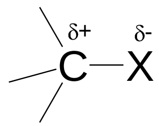
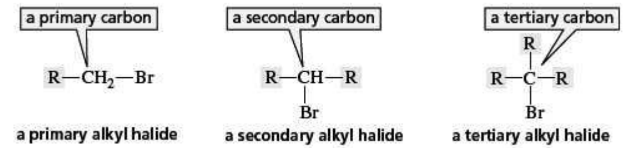
Alkyl halides

A compound with a halogen atom bonded to one of the sp^3 hybrid carbon atoms of an alkyl group



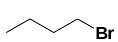
Primary, Secondary and Tertiary Alkyl halides

Alkyl: Halogen, X, is directly bonded to *sp*3 carbon



Nomenclature of Alkyl halides

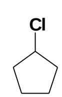
- **functional class nomenclature**
  - The alkyl group and the halide (*fluoride, chloride, bromide,* or *iodide*) are designated as separate words.
  - The alkyl group is named on the basis of its longest continuous chain beginning at the carbon to which the halogen is attached.



n-Butyl bromide

CH_3-I

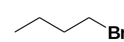
Methyl iodide



Cyclopentyl Chloride

Substitutive nomenclature

- **Substitutive nomenclature** of alkyl halides treats the halogen as a *halo-* (*fluoro-, chloro-, bromo-,* or *iodo-*) *substituent* on an alkane chain.
- The carbon chain is numbered in the direction that gives the substituted carbon the lower locant.



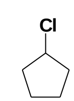
1-Bromo-butane

n-Butyl bromide

H_3C-I

Iodomethane

Methyl iodide



Chloro-cyclopentane

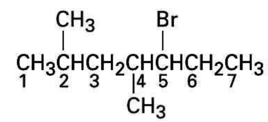
Cyclopentyl Chloride

Substitutive nomenclature

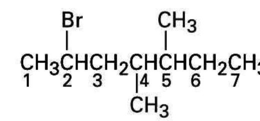
- When the carbon chain bears both a halogen and an alkyl substituent, the two substituents are considered of equal rank, and the chain is numbered so as to give the lower number to the substituent nearer the end of the chain.
- Substitutive names are preferred, but functional class names are sometimes more convenient or more familiar and are frequently encountered in organic chemistry.

Naming Alkyl Halides using Substitutive Nomenclature

- Find longest chain, name it as parent chain
  - (Contains double or triple bond if present)
  - Number from end nearest any substituent (alkyl or halogen)



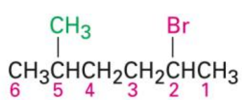
5-Bromo-2,4-dimethylheptane



2-Bromo-4,5-dimethylheptane

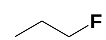
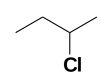
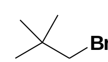
Naming Alkyl Halides using Substitutive Nomenclature

- Naming if Two Halides or Alkyl Are Equally Distant from Ends of Chain
- Begin at the end nearer the substituent whose name comes first in the alphabet

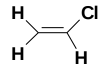
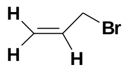
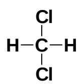


2-Bromo-5-methylhexane
(***NOT*** **5-bromo-2-methylhexane**)

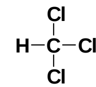
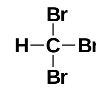
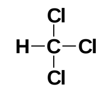
Common and IUPAC names of some Halides

Structure	IUPAC Name	Common Name
 ($CH_3CH_2CH_2F$)	1-Fluropropane	n-Propyl fluoride
 [$CH_3CH_2CH(Cl)CH_3$]	2-Chloro-butane	Sec Butyl Chloride
 [$(CH_3)_3CCH_2Br$]	1-Bromo-2,2-dimethyl-propane	Neo-pentyl bromide

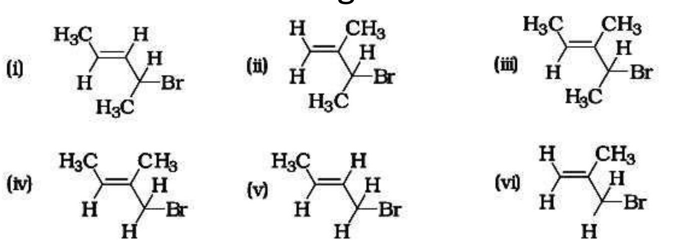
Common and IUPAC names of some Halides

Structure	IUPAC Name	Common Name
 (CH_2=CHCl)	Chloroethene	Vinyl Chloride
 (CH_2=$CHCH_2Br$)	3-Bromoethene	Allyl bromide
 (CH_2Cl_2)	Dichloromethane	Methylene Chloride

Common and IUPAC names of some Halides

Structure	IUPAC Name	Common Name
 ($CHCl_3$)	Trichloromethane	Chloroform
 ($CHBr_3$)	Tribromoethane	Bromoform
 (CCl_4)	Tetrachloromethane	Carbon tetrachloride

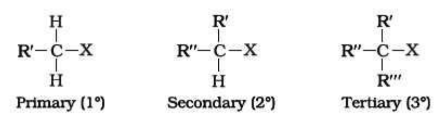
Q & A: Write IUPAC names of the following halides



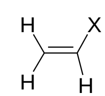
(i) 4-Bromopent-2-ene
(ii) 3-Bromo-2-methylbut-1-ene
(iii) 4-Bromo-3-methylpent-2-ene
(iv) 1-Bromo-2-methylbut-2-ene
(v) 1-Bromobut-2-ene
(vi) 3-Bromo-2-methylpropene

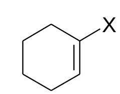
Classes of Halides

- Alkyl: Halogen, X, is directly bonded to *sp*3 carbon.



- Vinyl: X is bonded to *sp*2 carbon of alkene.





Classes of Halides

- Aryl: X is bonded to *sp*2 carbon on benzene ring.

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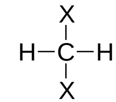
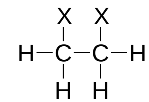
Dihalides

- Geminal dihalide: two halogen atoms are bonded to the same carbon



- Vicinal dihalide: two halogen atoms are bonded to adjacent carbons.



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Physical Properties of Alkyl halides: Bond length

- The C-X bond (where X denotes a halogen) of an alkyl halide is formed from the overlap of an SP^3 orbital of carbon with an SP^3 orbital of the halogen
- Fluorine uses a $2SP^3$ orbital, chlorine a $3SP^3$ orbital, bromine a $4SP^3$ orbital, and iodine a 5 SP^3 orbital.
- Since halogen atoms are more electronegative than carbon, the carbon halogen bond of alkyl halide is polarised; the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge.

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Physical Properties of Alkyl halides: Bond length and energy

- The electron density of the orbital decreases with increasing volume, the bond becomes longer and weaker as the size of the halogen increases.
- Since the size of halogen atom increases as we go down the group in the periodic table, fluorine atom is the smallest and iodine atom, the largest. Consequently the carbon-halogen bond length also increases from C—F to C—I.

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Physical Properties of Alkyl halides: Bond length and energy

Bond	Bond length/ppm (Å)	C-X bond energy/KJ mol^{-1}
CH3-F	139 (1.39)	452
CH3-Cl	178 (1.78)	351
CH3-Br	193 (1.93)	293
CH3-I	214 (2.14)	234

Physical Properties of Alkyl Halides: Colour and Smell

- Alkyl halides are colourless when pure. However, bromides and iodides develop colour when exposed to light.
- Many volatile halogen compounds have sweet smell.

Physical Properties of Alkyl Halides: Boiling Points

- The **boiling point (bp)** of a compound is the temperature at which the liquid form of the compound becomes a gas (vaporizes). In order for a compound to vaporize, the forces that hold the individual molecules close to each other in the liquid must be overcome.

Physical Properties of Alkyl Halides: Boiling Points

- If the molecules are held together by strong forces, it will take a lot of energy to pull the molecules away from each other, the compound will have a high boiling point.
- Boiling point of a compound depends on the strength of the attractive forces between the individual molecules.
- In contrast, if the molecules are held together by weak forces, only a small amount of energy will be needed to pull the molecules away from each other and the compound will have a low boiling point.

Physical Properties of Alkyl Halides: Boiling Points

- Both van der Waals forces and dipole–dipole interactions must be overcome in order for an alkyl halide to boil.
- As the halogen atom increases in size, the size of its electron cloud increases.
- As a result, both the van der Waals contact area and the *polarizability* of the electron cloud increase.

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Physical Properties of Alkyl Halides: Boiling Points

	Y				
	H	F	Cl	Br	I
CH_3-Y	−161.7	−78.4	−24.2	3.6	42.4
CH_3CH_2-Y	−88.6	−37.7	12.3	38.4	72.3
$CH_3CH_2CH_2-Y$	−42.1	−2.5	46.6	71.0	102.5
$CH_3CH_2CH_2CH_2-Y$	−0.5	32.5	78.4	101.6	130.5
$CH_3CH_2CH_2CH_2CH_2-Y$	36.1	62.8	107.8	129.6	157.0

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Physical Properties of Alkyl Halides: Boiling Points

- For the same alkyl group, the boiling points of alkyl halides decrease in the order:

  RI> RBr> RCl> RF.
- This is because with the increase in size and mass of halogen atom, the magnitude of van der Waal forces increases.
- The boiling points of isomeric haloalkanes decrease with increase in branching

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Physical Properties of Alkyl Halides: Boiling Points

- Methyl chloride, methyl bromide, ethyl chloride and some chlorofluoromethanes are gases at room temperature.
- Higher members are liquids or solids.

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Physical Properties of Alkyl Halides: Boiling Points

- Due to greater polarity of the carbon-halogen bond, as well as higher molecular mass as compared to the parent hydrocarbon, the intermolecular forces of attraction (dipole-dipole and van der Waals) are stronger in the halogen derivatives.
- That is why the boiling points of chlorides, bromides and iodides are considerably higher than those of the hydrocarbons of comparable molecular mass.

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Physical Properties of Alkyl Halides: Solubilities in Water

- *The haloalkanes are only very slightly soluble in water. In order for a* haloalkane to dissolve in water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules.
- Less energy is released when new attractions are set up between the haloalkane and the water molecules as these are not as strong as the original hydrogen bonds in water. As a result, the solubility of haloalkanes in water is low.

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Physical Properties of Alkyl Halides: Solubilities in Water

- In summary:
- Alkyl halides have some polar character, but only the alkyl fluorides have an atom that can form a hydrogen bond with water.
- Alkyl fluorides are the most water soluble of the alkyl halides.
- The other alkyl halides are less soluble in water

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Physical Properties of Alkyl Halides: Solubilities 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

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Physical Properties of Alkyl Halides: Solubilities in Organic Solvents

- However, haloalkanes tend to dissolve in organic solvents because the new intermolecular attractions between haloalkanes and solvent molecules have much the same strength as the ones being broken in the separate haloalkane and solvent molecules.

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Densities of Alkyl Halides

- Alkyl monofluorides and monochlorides less dense than water.
- Alkyl dichlorides, mono bromides, and monoiodides more dense than water i.e. Bromo, iodo and polychloro derivatives of hydrocarbons are heavier than water.
- The density increases with increase in number of carbon atoms, halogen atoms and atomic mass of the halogen atoms

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Uses of Alkyl Halides

- Solvents - degreasers and dry cleaning fluid
- Reagents for synthesis of other compounds
- Halothane $CF_3CHClBr$, is an Anesthetic
- $CHCl_3$ used originally (toxic and carcinogenic)
- Freons, chlorofluorocarbons or CFC's are used in fridges but are harmful to ozone layer. CF_2Cl_2, now replaced with CF_2CHCl, not as harmful to ozone layer (i.e. it is ozone friendly).
- Many Pesticides including DDT contain halogens.

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Uses of Alkyl Halides

- Propellants:
  - One major use of CFCs has been as propellants in aerosol inhalers for drugs used to treat asthma.
  - The conversion of these devices and treatments from CFC to halocarbons that do not have the same effect on the ozone layer is well under way.

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Uses of Alkyl Halides: Fire extinguishing

- Definition of halons
  - A class of simple hydrocarbon derivatives in which bromine, chlorine and fluorine are substituted for some or all of the hydrogen atoms.
  - These compounds are used mainly as fire-extinguishing gases, the two best known being Halon 1211 (CF_2BrCl) and Halon 1301 (CF_3Br).
  - The chemicals are long-lived in the troposphere and are implicated in the depletion of the ozone layer.

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Uses of Alkyl Halides (halons): Fire extinguishing

- At high temperatures, halons decompose to release halogen atoms that combine readily with active hydrogen atoms, quenching the flame propagation reaction even when adequate fuel, oxygen and heat remains.
- Halons are able to "poison" the fire at much lower concentrations than are required by fire suppressants using the more traditional methods of cooling, oxygen deprivation, or fuel dilution.

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Uses of Alkyl Halides: Fire extinguishing

- For example, Bromotrifluoromethane (Halon 1301, $CBrF_3$) total flooding systems are typically used at concentrations no higher than 7% volume per volume (v/v) in air, and can suppress many fires at 2.9% v/v.
- By contrast, carbon dioxide fire suppression flood systems are operated from 34% concentration by volume (surface-only combustion of liquid fuels) up to 75% (dust traps).

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Uses of Alkyl Halides: Fire extinguishing

- Carbon dioxide can cause severe distress at concentrations of 3 to 6%, and has caused death by respiratory paralysis in a few minutes at 10% concentration.
- Bromotrifluoromethane (Halon 1301) causes only slight giddiness at its effective concentration of 5%, and even at 15% persons remain conscious but impaired and suffer no long term effects.

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