Chapter 9

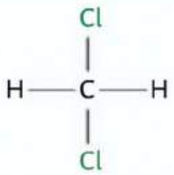
Haloalkanes and Haloarenes

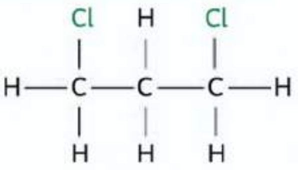
Classification & Nomenclature of Haloalkanes & Haloarenes

What are Haloalkanes and Haloarenes?

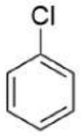
When a hydrogen atom in an aliphatic or aromatic hydrocarbon is replaced by halogen atoms then the compounds are termed **haloalkanes and haloarenes**. If a hydrogen atom is replaced from an aliphatic hydrocarbon by a halogen atom the resulting compound formed is called **haloalkane**. It is also known as **alkyl halide** and **halogenalkane**.

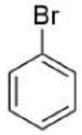

bromomethane

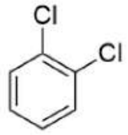

dichloromethane

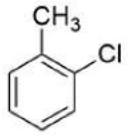

1,3-dichloropropane

However, if a hydrogen atom is replaced from an aromatic hydrocarbon by a halogen atom the resulting compound formed is known as **haloarene**. It is also known as **aryl halide or halogenoarene.** In a haloalkene (R – X), X represents the halogen group. It is attached to an sp_3 hybridized atom of an alkyl group whereas in haloarene (Ar – X) the halogen is attached to an sp_2 hybridized atom of an aryl group.


Chlorobenzene


Bromobenzene


1,2-dichlorobenzene


2-chlorotoluene

Classification of Haloalkanes and Haloarenes

They can be classified on the basis of:

- Number of Halogen atoms
- Compounds with sp^3 C—X Bond

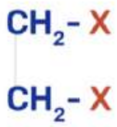
- Compounds having the sp^2 C-X Bond

1) Number of Halogen Atoms:

On the basis of the number of hydrogen, they can be divided into mono, di or poly (tri, tetra, and so on) compounds of haloalkanes and haloarenes. It is named depending on the number of halogen atom these compounds contain in their structures. For example,

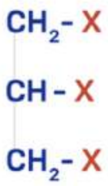
C_2H_5-X

(Monohaloalkane)



$$\begin{array}{l} CH_2-X \\ | \\ CH_2-X \end{array}$$

(Dihaloalkane)



$$\begin{array}{l} CH_2-X \\ | \\ CH-X \\ | \\ CH_2-X \end{array}$$

(Trihaloalkane)

2) Compounds with sp^3 C—X Bond:

These compounds can be further divided into three types. They are:

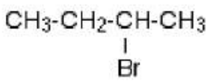
i) Alkyl Halides/Haloalkanes (R – X)

In this class, the halogen atom is attached to an alkyl group. The general homologous formula followed by this class is $C_nH_{2n+1}X$. They are further classified into mainly three types on the basis of the carbon atom to which the carbon-bearing halogen (X) atom is bonded- primary, secondary, and tertiary. This classification is based on the nature of the carbon atom to which the halogen is attached.

$CH_3-CH_2-CH_2-CH_2-Br$

1-bromobutane

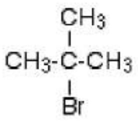
(primary)



$$CH_3-CH_2-\underset{\underset{Br}{|}}{CH}-CH_3$$

2-bromobutane

(secondary)



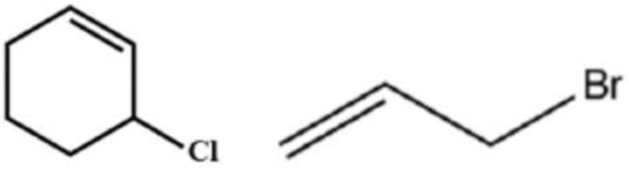
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3$$

2-bromo-2-methylpropane

(tertiary)

ii) Allylic Halides

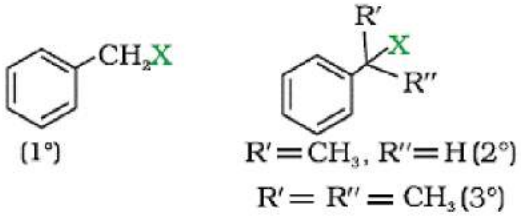
This classification of compounds is formed by bonding of halogen group having sp_3 hybridized carbon atom present next to a carbon-carbon double bond structure (C=C). The carbon-carbon double bond structure is also known as allylic carbon. Thus, the name allylic halides.



Allylic halide

(iii) Benzylic Halides

This type of compounds is formed when a halogen atom is attached to an sp_3 hybridized carbon atom. The sp_3 hybridized carbon atom should be present next to an aromatic ring in order to form benzyl halides.

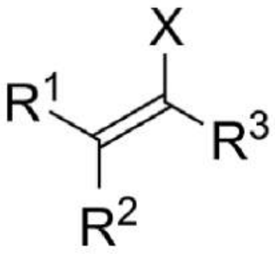


3) Compounds Having the sp^2 C-X Bond

This class of compounds includes vinyl halides and aryl halides.

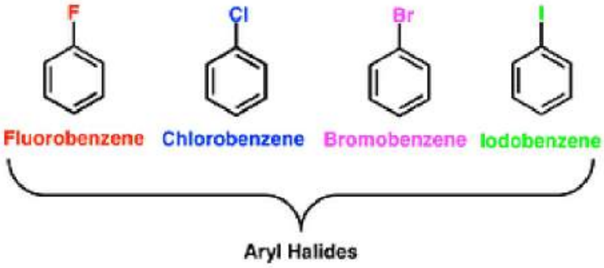
i) Vinyl Halides

These compounds are formed when a halogen atom is attached to an sp_2 hybridized carbon atom present next to a carbon-carbon double bond (C=C).



ii) Aryl Halides

This class of compounds is formed when the halogen group is bonded to an sp_2 - hybridized atom of carbon in an aromatic ring.



Nomenclature Of Haloalkanes and Haloarenes

- Initially, there was no proper system for the naming of compounds. Mostly there were trivial names that were used depending upon the country and region. These trivial names were based on the discoverer or the nature of the compound or its place of discovery.
- The system of trivial names was not standard and led to much confusion, thus raising the need for a standard system for the naming of organic compounds. IUPAC came up with a set of rules that are used universally for the naming of organic compounds.

There are two names associated with every compound:

Common name: It is different from a trivial name in the sense that it also follows a rule for its nomenclature.

IUPAC name: The IUPAC (International Union of Pure and Applied Chemistry) naming system is the standard naming system that chemists generally use.

Rules of Nomenclature

1. Find the longest carbon chain.
2. Number the longest carbon chain such that the carbon atom(s) to which the halogen(s) is/are attached get the lowest number(s).
3. Multiple halogen atoms are labelled with the Greek numerical prefixes such as di, tri, tetra, to denote the number of identical halogen atoms attached to a carbon atom. If more than one halogen atoms attached to the same carbon atom, the numeral is repeated that much time.
4. In case, different types of halogens are attached, they are named alphabetically.
5. The position of the halogen atom is indicated by writing the position and name of the halogen just before the name of the parent hydrocarbon.

Methodology of Writing Name

- First, write the root word for the parent hydrocarbon (depending upon the no. of carbon atoms in the longest carbon chain).
- Secondly, calculate the number of halogen atoms present. If there are multiple halogen atoms present, then arrange the halogens alphabetically in the prefix, labelling them with their respective positions. But, if the same halogen atom is present more than once then use the prefixes di, tri, tetra, etc.

Nomenclature of Haloalkanes

Alkyl halides are named in two ways. In the common system, the alkyl group is named first followed by an appropriate word chloride, bromide, etc. The common name of an alkyl halide is always written as two separate words. In the IUPAC system, alkyl halides are named haloalkanes. The other rules followed in naming compounds is:

- Select the longest chain of carbon atoms containing the halogen atom.
- Number the chain to give the minimum number to the carbon carrying halogen atom.
- If multiple bonds (double or triple bond) is present, then it is given the preference in numbering the carbon chain.
- The IUPAC name of any halogen derivative is always written as one word.

Compound	Common Name	IUPAC Name
CH_3-Cl	Methyl Chloride	Chloromethane
CH_3-CH_2-Br	Ethyl bromide	Bromoethane
CH_3-$C(CH_3)_2$-Br	tert-Butyl bromide	2-Bromo-2-methylpropane
$CHCl_3$	Chloroform	Trichloromethane
CH_3-$CH(Br)_2$	Ethylidene bromide	1,1-Dibromoethane
CH_2=CH-CH_2-I	Allyl iodide	3-Iodoprop-1-ene

Nomenclature of Haloarenes

- Aryl halides are named by prefixing "halo" to the name of the parent aromatic hydrocarbon.
- If there is more than one substituent on the ring then the relative positions of the substituents are indicated by mathematical numerals.

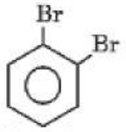
- In the common system, the relative position of two groups is shown by prefixes ortho, meta or para.

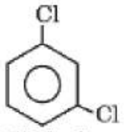
The common and IUPAC names of some representative haloarenes are given below:

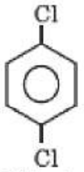

Chlorobenzene

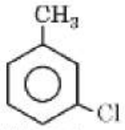

Bromobenzene

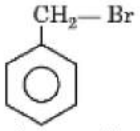

Iodobenzene


1,2-Dibromobenzene
(*ortho*-Dibromobenzene)


1, 3-Dichlorobenzene
(*meta*-Dichlorobenzene)

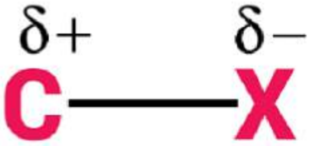

1,4-Dichlorobenzene
(*para*-Dichlorobenzene)


3-Chlorotoluene
(*meta*-Chlorotoluene)


Phenylbromomethane
(Benzyl bromide)

Nature of C-X Bond

It is essential to understand the nature of the C-X bond because it determines the reactivity of the compound having this kind of bond. The C-X bond is highly polar in nature because halogen atoms are electronegative and the carbon atom is electropositive. The difference in electronegativity results in the withdrawal of electron density from the sigma bond pair towards the halogen atom.
This result in the polarization of the C-X bond is polarized in a manner that the carbon atom develops a partial positive charge whereas the halogen atom in the bond develops a partial negative charge. Therefore, the carbon-halogen bond of an alkyl halide is polarized. This is represented as:



$$\overset{\delta+}{C}—\overset{\delta-}{X}$$

The electronegativity of the halogen group varies from one another. The size increases as we go down the group so the fluorine atom is the smallest one in the group and the iodine atom is the largest. Thus, fluorine has the highest electronegativity followed by chlorine then bromine and finally iodine.

Electronegativity of X: F(3.98) > Cl(3.16) > Br(2.96) > I(2.66). However, the electronegativity of the carbon atom is 2.55. The electronegativity difference between C-F is maximum. Therefore, C-F is the most polar among all of them.

Parameters Related to Nature of C-X Bond

(i) Bond Length (A_0)

The nature of the C-X bond depends upon the bond length between the carbon atom and halogen group. We have previously mentioned that size of the halogen group increases as we move down the group (F < Cl < Br < I). Consequently, the difference in the C-F bond will be the smallest and the C-I bond will be the largest.

(ii) Bond Enthalpy Order

The nature of the C-X bond depends upon bond enthalpy order. The size of the carbon and fluorine atom is very similar so the orbitals overlap (2p-2p overlap) into one another. This leads to the formation of a very strong bond. In C-I the atomic size of iodine is very large in comparison to carbon atom so the orbital interaction is very weak.

This results in the formation of weak bond strength. We can conclude that less the bond length stronger will be the bond. Hence, the bond length of C-F is 1.39 A^0. The stronger the bond, the amount of energy required increases to break that bond. Therefore, C-F has the highest bond enthalpy. The bond enthalpy order is: $\mathbf{C-F > C-Cl > C-Br > C-I}$

(iii) Dipole Moment

Dipole moment helps to calculate the polarity of a chemical bond within a molecule. It occurs due to the separation of positive and negative charges. It is the product of both charge and the distance between them. Bond dipole (μ) is given by the formula $\mathbf{\mu = q \times d}$

The **order of dipole moment** in C-X is $CH_3Cl > CH_3F > CH_3Br > CH_3I$.

Dipole moments of haloalkanes are:

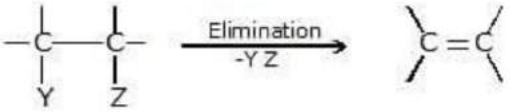
1. CH3F – 1.847D,
2. CH_3Cl – 1.860 D,
3. CH_3Br – 1.830 D,
4. CH_3I – 1.636 D

Can you notice the abnormal order of the dipole moment in the case where $CH_3Cl > CH_3F$? Even though fluorine is more electronegative than Chlorine but the C-F bond (139 pm) is shorter than the C-Cl bond C – Cl (178 pm). Thus, the dipole moment will be lower in the case of CH_3F in comparison to CH_3Cl.

Chemical Reaction: Elimination Reactions & Reaction with Metals

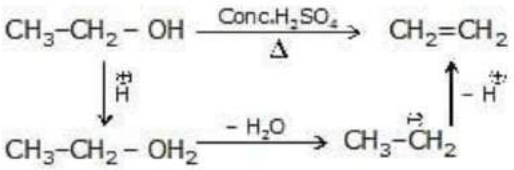
Elimination Reactions

In an elimination reaction, two atoms or groups (YZ) are removed from the substrate with the formation of a pi bond.



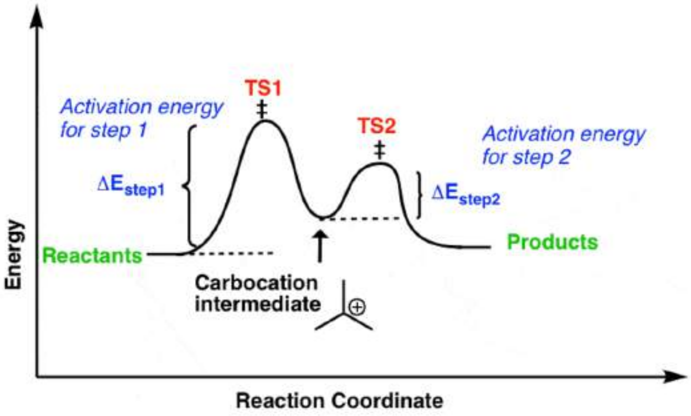
depending on the reagents and conditions involved, elimination may be a first-order (E_1) or second-order (E_2).

Dehydration of Alcohol (E_1)

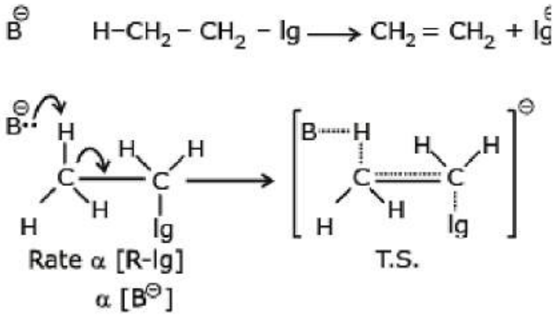


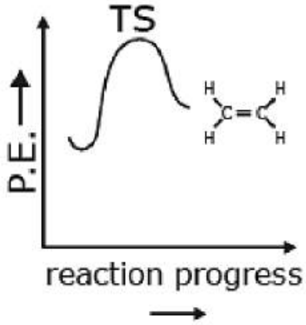
Characteristics of E_1 reaction

1. It is a unimolecular, two-step process
2. It is a first-order reaction
3. Reaction intermediate is carbocation, so rearrangement is possible
4. In the second step, a base abstracts a proton from the carbon atom adjacent to the carbocation and forms alkene.
5. Kinetics → Rate ∝ [Substrate]
   Rate = k[Substrate]



E_2- elimination:





Bimolecular reaction, second-order kinetic:

1. Leaving group leads when the base is taking proton from adjacent carbon.
2. It is a single step reaction
3. It shows elemental as well as kinetic isotopic effect with l_g as well as at b-position.
4. Normally Saytzaff product is major.
5. Transition state mechanism therefore rearrangement is not possible.
6. The orientation of the proton & leaving group should be antiperiplanar for E2.
7. **Positional orientation of elimination:** In most E_1 and E_2 eliminations gives two or more possible elimination products, the product with the most highly substituted double bond will predominate. This rule is called the Saytzeff or Zaitsev rule (i.e., most stable alkene will be the major product)
8. E_2-elimination is favour by:
    a. Strong base (RO^-, Alc. KOH)
    b. Polar aprotic solvent.
    c. High conc. of base.
    d. High temperature

Reactivity towards E_2: R - I > R - Br > R - Cl > R – F

Question 1: Predict the elimination products of the following reactions.

(a) Sec. butyl bromide + $\overset{+}{Na}O\overset{-}{E}t \xrightarrow{\Delta}$

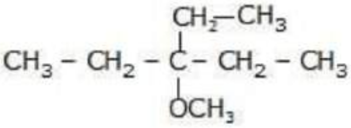
(b) 3-Bromo-3-ethylpentane + $CH_3OH \longrightarrow$

(c) 2-Bromo-3-ethylpentane + MeONa $\xrightarrow{\Delta}$

(d) 1-Bromo-2-methylcyclohexane + EtONa $\xrightarrow{\Delta}$

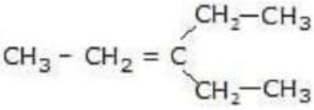
Sol. (a) $CH_3 - CH = CH - CH_3$

(b)

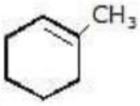


$CH_3 - CH_2 - \underset{OCH_3}{\overset{CH_2-CH_3}{C}} - CH_2 - CH_3$

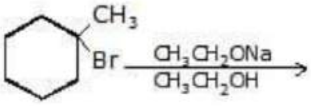
(c)



(d)



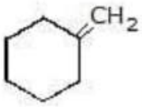
Question 2:



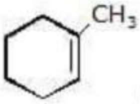
major + minor

Write the structure of major and minor product.

Sol.



(minor)



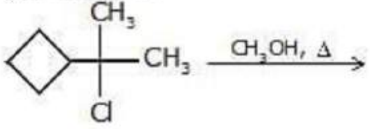
(major)

Comparison of E_1 and E_2 elimination:

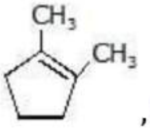
Promoting factors	**E_1**	**E_2**
(i) Base	Weak base	Strong base required
(ii) Solvent	Good ionizing solvent	Wide variety of solvent
(iii) Substrate	3° > 2° > 1°	3° > 2° > 1°

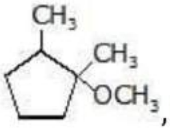
(iv) Leaving group	Better one required	Better one required
Characteristics		
(i) Kinetics	K [R- X], I order	K [R - X] [Base], IIst order
(ii) Orientation	Saytzeff alkene	Saytzeff alkene
(iii) Stereochemistry	No special geometry is required	transition state must be coplanar

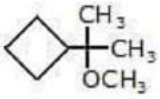
Question 3:



P + Q + R

Sol. P is 

, Q is 

, R 

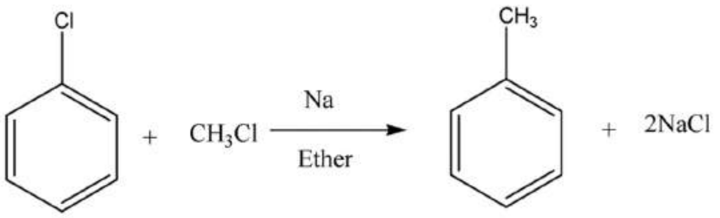
Question 4: Arrange the compounds of each set in order of reactivity towards dehydrohalogenation by a strong base

(a) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane
(b) 1-Bromo-3-methylbutane, 2-bromo-2-methylbutane-2-Bromo-3-methylbutane
(c) 1-Bromobutane,1-Bromo-2,2-dimethylpropane, 1-bromo-2-methylbutane, 1-Bromo-3-methylbutane

Reactions with Metals Haloarenes undergo few reactions with metals. Two primary reactions are:

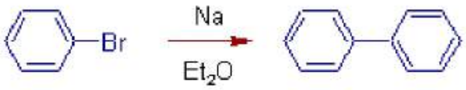
- Wurtz-Fittig Reaction
- Fittig Reaction

Wurtz-Fittig Reaction:
In this reaction, a mixture of alkyl halide reacts with an aryl halide in the presence of dry ether and sodium. The resultant product is alkyl arene.



Fittig Reaction:

In this reaction, a mixture of haloarenes reacts with sodium in the presence of dry ether. The resultant product is diaryl.



Polyhalogen Compounds

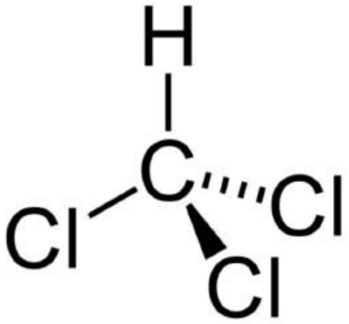
What is Polyhalogen Compounds?

The hydrocarbons or any carbon compounds containing more than one halogen atom (group 17 elements of the modern periodic table) are known as **polyhalogen compounds.**

Many of these compounds are useful in industry and agriculture. Some notable polyhalogen compounds are described below:

1. Trichloromethane (Chloroform), $CHCl_3$

Chloroform, also referred to as trichloromethane is an organic compound. Chloroform is an organic chemical compound initially employed as an ideal anaesthetic. It was first prepared in 1831. The chemical formula is CHCl3. It is a colourless, sweet-smelling dense liquid produced on a large scale.

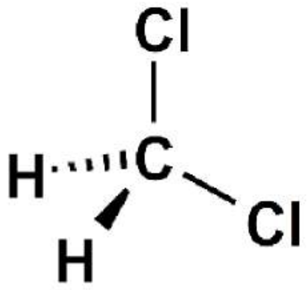


Uses of Chloroform:

1. Used as an anaesthetic and used in dentistry during root canal procedures.
2. The spectrum of pure chloroform is used as the reference or background, and pure cholesterol powder or cholesterol extract from milk products is dissolved in chloroform and used for FTIR analysis.
3. Chloroform was utilized in the past as an extraction dissolvable for fats, greases, oils, and different items; as a laundry spot.
4. Used as an indirect food additive in food packaging materials for adhesive components and as a component of food contact materials.

2. Dichloromethane, CH_2Cl_2

Dichloromethane is a geminal organic compound and is also called Methylene chloride or Methylene dichloride. It can be obtained naturally from oceanic sources, macroalgae, volcanoes, and wetlands. The majority of Methylene dichloride in the environment is due to industrial emissions. The chemical formula of Dichloromethane is CH_2Cl_2.

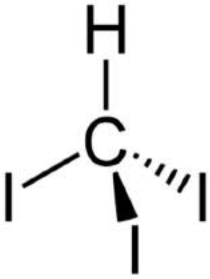


Uses of Dichloromethane:

1. Dichloromethane is used as a solvent in food technology
2. It is used in aerosol formulations.
3. It is an ethane foam blowing agent.
4. Used as a solvent in the manufacturing of pharmaceutical products.
5. CH_2Cl_2 is used as a degreasing agent.
6. Used in the manufacturing of electronics.

3. Iodoform

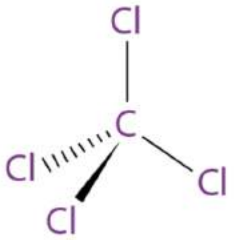
Iodoform which is also called triiodomethane is a yellow crystalline solid. It is insoluble in water but soluble in solvents like ethanol, chloroform, and ether. It is hydrolyzed to give sodium methanoate (sodium formate) when treated with an aqueous sodium hydroxide solution.



Uses of Iodoform:
Iodoform was used earlier as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to the iodoform itself. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

4. Tetrachloromethane (Carbon Tetrachloride)

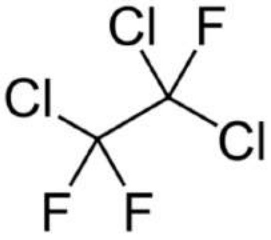
- It is a colourless liquid with a "sweet" smell that can be detected at low levels. The molecular formula of carbon tetrachloride is CCl4.
- It is used in the manufacturing of refrigerants, as a cleaning agent and was also used as a fire extinguisher.
- Medically, it is one of the most potent hepatotoxins (toxic to the liver) and is widely used in scientific research to evaluate hepatoprotective agents.
- When carbon tetrachloride is released into the air, it rises in the atmosphere and depletes the ozone layer. Depletion of the ozone layer is believed to increase human exposure to ultraviolet rays, leading to increased skin cancer, eye diseases and disorders, and possible disruption of the immune system.



5. Freons (CFCs)

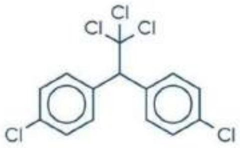
- Freons are the chlorofluorocarbon compounds of methane and ethane. The chlorofluorocarbon compounds refer to the compounds having mainly carbon, fluorine, and chlorine. Freons is the brand name for this group of compounds coined by DuPont.

- They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases.
- Freon 12 or R-12 (CCl2F2) is one of the most common representatives of this group. It is manufactured from tetrachloromethane by Swarts reaction.
- These are usually produced for aerosol propellants, refrigeration and air conditioning purposes.



6. DDT (p, p'-Dichlorodiphenyltrichloroethane)

- It is a colourless, crystalline, tasteless and almost odourless organochloride known for its insecticidal
- It was the first chlorinated organic insecticides prepared in 1873. But in 1939, Paul Miller identified the different uses of DDT. Paul Muller was awarded the Nobel Prize in Medicine and Physiology in 1948 for this discovery.
- It became popular because of its effectiveness against the mosquito that spreads malaria and lice that carry typhus.
- But due to the ill-effects of DDT such as chemical instability and fat solubility, it got banned in many countries



DDT

Methods of Preparation of Haloalkane & Haloarenes

Haloalkanes and Haloarenes can be prepared from other organic compounds by numerous methods. Different methods of preparation include **conversion of alcohols to alkyl halides**, **the addition of halogens to alkenes**, and **hydrohalogenation of alkenes**. The preparation techniques were so reliable and efficient that they became an inevitable part of industrial chemistry.

There are primarily 4 different types of preparation techniques of Haloalkanes and Haloarenes.

1. Alcohols
2. Hydrocarbons
3. Alkenes by addition of hydrogen halides and halogens
4. Halogen exchange reaction.

So let's learn about the **methods of preparation of Haloalkanes and Haloarenes.**

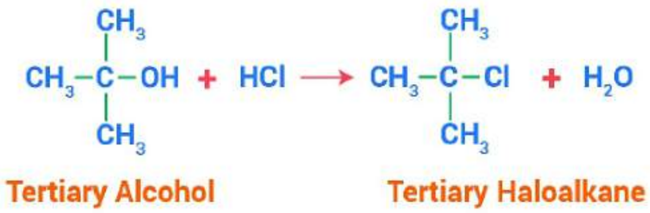
Preparation of Haloalkanes:

1. From Alcohols:

Alkyl halides can easily be prepared from alcohols upon the addition of halides. In this reaction, the hydroxyl group of alcohol is replaced with the halogen atom attached to the other compound involved. This reaction requires a catalyst for primary and secondary alcohols whereas it doesn't require any catalyst for tertiary alcohols.

The general reaction looks like this: $ROH + HX \rightarrow RX + H_2O$

a. Reaction with HCl:



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH + HCl \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl + H_2O$$

b. Reaction with Bromine: $CH_3CH_2OH + HBr \rightarrow CH_3CH_2Br + H_2O$

c. Reaction with Phosphorous Halide:

$$3CH_3CH_2CH_2OH + PCl_3 \rightarrow 3CH_3CH_2CH_2Cl + H_3PO_3$$

d. Reaction with Thionyl Chloride:

$$CH_3CH_2CH_2OH + SOCl_2 \rightarrow CH_3CH_2CH_2Cl + SO_2 + HCl$$

2. From Alkenes:

The addition of hydrogen halides to alkenes follows either Markovnikov's rule or exhibit the Kharash effect. All the electrophilic addition reactions of alkenes following the Markovnikov rule are known as Markovnikov addition reactions. A general example of such reaction is given below:

$$\underset{\text{Alkene}}{R-CH=CH_2}+H-X\rightarrow \underset{\text{Hydrogen halide}}{R-CH_2}-CH_2X \text{ OR } R-\underset{\text{Alkyl halide}}{CH_2X-CH_2}$$

$$\underset{\text{Symmetric alkene}}{R-CH=CH-R}+\underset{\text{Hydrogen chloride}}{H-Cl}\rightarrow \underset{\text{Alkyl chloride}}{R-CH_2-CHCl-R}$$

$$\underset{\text{Unsymmetric alkene}}{R-CH=CH-R'}+H-X\rightarrow \underset{\text{Hydrogen chloride}}{R-CH_2-CHX-R'}\rightarrow \underset{\text{Alkyl halide}}{R-CHX-CH_2-R'}$$

3. From Free Radical Halogenation:

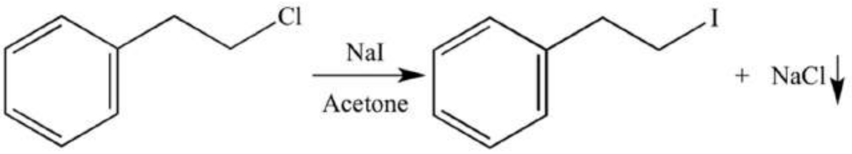
In free radical halogenation, we get a mixture of mono-substituted, di-substituted, tri-substituted, and even tetra-substituted halo-alkanes (alkyl halides). Since we require only one type of alkyl halide and not all in the form of a mixture, So this method is not used.

$$CH_3CH_2CH_2CH_3\xrightarrow{Cl_2/UVlight}CH_3CH_2CHClCH_3+CH_3CH_2CH_2CH_2Cl$$

4. From Halogen Exchange:

a. Finkelstein Reaction:

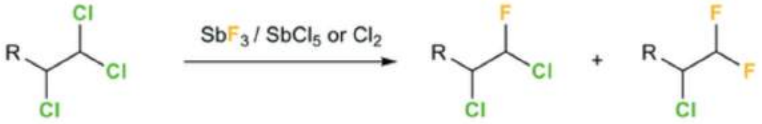
In this reaction, an alkyl chloride or alkyl bromide reacts with sodium iodide in acetone to form alkyl iodides.



The solubility difference of alkyl halides in acetone is used for driving the reaction in the forward direction. We know that sodium iodide is soluble in acetone but NaCl or NaBr are insoluble. Therefore, they precipitate out in the reaction which is easy to remove from the reaction mixture.

b. Swartz Reaction:

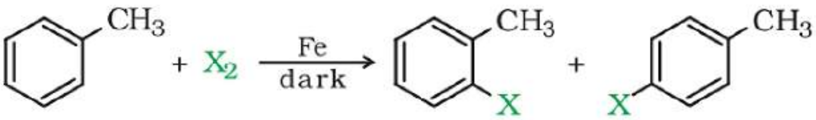
In this reaction, alkyl fluorides formation is possible by heating of Alkyl fluorides RBr/RCl. The reaction is carried out in the presence of metallic fluoride such as SbF_3, Hg_2F_2, AgF, CoF_2.



Preparation of Haloarenes:

1. From hydrocarbons by Electrophilic Substitution Reactions

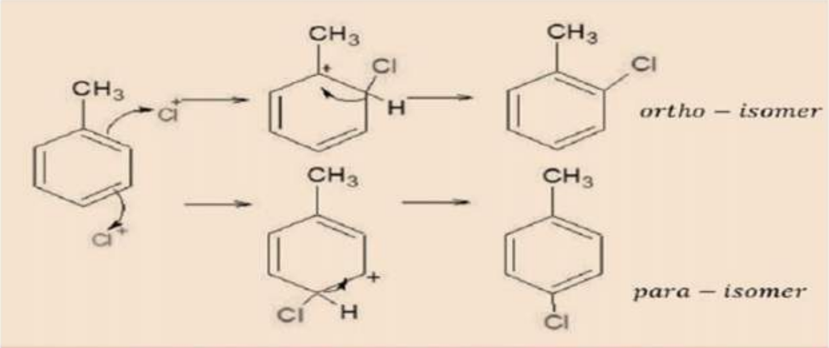
Aryl halides can be prepared by electrophilic aromatic substitution of arenes with halogens in the presence of a Lewis acid.



o-Halotoluene *p*-Halotoluene

Mechanism of Electrophilic Substitution Reaction:

In the above reaction, two different isomers of the aryl chlorides are formed. They are Ortho and para isomer. The π-electron in the benzene ring attacks the Cl+ electrophile to produce an intermediate complex. However, the H+ bond from the intermediate complex moves in order to compensate for the positive charge of the carbon atom.
Thus the reaction forms two different isomers of the product-ortho and para. The melting points of both the isomer differ significantly. And para-isomer has a higher boiling point than ortho-isomer. Therefore, they can be easily separated from each other.



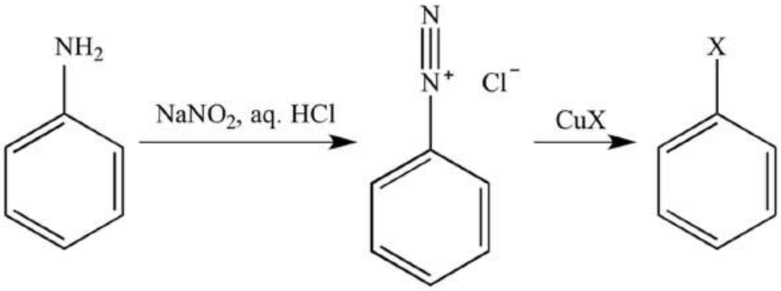
Mechanism of Electrophilic Substitution Reaction

2. From amines by Sandmeyer's reaction:

Sandmeyer's Reaction is a two-step method that includes:

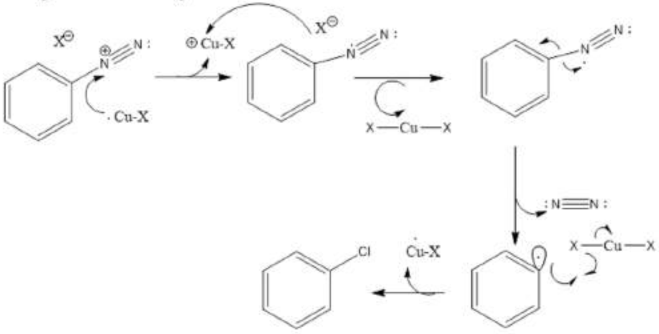
1. Diazonium salt formation
2. Diazonium salt reaction with a cuprous halide (Cu_2X_2)

Primary aromatic amine reacts with sodium nitrite in the presence of cold mineral acid to form the diazonium salt. In this case, HNO_2 is prepared within the reaction by reacting sodium nitrite and HX at a temperature of 273-278K.



Mechanism of the Sandmeyer's Reaction:

In the first step: $NaNO_2 + HCl \rightarrow HNO_2 + NaCl$
The HNO_2 formed in the presence of H^+ undergo protonation to form NO^+ as the electrophile. The lone pair of the atom from the primary amine will react with the electrophile to form an intermediate compound which further gives diazonium salt after elimination of H_2O. In the second step, the diazonium salt reacts with cuprous halide to form the respective aryl halide



Physical Properties of Haloalkanes & Haloarenes

Physical Properties of Haloalkanes

Haloalkanes are hydrocarbons in which hydrogen in a normal alkane is replaced by a halogen (group 17 elements). The physical properties of haloalkanes are mostly like a normal covalent compound. Halogens not being much reactive functional group as a carboxyl group or aldehyde doesn't affect the overall physical properties by much. Still, few differences can be seen as we move down in the homologous series of the haloalkanes group due to the difference in atomic masses of the compound.

1. Colour

Alkyl halides are colourless when pure but bromides and iodides develop colour when exposed to light because they decompose into halogens.

$$2R\text{–}I \rightarrow R\text{–}R + I_2$$

2. Melting and Boiling Points

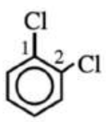
- The melting points and boiling points of haloalkanes are higher than those of corresponding hydrocarbons due to the higher molecular mass of haloalkanes.
- The melting and boiling points increase with the increase in size due to higher van der Waal's forces. Hence the order is : $R-I > R-Br > R-Cl > R-F$
- The boiling points of isomeric haloalkanes decrease with an increase in branching as the surface area decreases on branching and Vander Waal's forces decrease.

Boiling point decreases with branching

$$CH_3CH_2CH_2CH_2Cl > (CH_3)_2CHCH_2Cl > (CH_3)_3CCl$$

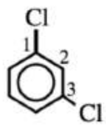
- The boiling points of isomeric dihalobenzene are nearly the same.
- The melting point of p-dihalobenzene is always higher than those of the o- and p- isomers. Because p-isomers are more symmetrical and hence their molecules pack closely in the crystal lattice. This leads to stronger molecular forces of attraction.

o-dichlorobenzene



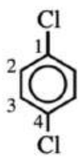
Unsymmetrical

m-dichlorobenzene



Unsymmetrical

p-dichlorobenzene



Symmetrical

3. Solubility

- Haloalkanes and haloarenes, though polar, are immiscible with water because they neither form H-bond nor break the already existing H-bonds (because the new attraction of water and haloalkanes is weaker).
- Haloalkanes are soluble in organic solvents of low polarity like ether, benzene etc. because new intermolecular forces are similar to those in the low polarity solvents.

4. Density

- Alkyl fluorides and alkyl chlorides are generally lighter than water whereas alkyl bromides and alkyl iodides are heavier. The relative densities follow the order: RI > RBr > RCl.
- The densities of the alkyl halides decrease as the size of the alkyl group increases.

5. Stability

The stability of the haloalkanes having the same alkyl group decreases in the order: **R–F > R–Cl > R–Br > R–I** since the strength of the C–X bond decreases in the order: **C–F > C–Cl > C–Br > C–I**

6. Dipole Moment

The dipole moment of methyl halides follows the order: $CH_3Cl > CH_3F > CH_3Br > CH_3I$. Due to the very small size of F, fluorides have lower dipole moments than chlorides.