

Introduction to Organic Chemistry

CHEM 108

Credit hrs.: (3+1)

King Saud University

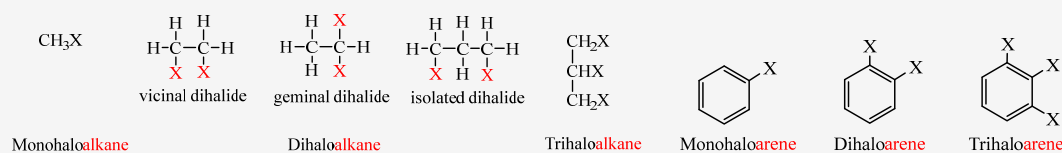
College of Science, Chemistry Department

CHAPTER 4: Organic halides

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Classification of Haloalkanes and Haloarenes

- The replacement of hydrogen atom(s) in a hydrocarbon, aliphatic or aromatic, by halogen atom(s) ($X = F, Cl, Br, \text{ or } I$; *fluoro, chloro, bromo, and iodo compounds*) results in the formation of alkyl halide (**haloalkane**) and aryl halide (**haloarene**).
- On the basis of number of halogen atoms; **Haloalkanes** and **haloarenes** may be classified as follows: **mono, di, or polyhalogen (tri-,tetra-, etc.)** compounds depending on whether they contain one, two or more halogen atoms in their structures.



- Monohalocompounds** may further be classified according to the hybridization of the carbon atom to which the halogen is bonded, as following:



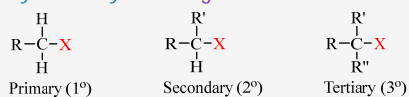
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Classification of Haloalkanes and Haloarenes

Compounds Containing sp^3 C—X Bond (X= F, Cl, Br, I)

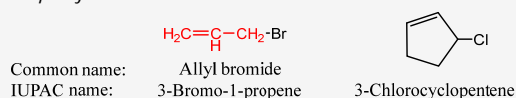
(a) Alkyl halides or haloalkanes (R—X)

- The halogen atom is bonded to an alkyl group (R) & the *general formula* is $C_nH_{2n+1}X$.
- They are classified as *primary*, *secondary* or *tertiary* according to the nature of carbon to which halogen is attached.



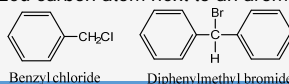
(b) Allylic halides

- The halogen atom is bonded to an sp^3 -hybridized carbon atom next to carbon-carbon double bond (C=C).



(c) Benzylic halides

- The halogen atom is bonded to an sp^3 -hybridized carbon atom next to an aromatic ring.



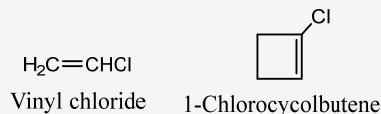
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Classification of Haloalkanes and Haloarenes

Compounds Containing sp^2 C—X Bond (X= F, Cl, Br, I)

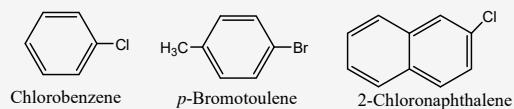
(a) Vinylic halides

- These are the compounds in which the halogen atom is bonded to an sp^2 -hybridized carbon atom of a carbon-carbon double bond (C=C).



(b) Aryl halides

- These are the compounds in which the halogen atom is bonded to the sp^2 -hybridized carbon atom of an aromatic ring.



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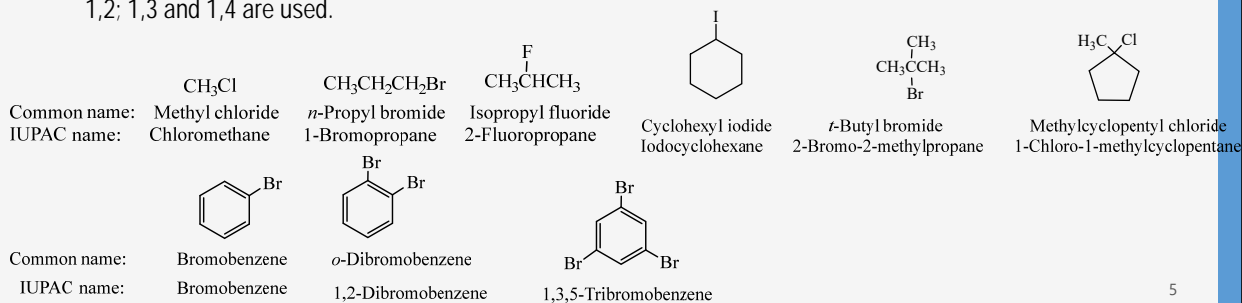
Nomenclature of Haloalkanes and Haloarenes

Haloalkanes

- o **Common names**; alkyl halides are derived by naming the alkyl group followed by the halide. *Alkyl halide*
- o **IUPAC system**; alkyl halides are named as *halosubstituted hydrocarbons*.

Haloarenes

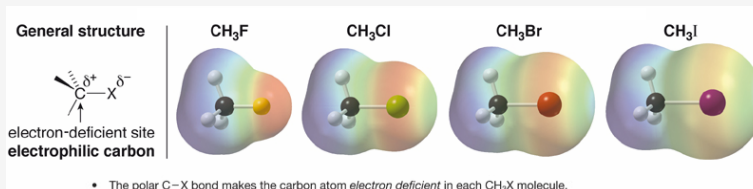
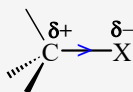
- o Haloarenes are the common as well as IUPAC names of *aryl halides*.
- o For dihalogen derivatives, the prefixes *o*-, *m*-, *p*- are used in common system but in IUPAC system, the numerals 1,2; 1,3 and 1,4 are used.



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Nature of C-X Bond C-X Bond

- o Since halogen atoms are more electronegative than carbon, the *carbon-halogen bond of alkyl halide is polarized*; the *carbon atom bears a partial positive charge* whereas the *halogen atom bears a partial negative charge*.



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Physical Properties of Organic Halides

➤ Solubility

- All organic halides are insoluble in water.
- All organic halides are soluble in common organic solvents (benzene, ether, etc.).

➤ Density

- The simple monofluoro and monochloro compounds are less dense than water,
- The monobromo and monoiodo derivatives have densities greater than water.
- As the number of halogen atoms increases, the density increases.

Group	Fluoride		Chloride		Bromide		Iodide	
	bp (°C)	Density (g mL ⁻¹)	bp (°C)	Density (g mL ⁻¹)	bp (°C)	Density (g mL ⁻¹)	bp (°C)	Density (g mL ⁻¹)
Methyl	-78.4	0.84 ⁶⁰	-23.8	0.92 ²⁰	3.6	1.73 ⁰	42.5	2.28 ²⁰
Ethyl	-37.7	0.72 ²⁰	13.1	0.91 ¹⁵	38.4	1.46 ²⁰	72	1.95 ²⁰
Propyl	-2.5	0.78 ⁻³	46.6	0.89 ²⁰	70.8	1.35 ²⁰	102	1.74 ²⁰
Butyl	32	0.78 ²⁰	78.4	0.89 ²⁰	101	1.27 ²⁰	130	1.61 ²⁰
CH ₂ =CH-	-72	0.68 ²⁶	-13.9	0.91 ²⁰	16	1.52 ¹⁴	56	2.04 ²⁰
CH ₂ =CHCH ₂ -	-3		45	0.94 ²⁰	70	1.40 ²⁰	102-103	1.84 ²²
C ₆ H ₅ -	85	1.02 ²⁰	132	1.10 ²⁰	155	1.52 ²⁰	189	1.82 ²⁰
C ₆ H ₅ CH ₂ -	140	1.02 ²⁵	179	1.10 ²⁵	201	1.44 ²²	93 ¹⁰	1.73 ²⁵

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Physical Properties of Organic Halides

➤ Boiling points

- Within a series of halides, the boiling points increase with increasing molecular weights.
This is due to the increase in van der Waals forces when the size and mass of the halogen atom increases.
- Within a homologous series, the boiling points also increase regularly with molecular weights.
- Within a series of isomers, the straight-chain compound has the highest boiling point, and the most branched isomer the lowest boiling point.
- Haloalkanes generally have a boiling point that is higher than the alkane they are derived from due to
 - The increased molecular weight due to the large halogen atoms
 - The increased intermolecular forces due to the polar bonds, and the increasing polarizability of the halogen.

Size of hydrocarbon part		Type of halogen		# of halogen atoms	
Compound	bp [°C]	Compound	bp [°C]	Compound	bp [°C]
CH ₃ -Cl	-24	CH ₃ CH ₂ -F	-38	CH ₃ Cl	-24
CH ₃ CH ₂ -Cl	12	CH ₃ CH ₂ -Cl	12	CH ₂ Cl ₂	40
CH ₃ CH ₂ CH ₂ -Cl	47	CH ₃ CH ₂ -Br	38	CHCl ₃	61
CH ₃ CH ₂ CH ₂ CH ₂ -Cl	78	CH ₃ CH ₂ -I	72	CCl ₄	77

For comparison: CH₃-CH₃ bp - 89 °C

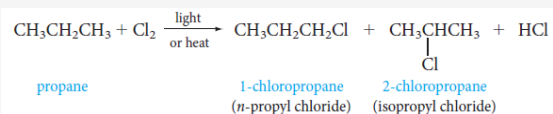
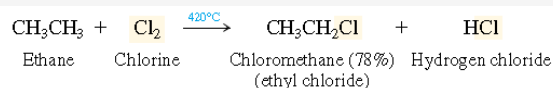
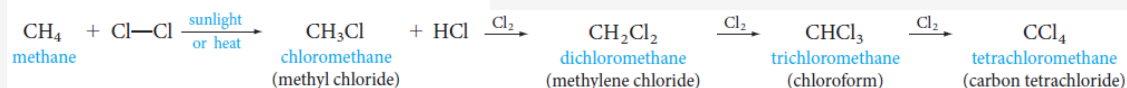
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Preparation of Halogen Compounds

From Hydrocarbons

(a) By free radical halogenation; Alkyl halide

Free radical chlorination or bromination of alkanes gives a complex mixture of isomeric mono- and polyhaloalkanes,



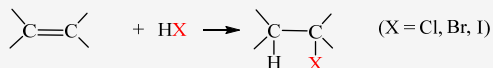
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Preparation of Halogen Compounds

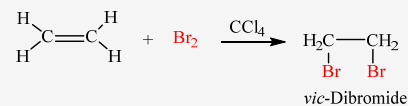
From Hydrocarbons

(b) From alkenes

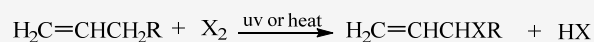
- (i) **Addition of hydrogen halides:** an alkene is converted to corresponding **alkyl halide** by reaction with hydrogen chloride, hydrogen bromide or hydrogen iodide.



- (ii) **Addition of halogens:** addition of bromine in CCl_4 to an alkene resulting in the synthesis of **vic-dibromides**.



- (iii) **Halogenation of alkenes: Allyl halides**



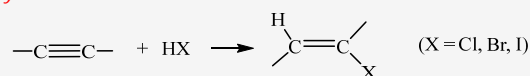
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Preparation of Halogen Compounds

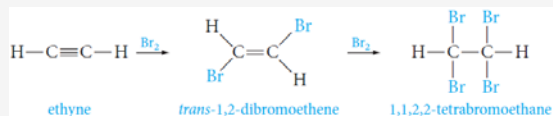
From Hydrocarbons

(c) From Alkynes

(i) *Addition of HX to alkynes: Vinyl halides*



(ii) *Addition of Halogen: Bromine adds to alkynes and the addition occurs mainly trans.*



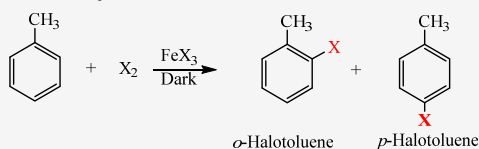
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Preparation of Halogen Compounds

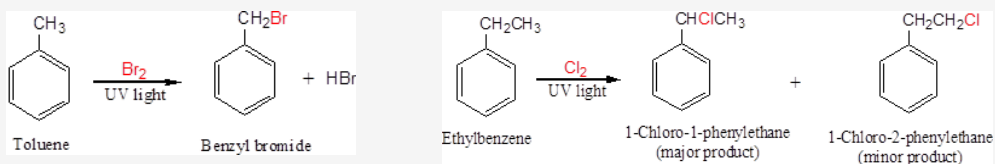
From Hydrocarbons

(d) By electrophilic substitution; Aryl halide

(i) *Aryl chlorides and bromides* can be easily prepared by electrophilic substitution of arenes with chlorine and bromine, respectively in the presence of Lewis acid catalysts like iron or iron(III) chloride.



(ii) *Halogenation of an Alkyl Side Chain of Benzene derivatives; Benzyl halides*

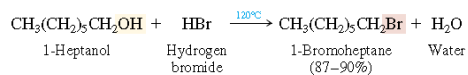
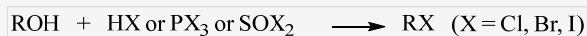


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Preparation of Halogen Compounds

From Alcohols

The hydroxyl group of an alcohol is replaced by halogen on reaction with concentrated halogen acids, phosphorus halides or thionyl chloride.

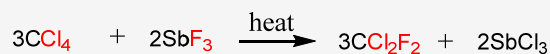


Halogen Exchange

(i) **Alkyl iodides** are often prepared by the reaction of alkyl chlorides/bromides with NaI in dry acetone. This reaction is known as Finkelstein reaction.



The manufacture of chlorofluoro compounds, known as Freons.



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Reactions of Haloalkanes

The reactions of organic halides fall into three categories

(i) **Nucleophilic substitution, or S_N , reactions.**

Those in which the halogen is replaced by some other atom or group.

(ii) **Elimination, or E, reactions.**

Those that involve the loss of HX from the halide.

(iii) **Reaction with metals (Formation of organometallic compounds).**

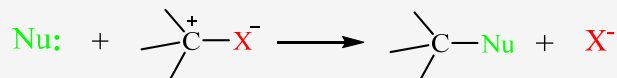
Those that involve reaction with certain metals.

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Reactions of Haloalkanes

Nucleophilic Substitution (S_N) Reactions

- A nucleophile reacts with haloalkane (the substrate) having a partial positive charge on the carbon atom bonded to halogen.
- The overall process describing any S_N reaction is



Nu: is the nucleophile.

The nucleophile has an unshared electron pair available for bonding.

X is the leaving group.

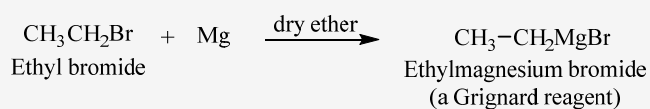
The leaving group is also a nucleophile.

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Reactions of Haloalkanes

Reaction with Metals

- Most organic chlorides, bromides, and iodides react with certain metals to give **organo-metallic compounds**, molecules with **carbon-metal bonds**.
- **Grignard reagents** are obtained by the reaction of alkyl or aryl halides with metallic magnesium in dry ether as the solvent.



- **Grignard reagents** react readily with any source of protons to give hydrocarbons.



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