Class : 11

2023 – 24

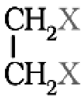
HALOALKANES AND HALOARENES

Classification:

On the Rasis of Number of Halogen Atoms: These may be classified as mono, di, or polyhalogen (tri-, tetra-, etc.) compounds depending on whether they contain one, two or more halogen atoms in their structures.

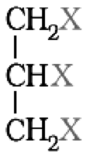
C_2H_5X

Monohaloalkane



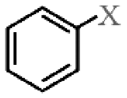
CH_2X-CH_2X

Dihaloalkane

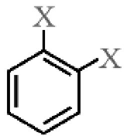


$CH_2X-CHX-CH_2X$

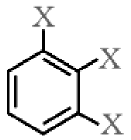
Trihaloalkane



Monohaloarene



Dihaloarene

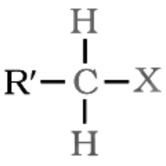


Trihaloarene

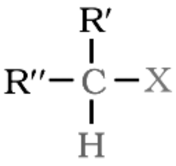
Compounds Containing s^3C − X Bond ($X = F, C, Br, I$)

Alkyl halides or haloalkanes (R − X) : In alkyl halides, the halogen atom is bonded to an alkyl group (*R*). They form a homologous series represented by $C_nH_{2n+1}X$.

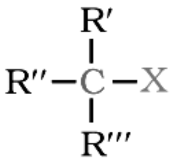
They are further classified as primary, secondary or tertiary according to the nature of carbon to which halogen is attached.



Primary (1°)

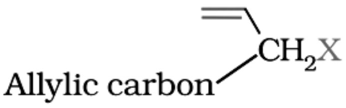


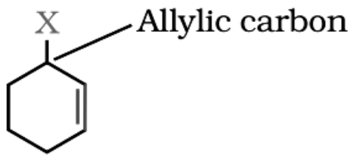
Secondary (2°)



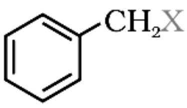
Tertiary (3°)

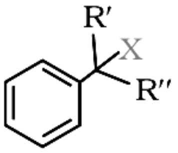
Allylic halides: These are the compounds in which the halogen atom is bonded to an sp^3-hybridised carbon atom adjacent to carbon-carbon double bond ($C-C$) i.e. to an allylic carbon.





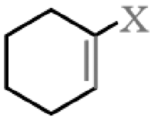
Benzylic halides: These are the compounds in which the halogen atom is bonded to an sp^3-hybridised carbon atom attached to an aromatic ring.


(1°)

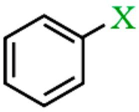

$R' = CH_3$, $R'' = H$ (2°)
$R' = R'' = CH_3$ (3°)

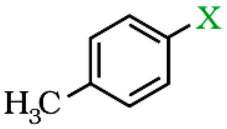
Compounds Containing $sp^2\mathrm{C-X}$ Bond

Vinylic halides: These are the compounds in which the halogen atom is bonded to a sp^2-hybridised carbon atom of a carbon-carbon double bond ($\mathrm{C=C}$).



- **Aryl halides:** These are the compounds in which the halogen atom is directly bonded to the sp^2-hybridised carbon atom of an aromatic ring.

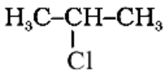
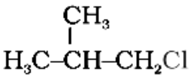
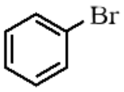
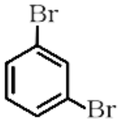
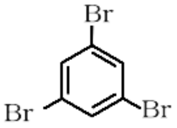
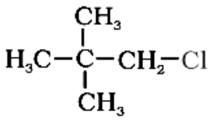
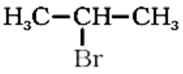




Nomenclature

The common names of alkyl halides are derived by naming the alkyl group followed by the name of halide.

- In the IUPAC system of nomenclature, alkyl halides are named as halosubstituted hydrocarbons.
- For mono halogen substituted derivatives of benzene, common and IUPAC names are the same. For dihalogen derivatives, the prefixes $0, m$-, p-are used in common system but in IUPAC system, the numerals 1,2: 1,3 and 1,4 are used.

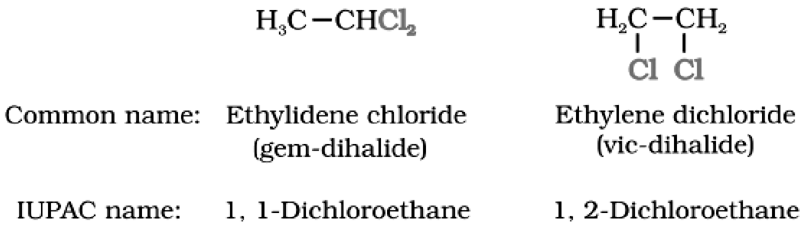
	$CH_3CH_2CH_2Br$	 $H_3C-\underset{\underset{Cl}{\vert}}{CH}-CH_3$	 $H_3C-\overset{\overset{CH_3}{\vert}}{CH}-CH_2Cl$
Common name:	n-Propyl bromide	Isopropyl chloride	Isobutyl chloride
IUPAC name:	1-Bromopropane	2-Chloropropane	1-Chloro-2-methylpropane
			
Common name:	Bromobenzene	*m*-Dibromobenzene	*sym*-Tribromobenzene
IUPAC name:	Bromobenzene	1,3-Dibromobenzene	1,3,5-Tribromobenzene
		 $H_3C-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-CH_2-Cl$	 $H_3C-\underset{\underset{Br}{\vert}}{CH}-CH_3$
IUPAC name:		1-Chloro-2,2-dimethylpropane	2-Bromopropane

Common Name: n-Propyl bromide TUPAC Name: -Bromopropane
Isopropyl chloride
2-Chloropropane
Isobutyl chloride
1-Chloro-2-methylpropane

Common Name: Bromobenzene m-Dibromobenzenc sym-Tribromobenzene
IUPAC Name: Bromobenzene 1,3-dibromobenzene 1,3,5-Tribromobenzene

The dihaloalkanes having the same type of halogen atoms are named as alkylidene or alkylene dihalides. The dihalo-compounds having both the halogen atoms are further classified as geminal halides or gem-dihalides when both the halogen atoms are present on the same carbon atom of the chain and vicinal halides or vic-dihalides when halogen atoms are present on adjacent carbon atoms.

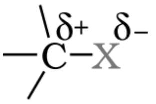
In common name system, gem-dihalides are named as alkylidene halides and vic-dihalides are named as alkylene dihalides.
In IUPAC system, they are named as dihaloalkanes.



	$H_3C-CHCl_2$	$H_2C(Cl)-CH_2(Cl)$
Common name:	Ethylidene chloride (gem-dihalide)	Ethylene dichloride (vic-dihalide)
IUPAC name:	1, 1-Dichloroethane	1, 2-Dichloroethane

Nature of $C.X$ Bond

Halogen atoms are more electronegative than carbon, therefore, carbonhalogen bond of alkyl halide is polarised; the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge.



As we go down the group in the periodic table, the size of halogen atom increases,

- Fluorine atom is the smallest and iodine atom is the largest. Consequently the carbon-halogen bond length also increases from $C-F$ to $C-I$.

Methods of Preparation of Haloalkanes:

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

From Alcohols : 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 the alcohol with concentrated HCl at room temperature.

Good yields of R - I may be obtained by heating alcohols with sodium or potassium iodide in 95% orthophosphoric acid. The order of reactivity of alcohols with a given haloacid is $3^{\circ} > 2^{\circ} > 1^{\circ}$.

$$R\text{-}OH+HCl\xrightarrow{ZnCl_2}R\text{-}Cl+H_2O$$
$$R\text{-}OH+NaBr+H_2SO_4\longrightarrow R\text{-}Br+NaHSO_4+H_2O$$
$$3R\text{-}OH+PX_3\longrightarrow 3R\text{-}X+H_3PO_3(X=Cl,Br)$$
$$R\text{-}OH+PCl_5\longrightarrow R\text{-}Cl+POCl_3+HCl$$
$$R\text{-}OH\xrightarrow[X_2=Br_2,I_2]{redP_2/X_2}R\text{-}X$$
$$R\text{-}OH+SOCl_2\longrightarrow R\text{-}Cl+SO_2+HCl$$

Thionyl chloride is preferred because in this reaction alkyl halide is formed along with gases SO_2 and HCl. 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.

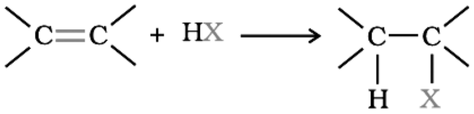
From Hydrocarbons :

From alkanes by free radical halogenation.

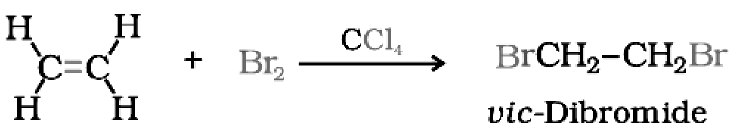
$$CH_3CH_2CH_2CH_3\xrightarrow[\text{or heat}]{Cl_2/\text{UV light}}CH_3CH_2CH_2CH_2Cl+CH_3CH_2CHClCH_3$$

From alkenes:

- **Addition of hydrogen halides:**



- **Addition of halogens(Markovnikov's rule):**



- **By Halogen Exchange :** Alkyl iodides are often prepared by the reaction of alkyl chlorides/ bromides with Nal in dry acetone. This reaction is known as Finkelstein reaction.

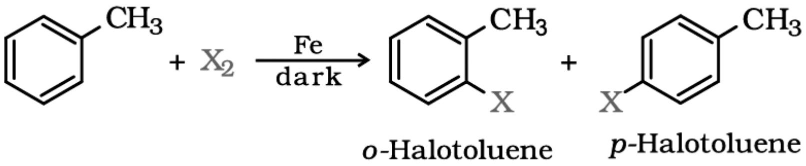
$$R-X+NaI\longrightarrow R-I+NaX\ (X=Cl,Br)$$

- NaCl or NaBr thus formed is precipitated in dry acetone. It facilitates the forward reaction according to Le Chatelier's Principle.
- **Swartz reaction:** The synthesis of alkyl fluorides is best accomplished by heating an alkyl chloride/bromide in the presence of a metallic fluoride such as $AgF, Hg_2\ F_2, CoF_2$ or SbF_3.

$$H_3C-Br+AgF\longrightarrow H_3C-F+AgBr$$

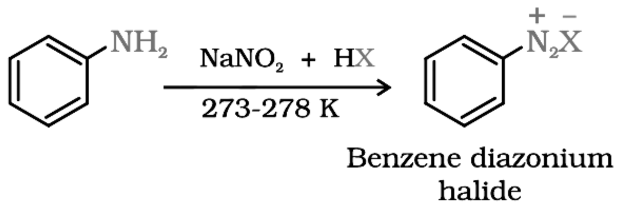
Preparation of Haloarenes:

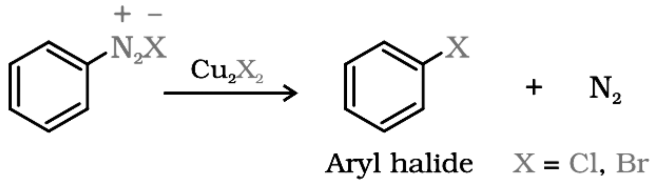
From hydrocarbons by electrophilic substitution: Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts like iron or iron(III) chloride.



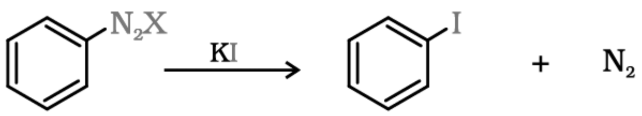
- The ortho and para isomers can be easily separated due to large difference in their melting points.
- Reactions with iodine are reversible in nature and require the presence of an oxidising agent (HNO_3, HIO_4) to oxidise the HI formed during iodination.
- Fluoro compounds are not prepared by this method due to high reactivity of fluorine.

- **From amines by Sandmeyer's reaction:** When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed. Mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by $-Cl$ or $-Br$.





- Replacement of the diazonium group by iodine does not require the presence of cuprous halide and is done simply by shaking the diazonium salt with potassium iodide.



Physical Properties:

- Alkyl halides are colourless when pure. However, bromides and iodides develop colour when exposed to light. Many volatile halogen compounds have sweet smell.
- Methyl chloride, methyl bromide, ethyl chloride and some chlorofluoromethanes are gases at room temperature. Higher members of liquids or solids.

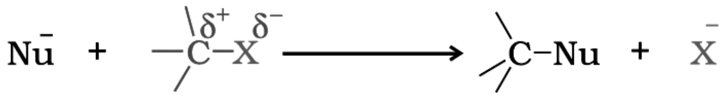
- Due to greater polarity as well as higher molecular mass as compared to the parent hydrocarbon, the intermolecular forces of attraction (dipole-dipole and van der Waals) are stronger in the halogen derivatives that is why the boiling points of chlorides, bromides and iodides are considerably higher than those of the hydrocarbons of comparable molecular mass.
- The attractions get stronger as the molecules get bigger in size and have more electrons.
- 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.
- Boiling points of isomeric dihalobenzenes are very nearly the same. However, the para-isomers are high melting as compared to their ortho and metaisomers. It is due to symmetry of para-isomers that fits in crystal lattice better as compared to ortho- and meta-isomers.
- 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. The haloalkanes are very slightly soluble in water. However, haloalkanes tend to dissolve in organic solvents because the new intermolecular attractions between haloalkanes and solvent molecules have the same strength as the ones being broken in the separate haloalkane and solvent molecules.

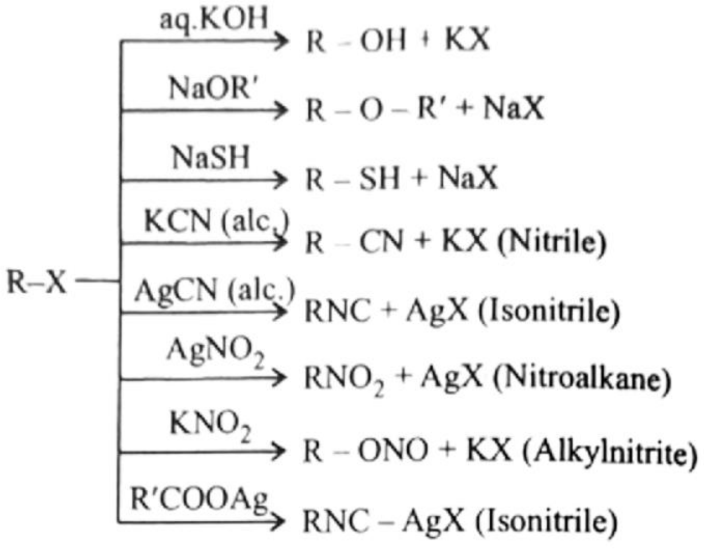
Chemical Reactions

Reactions of Haloalkanes:

Nucleophilic Substitution Reaction: The reaction in which a nucleophile replaces already existing nucleophile in a molecule is called nucleophilic substitution reaction.

- A substitution reaction takes place and halogen atom, called leaving group departs as halide ion. Since the substitution reaction is initiated by a nucleophile, it is called nucleophilic substitution reaction.

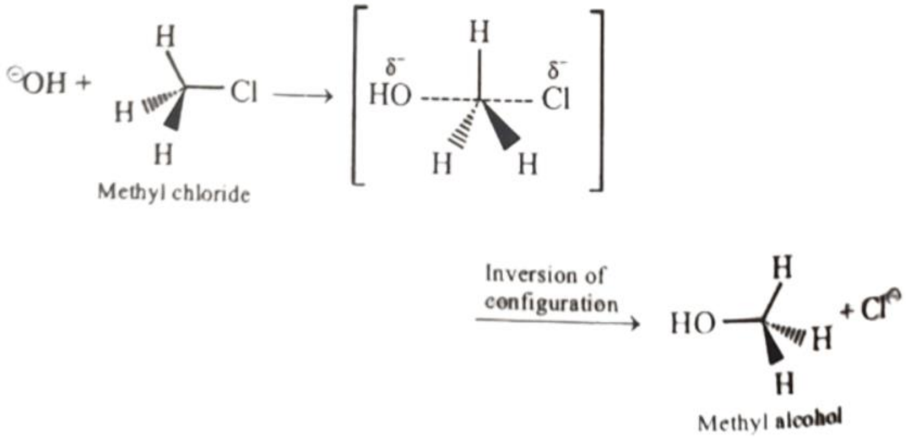




- Groups like cyanides and nitrites possess two nucleophilic centres and are called ambident nucleophiles. Actually cyanide group is a hybrid of two contributing structures and therefore can act as a nucleophile in two different ways $[-\mathrm{C}=\mathrm{N} \leftrightarrow : \mathrm{C}-\mathrm{N}^{-}]$, i.e., linking through carbon atom resulting in alkyl cyanides and through nitrogen atom leading to isocyanides.

- Similarly nitrite ion also represents an ambident nucleophile with two different points of linkage $[\,{}^{-}\mathrm{O}-\ddot{\mathrm{N}}=\mathrm{O}]$.
- The linkage through oxygen results in alkyl nitrites while through nitrogen atom, it leads to nitroalkanes.

- **Mechanism:** This reaction has been found to proceed by two different mechanism which are described below: **Substitution nucleophilic bimolecular $(\mathrm{S_N}{}^2)$:** The reaction between $\mathrm{CH_3Cl}$ and hydroxide ion to yield methanol and chloride ion follows a second order kinetics.



- In the transition state, carbon is simultaneously bonded to five atoms. So it will be unstable and cannot be isolated.

- Of the simple alkyl halides, methyl halides react most rapidly in $\mathrm{S_N}{}^2$ reactions because there are only three small hydrogen atoms. Tertiary halides are the least reactive because bulky groups hinder the approaching nucleophiles. Thus the order of reactivity followed is: Primary halide > Secondary halide > Tertiary halide.

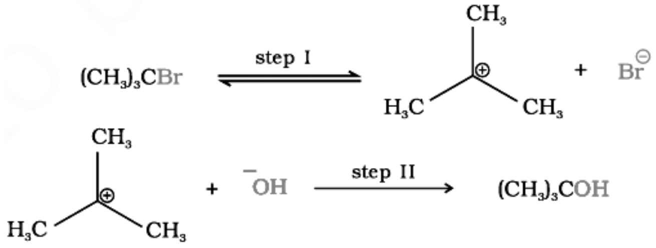
- **Substitution nucleophilic unimolecular $(\mathrm{S_N1})$**: $\mathrm{S_N1}$ reactions are generally carried out in polar protic solvents.

- The reaction between teri-butyl bromide and hydroxide ion yields teri-butyl alcohol and follows the first order kinetics.

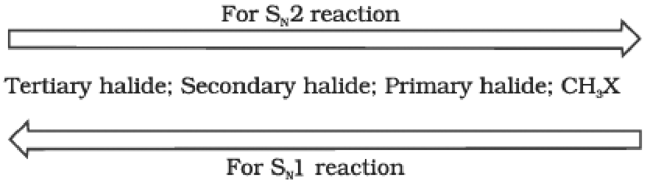
$$(\mathrm{CH_3})_3\mathrm{CBr} + \mathrm{OH} \longrightarrow (\mathrm{CH_3})_3\mathrm{COH} + \mathrm{Br}^{-}$$

2-Bromo-2-methylpropane   2-Methylpropan - 2-ol

- It occurs in two steps. In step 1, the polarised $\mathrm{C}-\mathrm{Br}$ bond undergoes slow cleavage tó produce a carbocation and a bromide ion. The carbocation thus formed is then attacked by nucleophile in step II to complete the substitution reaction.



- Step I is the slowest and reversible. Since the rate of reaction depends upon the slowest step, the rate of reaction depends only on the concentration of alkyl halide and not on the concentration of hydroxide ion.
- Further, greater the stability of carbocation, greater will be its ease of formation from alkyl halide and faster will be the rate of reaction.
- The order of reactivity of alkyl halides towards $S_N 1$ and $S_N{}^2$ reactions as follows:



For a given alkyl group, the reactivity of the halide, $R-X$, follows the same order in both the mechanisms

$$\mathrm{R-I > R-Br > R-Cl > R-F.}$$

Stereochemical aspects of nucleophilic substitution reactions

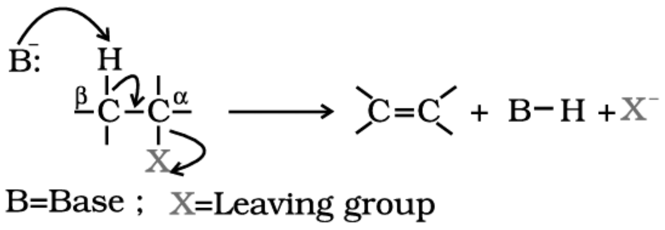
- **Optical activity:** Plane of plane polarised light produced by passing ordinary light through Nicol prism is rotated when it is passed through the solutions of certain compounds. Such compounds are called **optically active** compounds.
- If the compound rotates the plane of plane polarised light to the right, i.e., clockwise direction, it is called dextrorotatory (Greek for right rotating) or the d-form and is indicated by placing a positive $(+)$ sign before the degree of rotation.
- If the light is rotated towards left (anticlockwise direction), the compound is said to be laevo-rotatory or the 1 - form and a negative $(-)$ sign is placed before the degree of rotation.
- Such $(+)$ and $(-)$ isomers of a compound are called optical isomers and the phenomenon is termed as optical isomerism.
- Molecular asymmetry, chirality and enantiomers: Dutch scientist, J. Van't Hoff and French scientist, C. Le Bel in the year (1874), independently argued that the spatial arrangement of four groups (valencies) around a central carbon is tetrahedral and if all the substituents attached to that carbon are different, the mirror image of the molecule is not superimposed (overlapped) on the molecule; such a carbon is called asymmetric carbon or stereocentre. The molecule would lack symmetry and is referred to as asymmetric molecule.
- The objects which are nonsuperimposable on their mirror image (like a pair of hands) are said to be chiral and this property is known as chirality.
- Chiral molecules are optically, which are, superimposable on their mirror images are called achiral. These molecules are optically inactive.
- The stereoisomers 'related to each other as nonsuperimposable mirror images are called enantiomers.
- Enantiomers possess identical physical properties namely, melting point, boiling point, refractive index, etc. They only differ with respect to the rotation of plane polarised light. If one of the enantiomer is dextrorotatory, the other will be laevo rotatory. However, the sign of optical rotation is not necessarily related to the absolute (actual) configuration of the molecule.
- A mixture containing two enantiomers in equal proportions will have zero optical rotation, as the rotation due to one isomer will be cancelled by the rotation due to the other isomer. Such a mixture is known as racemic mixture or racemic modification.

- A racemic mixture is represented by prefixing dl or ($\pm$) before the name.

- The process of conversion of enantiomer into a racemic mixture is known as racemisation.
- **Retention:** Retention of configuration is the preservation of the spatial arrangement of bonds to an asymmetric centre during a chemical reaction or transformation.
- **Inversion, retention and recemisation:** If the spatial arrangement of bonds to a chiral centre is not retained it is called inversion.

The S_N2 reactions of optically active halides are accompanied by inversion of configuration.
In case of optically active alkyl halides, $\mathrm{S_N1}$ reactions are accompanied by partial racemisation.

- **Elimination reactions:** When a haloalkane with β-hydrogen atom is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen atom from β-carbon and a halogen atom from the α-carbon atom.



- As a result, an alkene is formed as a product. Since β-hydrogen atom is involved in elimination, it is often called β-elimination.
- **Saytzeff rule :** In dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms.

- **Elimination versus substitution :** An alkyl halide with β-hydrogen atoms when reacted with a base or a nucleophile has two competing routes: substitution ($\mathrm{S_N1}$ and $\mathrm{S_N2}$) and elimination. Which route will be taken up depends upon the nature of alkyl halide, strength and size of base/nucleophile and reaction conditions.
- Thus, a bulkier nucleophile will prefer to act as a base and abstracts a proton rather than approach a tetravalent carbon atom (steric reasons) and vice-versa.
- Similarly, a primary alkyl halide will prefer a $\mathrm{S_N2}$ reaction, a secondary halide- $\mathrm{S_N2}$ or elimination depending upon the strength of base) nucleophile and a tertiary halide- $\mathrm{S_N1}$ or elimination depending upon the stability of carbocation or the more substituted alkene.

Reaction with metals: Most organic chlorides, bromides and iodides react with certain metals to give compounds containing carbon-metal bonds. Such compounds are known as organo-metallic compounds.

$$\mathrm{CH_3CH_2Br + Mg \rightarrow \underset{\text{Grignard reagent}}{CH_3CH_2MgBr}}$$

- In the Grignard reagent, the magnesium halogen bond is essentially ionic.

$$\overset{\delta}{\mathrm{R}} - \overset{\delta^+}{\mathrm{M}}\overset{\delta}{\mathrm{X}}$$

- Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons. Even water, alcohols, amines arc sufficiently acidic to convert them to corresponding hydrocarbons.

$$\mathrm{RMgX + H_2O \longrightarrow RH + Mg(OH)X}$$

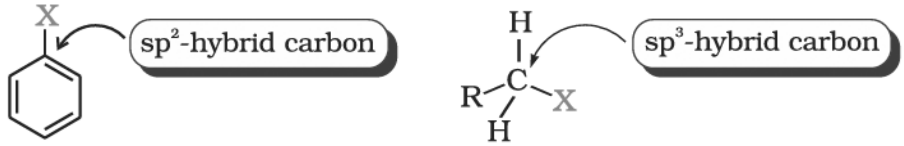
- Alkyl halides react with sodium in dry ether to give hydrocarbons containing double the number of carbon atoms present in the halide. This reaction is known as Wurtz reaction.

$$2\mathrm{RX} + 2\mathrm{Na} \longrightarrow \mathrm{RR} + 2\mathrm{NaX}$$

Reactions of Haloarenes

Nucleophilic substitution: Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

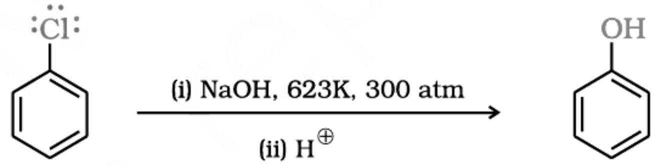
- **Resonance effect :** In haloarenes, the electron pairs on halogen atom are in conjugation with p-electrons of the ring.
- $\mathrm{C}-\mathrm{Cl}$ bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.
- **Difference in hybridisation of carbon atom in $\mathbf{C}-\mathbf{X}$:**



- The sp^2 hybridised carbon with a greater s-character is more electronegative and can hold the electron pair of $\mathrm{C}-\mathrm{X}$ bond more tightly than sp^3-hybridised carbon in haloalkane with less $s-$ charareter. Thus, C-Cl bond length in haloalkane is 177pm while in haloarene is 169pm.

- Since it is difficult to break a shorter bond than a longer bond, therefore, haloarenes arc less reactive than haloalkanes towards nucleophilic substitution reaction.

- **Instability of phenyl cation:** In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore, $\mathrm{S_N}$I mechanism is ruled out. Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.
- **Replacement by hydroxyl group:** Chlorobenzene can be converted into phenol by heating in aqueous sodium hydroxide solution at a temperature of 623 K and a pressure of 300 atmospheres.

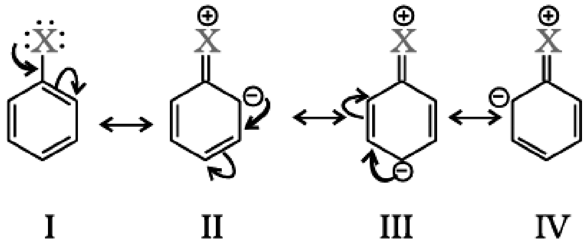


- The presence of an electron withdrawing group $(-\mathrm{NO_2})$ at orthoand para-positions increases the reactivity of haloarenes.
  The effect is pronounced when $(-\mathrm{NO_2})$ group is introduced at ortho and para-positions. However, no effect on reactivity of haloarenes is observed by the presence of electron withdrawing group at meta-position.
- The presence of nitro group at ortho- and para-positions withdraws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on haloarene.

The negative charge appeared at ortho- and para- positions with respect to the halogen substituent is stabilised by $-NO_2$ group while in case of meta-nitrobenzene, none of the resonating structures bear the negative charge on carbon atom bearing the $-NO_2$ group. Therefore, the presence of nitro group at meta-position does not stabilise the negative charge and no effect on reactivity is observed by the presence of $-NO_2$ group at metaposition.

Electrophilic substitution reactions

- Haloarenes undergo the usual electrophilic reactions of the benzene ring such as halogenation, nitration, sulphonation and Friedel Crafts reactions. Halogen atom besides being slightly deactivating is o, p-directing; therefore, further substitution occurs parapositions with respect to the halogen atom. The o, p-directing influence of halogen atom can be casily understood if we consider the resonating structures of halobenzene as shown:

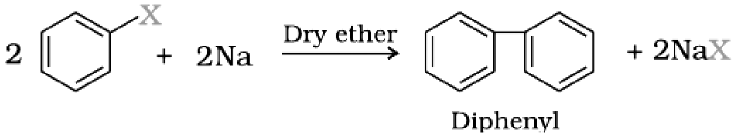


- Due to resonance, the electron density increases more at ortho. and para-positions than at meta-positions. Further, the halogen atom because of its -1 effect has some tendency to withdraw electrons from the benzene ring. As a result, the ring gets somewhat deactivated as compared to benzene and hence the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.

Reaction with metals:

- **Wurtz-Fittig reaction :** A mixture of an alkyl halide and aryl halide gives an alkylarene when treated with sodium in dry ether and is called Wurtz-Fitting reaction.

- **Fittig reaction :** Aryl halides also give analogous compounds when treated with sodium in dry ether, in which two aryl groups are joined together. It is called Fittig reaction.



Polyhalogen Compounds

- Carbon compounds containing more than one halogen atom are usually referred to as polyhalogen compounds. Many of these compounds are useful in industry and agriculture.

- **Dichloro-methane (Methylene chloride) :** Dichloro-methane is widely used as a solvent as a paint remover, as a propellant in aerosols, and as a process solvent in the manufacture of drugs. It is also used as a metal cleaning and finishing solvent.

- In humans, direct skin contact with methylene chloride causes intense burning and mild redness of the skin. Direct contact with the eyes can burn the cornea.

Trichloro-methane (Chloroform) : Chemically, chloroform is employed as a solvent for fats, alkaloids, iodine and other substances.

- The major use of chloroform today is in the production of the freon refrigerant $R-22$.
- Chronic chloroform exposure may cause damage to the liver (where chloroform is metabolised to phosgene) and to the kidneys, some people develop sores when the skin is immersed in chloroform.
- Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas, carbonyl chloride, also known as phosgene.

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

Triiodo-methane (Iodoform) : It was used earlier as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to iodoform itself.

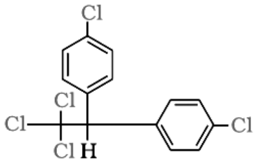
Tetrachloro-methane (Carbon tetrachloride): It is produced in large quantities for use in the manufacture of refrigerants and propellants for aerosol cans.

It is also used as feedstock in the synthesis of chlorofluorocarbons and other chemicals, pharmaceutical manufacturing, and general solvent use.

When carbon tetrachloride is released into the air, it rises to the atmosphere and depletes the ozone layer. **Freons :** The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. They are extremely stable, unreactive, non-toxic, noncorrosive and easily liquefiable gases. Freon $12(CCl_2\,F_2)$ is one of the most common freons in industrial use.

It is manufactured from tetrachloromethane by Swarts reaction. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes. In stratosphere, freon is able to initiate radical chain reactions that can upset the natural ozone balance

p, p'-Dichlorodiphenyltrichlorocthane (DDT) : DDT, the first chlorinated organic insecticides, was originally prepared in 1873.



DDT

DDT is not metabolised very rapidly by animals; instead, it is deposited and stored in the fatty tissues.

Tips/Tricks/Techniques One-Liners

Prediction of number of optical isomers in compounds having chiral centre:

(i) When the molecule is chiral.

Number of d and l isomers $(a) = 2^n$. Number of meso forms $(m) = 0$

$\therefore$ Total number of optical isomers $= (a + m) = 2^n$

Where n is the number of differently substituted chiral carbon atom(s).

(ii) When the molecule is symmetrical and has even number of chiral carbon atoms.

Number of d and $/$ isomers $(a) = 2^{(n-1)}$, Number of mesoforms $(m) = 2^{(n/2)-1}$

$\therefore$ Total number of optical isomers $= (a + m)$

(iii) When the molecule is symmetrical and has an odd number of chiral carbon atoms.

Number of d and l forms $(a) = 2^{(n-1)} - 2^{\left(\frac{n-1}{2}\right)}$

Number of meso forms $(m) = 2^{\left(\frac{n-1}{2}\right)}$

$\therefore$ Total number of opital isomers $= (a + m) = 2^{(n-1)}$

Trends in nucleophilicity:

(i) A species with a negative charge is a stronger nucleophile than a similar neutral species. In particular, a base is a stronger nucleophile than its conjugate acid.

$$\ddot{O}H > H_2\ddot{O}:;\ddot{S}H > H_2\ddot{S};;\ N\ddot{H}_2 > \ddot{N}H_3$$

(ii) With increase in electronegativity, nucleophilicity decreases from left to right in the periodic table.

$$:\ddot{O}H > \ddot{F}:;\ :NH_3 > H_2\ddot{O};\ R_3P: > R_2\ddot{S}:$$

(iii) Nucleophilicity increases down the periodic table, following the increase in size and polarizability.

$$I^- > Br^- > Cl^- > F^-; -SeH > -SH > -OH; R_3P: > R_3\ N:$$

The rate of S_N1 is independent of the nature of the nucleophile (stronger or weaker) because here the nucleophile attacks on the carbocation (a fast step). The net result is that, other things being equal, a strong nucleophile favours the $S_N{}^2$ reaction, and a weak nucleophile favours the S_N1 reaction.

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