

1. Introduction and Classification

Haloalkanes (alkyl halides) and haloarenes (aryl halides) are formed by the replacement of hydrogen atom(s) in an aliphatic or aromatic hydrocarbon by halogen atom(s) (F, Cl, Br, I).

Classification based on the nature of the C-X bond:

- **Compounds containing sp^3 C-X bond:**
 - **Alkyl halides ($R-X$):** The halogen is attached to an alkyl group. They are sub-classified as primary (1°), secondary (2°), or tertiary (3°) depending on the carbon atom to which the halogen is attached.
 - **Allylic halides:** The halogen is bonded to an sp^3 -hybridized carbon adjacent to a carbon-carbon double bond ($C=C-C-X$).
 - **Benzylic halides:** The halogen is bonded to an sp^3 -hybridized carbon attached to an aromatic ring.
- **Compounds containing sp^2 C-X bond:**
 - **Vinylic halides:** The halogen is bonded to an sp^2 -hybridized carbon of a carbon-carbon double bond ($C=C-X$).
 - **Aryl halides (Haloarenes):** The halogen is bonded directly to the sp^2 -hybridized carbon of an aromatic ring.

2. Nomenclature

- **Common Names:** Alkyl group name + halide (e.g., n-propyl bromide, isobutyl chloride).
- **IUPAC Names:** Halogen is treated as a substituent. The prefix *halo-* (fluoro, chloro, bromo, iodo) is attached to the parent

alkane/arene name with proper numbering to give the lowest locant to the halogen.

- **Example:** $CH_3CH_2CH_2Br$ is 1-Bromopropane.
- **Example:** Benzene ring with Cl is Chlorobenzene. If two halogens are present, numbering dictates the position (e.g., 1,2-Dichlorobenzene).

3. Nature of the C-X Bond

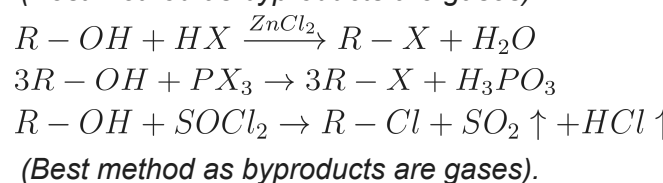
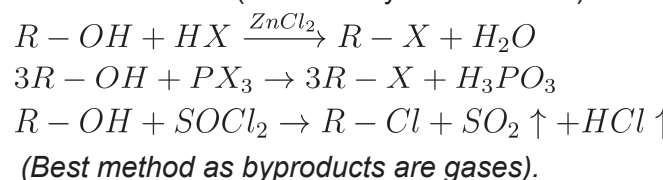
Halogen atoms are more electronegative than carbon, making the carbon-halogen bond polarized. The carbon atom bears a partial positive charge (δ^+) and the halogen a partial negative charge (δ^-).

- **Bond Length:** Increases as the size of the halogen increases:
 $C-F < C-Cl < C-Br < C-I$.
- **Bond Enthalpy:** Decreases as bond length increases:
 $C-F > C-Cl > C-Br > C-I$.
- **Dipole Moment:** Generally decreases down the group, but the dipole moment of CH_3Cl is slightly higher than CH_3F due to the much larger bond length of C-Cl compensating for the lower electronegativity of Cl.

4. Methods of Preparation

A. Preparation of Haloalkanes

1. **From Alcohols:** (Most widely used method)



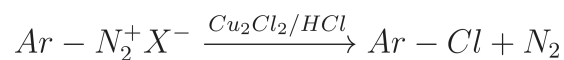
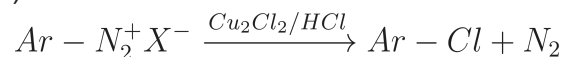
2. **From Hydrocarbons:**

- **Free radical halogenation of alkanes:** Yields a complex mixture of isomeric mono- and polyhaloalkanes.
- **Electrophilic addition to alkenes:** Follows Markovnikov's rule.
 $R-CH=CH_2 + HX \rightarrow R-CH(\lambda)CH_2X$
 $R-CH=CH_2 + HX \rightarrow R-CH_2CH(\lambda)X$

3. Halogen Exchange:

- **Finkelstein Reaction (For Alkyl Iodides):**
 $R-X + NaI \xrightarrow{\text{dry acetone}} R-I + NaX$
 (Where X = Cl, Br)
- **Swarts Reaction (For Alkyl Fluorides):** Heating an alkyl chloride/bromide in the presence of a metallic fluoride like AgF , Hg_2F_2 , or CoF_3 .

then treating it with Cuprous halide (Cu_2X_2).



5. Physical Properties

- **Melting and Boiling Points:** Higher than parent hydrocarbons due to greater polarity and molecular mass (stronger dipole-dipole and van der Waals forces).
 - For the same alkyl group:
 $R-I > R-Br > R-Cl > R-F$
 - For isomeric haloalkanes: Boiling point *decreases* with an increase in branching (due to decreased surface area and weaker van der Waals forces).
 - For isomeric dihalobenzenes: para-isomers have higher melting points than ortho/meta isomers due to symmetry, which allows them to fit better in the crystal lattice.
- **Density:** Increases with the number of carbon atoms, halogen atoms, and the atomic mass of the halogen.
- **Solubility:** Haloalkanes are heavily polar but are **insoluble in water** because they cannot form hydrogen bonds with water molecules, nor can they break the existing hydrogen bonds between water molecules. They are soluble in organic solvents.



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B. Preparation of Haloarenes

1. **Electrophilic Substitution:** Direct halogenation of benzene using X_2 in the presence of Lewis acids ($FeCl_3$, $AlCl_3$).
2. **Sandmeyer's Reaction:** Converting a primary aromatic amine to a diazonium salt,

6. Chemical Properties

A. Reactions of Haloalkanes

1. **Nucleophilic Substitution Reactions (S_N):** A nucleophile (Nu^-) replaces the halogen atom.
 - **S_N2 Mechanism (Substitution Nucleophilic Bimolecular):** Occurs in a single step via a transition state.

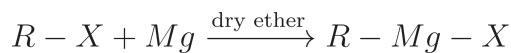
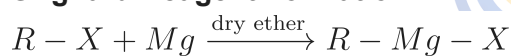
The nucleophile attacks from the back, leading to **inversion of configuration**. Order of reactivity: $1^\circ > 2^\circ > 3^\circ$ (due to steric hindrance).

- **S_N1 Mechanism (Substitution Nucleophilic Unimolecular):** Occurs in two steps. Step 1 forms a planar carbocation intermediate. Step 2 involves nucleophilic attack from either side, leading to **racemization**. Order of reactivity: $3^\circ > 2^\circ > 1^\circ$ (driven by carbocation stability).

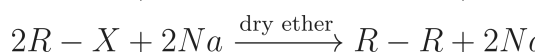
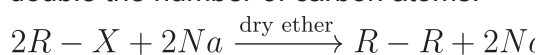
- Elimination Reactions (β -elimination):** When heated with alcoholic KOH, a hydrogen atom from the β -carbon and the halogen from the α -carbon are eliminated to form an alkene. Follows **Zaitsev's Rule** (the more highly substituted alkene is the major product).

- Reaction with Metals:**

- **Grignard Reagent Formation:**



- **Wurtz Reaction:** Two alkyl halides react with sodium in dry ether to form a symmetrical alkane with double the number of carbon atoms.



B. Reactions of Haloarenes

Haloarenes are **extremely less reactive** towards nucleophilic substitution due to resonance stabilization (partial double bond character of C-X bond) and the sp^2 hybridized state of the carbon atom.

- Electrophilic Substitution Reactions:** The halogen atom is ortho-para directing (due to resonance, +R effect) but deactivating (due to inductive effect, -I effect).
- Reaction with Metals:**

- **Wurtz-Fittig Reaction:** A mixture of an alkyl halide and aryl halide gives an alkylarene.
- **Fittig Reaction:** Two aryl halides react with sodium to form a diaryl (biphenyl).



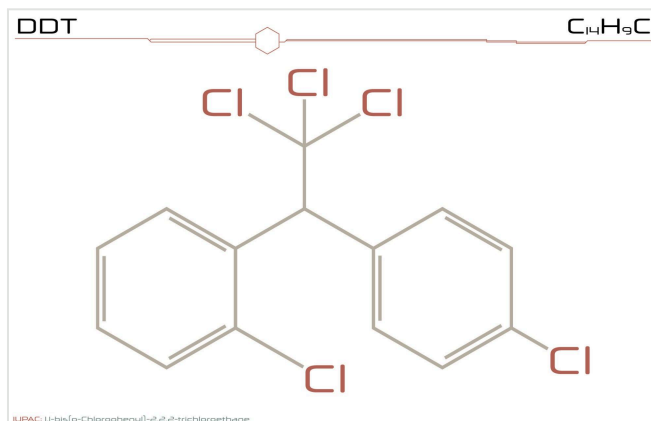
7. Stereochemical Aspects of S_N Reactions

- **Plane Polarized Light:** Light vibrating in only one plane.
- **Optical Activity:** The ability of certain compounds to rotate the plane of polarized light.
 - **Dextrorotatory (d or $+$):** Rotates light to the right (clockwise).
 - **Laevorotatory (l or $-$):** Rotates light to the left (anticlockwise).
- **Chirality:** A molecule that is non-superimposable on its mirror image is chiral (optically active). It usually contains an asymmetric carbon atom (bonded to four different groups).
- **Enantiomers:** Non-superimposable mirror image isomers. They have identical physical

properties but rotate plane-polarized light in opposite directions.

- **Retention:** The spatial arrangement of bonds to an asymmetric center remains the same during a reaction.
- **Inversion:** The spatial arrangement is inverted (like an umbrella turning inside out), characteristic of S_N2 reactions.
- **Racemization:** A mixture containing equal amounts of enantiomers (*d* and *l*) has zero optical rotation. This is called a racemic mixture, characteristic of S_N1 reactions.

toxicity to fish, non-biodegradability, and tendency to accumulate in the food chain (biomagnification).



8. Important Polyhalogen Compounds

- **Dichloromethane (CH_2Cl_2):** Used as a solvent and paint remover. Harms the central nervous system.
- **Chloroform ($CHCl_3$):** Used as a solvent. Slowly oxidizes in air in the presence of light to form an extremely poisonous gas, phosgene ($COCl_2$). It is stored in closed dark colored bottles.
- **Iodoform (CHI_3):** Used formerly as an antiseptic, but replaced due to its objectionable smell. The antiseptic property is due to the liberation of free iodine.
- **Carbon Tetrachloride (CCl_4):** Used in fire extinguishers (under the name Pyrene) and as a solvent. Exposure causes liver damage and ozone layer depletion.
- **Freons (Chlorofluorocarbons/CFCs):**
 E.g., Freon-12 (CCl_2F_2). Used as refrigerants and aerosol propellants. Highly responsible for ozone layer depletion in the stratosphere.
- **DDT (p,p'-Dichlorodiphenyltrichloroethane):**
 The first chlorinated organic insecticide. Banned in many countries due to its high