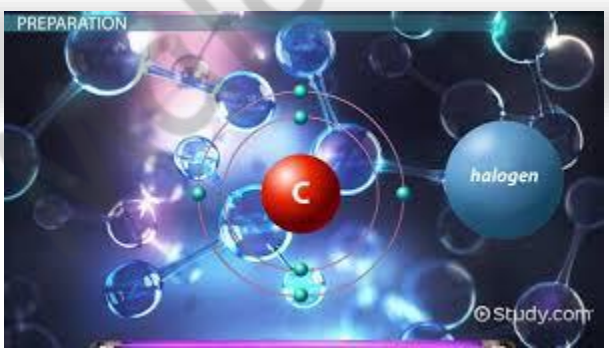
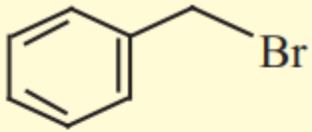
CHP. 10

Halogen Derivatives



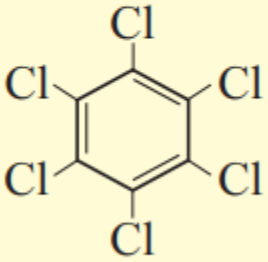
Identify the functional group in the following compounds ?

i. 

(Benzyl bromide)

ii. CCl_2F_2

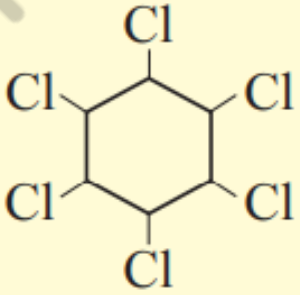
(Freon - 12)

iii. 

(Hexachlorobenzene)

iv. $Cl - CH = CCl_2$

(Westrosol)

v. 

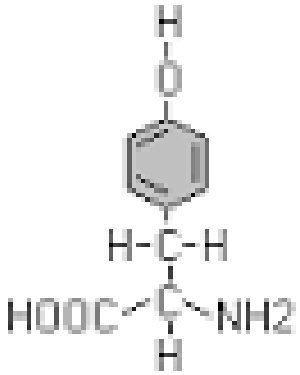
(Hexachlorocyclohexane)

Halogen Derivatives

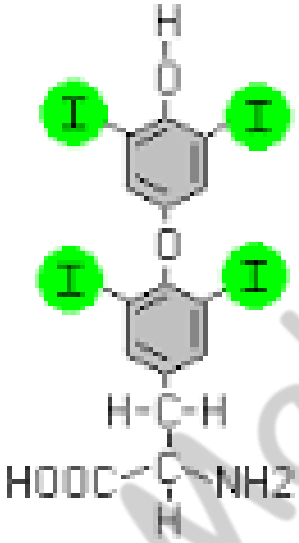
The parent family of organic compounds is hydrocarbon.

Def Replacement of hydrogen atom/s in aliphatic or aromatic hydrocarbons by halogen atom/s results in the formation of halogen derivatives of hydrocarbons

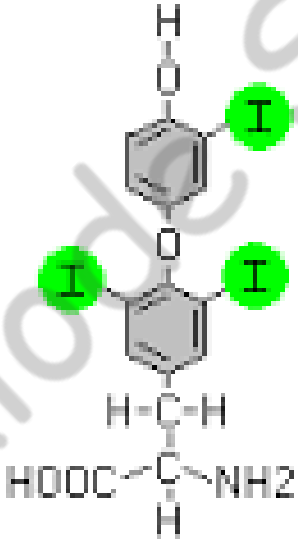
Find out the structures of two thyroid hormones T_3 (triiodothyronine) and T_4 (thyroxine). How do these help our body ?



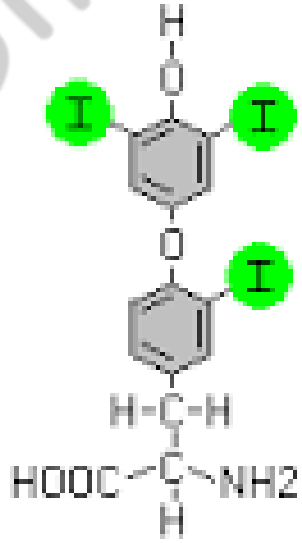
Tyrosine



Thyroxine (T4)



Triiodothyronine (T3)



"Reverse T3" (inactive)

10.1 Classification of halogen derivatives :

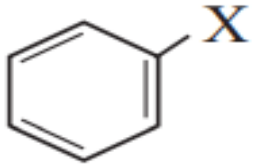
Halogen derivatives of hydrocarbons are classified mainly in two ways

a. **On the basis of hydrocarbon skeleton to which halogen atom is bonded, the halogen derivatives are classified as**

$CH_3 - CH_2 - X$ (Haloalkane)

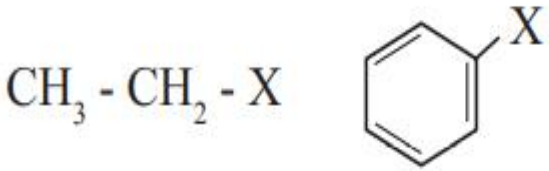
$CH_2 = CH - X$ (Haloalkene)

$HC \equiv C - X$ (Haloalkyne)

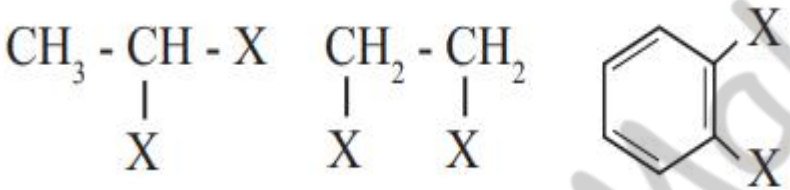


(Haloarene)

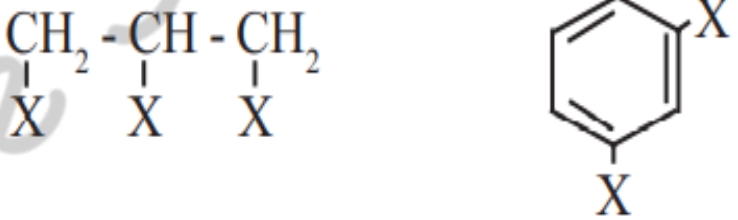
b. On the basis of number of halogen atoms, halogen derivatives are classified as mono, di, tri or poly halogen compounds.



Monohalogen compounds



Dihalogen compounds



Trihalogen compounds

We will consider classification of mono halogen derivatives in more detail.

10.1.1 Classification of monohalogen compounds :

Monohalogen compounds are further classified on the basis of position of halogen atom and the type of hybridization of carbon to which halogen is attached

a. Alkyl halides or haloalkanes :

b. Allylic halides :

c. Benzylic halide

d. Vinylic halides :

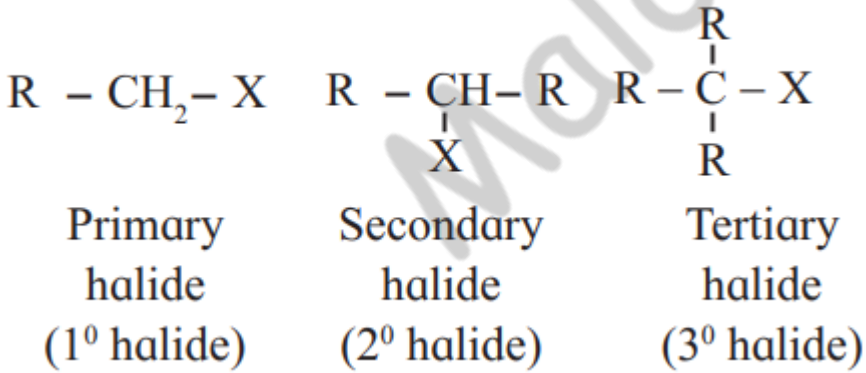
e. Haloalkyne :

f. Aryl halides or haloarenes :

a. Alkyl halides or haloalkanes :

In alkyl halides or haloalkanes the halogen atom is bonded to sp3 hybridized carbon which is a part of saturated carbon skeleton.

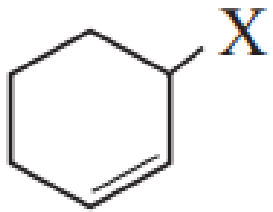
Alkyl halides may be primary, secondary or tertiary depending on the substitution state of the carbon to which halogen is attached :



b. Allylic halides

: In allylic halides, halogen atom is bonded to a sp3 hybridized carbon atom next to a carbon-carbon double bond.

$CH_2 = CH - CH_2 - X$



c. Benzylic halide :

In benzylic halides halogen atom is bonded to a sp3 hybridized carbon atom which is further bonded to an aromatic ring.

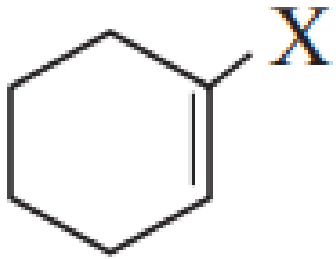
aromatic ring.

d. Vinylic halides

: In vinylic halides halogen atom is bonded to a sp2 hybridized carbon atom of aliphatic chain.

Vinylic halide is a haloalkene.

$CH_2 = CH - X$



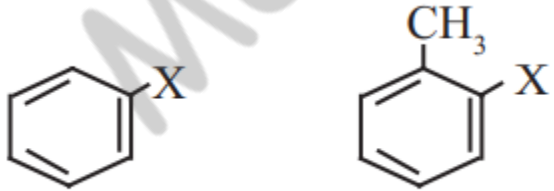
e. Haloalkyne

: When a halogen atom is bonded to a sp hybridized carbon atom it is a haloalkyne.

$$CH \equiv C - X$$

f. Aryl halides or haloarenes :

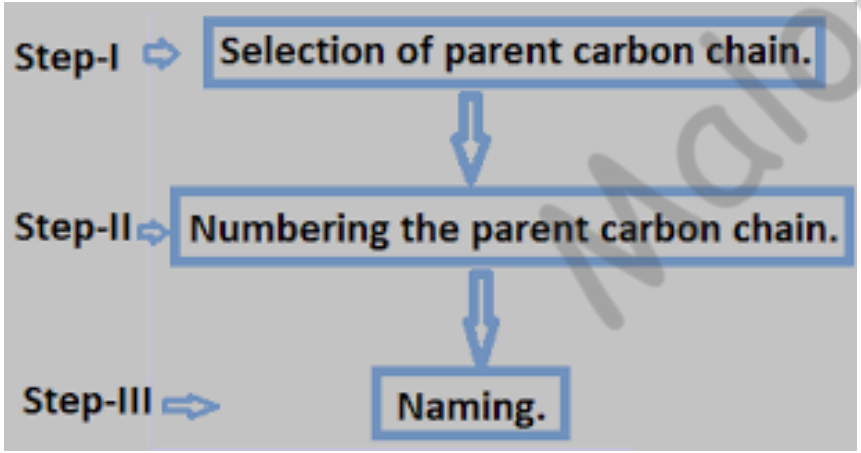
In aryl halides, halogen atom is directly bonded to the sp2 hybridized carbon atom of aromatic ring.



10.2 Nomenclature of halogen derivatives

alkyl halides are named as haloalkanes.

Aryl halides are named as haloarenes



Naming

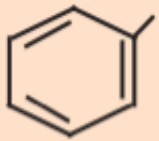
Locant – Prefix – Parent – Suffix

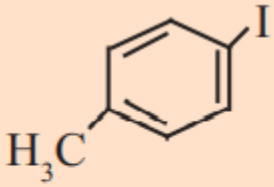
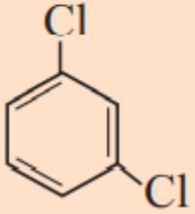
Locant: Where are the substituents?

Prefix: What are the substituents?

Parent: How many carbons?

Suffix: What is primary functional group?

Formula	Common name	IUPAC name
CH_2Cl_2	Methylene chloride	Dichloromethane
CH_3CH_2Br	Ethyl bromide	Bromoethane
$CH_3CH(Cl)CH_3$	Isopropyl chloride	2-Chloropropane
$(CH_3)_2$ CH - CH_2Br	Isobutyl bromide	1-Bromo-2-methylpropane
$(CH_3)_3$ C Br	Tert-butyl bromide	2-Bromo-2-methyl-propane
$(CH_3)_3$ C CH_2Cl	Neopentyl chloride	1-Chloro-2, 2-dimethyl propane
CH_2 = CH - Cl	Vinyl chloride	1-Chloroethene
CH_2 = CH - CH_2Br	Allyl bromide	3-Bromopropene
CH ≡ C - Cl	Chloro acetylene	Chloroethyne
 CH_2I	Benzyl iodide	Iodophenylmethane

	p-Iodotoluene	1-Iodo-4-methyl benzene or 4-Iodotoluene
	m-dichlorobenzene	1, 3-dichlorobenzene

Can you recall ?

- In IUPAC system of nomenclature does the functional group 'halogen' appear as a suffix or prefix ?
- What are the trivial names of laboratory solvents $CHCl_3$ and CCl_4 ?

1. State Markownikoff's Rule.

2. Identify the product of the following reaction.

(i)

$+ Cl_2 \xrightarrow[AlCl_3]{\text{Anhydrous}}$ _____

Benzene

(ii) Name the type of halide produced in the following reaction.

(iii) What type of reaction are shown by benzene.

Q. How will you prepare 1-bromobutane from 1-butene.

Q. How will you obtain 2-chloropropene from propane.

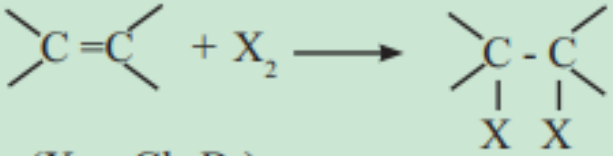
Problem 10.1 : How will you obtain 1-bromo-1-methylcyclohexane from alkene?

Write possible structures of alkene and the reaction involved.

Solution :

Do you know ?

Alkenes form additon product, vicinal dihalide, with chlorine or bromine usually in inert solvent like CCl_4 at room temperature.



(X = Cl, Br)

Do you know ?

When alkenes are heated with Br_2 or Cl_2 at high temperature, hydrogen atom of allylic carbon is substittued with halogen atom giving allyl halide.

$$CH_2 = CH - CH_3 + Cl_2 \longrightarrow CH_2 = CH - CH_2Cl + HCl$$

10.4 Physical properties :

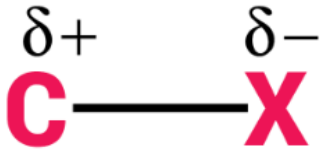
Physical properties of alkyl halides are considerably different from those of corresponding alkanes.

The boiling point of alkyl halides is determined by polarity of the C-X bond as well as the size of halogen atoms.

1 Nature of intermolecular forces
2 Boiling point
3 Solubility

1 Nature of intermolecular forces

Halogens (X = F, Cl, Br and I) are more electronegative than carbon.

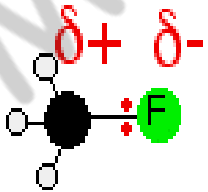


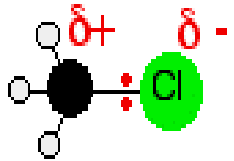
polar covalent bond

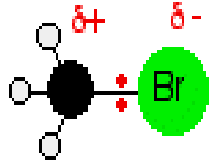
moderately polar compounds.

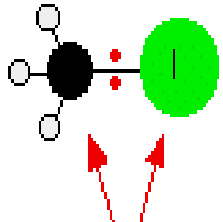
Table 10.2 : Bond parameters of C-X bond

Bond	Bond length/ (pm)	Bond en-thalpy/ (kJ mol^{-1})	Dipole moment/ debye
CH_3 - F	139	452	1.847
CH_3 - Cl	178	351	1.860
CH_3 - Br	193	293	1.830
CH_3 - I	214	234	1.636



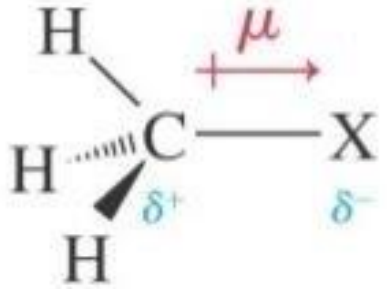






Dipole Moments

- Electronegativities of the halides:
  F > Cl > Br > I
- Bond lengths increase as the size of the halogen increases:
  C—F < C—Cl < C—Br < C—I
- Bond dipoles:
  C—Cl > C—F > C—Br > C—I
  1.56 D 1.51 D 1.48 D 1.29 D
- Molecular dipoles depend on the geometry of the molecule.



19. Among the following, the molecule with the highest dipole moment is _____.

[IIT JEE (Screening) 2003]

(A) CH_3Cl (B) CH_2Cl_2

(C) $CHCl_3$ (D) CCl_4

2 Boiling point

Boiling points of alkyl halides are considerably higher than those of corresponding alkanes due to higher polarity and higher molecular mass

van der Waals force increases with increase in size and mass of halogen.

Thus boiling point of alkyl halide decreases in the order RI > RBr > RCl > RF

For example, :

Haloal-kane	CH_3F	CH_3Cl	CH_3Br	CH_3I
Boiling point (K)	194.6	248.8	276.6	315.4

boiling point rises with increasing carbon number

boiling point increases
With increase in
Molecular Weight

For example,

Haloalkane	Boiling point (K)
CH_3Cl	248.8
CH_3CH_2Cl	285.5
$CH_3CH_2CH_2Cl$	320.0
$CH_3CH_2CH_2CH_2Cl$	351.5

For isomeric alkyl halides, boiling point decrease with increased branching as surface area decreases on branching and van der Waals forces decrease.

Haloalkane	Boiling point (K)
$CH_3CH_2CH_2CH_2Br$	375
$CH_3-\underset{\displaystyle Br}{\underset{\vert}{CH}}-CH_2-CH_3$	364
$CH_3-\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle Br}{\underset{\vert}{C}}}}-CH_3$	346

3 Solubility

Haloalkanes are soluble in organic solvents but insoluble in water

Alkyl halides cannot form hydrogen bonds with water.

In addition to this, the attraction between alkyl halide molecules is stronger than attraction between alkyl halide and water

Alkyl halides are soluble in non-polar organic solvents

From Exercise

Q. 3. Give reasons

ii. Alkyl halides though polar are immiscible with water.

Ans :- i. Alkyl halides cannot form hydrogen bonds with water.

ii. In addition to this, the attraction between alkyl halide molecules is stronger than attraction between alkyl halide and water.

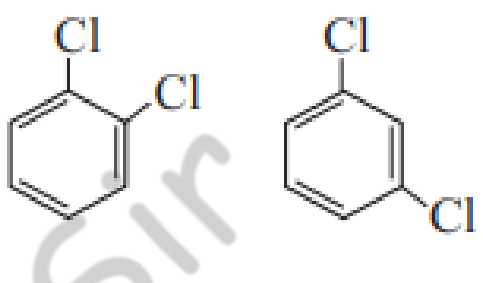
Hence, alkyl halides though moderately polar are immiscible with water

Aryl halides are also **insoluble in water** but soluble in organic solvents.

If aryl halides are not modified by presence of any other functional group, they show properties similar to corresponding alkyl halides.

The isomeric dihalobenzenes have nearly the same boiling points, but melting points of these isomers show variation.

Melting point of para isomer is quite high compared to that of ortho or meta isomer



b.p./K	453	446	448
m.p./K	256	249	323

This is because of its symmetrical structure which can easily pack closely in the crystal lattice. As a result intermolecular forces of attraction are stronger

Problem 10.2 Arrange the following compounds in order of increasing boiling points : bromoform, chloromethane, dibromomethane, bromomethane.

$$CH_3Cl < CH_3Br < CH_2Br_2 < CHBr_3$$

Arrange each set of compounds in order of increasing boiling points:

i. **Bromomethane, bromoform, chloromethane, dibromomethane.**

ii. 1-Bromopropane , Isopropyl bromide , 1-Bromobutane

iii. 1-Chloropropane , Isopropyl chloride , 1-Chlorobutane

The decreasing order of boiling points of alkyl halides is [EAMCET 1980; CBSE PMT 1997; BHU 1999; AIIMS 20011]

1. RF > RCl > RBr > RI
2. RBr > RCl > RCl > RF
3. RI > RBr > RCl > RF
4. RCl > RF > RI > RBr

Arrange the following compounds in-decreasing order of their boiling points

[IIT JEE 2016]

(i) CH_3Br
(ii) CH_3CH_2Br
(iii) $CH_3CH_2CH_2Br$
(iv) $CH_2CH_2CH_2CH_2Br$

(a) (i) > (ii) > (iii) > (iv)
(b) (iv) > (iii) > (ii) > (i)
(c) (i) > (iii) > (ii) > (iv)
(d) (iii) > (iv) > (i) > (ii)