Methylene halides	Haloforms	Carbon tetrahalide
	CH_2Cl_2	$CHCl_3$	CCl_4
IUPAC name:	dichloromethane	trichloromethane	tetrachloromethane
common name:	methylene chloride	chloroform	carbon tetrachloride

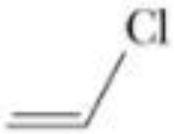
$CH_3{-}Br$	$CH_3CH_2CH_2{-}F$	$\overset{\displaystyle I}{\overset{\vert}{CH_3{-}CH{-}CH_2CH_3}}$	$(CH_3)_3C{-}Cl$
	1°	2°	3°
bromomethane	1-fluoropropane	2-iodobutane	2-chloro-2-methylpropane
methyl bromide	*n*-propyl fluoride	*sec*-butyl iodide	*tert*-butyl chloride

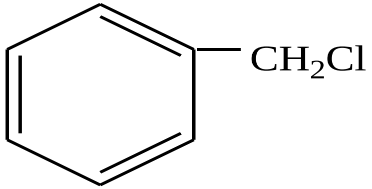
	$CH_3CH_2{-}F$	$\overset{\displaystyle Cl}{\overset{\vert}{CH_2}}CH_2CH_2CH_3$	$\overset{\displaystyle Br}{\overset{\vert}{CH_3{-}CH{-}CH_3}}$
IUPAC name:	fluoroethane	1-chlorobutane	2-bromopropane
common name:	ethyl fluoride	*n*-butyl chloride	isopropyl bromide

		
IUPAC name:	iodocyclohexane	*trans*-1-chloro-3-methylcyclopentane
common name:	cyclohexyl iodide	(none)

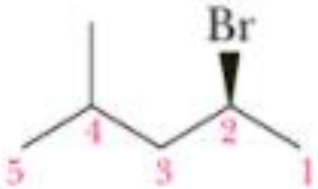
	$\overset{\displaystyle CH_2{-}I}{\overset{\vert}{CH_3CH_2{-}CH{-}CH_2CH_3}}$	$\overset{\displaystyle CH_2CH_2{-}F}{\overset{\vert}{CH_3CH_2CH_2{-}CH{-}CH_2CH_2CH_3}}$
IUPAC name:	3-(iodomethyl)pentane	4-(2-fluoroethyl)heptane



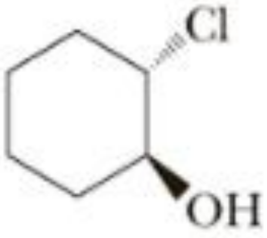




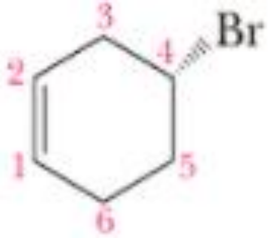
IUPAC:	**(*R*)-2-Bromobutane**	**Chloroethene**	**3-Chloropropene**	**Chloromethyl benzene**
Common:	**((*R*)-*sec*-Butyl bromide)**	**(Vinyl chloride)**	**(Allyl chloride)**	**(Benzyl Chloride)**



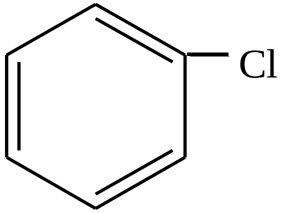
(*S*)-2-Bromo-4-methylpentane



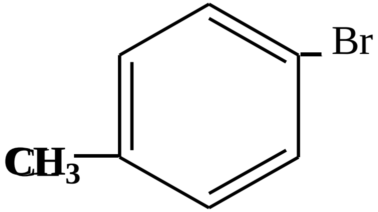
(1*S*,2*S*)-2-Chlorocyclohexanol



(*R*)-4-Bromocyclohexene



Chlorobenzene



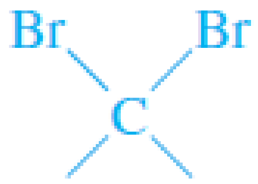
***p*-Bromo toluene**

Note:

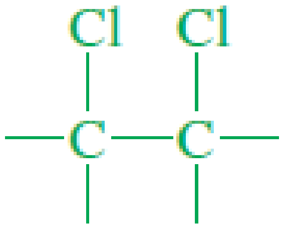
Systematic name	**Common name**
substituted alkane	alkyl group attached to halogen plus *halide*
CH_3Br bromomethane	CH_3Br methyl bromide
CH_3CH_2Cl chloroethane	CH_3CH_2Cl ethyl chloride

Types of Dihalides

- A **geminal dihalide** (Latin, *geminus*, "twin") has the two halogen atoms bonded to the same carbon atom.
- A **vicinal dihalide** (Latin, *vicinus*, "neighboring") has the two halogens bonded to adjacent carbon atoms.



a geminal dibromide

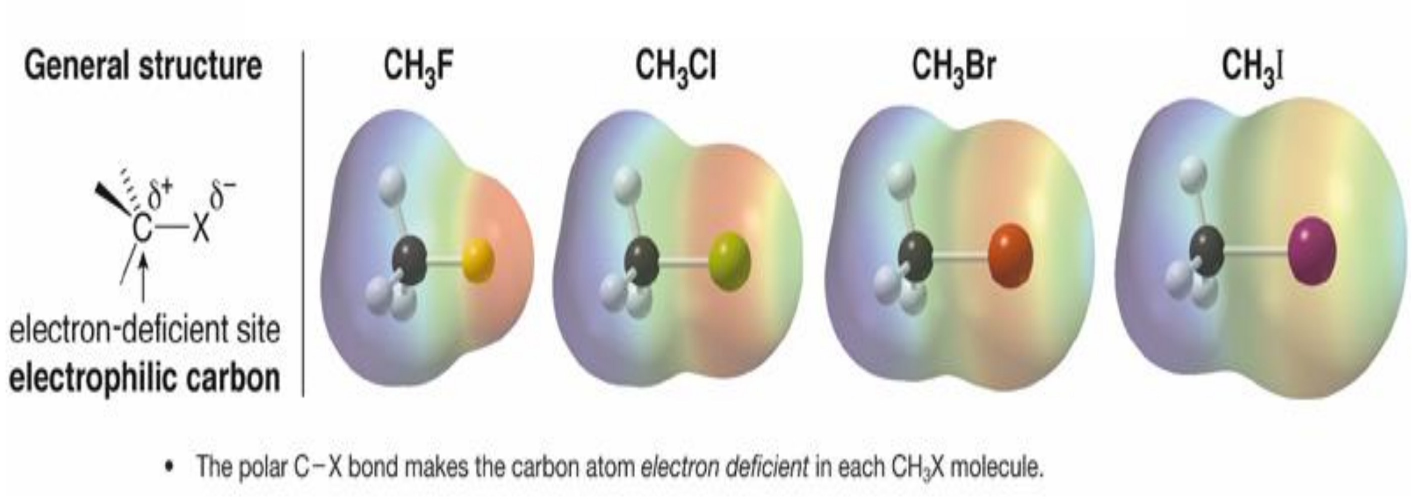


a vicinal dichloride

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.



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.

Table 3.7 Solubilities of Alkyl Halides in Water

CH_3F very soluble	CH_3Cl soluble	CH_3Br slightly soluble	CH_3I slightly soluble
CH_3CH_2F soluble	CH_3CH_2Cl slightly soluble	CH_3CH_2Br slightly soluble	CH_3CH_2I slightly soluble
$CH_3CH_2CH_2F$ slightly soluble	$CH_3CH_2CH_2Cl$ slightly soluble	$CH_3CH_2CH_2Br$ slightly soluble	$CH_3CH_2CH_2I$ slightly soluble
$CH_3CH_2CH_2CH_2F$ insoluble	$CH_3CH_2CH_2CH_2Cl$ insoluble	$CH_3CH_2CH_2CH_2Br$ insoluble	$CH_3CH_2CH_2CH_2I$ insoluble

Physical Properties

The boiling point

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

- Alkyl halides have higher melting point than the corresponding alkanes, alkenes, and alkynes because:

    1. Polarity

    2. Molecular weight

        - **(In series of halides BP. F <Cl <Br <I)**

$CH_3CH_2CH_2F$	**$CH_3CH_2CH_2Br$**	**$CH_3CH_2CH_2I$**
bp= 47^0C	**bp= 71^0C**	**bp= 102^0C**

- Ethane (bp -89°C) & bromomethane (bp 4°C)
- butyl bromide, bp 100°C & *tert*-butyl bromide, bp 72°C.

Preparation Of Halocompounds

1- Direct halogenation of hydrocarbons

A. **Halogenation of alkanes**
B. **Halogenation of alkenes**
C. **Halogenation of alkynes**
D. **Halogenation of aromatic ring and alkyl benzenes**

2- Conversion of alcohols: alkyl halides

Preparation Of Halocompounds

1- Direct halogenation of hydrocarbons

A. Halogenation of alkanes:

$$R{-}H \;+\; X_2 \xrightarrow{\text{UV or heat}} R{-}X \;+\; HX \quad (X{=}Cl,\ Br)$$

$$CH_4 \;+\; Cl_2 \xrightarrow{\text{heat}} CH_3Cl \;+\; HCl$$

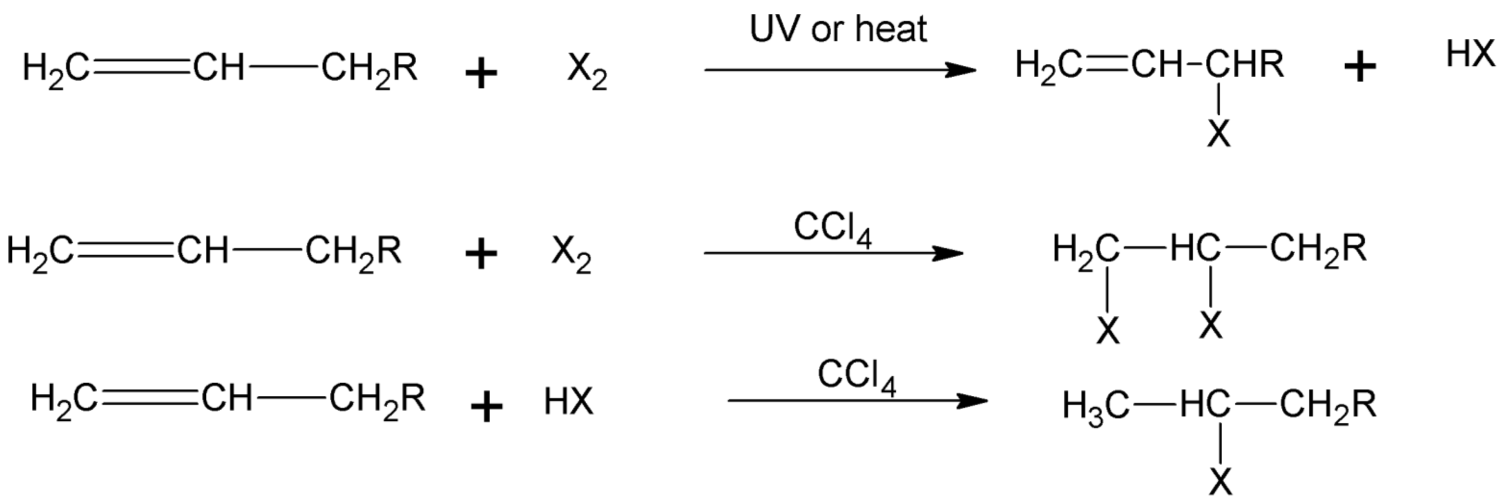
Methane → **Chloromethane (Methyl chloride)**

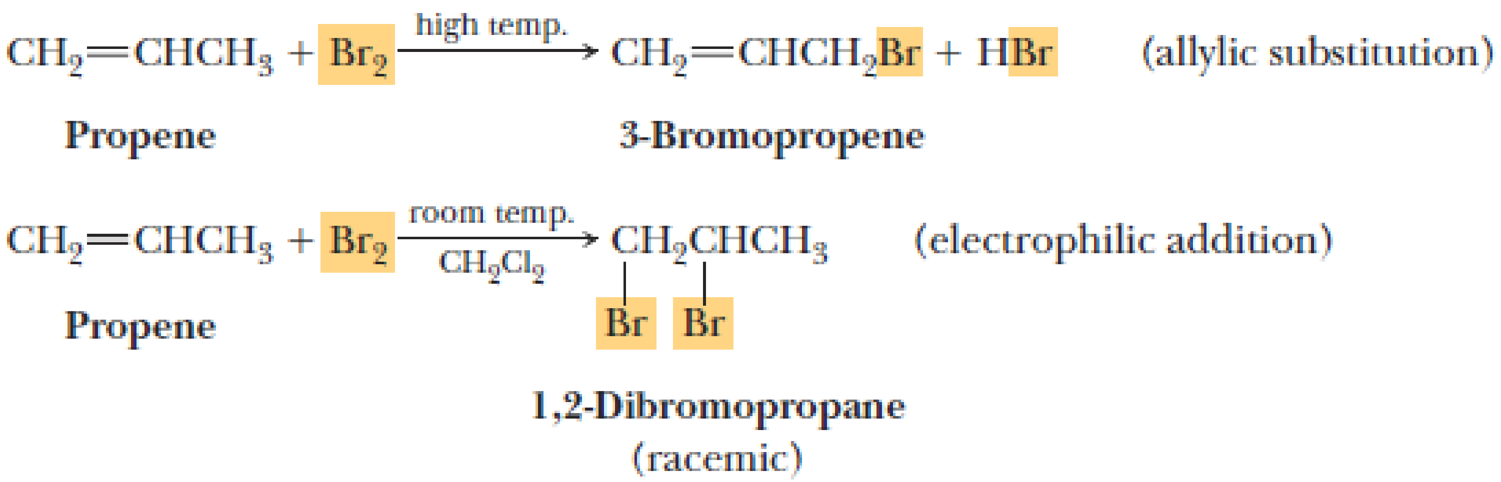
$$\begin{array}{c} CH_3 \\ | \\ CH_3CH \\ | \\ CH_3 \end{array} \;+\; Br_2 \xrightarrow{\text{heat}} \begin{array}{c} CH_3 \\ | \\ CH_3CBr \\ | \\ CH_3 \end{array} \;+\; HBr$$

2-Methylpropane (Isobutane) → **2-Bromo-2-methylpropane (*tert*-Butyl bromide)**

Preparation Of Halocompounds

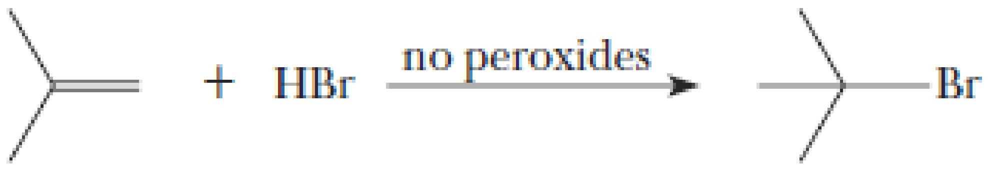
B. Halogenation of alkenes:





Note:

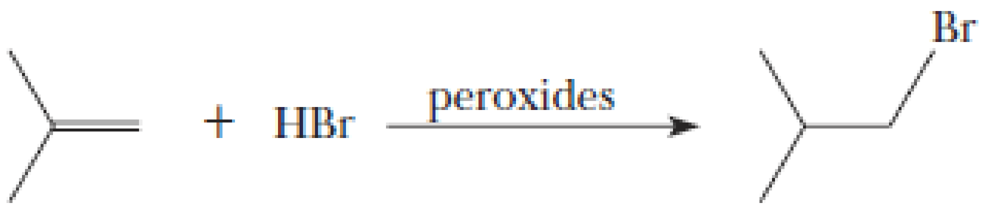
Markovnikov addition



2-Methylpropene

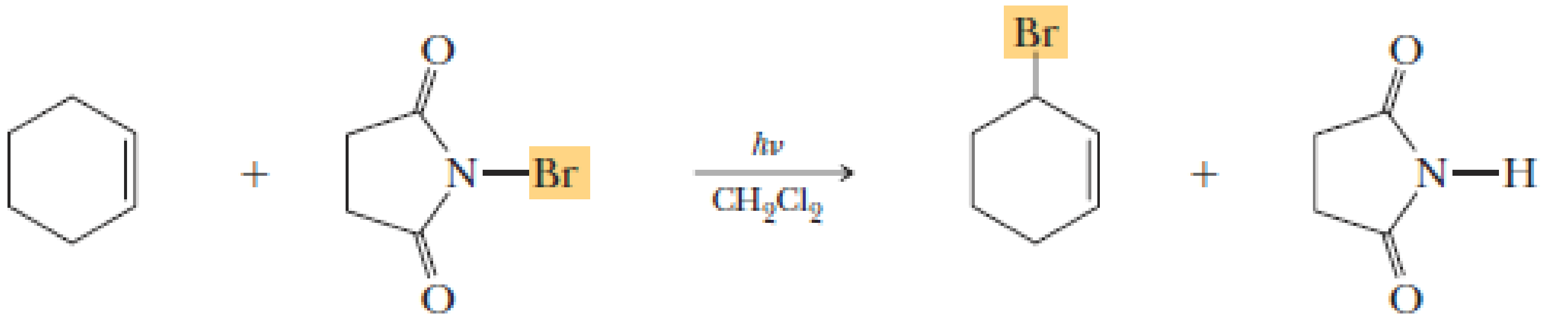
2-Bromo-2-methylpropane

Non-Markovnikov addition



2-Methylpropene

1-Bromo-2-methylpropane



Cyclohexene

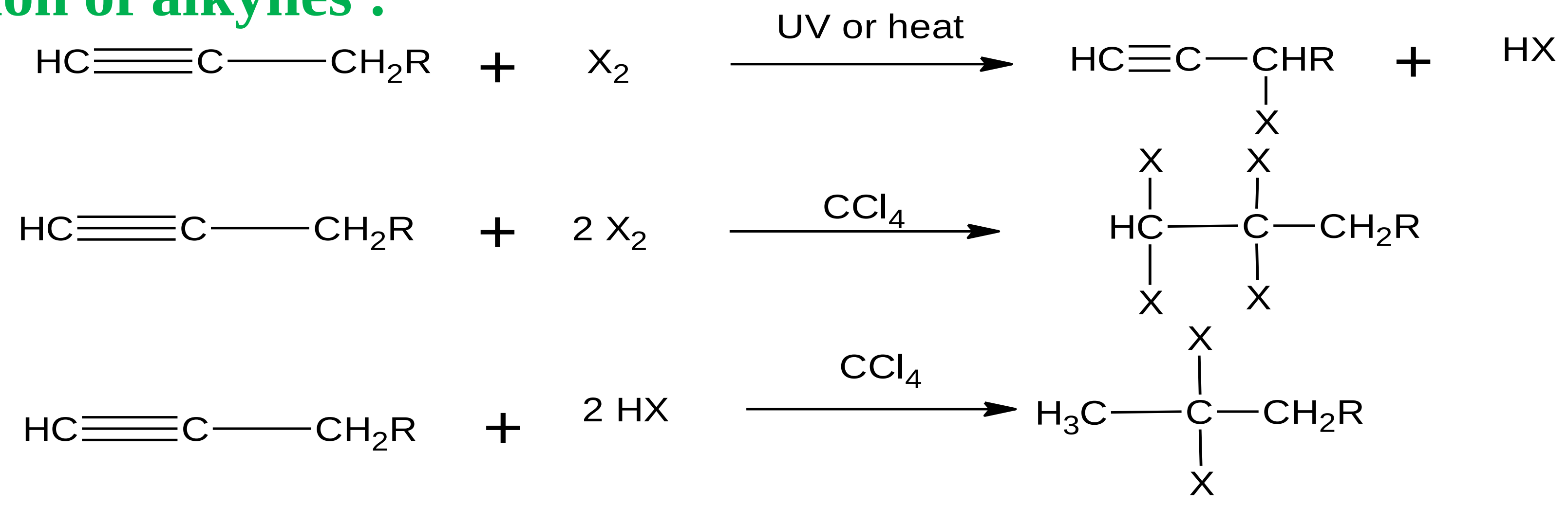
N-Bromosuccinimide (NBS)

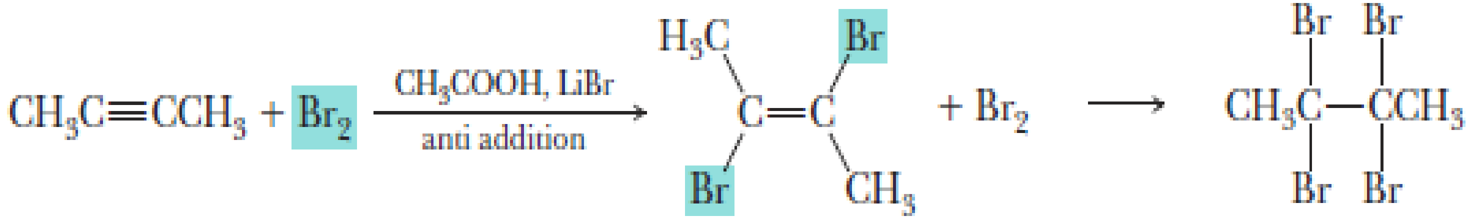
3-Bromocyclohexene (racemic)

Succinimide

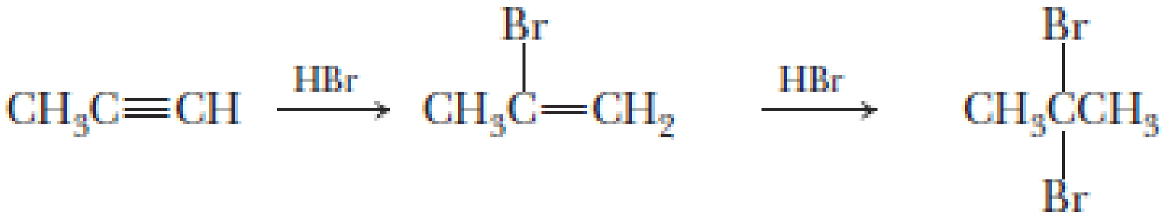
Preparation Of Halocompounds

C. Halogenation of alkynes :





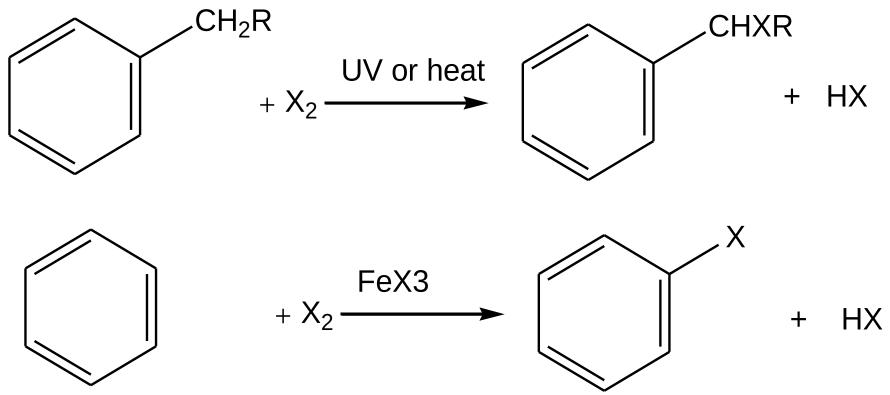
2-Butyne **(*E*)-2,3-Dibromo-2-butene** **2,2,3,3-Tetrabromobutane**

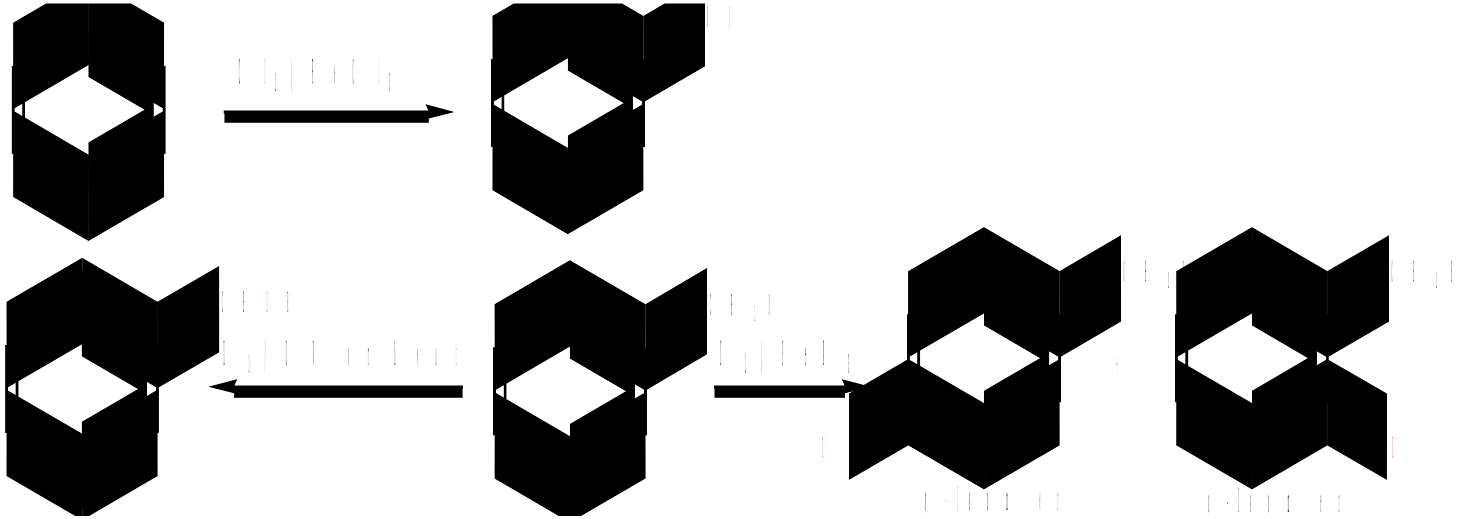


Propyne **2-Bromopropene** **2,2-Dibromopropane**

Preparation Of Halocompounds

D. Halogenation of aromatic ring and alkyl benzenes:



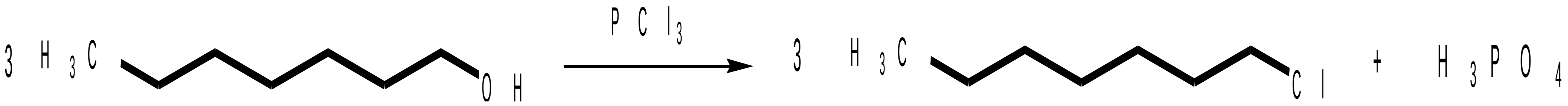


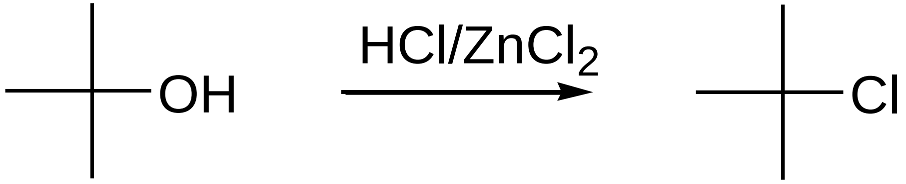
Preparation Of Halocompounds

2-Conversion of alcohols: alkyl halides (*Nucleophilic Substitution*)

$$R-OH \xrightarrow[\substack{\text{or } SOCl_2 \\ \text{or } PCl_3 \\ \text{or } PCl_5}]{HCl/ZnCl_2} R-Cl$$

- Concentrated halogen acid; HX - Phosphorus halides; PX_3 or PX_5 or Thionyl chloride ;$SOCl_2$





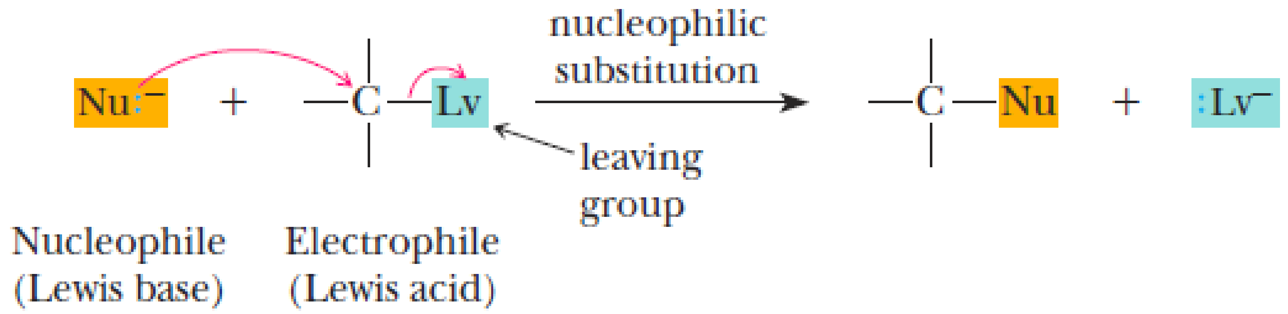
Reactions of Organic Halides

1. **Nucleophilic Substitution Reactions**
2. **Elimination Reactions**
3. **Formation of Grignard reagent and its reactions**
4. **Reduction of alkyl halides**

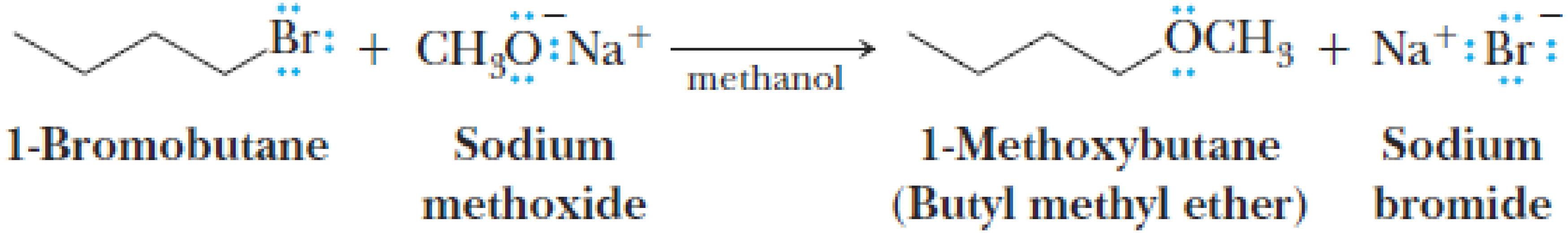
   - **Reduction by Zinc metal and acids or by metal hydrides**
   - **Reduction by sodium metal (coupling reaction)**
   - **Reduction using lithium dialkyl cuprate**

Reactions of Organic Halides

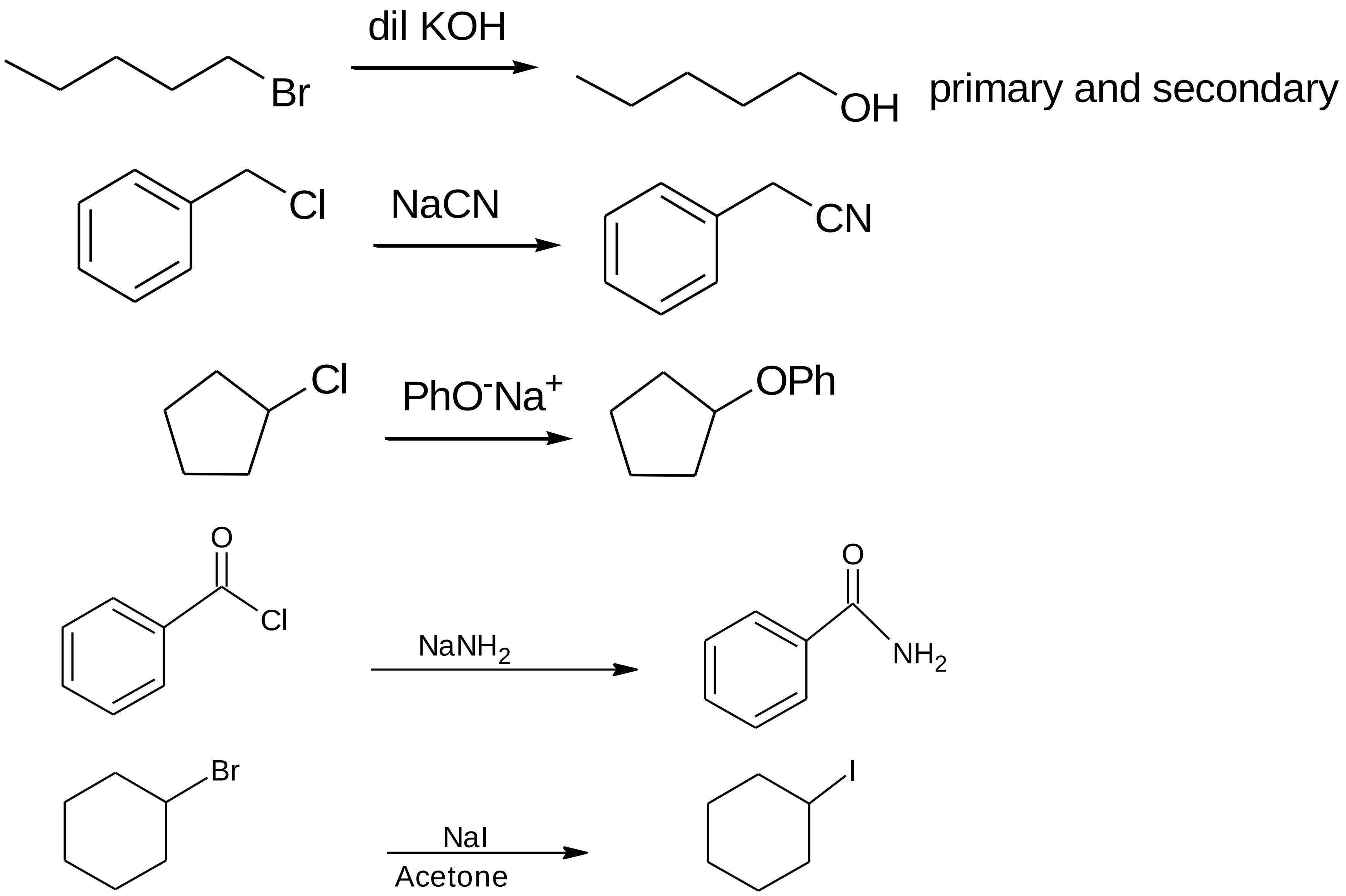
1- Nucleophilic Substitution Reactions



Nu= $\ddot{O}H$, $\ddot{O}R$, $\ddot{O}COR$, $\ddot{N}H_2$, $R\ddot{N}H$, $\ddot{S}H$, $\ddot{S}R$, $CN^{\ominus}$, $X^{\ominus}$, $HC{\equiv}C^{\ominus}$, $RC{\equiv}C^{\ominus}$,



Reactions of Organic Halides



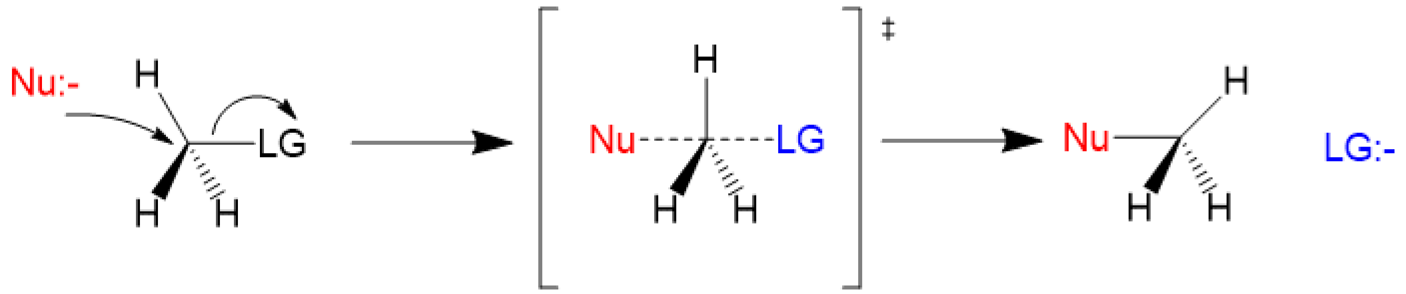
Reaction: $Nu{:}^- + CH_3Br \longrightarrow CH_3Nu + {:}Br{:}^-$

Nucleophile	Product	Class of Compound Formed
$^-{:}OH \longrightarrow$	CH_3OH	An alcohol
$^-{:}OR \longrightarrow$	CH_3OR	An ether
$^-{:}SH \longrightarrow$	CH_3SH	A thiol (a mercaptan)
$^-{:}SR \longrightarrow$	CH_3SR	A sulfide (a thioether)
$^-{:}C{\equiv}CH \longrightarrow$	$CH_3C{\equiv}CH$	An alkyne
$^-{:}C{\equiv}N{:} \longrightarrow$	$CH_3C{\equiv}N{:}$	A nitrile
${:}I{:}^- \longrightarrow$	$CH_3I{:}$	An alkyl iodide
$^-{:}N{=}\overset{+}{N}{=}N{:}^- \longrightarrow$	$CH_3{-}N{=}\overset{+}{N}{=}N{:}^-$	An alkyl azide
${:}NH_3 \longrightarrow$	$CH_3NH_3^+$	An alkylammonium ion
${:}O(H){-}H \longrightarrow$	$CH_3\overset{+}{O}(H){-}H$	An alcohol (after proton is taken away)
${:}O(H){-}CH_3 \longrightarrow$	$CH_3\overset{+}{O}(H){-}CH_3$	An ether (after proton is taken away)

Nucleophilic Substitution Mechanism

- The SN2 mechanism:

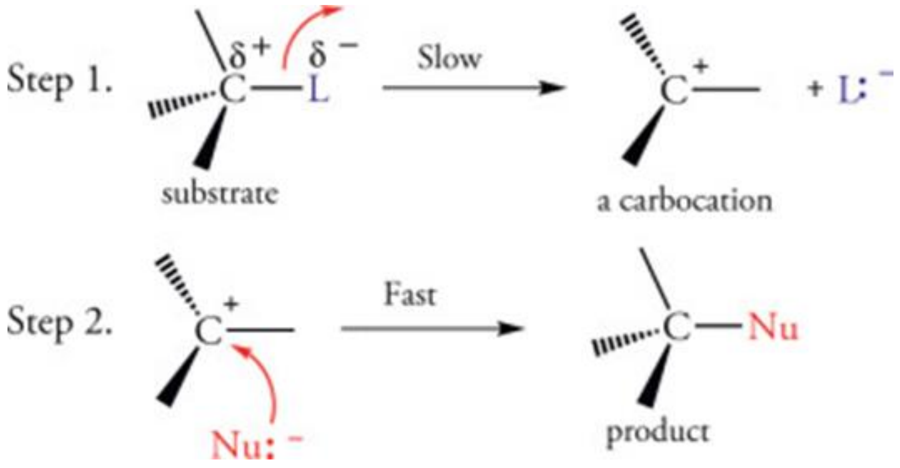
is a one –step process in which the bond to the leaving group begins to break as the bond to nucleophile begins to form



Nucleophilic Substitution Mechanism

- The SN1 mechanism:

Is a two process: the bond between the carbon and leaving group breaks first and then the resulting carbocation combines with nucleophile



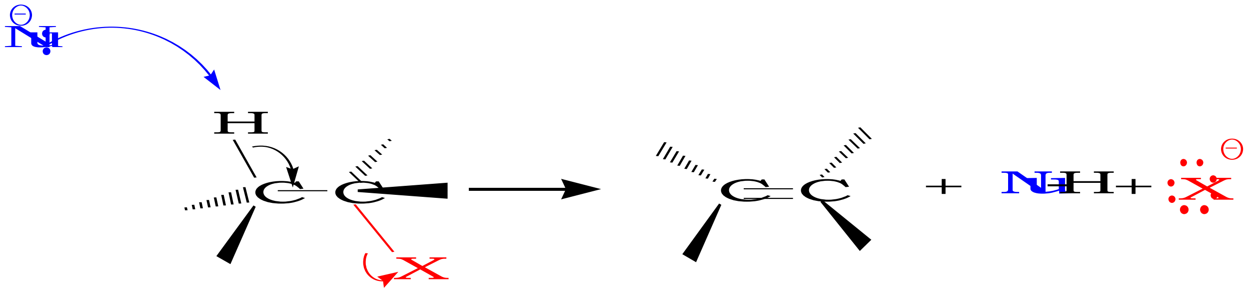
Nucleophilic Substitution Mechanism

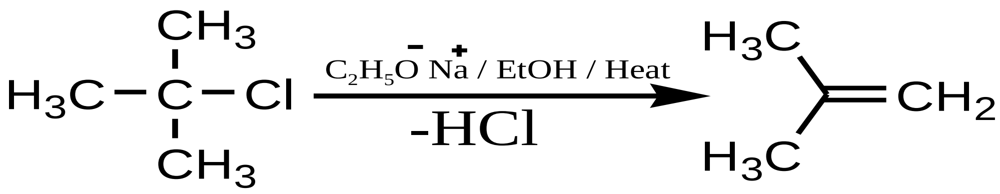
- Comparison of SN2 and SN1

Reactions of Organic Halides

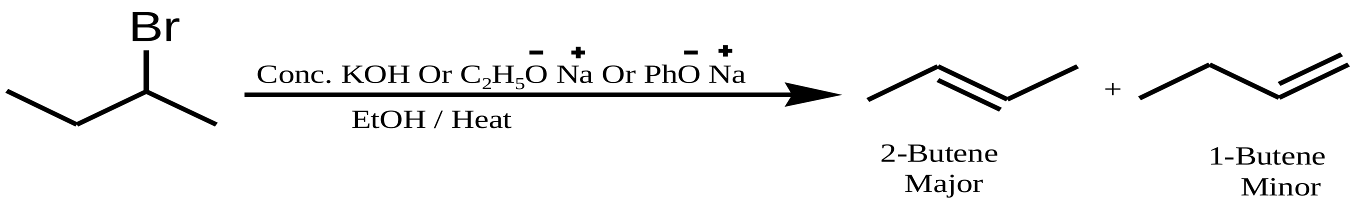
2- Elimination Reactions

- Alkyl halides can lose HX molecule to give an alkene.





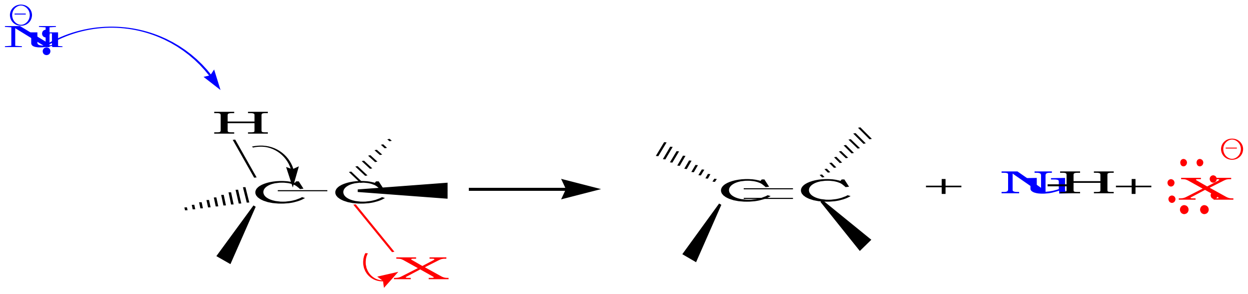
- If the haloalkane is unsymmetrical (e.g. 2-bromobutane or 2-bromopentane) a mixture of isomeric alkene products is obtained.



Reactions of Organic Halides

Elimination Reactions mechanism

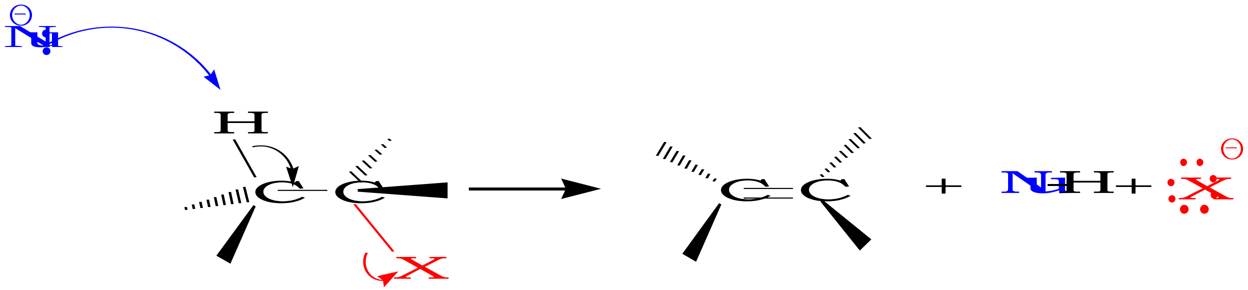
E2



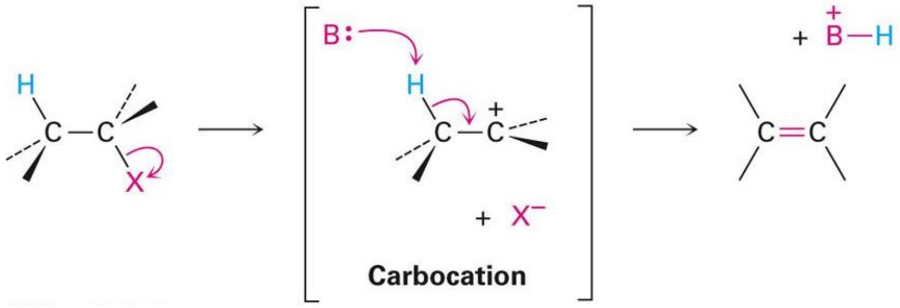
• Reactions of Organic Halides

Elimination Reactions mechanism

- E2



- E1



Reactions of Organic Halides

3- Formation of Grignard reagent and its reactions:

$$R{-}X + Mg \xrightarrow{\text{Dry ether}} R{-}MgX \quad (X{=}Cl, Br, I)$$

$$Ar{-}X + Mg \xrightarrow{\text{Dry ether}} Ar{-}MgX \quad (X{=}Cl, Br, I)$$

- **Reactions of Grignard reagent**

$$R{-}MgX \xrightarrow{H_2O} R{-}H + Mg(OH)X$$

$$R{-}MgX \xrightarrow{R'OH} R{-}H + Mg(OR')X$$

$$R{-}MgX \xrightarrow{HC\equiv CH} R{-}H + Mg(HC\equiv C)X$$

Reactions of Organic Halides

4- Reduction of alkyl halides:

- **Reduction by Zinc metal and acids or by metal hydrides**

$$CH_3CH_2CH_2Br \quad + \quad Zn \xrightarrow{H^+} CH_3CH_2CH_3 \quad + ZnBr_2$$

$$CH_3CH_2CH_2CH_2Br \xrightarrow[2)\ H_3O^+]{1)\ LiAlH_4\ /\ ether} CH_3CH_2CH_2CH_3$$

- **Reduction by sodium metal (coupling reaction)**

$$2\ H_3C\text{—}Br \quad + \quad 2\ Na \longrightarrow H_3C\text{—}CH_3 \quad + \quad 2\ NaBr$$

- **Reduction using lithium dialkyl cuprate**

$$(CH_3CH_2)_2CuLi \quad + \quad CH_3Br \longrightarrow CH_3CH_2CH_3$$

Quotations