108 Chem

Chapter 4

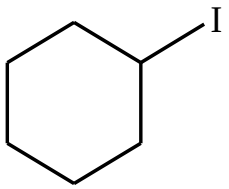
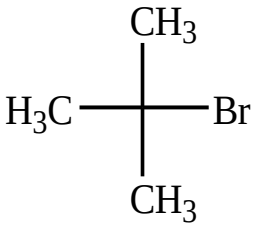
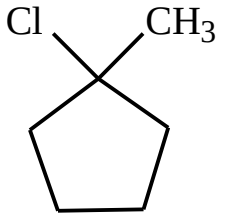
Organic Halogen compounds

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*).

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°), secondary (2°) or tertiary (3°))

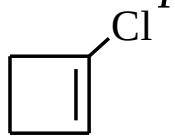
Compound	CH_3-Cl	CH_3-CH_2-Br	$(CH_3)_2$-CHF
Common name	Methyl Chloride	Ethyl bromide	Isopropyl fluoride
IUPAC name	Chloromethane	Bromoethane	2-Fluoropropane
Class	1°	1°	2°
Compound			
Common name	Cyclohexyl Iodide	t.Butyl bromide	Methylcyclopentyl chloride
IUPAC name	Iodocyclohexane	2-Bromo-2-methylpropane	1-Chloro-1-methylcyclopentane
Class	2°	3°	3°

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

$CH_2=CHBr$

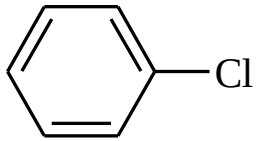
Common name: Vinyl bromide

IUPAC name: Bromoethene

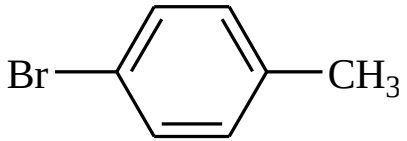


1-Chlorocyclobutene

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



Chlorobenzene



Common name: *p*-Bromotoluene

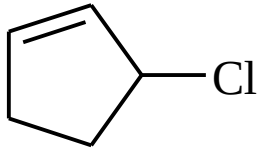
IUPAC name: 4-Bromotoluene

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

$CH_2=CHCH_2Cl$

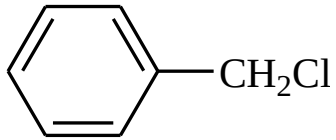
Common name: Allyl chloride

IUPAC name: 3-Chloro-1-propene



3-Chlorocyclopentene

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

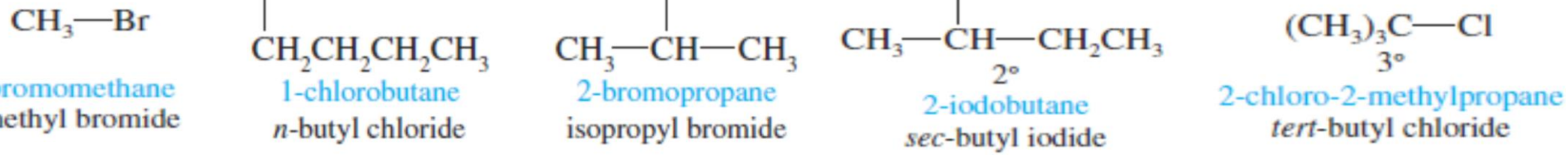


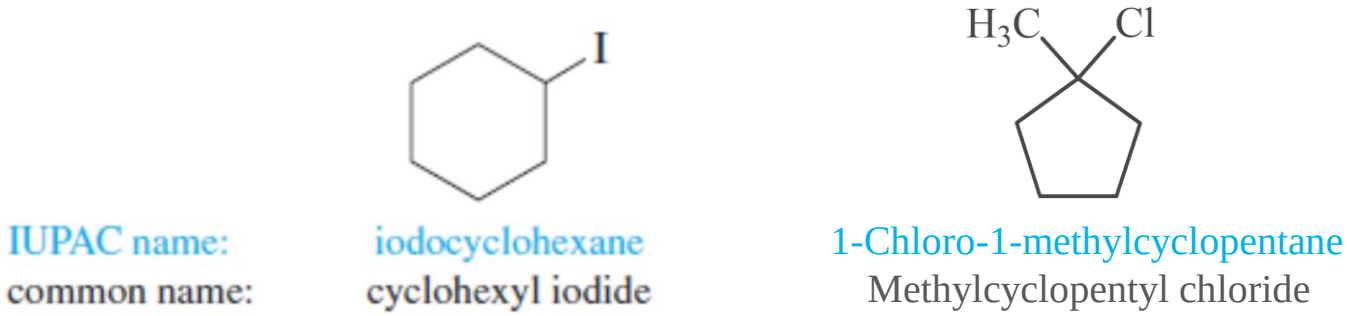
Common name: Benzyl Chloride

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.

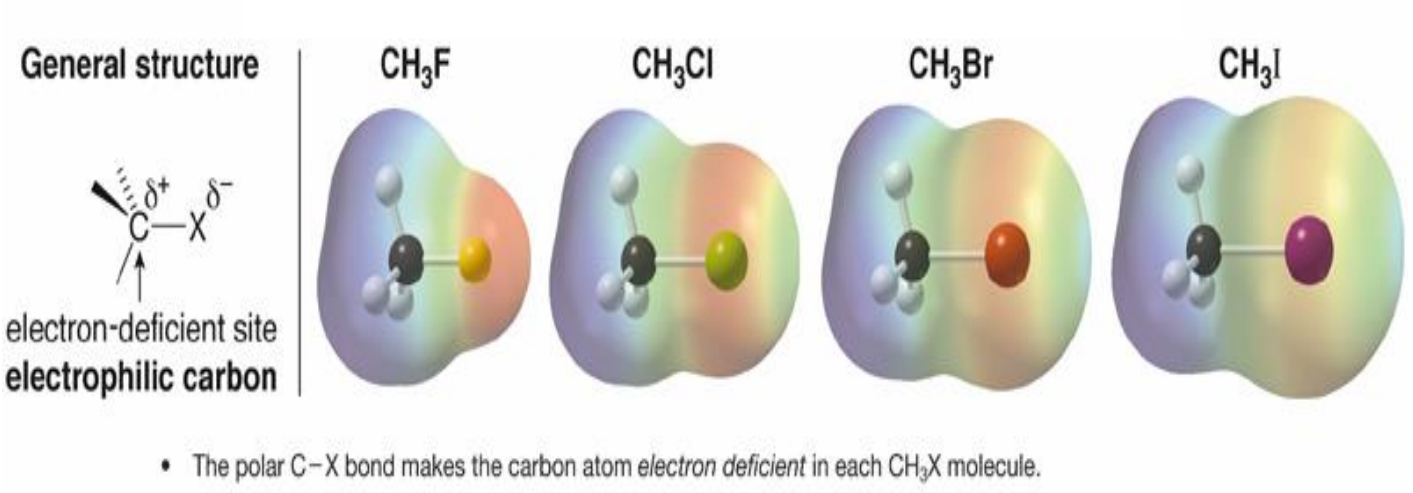




Physical Properties

Polarity

- Fluorine, chlorine, bromine and iodine 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.

The boiling point

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

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

- 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)

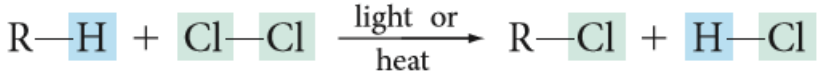
- Branching of the alkane chain lowers the boiling point.

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

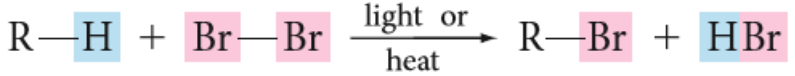
Preparation Of Organic Halides

1- Direct halogenation of hydrocarbons

A. Halogenation of alkanes: Substitution reaction called Free-Radical Reaction

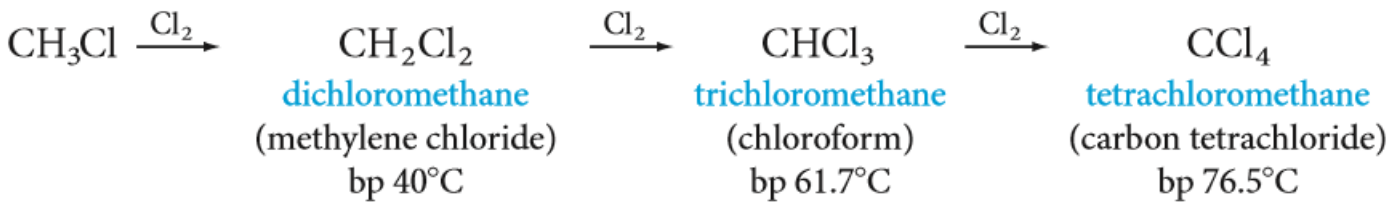


Chlorination



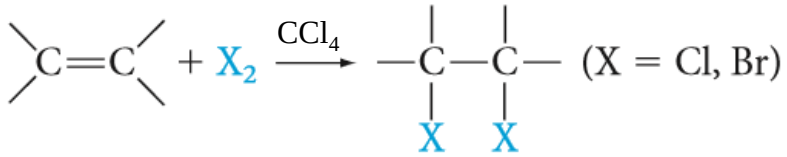
Bromination

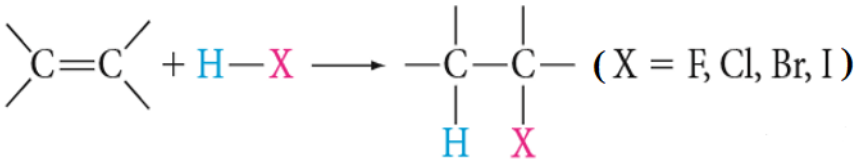
- If excess halogen is present:



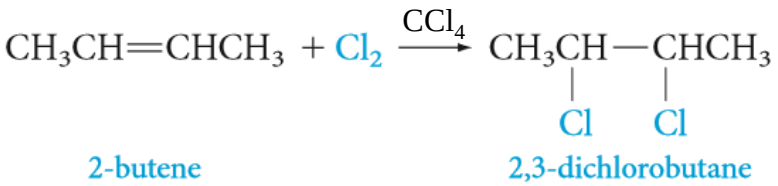
Preparation Of Organic Halides

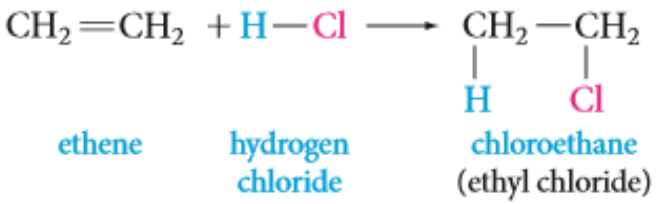
B. Halogenation of alkenes: Electophilic Addition

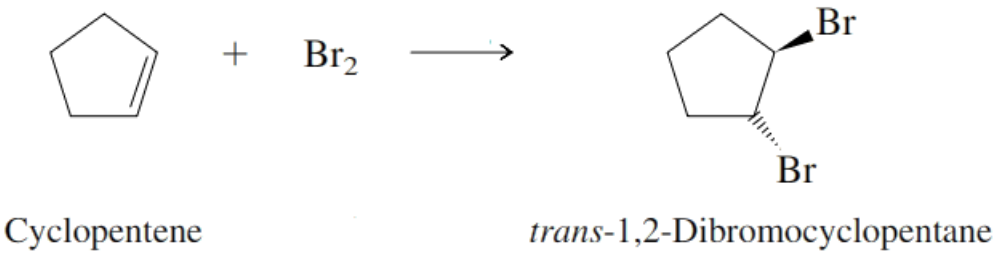


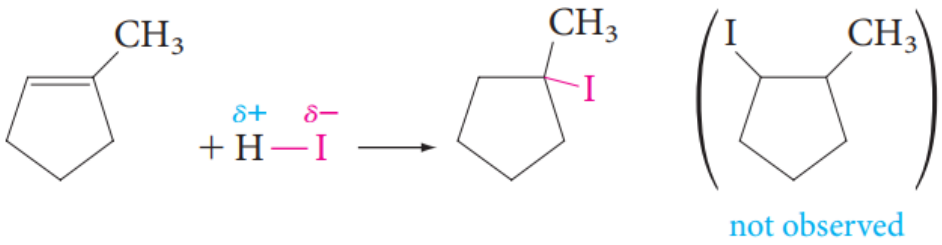


Markovnikov's Rule



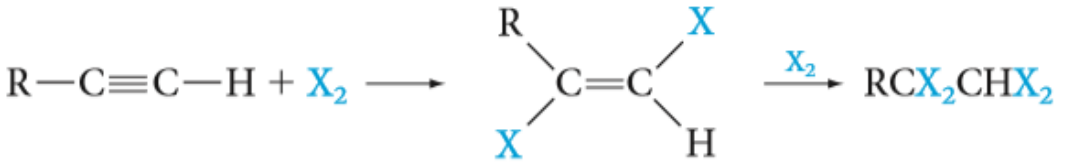


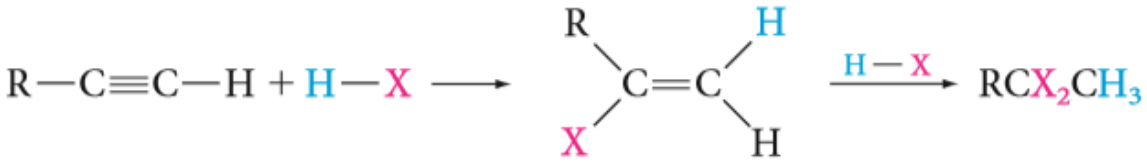




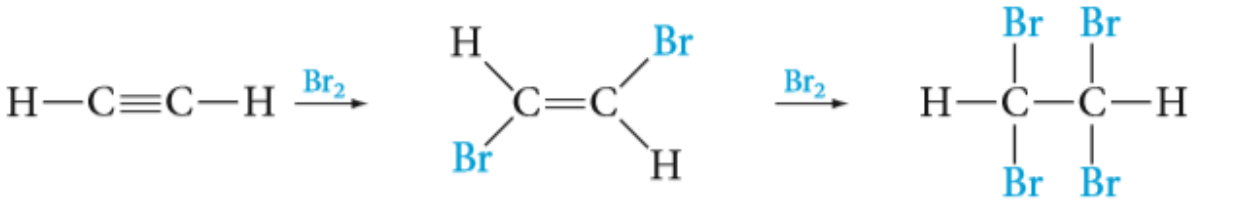
Preparation Of Organic Halides

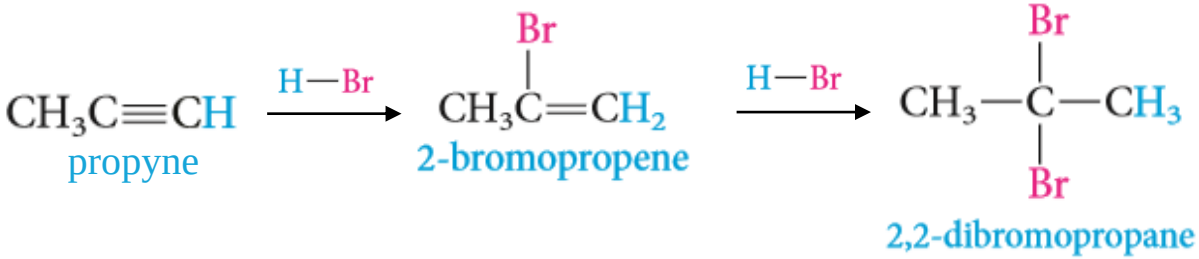
C. Halogenation of alkynes : Electophilic Addition





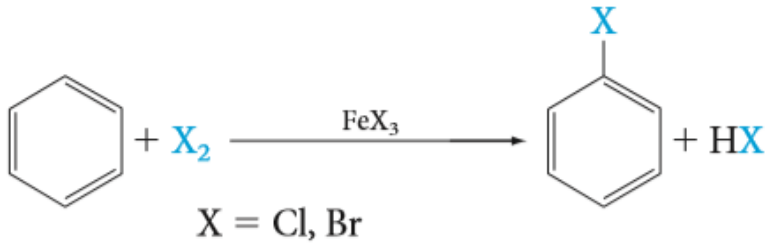
Markovnikov's Rule



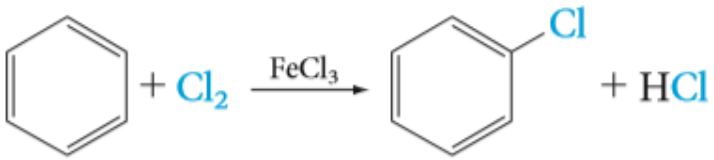


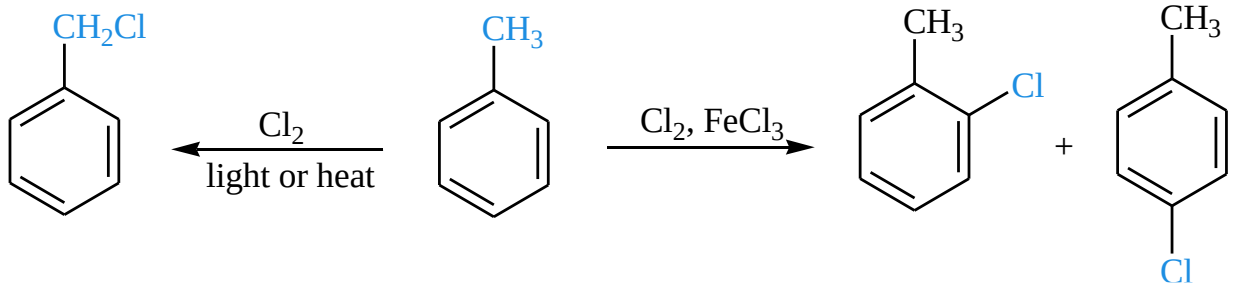
Preparation Of Organic Halides

D. Halogenation of aromatic ring and alkyl benzene:



Electrophilic Aromatic Substitution



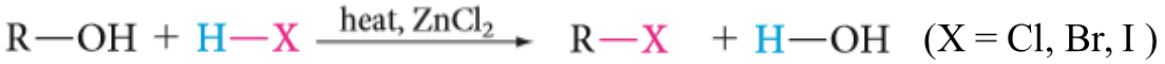


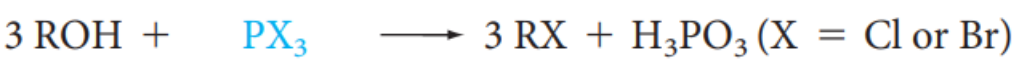
Radical halogenation

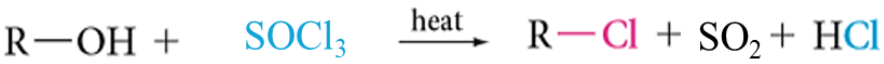
Electrophilic Aromatic Substitution

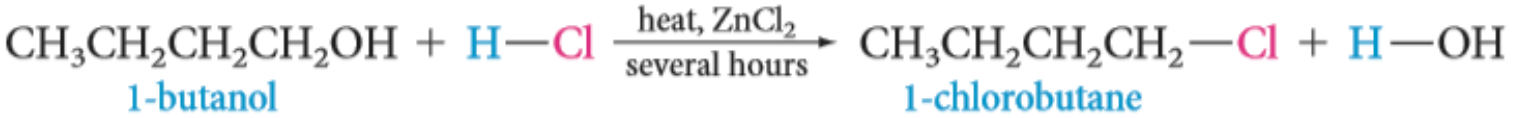
Preparation Of Organic Halides

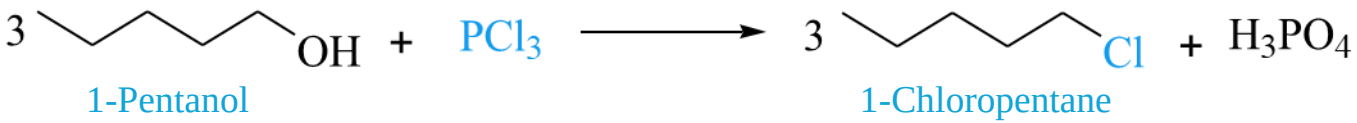
2-Conversion of alcohols into alkyl halides: Nucleophilic Substitution









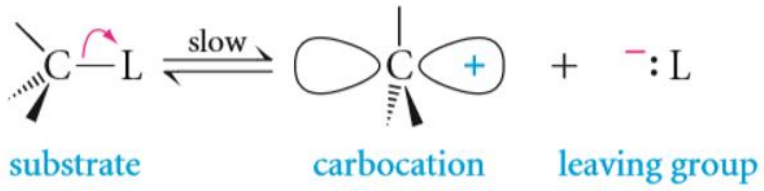


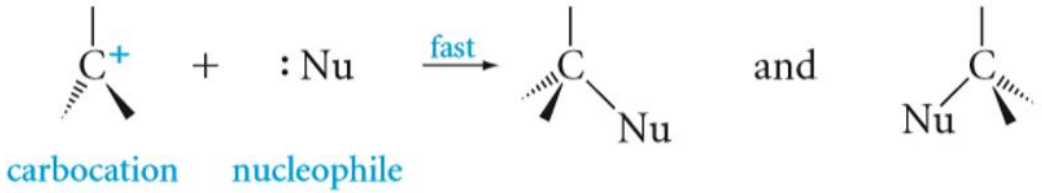
Reactions Of Organic Halides

1- Nucleophilic Substitution Reactions (S_N1 and S_N2)

S_N2 : Bimolecular Nucleophilic Substitution

S_N1 : Unimolecular Nucleophilic Substitution





Reactions Of Organic Halides

Reactions of Common Nucleophiles with Alkyl Halides:

Nu		R—Nu		
Formula	**Name**	**Formula**	**Name**	**Comments**
Oxygen nucleophiles				
1. $HO:^-$	hydroxide	$R-\ddot{O}H$	alcohol	
2. $RO:^-$	alkoxide	$R-\ddot{O}R$	ether	
3. $H\ddot{O}H$	water	$R-\overset{\pm}{O}(H)H$	alkyloxonium ion	These ions lose a proton and the products are alcohols and ethers. $\xrightarrow{-H^+}$ $R\ddot{O}H$ (alcohol)
4. $R\ddot{O}H$	alcohol	$R-\overset{\pm}{O}(R)H$	dialkyloxonium ion	$\xrightarrow{-H^+}$ $R\ddot{O}R$ (ether)
5. $R-C(=O)-\ddot{O}:^-$	carboxylate	$R-\ddot{O}C(=O)-R$	ester	
Nitrogen nucleophiles				
6. $\ddot{N}H_3$	ammonia	$R-\overset{+}{N}H_3$	alkylammonium ion	With a base, these ions readily lose a proton to give amines. $\xrightarrow{-H^+}$ $R\ddot{N}H_2$
7. $R\ddot{N}H_2$	primary amine	$R-\overset{+}{N}H_2R$	dialkylammonium ion	$\xrightarrow{-H^+}$ $R_2\ddot{N}H$
8. $R_2\ddot{N}H$	secondary amine	$R-\overset{+}{N}HR_2$	trialkylammonium ion	$\xrightarrow{-H^+}$ $R_3N:$
9. $R_3\ddot{N}$	tertiary amine	$R-\overset{+}{N}R_3$	tetraalkylammonium ion	

Reactions Of Organic Halides

Reactions of Common Nucleophiles with Alkyl Halides:

Sulfur nucleophiles				
10. $HS:^-$	hydrosulfide	$R—SH$	thiol	
11. $RS:^-$	mercaptide	$R—SR$	thioether (sulfide)	
12. $R_2S:$	thioether	$R—S^+R_2$	trialkylsulfonium ion	
Halogen nucleophiles				
13. $:I:^-$	iodide	$R—I:$	alkyl iodide	The usual solvent is acetone. Sodium iodide is soluble in acetone, but sodium bromide and sodium chloride are not.
Carbon nucleophiles				
14. $^-:C\equiv N:$	cyanide	$R—C\equiv N:$	alkyl cyanide (nitrile)	Sometimes the isonitrile, $R—\overset{+}{N}\equiv\overset{-}{C}:$, is formed.
15. $^-:C\equiv CR$	acetylide	$R—C\equiv CR$	alkyne	

Reactions Of Organic Halides

The S_N1 and S_N2 Mechanisms Compared

- Class of Alkyl halide
- Solvent polarity
- Nucleophile

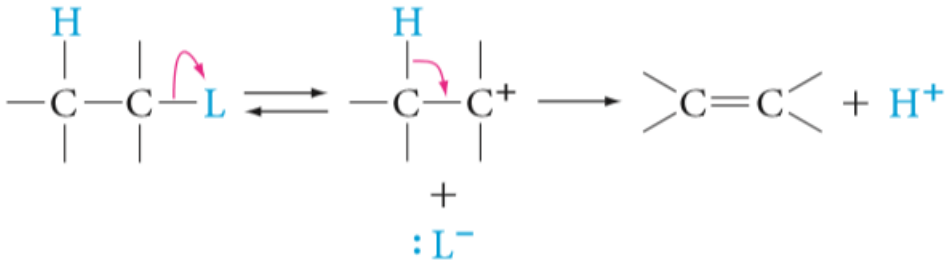
Variables	S_N2	S_N1
Halide structure		
Primary or CH_3	Common	Rarely*
Secondary	Sometimes	Sometimes
Tertiary	Rarely	Common
Stereochemistry	Inversion	Racemization
Solvent	Rate is retarded by polar protic solvents and increased by polar aprotic solvents	Because the intermediates are ions, the rate is increased by polar solvents
Nucleophile	Rate depends on nucleophile concentration; mechanism is favored when the nucleophile is an anion	Rate is independent of nucleophile concentration; mechanism is more likely with neutral nucleophiles

Reactions Of Organic Halides

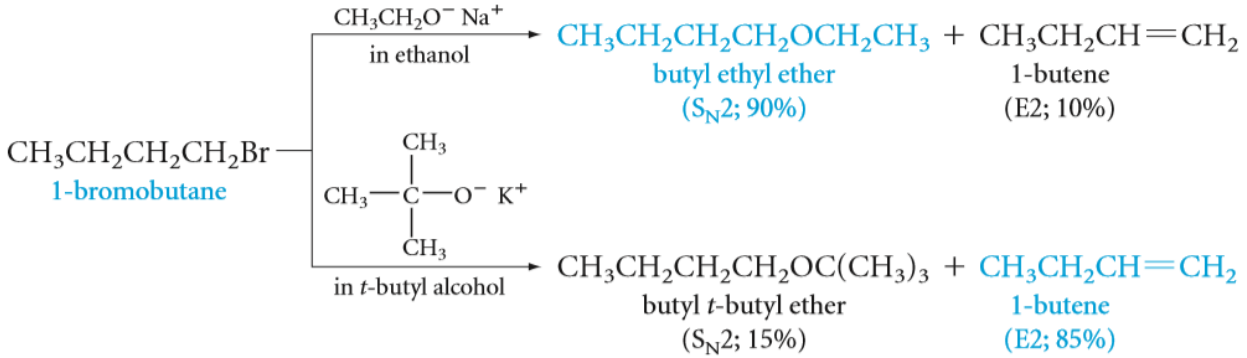
2- Elimination Reactions (E1 and E2)

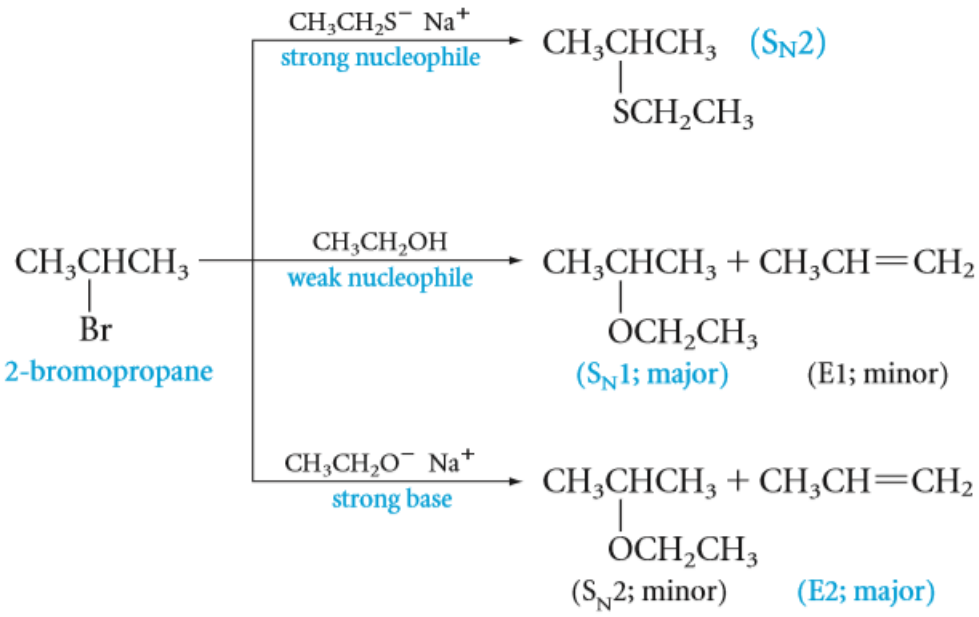
E2 : Bimolecular Elimination

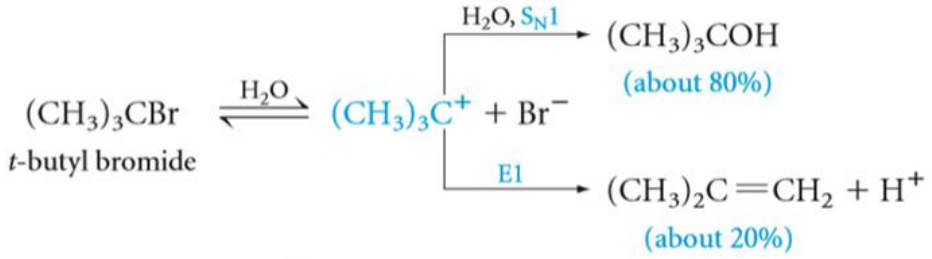
E1 : Unimolecular Elimination



Substitution and Elimination in Competition:







Zaitsev's Rule

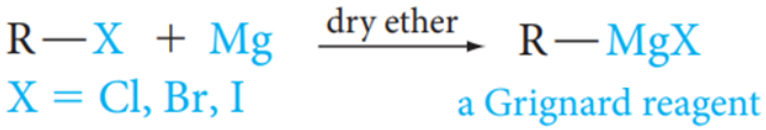
Hint:

Overall Summary of S_N1, S_N2, E1, and E2 Reactions

CH_3X			
Methyl	1°	2°	3°
	Bimolecular (S_N2/E2) Reactions Only		S_N1/E1 or E2
Gives S_N2 reactions	Gives mainly S_N2 except with a hindered strong base [e.g., $(CH_3)_3CO^-$] and then gives mainly E2.	Gives mainly S_N2 with weak bases (e.g., I^-, CN^-, RCO_2^-) and mainly E2 with strong bases (e.g., RO^-).	No S_N2 reaction. In solvolysis gives S_N1/E1, and at lower temperatures S_N1 is favored. When a strong base (e.g., RO^-) is used, E2 predominates.

Reactions Of Organic Halides

3- Formation of Grignard reagent and its reactions:



Reactions of Grignard reagent: