

CHEM 241

Organic Chemistry II

PRE-REQUISITES COURSE; CHEM 240
CREDIT HOURS; 2 (2+0)

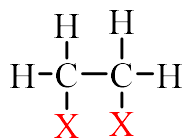
Organo-halogen Compounds

Classification of Haloalkanes and Haloarenes

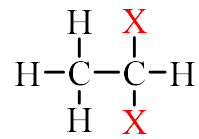
- The replacement of hydrogen atom(s) in a hydrocarbon, aliphatic or aromatic, by halogen atom(s) ($X = F, Cl, Br, \text{ or } I$; fluoro, chloro, bromo, and iodo compounds) results in the formation of alkyl halide (**haloalkane**) and aryl halide (**haloarene**)

- On the basis of number of halogen atoms; **Haloalkanes** and **haloarenes** may be classified as follows:

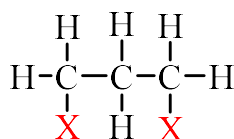
mono, *di*, or *polyhalogen* (tri-, tetra-, etc.) compounds depending on whether they contain one, two or more halogen atoms in their structures.



vicinal dihalide



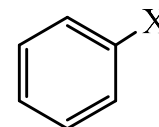
geminal dihalide



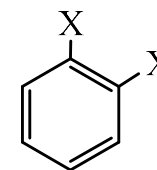
isolated dihalide



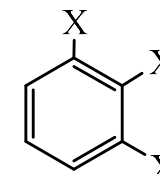
Trihaloalkane



Monohaloarene



Dihaloarene



Trihaloarene

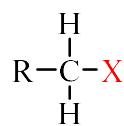
- **Monohalocompounds** may further be classified according to the hybridization of the carbon atom to which the halogen is bonded, as following:

Classification of Haloalkanes and Haloarenes

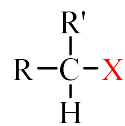
Compounds Containing sp^3 C—X Bond (X= F, Cl, Br, I)

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

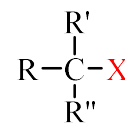
- The halogen atom is bonded to an alkyl group (R) & the *general formula* is $C_nH_{2n+1}X$.
- They are classified as *primary*, *secondary* or *tertiary* according to the nature of carbon to which halogen is attached.



Primary (1°)



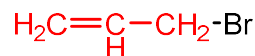
Secondary (2°)



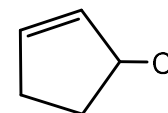
Tertiary (3°)

(b) Allylic halides

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



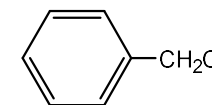
Common name: Allyl bromide
IUPAC name: 3-Bromo-1-propene



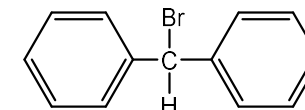
3-Chlorocyclopentene

(c) Benzylic halides

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



Benzyl chloride



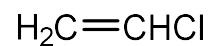
Diphenylmethyl bromide

Classification of Haloalkanes and Haloarenes

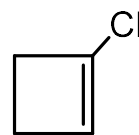
Compounds Containing sp^2 C—X Bond (X= F, Cl, Br, I)

(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).



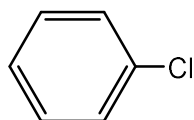
Vinyl chloride



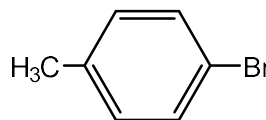
1-Chlorocyclobutene

(b) Aryl halides

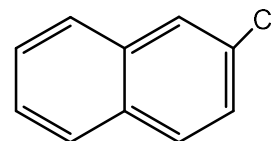
- These are the compounds in which the halogen atom is bonded to the sp^2 -hybridized carbon atom of an aromatic ring.



Chlorobenzene



p-Bromotoluene



2-Chloronaphthalene

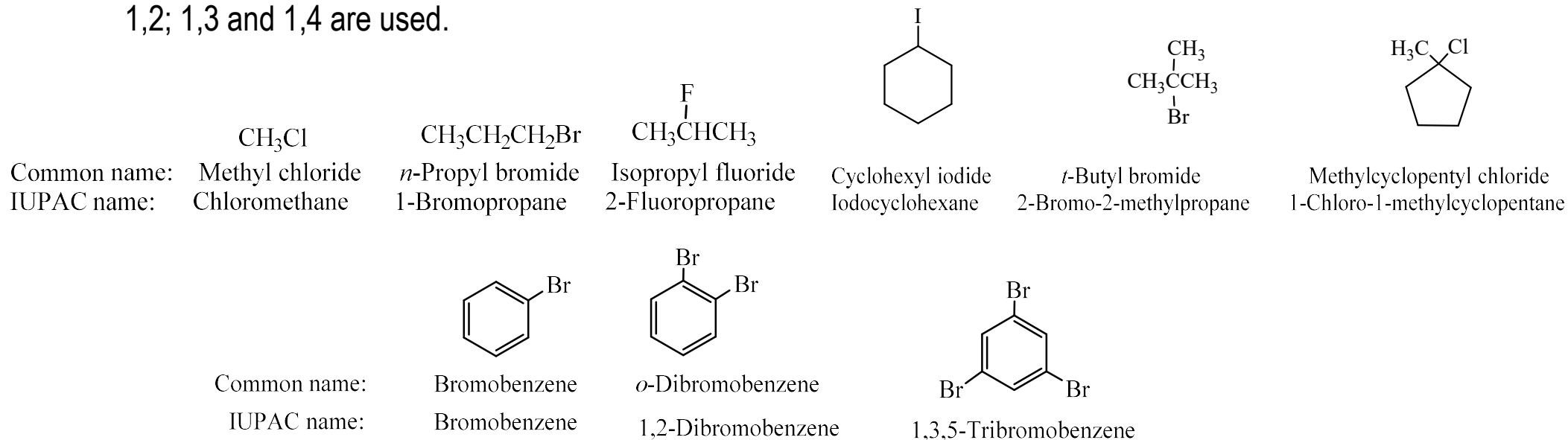
Nomenclature of Haloalkanes and Haloarenes

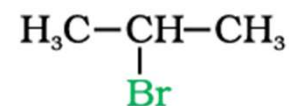
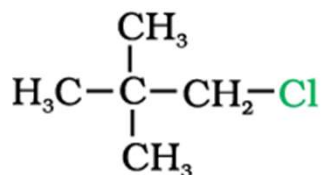
Haloalkanes

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

Haloarenes

- Haloarenes are the common as well as IUPAC names of **aryl halides**.
- 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.





IUPAC name:

1-Chloro-2,2-dimethylpropane

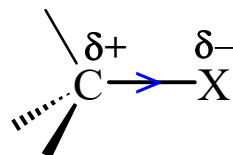
2-Bromopropane

Common and IUPAC Names of some Halides

Structure	Common name	IUPAC name
$\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$	sec-Butyl chloride	2-Chlorobutane
$(\text{CH}_3)_3\text{CCH}_2\text{Br}$	neo-Pentyl bromide	1-Bromo-2,2-dimethylpropane
$(\text{CH}_3)_3\text{CBr}$	tert-Butyl bromide	2-Bromo-2-methylpropane
$\text{CH}_2=\text{CHCl}$	Vinyl chloride	Chloroethene
$\text{CH}_2=\text{CHCH}_2\text{Br}$	Allyl bromide	3-Bromopropene
	<i>o</i> -Chlorotoluene	1-Chloro-2-methylbenzene or
	Benzyl chloride	2-Chlorotoluene Chlorophenylmethane
CH_2Cl_2	Methylene chloride	Dichloromethane
CHCl_3	Chloroform	Trichloromethane
CHBr_3	Bromoform	Tribromomethane
CCl_4	Carbon tetrachloride	Tetrachloromethane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{F}$	n-Propyl fluoride	1-Fluoropropane

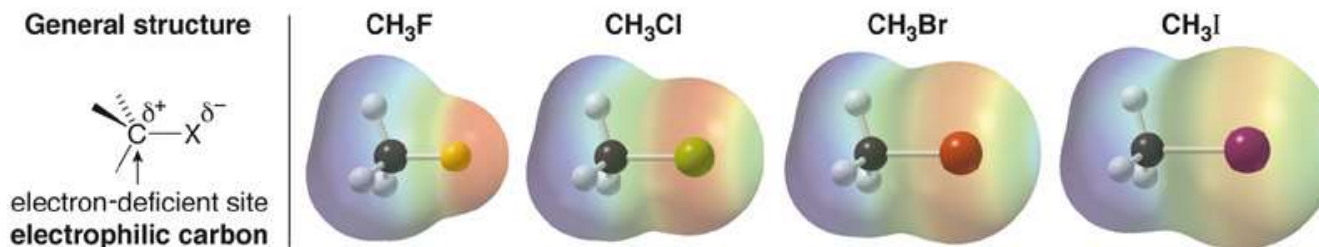
Nature of C-X Bond C-X Bond

- 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**.



Carbon-Halogen (C—X) Bond Lengths, Bond Strength and Dipole Moments

Bond	Bond Length (Å)	Bond Strength (kJ/mol)	Dipole moment (Debye)
CH ₃ -F	1.39	452	1.847
CH ₃ -Cl	1.78	351	1.860
CH ₃ -Br	1.93	293	1.830
CH ₃ -I	2.14	234	1.636



- The polar C—X bond makes the carbon atom *electron deficient* in each CH₃X molecule.

Importance of Organohalogen Compounds

a) Solvents: Alkyl halides are used as solvents for relatively non-polar compounds: CCl_4 , CHCl_3 , CCl_3CH_3 , CH_2Cl_2 ,etc.

They are good solvents for fats and oils.

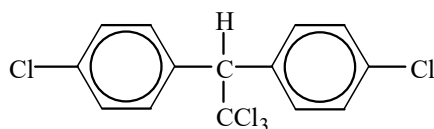
Polychloro compounds, such as trichloroethylene and tetrachloroethylene, are widely used as solvents for dry cleaning.

b) Reagents:

- Alkyl halides are used as the starting materials for the synthesis of many compounds.
- Alkyl halides are used in nucleophilic reactions, elimination reactions, formation of organometallics, and etc.

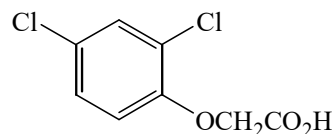
c) Refrigerants: Freons (ChloroFluoroCarbon)

d) Pesticides: DDT, Aldrin, Chlordan



DDT: [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane]

e) Herbicides: Kills broad leaf weeds but allow narrow leaf plants to grow unharmed and in greater yield



2,4-D
2,4-dichlorophenoxyacetic acid

f) Chlorine containing antibiotic, chloramphenicol: is very effective for the treatment of typhoid fever.

g) Our body produces iodine containing hormone, thyroxine: the deficiency of which causes a disease called goiter.

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	Flouride		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

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.

	Flouride	Chloride	Bromide	Iodine
Group	bp	bp	bp	bp
Methyl	-78.4	-28.8	-3.6	42.5
Ethyl	-37.7	13.1	38.4	72
Propyl	-2.5	46.6	70.8	102
Isopropyl	-9.4	34	59.4	89.4
Butyl	32	78.4	101	130
Sec-butyl		68	91.2	120
Tert-butyl		51	73.3	100

BOILING POINT TRENDS

Size of hydrocarbon part

Compound	bp [°C]
CH ₃ -Cl	-24
CH ₃ CH ₂ -Cl	12
CH ₃ CH ₂ CH ₂ -Cl	47
CH ₃ CH ₂ CH ₂ CH ₂ -Cl	78

Type of halogen

Compound	bp [°C]
CH ₃ CH ₂ -F	-38
CH ₃ CH ₂ -Cl	12
CH ₃ CH ₂ -Br	38
CH ₃ CH ₂ -I	72

of halogen atoms

Compound	bp [°C]
CH ₃ Cl	-24
CH ₂ Cl ₂	40
CHCl ₃	61
CCl ₄	77

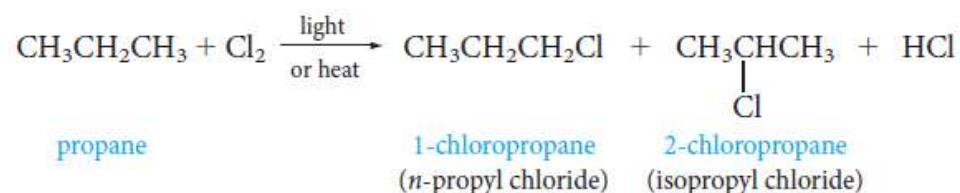
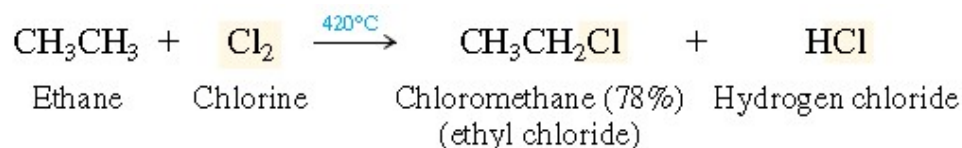
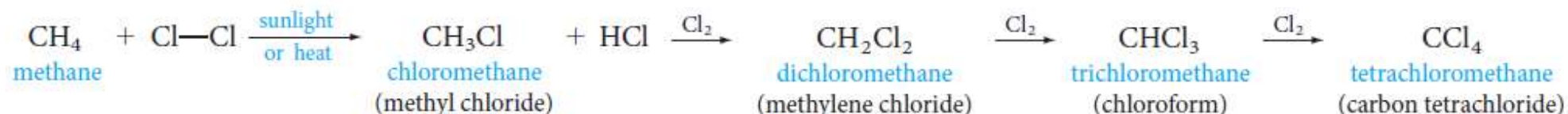
For comparison: CH₃-CH₃ bp - 89 °C

Preparation of Halogen Compounds

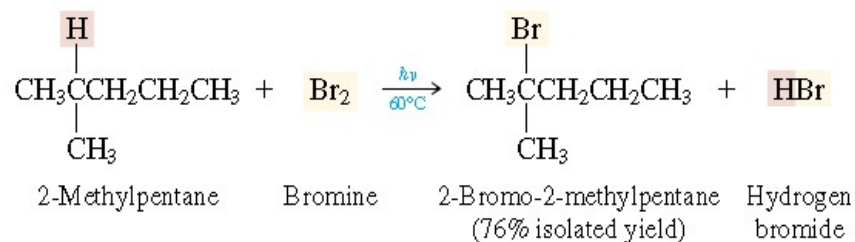
From Hydrocarbons

(a) By free radical halogenation; Alkyl halide

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



- **Rate of halogenation:** $\text{R}_3\text{CH} > \text{R}_2\text{CH}_2 > \text{RCH}_3$
(tertiary)
(secondary)
(primary)

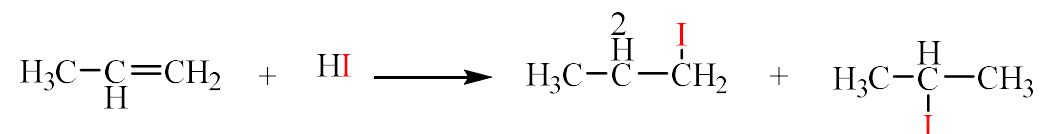
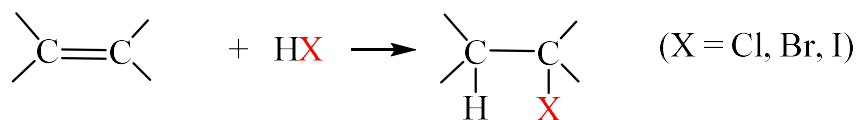


Preparation of Halogen Compounds

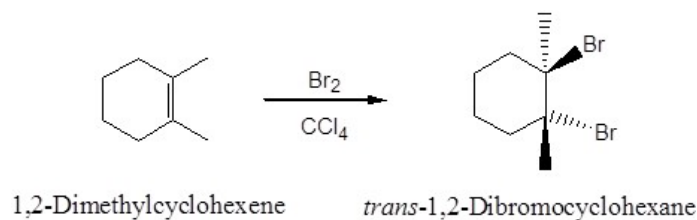
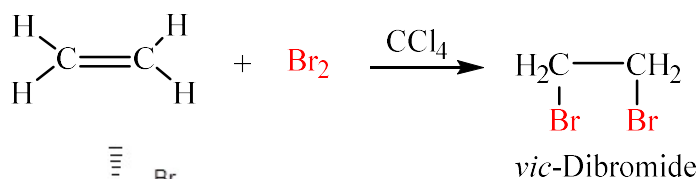
From Hydrocarbons

(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.



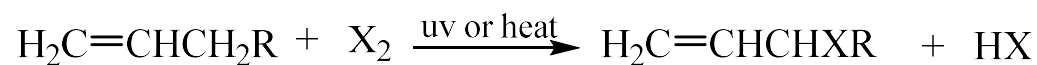
- (ii) **Addition of halogens:** addition of bromine in CCl_4 to an alkene resulting in the synthesis of **vic-dibromides**.



Preparation of Halogen Compounds

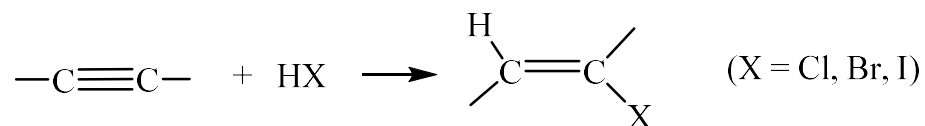
From Hydrocarbons

(iii) *Halogenation of alkenes: Allyl halides*

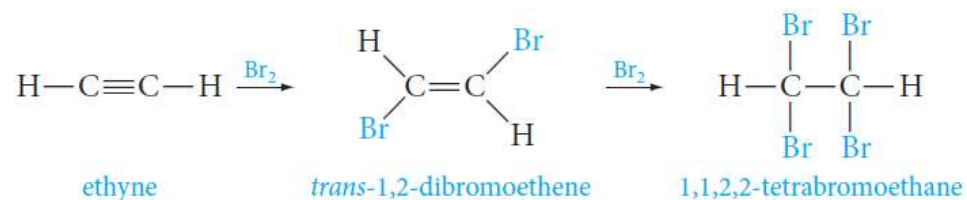


(c) From Alkynes

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



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

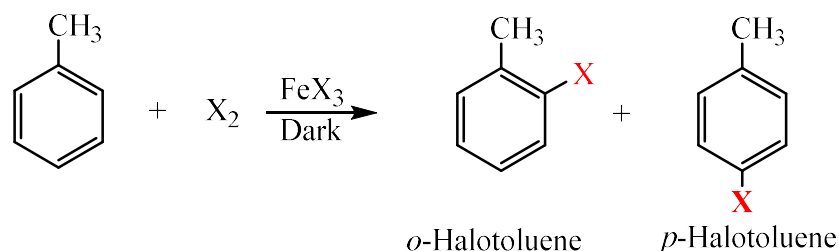


Preparation of Halogen Compounds

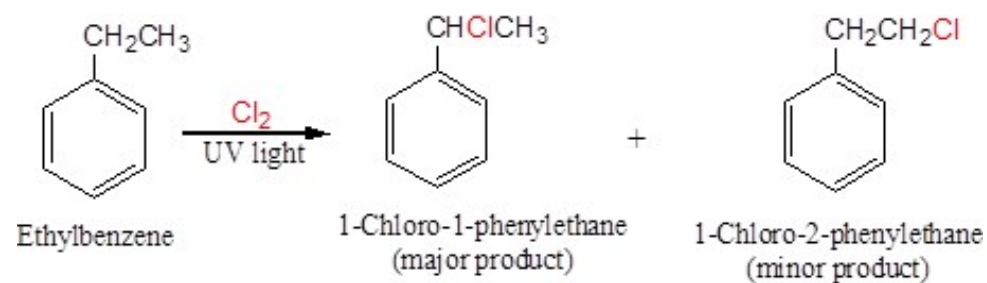
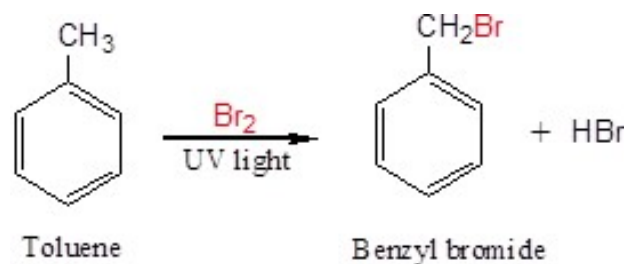
From Hydrocarbons

(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**

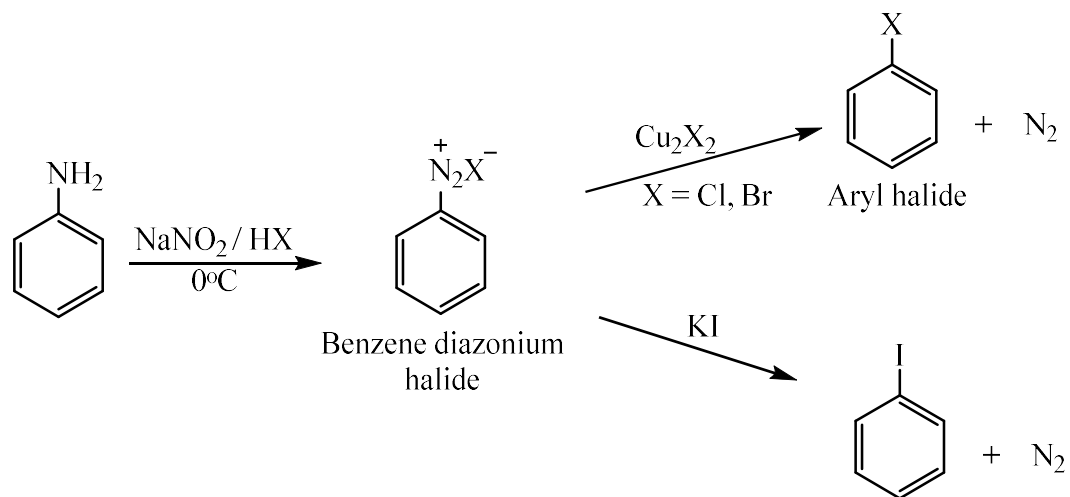


Preparation of Halogen Compounds

From Hydrocarbons

(e) Sandmeyer's reaction; Aryl halide

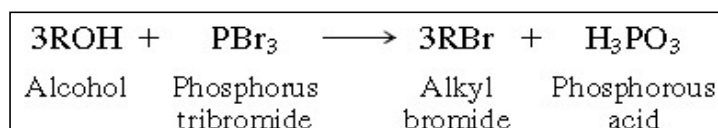
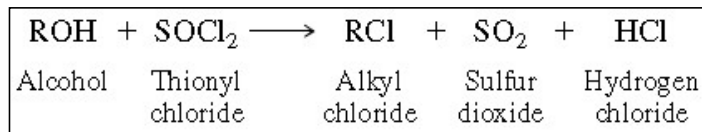
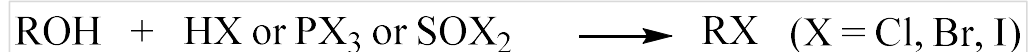
- Mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide or potassium iodide results in the replacement of the diazonium group by $-Cl$ or $-Br$ or $-I$.



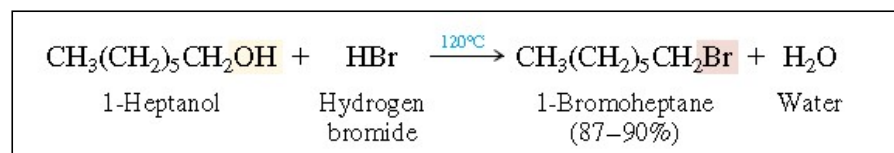
Preparation of Halogen Compounds

From Alcohols

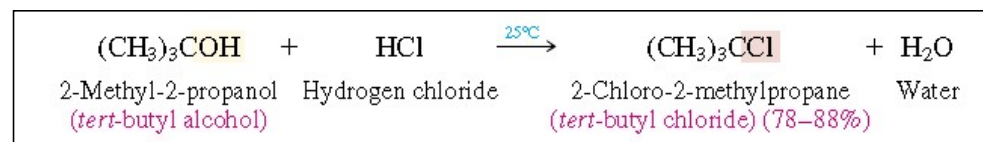
The hydroxyl group of an alcohol is replaced by halogen on reaction with concentrated halogen acids, phosphorus halides or thionyl chloride.



- The reactions of **primary** and **secondary alcohols** with HCl require the presence of a catalyst, ZnCl_2 .



- With **tertiary alcohols**, the reaction is conducted by simply shaking with concentrated HCl at room temperature.



- The **order of reactivity of alcohols** is $3^\circ > 2^\circ > 1^\circ$.
- The above methods are not applicable for the preparation of **aryl halides** because the carbon-oxygen bond in phenols has a partial double bond character and is difficult to break being stronger than a single bond.

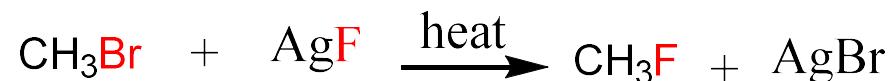
Preparation of Halogen Compounds

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**.



- (ii) The synthesis of **alkyl fluorides** is best accomplished by heating an alkyl chloride/bromide in the presence of a metallic fluoride such as AgF, Hg₂F₂, CoF₂ or SbF₃. The reaction is termed as **Swarts reaction**.



The manufacture of chlorofluoro compounds, known as Freons.

