HALOALKANES AND HALOARENES

- A haloalkane is formed by the replacement of hydrogen atoms in aliphatic hydrocarbon.
- It contains halogen atoms attached to an SP^3 hybridised carbon atom of an alkyl group.
- A haloarene is formed by the replacement of hydrogen atoms in an aromatic hydrocarbon by halogen atoms.
- It contains halogen atoms attached to an SP^2 hybridised carbon atom of an aryl group.

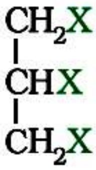
CLASSIFICATION

ON THE BASIS OF NUMBER OF HALOGEN ATOMS

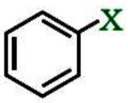
- Classified as mono, di or poly halogen compounds depending on whether they contain one, two or more halogen atoms in their structures.

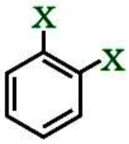
C_2H_5X

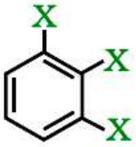
CH_2X-CH_2X



$CH_2X-CHX-CH_2X$





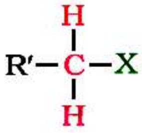


Monohaloalkane Dihaloalkane Trihaloalkane Monohaloarene Dihaloarene Trihaloarene

COMPOUNDS CONTAINING $SP^3C—X$ BOND

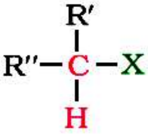
ALKYL HALIDES OR HALOALKANES

- The halogen atom is bonded to an alkyl group.
- Their homologous series can be represented as $C_nH2_{n+1}X$.
- Further classified as 1^0, 2^0 and 3^0 depending on the nature of carbon to which halogen is attached.



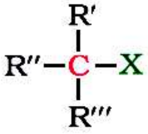
$R'-CH_2-X$

Primary (1°)



$R''-CH(R')-X$

Secondary (2°)

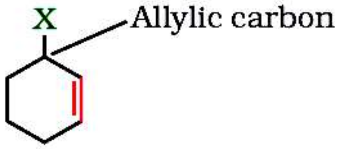


$R''-C(R')(R''')-X$

Tertiary (3°)

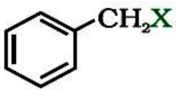
1. ALLYLIC HALIDES

- Compounds in which halogen atom is bonded to an SP^3 hybridised carbon atom next to C—C double bond.

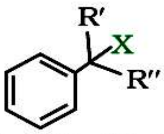


2. BENZYLIC HALIDES

- Compounds in which the halogen atom is bonded to an SP^3 hybridised carbon atom next to an aromatic ring.



(1°)



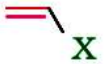
$R'=CH_3$, $R''=H$ (2°)

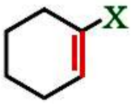
$R' = R'' = CH_3$ (3°)

COMPOUNDS CONTAINING $SP^2C—X$ BOND

1. VINYLIC HALIDES

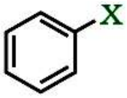
- Compounds in which, the halogen atom is bonded to an SP^2 hybridised carbon atom of C—C double bond.

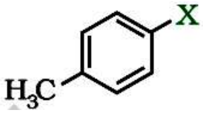




2. ARYL HALIDES

- Compounds in which, the halogen atom is bonded to an SP^2 hybridised carbon atom of the aromatic ring.





NOMENCLATURE

1. COMMON SYSTEM

- Alkyl halides are derived by naming the alkyl group followed by the halide.

2. IUPAC SYSTEM

- Alkyl halides are named as halo substituted hydrocarbons.
- Aryl halides are named as halo arenes according to common as well as IUPAC system.
- For dihalogen derivatives, the prefixes ortho, meta and para are used in the common system.
- According to the IUPAC system, the numerals 1,2 1,3 and 1,4 are used.
- The dihalo derivatives having the same type of halogen atoms are named as alkylidine or alkylene derivatives.
- The dihalo compounds having the same type of halogen atoms are further classified as germinal halides and vicinal halides.

- In common system, Gem dihalides are named as alkylidine halides and Vicinal dihalides are named as alkylene dihalides.
- In the IUPAC system, they are named as dihalo alkanes.

NOTE

GEMINAL DIHALIDES [GEM DIHALIDES]

- Halogen atoms are present on the same carbon atom.

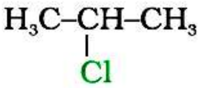
VICINAL DIHALIDES [VIC DIHALIDES]

- Halogen atoms are present on the adjacent carbon atoms.

EXAMPLES

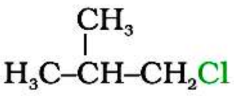
$CH_3CH_2CH_2Br$

n-Propyl bromide
1-Bromopropane



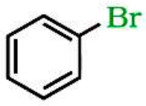
$H_3C-\underset{Cl}{CH}-CH_3$

Isopropyl chloride
2-Chloropropane

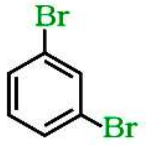


$H_3C-\overset{CH_3}{CH}-CH_2Cl$

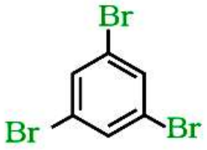
Isobutyl chloride
1-Chloro-2-methylpropane



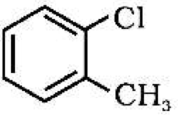
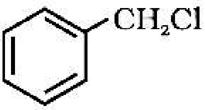
Bromobenzene
Bromobenzene



m-Dibromobenzene
1,3-Dibromobenzene

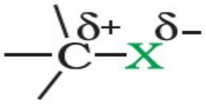


sym-Tribromobenzene
1,3,5-Tribromobenzene

Structure	Common name	IUPAC name
$CH_3CH_2CH(Cl)CH_3$	sec-Butyl chloride	2-Chlorobutane
$(CH_3)_3CCH_2Br$	neo-Pentyl bromide	1-Bromo-2,2-dimethylpropane
$(CH_3)_3CBr$	tert-Butyl bromide	2-Bromo-2-methylpropane
$CH_2 = CHCl$	Vinyl chloride	Chloroethene
$CH_2 = CHCH_2Br$	Allyl bromide	3-Bromopropene
	*o*-Chlorotoluene	1-Chloro-2-methylbenzene or 2-Chlorotoluene
	Benzyl chloride	Chlorophenylmethane
CH_2Cl_2	Methylene chloride	Dichloromethane
$CHCl_3$	Chloroform	Trichloromethane
$CHBr_3$	Bromoform	Tribromomethane
CCl_4	Carbon tetrachloride	Tetrachloromethane
$CH_3CH_2CH_2F$	n-Propyl fluoride	1-Fluoropropane

NATURE OF CARBON—HALOGEN BOND

- Halogen atoms are more electronegative than carbon atom.
- The Carbon—Halogen bond of alkyl halide is polarized.
- The carbon atom bears a partial +ve charge and the halogen atom bears a partial –ve charge.



METHODS OF PREPARATION

1. FROM ALCOHOLS

- When an alcohol is treated with conc. Halogen acids, Phosphorous halides or thionyl chloride, the hydroxyl group of alcohol is replaced by halogen.

$$R–OH + HCl \xrightarrow{ZnCl_2} R–Cl + H_2O$$

$$R–OH + NaBr + H_2SO_4 \longrightarrow R–Br + NaHSO_4 + H_2O$$

$$3R–OH + PX_3 \longrightarrow 3R–X + H_3PO_3 \quad (X = Cl, Br)$$

$$R–OH + PCl_5 \longrightarrow R–Cl + POCl_3 + HCl$$

$$R–OH \xrightarrow[X_2=Br_2,I_2]{red\ P/X_2} R–X$$

$$R–OH + SOCl_2 \longrightarrow R–Cl + SO_2 + HCl$$

2. FROM HYDROCARBONS

BY FREE RADICAL HALOGENATION

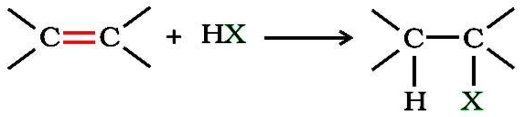
- Free radical chlorination or bromination of alkanes gives a complete mixture of isomeric mono and poly haloalkanes.

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

3. FROM ALKENES

A. ADDITION OF HYDROGEN HALIDES

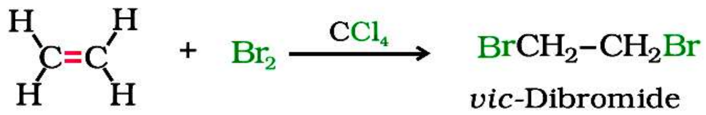
- An alkene is converted to an alkyl halide by reaction with HCl, HBr or HI.



$$CH_3CH=CH_2 + H{-}I \longrightarrow \underset{\text{minor}}{CH_3CH_2CH_2I} + \underset{\text{major}}{CH_3CHICH_3}$$

B. ADDITION OF HALOGENS

- Addition of Bromine in CCl_4 to an alkene gives Vic-dibromides.



4. HALOGEN EXCHANGE

1. FINKELSTEIN REACTION

- Alkyl iodides are prepared by the reaction of alkyl chlorides or alkyl bromides with NaI in dry acetone.
- This reaction is known as Finkelstein reaction

$$R{-}X + NaI \longrightarrow R{-}I + NaX$$

2. SWARTZ REACTION

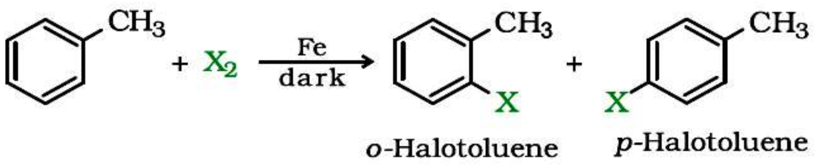
- Alkyl fluorides are synthesized by heating an alkyl chlorides or alkyl bromides in the presence of a metallic fluoride such as AgF, HgF_2, CaF_2 or SbF_3.
- This reaction is known as Swartz reaction.

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

PREPARATION OF HALOARENES

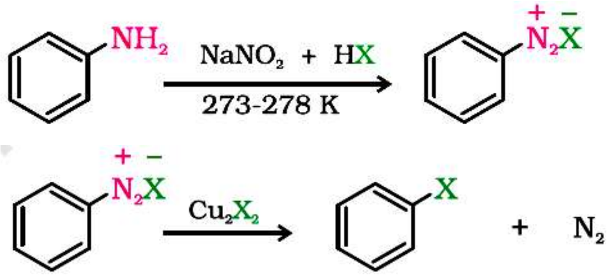
1. FROM HYDROCARBONS BY ELECTROPHILIC SUBSTITUTION

- Aryl bromides and chlorides can be prepared by the electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts like Iron or Iron (III)chloride

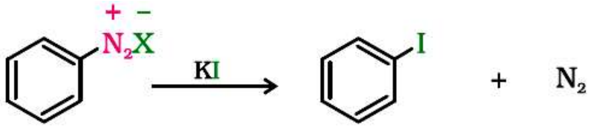


2. FROM AMINES BY SANDMEYERS REACTION

- When an aromatic primary amine, dissolved in cold aqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed.



- Replacement of the diazonium group by iodine does not require the presence of cuprous halide.
- It is done by shaking the diazonium salt with KI.



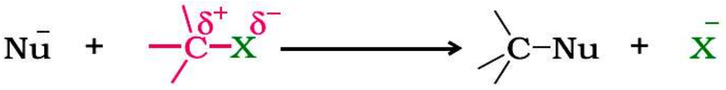
CHEMICAL PROPERTIES

1. REACTIONS OF HALOALKANES

- Classified into three categories.
- Nucleophilic substitution
- Elimination reaction
- Reaction with metals

NUCLEOPHILIC SUBSTUTION REACTIONS [S_N REACTIONS]

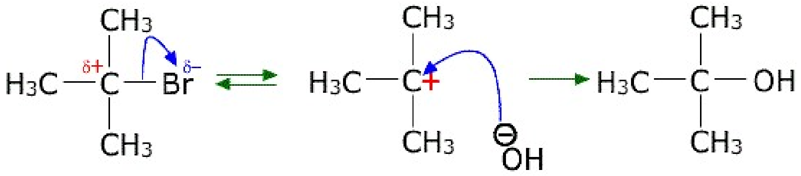
- Reaction in which an atom or group of a molecule is replaced by a nucleophile.
- A nucleophile reacts with a halo alkane having a partial positive charge on the carbon atom bonded to halogen.
- A substitution reaction takes place and halogen atom (leaving group) departs as a halide ion.



TYPES OF NUCLEOPHILIC SUBSTUTION REACTIONS

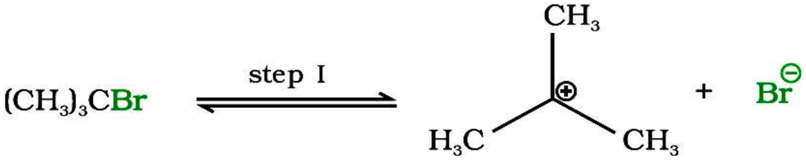
SUBSTITUTION NUCLEOPHILIC UNIMOLECULAR [S_N1 REACTIONS]

- The rate of a nucleophilic substitution reaction depends only on the concentration of the substrate and is independent of the concentration of the nucleophile. Rate ∞ [Substrate]
- S_N1 Reactions are carried out in polar protic solvents like water, alcohol, acetic acid etc.
- The reaction between tert-butyl bromide and hydroxide ion gives tert-butyl alcohol.
- It follows first order kinetics.



MECHANISM

- The reaction occurs in two steps
- **STEP-1:** Slow ionisation of the alkyl halide to give a carbocation.
- It is the rate determining step.



- **STEP-2:** The carbocation combines with the nucleophile to form an alcohol.
- This step is the fast step.

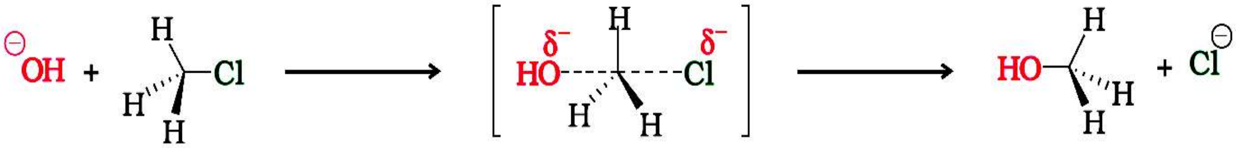
- Greater the stability of carbocation, greater will be its ease of formation from alkyl halide and faster will be the rate of reaction.
- Tertiary alkyl halides undergo S_N1 reaction very fast.
- Because the stability of tertiary carbocations is very high.

SUBSTITUTION NUCLEOPHILIC BIMOLECULAR S_N2 REACTIONS

- Rate of a nucleophilic substitution reaction depends on both the concentrations of the substrate and the nucleophile.

$$\text{Rate} \propto [\text{Substrate}][\text{Nucleophile}]$$

- Hydrolysis of a primary alkyl halide.
- The reaction between CH_3Cl and a hydroxide ion to give methanol and a chloride ion.



MECHANISM

- The reaction occurs in a single step.
- The nucleophile OH^- ion approaches the alkyl halide molecule from the side opposite to that of the departing group Cl^-.
- The incoming group OH^- will start to form a bond with the carbon bearing the halogen.
- At the same time, the leaving group Cl^- will start to take the grip of the bonding electron pair towards it.
- A high energy state called transition state is attained which is converted into products.

- The order of reactivity of alkyl halides is 1^0 halide > 2^0 halide > 3^0 halide

STEREOCHEMICAL ASPECTS OF NUCLEOPHILIC SUBSTITUTION REACTIONS

- An S_N2 reaction proceeds with complete stereochemical inversion.
- An S_N1 reaction proceeds with racemization.

PLANE POLARISED LIGHT

- Under ordinary conditions, light can vibrate in all directions to the path of propagation.
- Light vibrating in only one plane is called a plane polarized light.

OPTICAL ACTIVITY

- The phenomenon of rotating the plane of the plane polarized light to the left or right is called optical activity.
- The compounds exhibiting this property are called optically active compounds.
- The optically active compounds exist in two isomeric forms. They are

1. DEXTROROTATORY OR (+) FORM

- The isomers which rotate the plane polarized light to the right.

2. LAEVOROTATORY OR (-) FORM

- The isomers which rotate the plane polarized light to the left.

STEREOCENRE OR CHIRALITY CENTRE

- A carbon atom bonded to four different atoms or groups.
- The chirality centre is represented by an asterisk (*).

CHIRALITY

- The term chirality means having handedness.
- Chirality is derived from the Greek word 'Kheir' meaning hand.
- A molecule which is not super imposable on its mirror image is chiral.
- Human hand, shoes, gloves, alphabets like B, C, D, E etc are chiral objects.

ACHIRAL MOLECULE

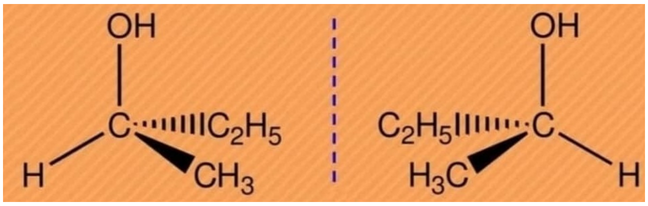
- An object or molecule which are super impossible on its mirror image is said to be achiral.
- Eg: Spoon, alphabets like A, H, I, M, O etc.

CAUSE OF OPTICAL ACTIVITY

- The necessary condition for a molecule to exhibit optical isomerism is dissymmetry or chirality.
- The compound contains asymmetric carbon.
- They have non-superimposable mirror image.

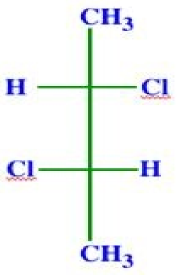
ENANTIOMERS

- Stereoisomers which are related to one another as an object and its non-superimposable mirror images are called enantiomers.
- Eg: Butan-2-ol

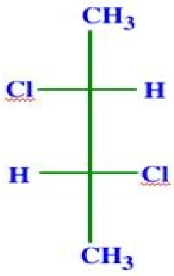


DIASTEREOISOMERS

- Stereoisomers which are non-superimposable and are not related as object and its mirror images are called diastereoisomers.
- Eg: 2,3-Dichlorobutane



1



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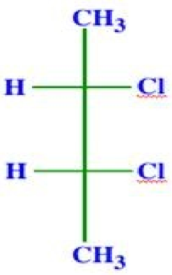

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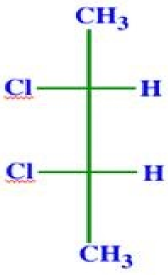


4

- Structures 1 and 3, 2 and 4 are diastereoisomers.

RACEMIC MIXTURE OR RACEMIC MODIFICATION

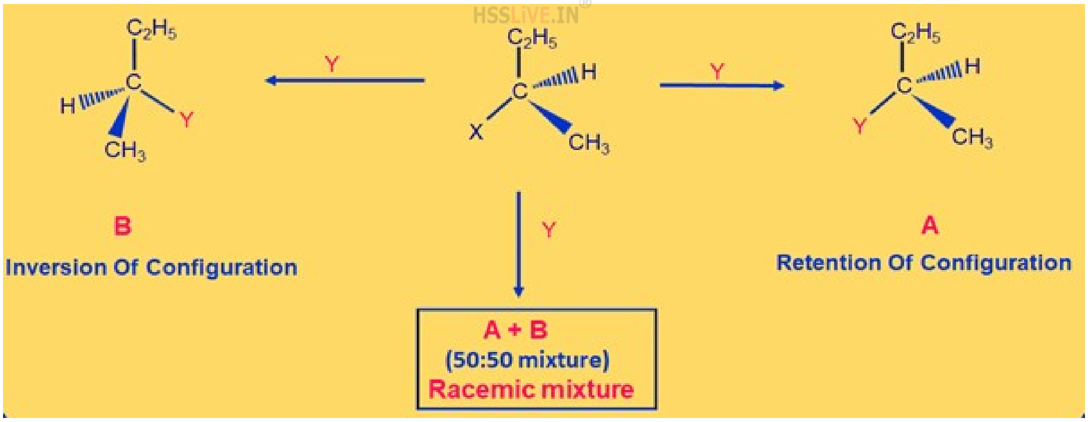
- A mixture containing two enantiomers in equal proportions will have zero optical rotation.
- This is because the rotation due to one isomer will be cancelled by the rotation due to the other isomer.
- Such a mixture is known as Racemic Mixture or Racemic Modification.
- It may be represented as (±) form or dl form.

RACEMISATION

- The process of converting an Enantiomer into a racemic mixture.

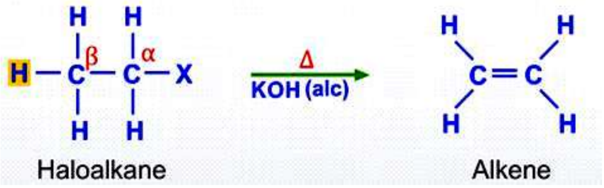
RETENTION

- The preservation of integrity of the spatial arrangement of bonds to an assymetric centre during a chemical reaction or transformation.



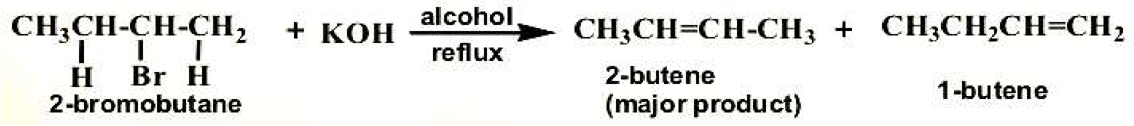
ELIMINATION REACTIONS [BETA ELIMINATION]

- When a halo alkane with β hydrogen atom is heated with alcoholic solution of KOH, there is elimination of hydrogen atom from the β carbon and a halogen atom from the α carbon atom.
- As a result, an alkene is formed as product.
- Since β hydrogen atom is involved in elimination, the reaction is called β elimination.



SAYTZEFF RULE

- In dehydrohalogenation reactions, the preferred product is that alkene which has greater number of alkyl groups attached to the doubly bonded carbon atoms.



$$CH_3\underset{H}{C}H-\underset{Br}{C}H-\underset{H}{C}H_2 + KOH \xrightarrow[reflux]{alcohol} CH_3CH=CH-CH_3 + CH_3CH_2CH=CH_2$$

3. REACTION WITH METALS

ORGANOMETALLIC COMPOUNDS

- organic halides react with certain metals to give compounds containing carbon-metal bonds.
- Such compounds are known as organo-metallic compounds
- Eg: Alkyl Magnesium Halides commonly known as Grignard Reagents.
- Grignard reagent is prepared by the reaction of haloalkanes with magnesium metal in dry ether.

$$CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} CH_3CH_2MgBr$$

In Grignard reagent, the C—Mg bond is covalent but highly polar with carbon pulling electrons from electropositive magnesium.

$$\overset{\delta-}{R}-\overset{\delta+}{Mg}\ \overset{\delta-}{X}$$

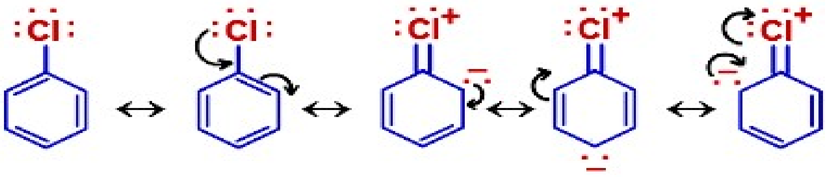
REACTIONS OF HALOARENES

NUCLEOPHILIC SUBSTITUTION REACTIONS

- Aryl halides are less reactive towards nucleophilic substitution reactions.
- It is due to the following reasons

A. RESONANCE EFFECT

In haloarenes, the electron pairs on halogen atoms are in conjugation with π electrons of the ring.



B. DIFFERENCE IN HYBRIDISATION OF CARBON ATOM IN C—X BOND

- In haloalkanes, the carbon atom attached to halogen is SP^3 hybridised.
- In haloarenes, the carbon atoms attached to halogen is SP^2 hybridised.

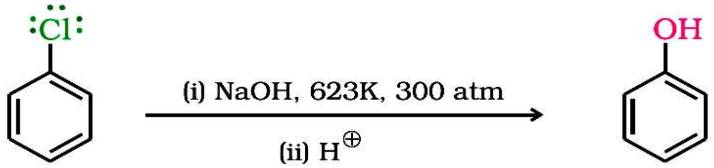
C. INSTABILITY OF PHENYL CARBOCATION

- In haloarenes, the phenyl carbocation formed as a result of self-ionization will not be stabilized by resonance.

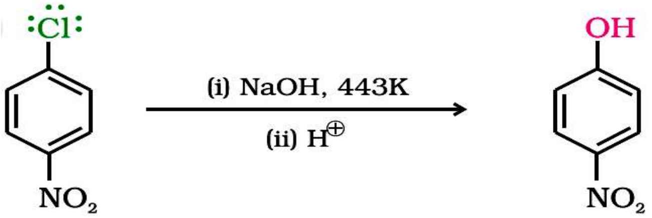
D. Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.

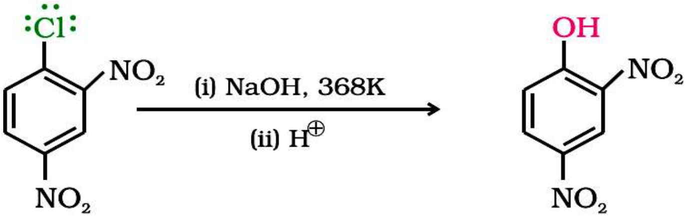
REPLACEMENT BY HYDROXYL GROUP

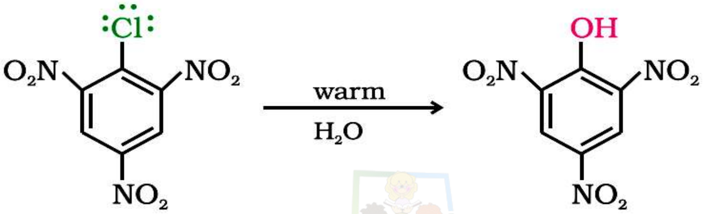
- Chlorobenzene can be converted into phenol by heating in aqueous NaOH solution at a temperature of 623 K and a pressure of 300 atm.



- ➢ The presence of electron withdrawing group (-NO_2) at ortho and para positions increases the reactivity of haloarenes.



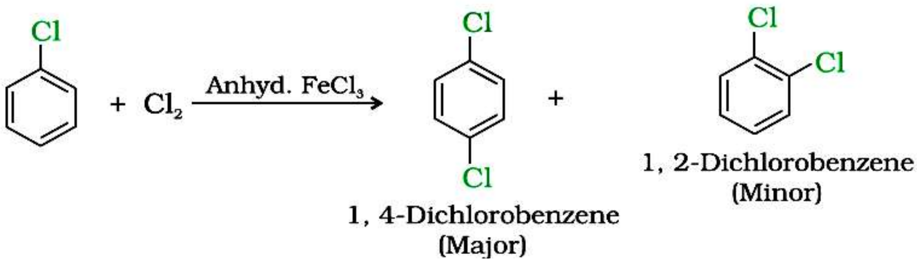




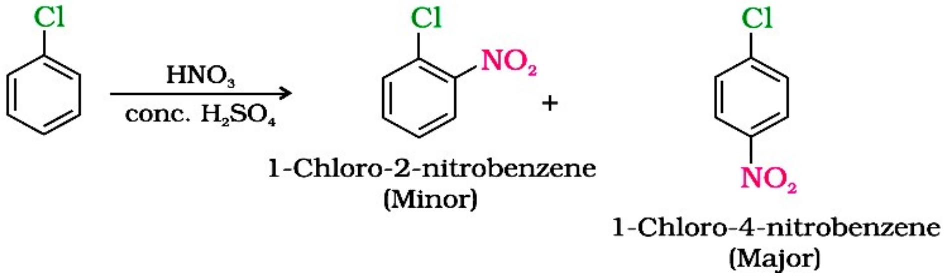
ELECTROPHILIC SUBSTTUTION REACTIONS

- ➢ Halogen atom is ortho-para directing due to resonance.
- ➢ The electron density increases more at ortho and para positions than at meta positions.

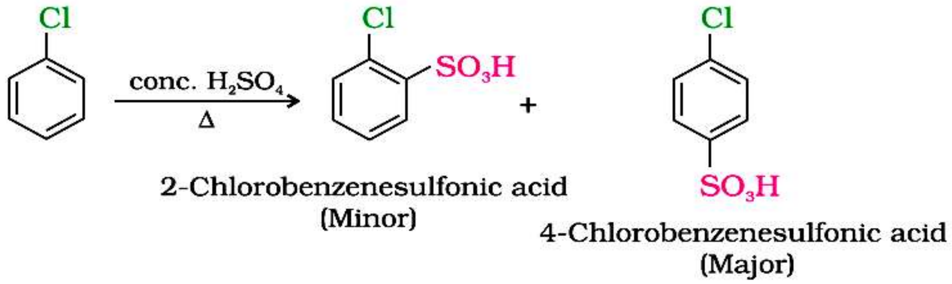
A. HALOGENATION



B. NITRATION



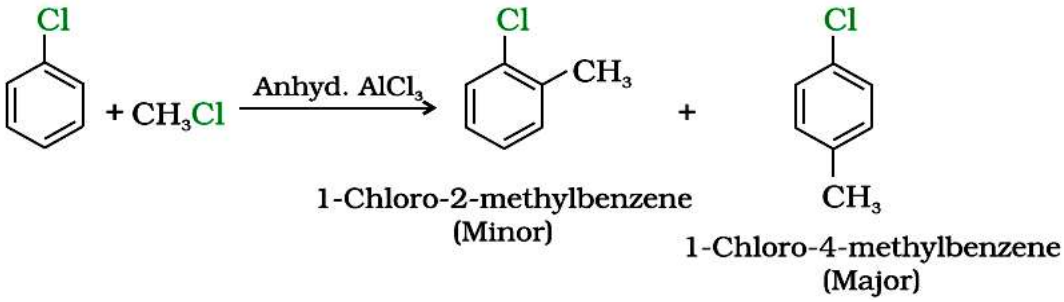
C. SULPHONATION



2-Chlorobenzenesulfonic acid (Minor)

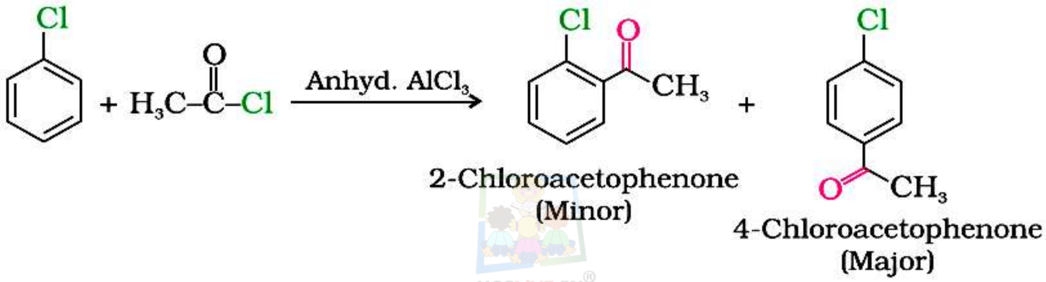
4-Chlorobenzenesulfonic acid (Major)

D. FRIEDEL CRAFTS REACTION



1-Chloro-2-methylbenzene (Minor)

1-Chloro-4-methylbenzene (Major)



2-Chloroacetophenone (Minor)

4-Chloroacetophenone (Major)

REACTION WITH METALS

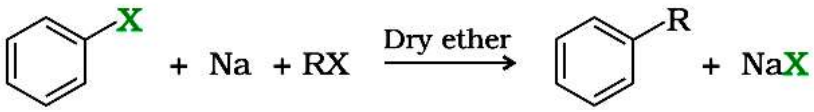
1. WURTZ REACTION

- Alkyl halide react with sodium in dry ether to give hydrocarbons containing double the number of carbon atom present in the halide.

$$2RX + 2Na \longrightarrow RR + 2NaX$$

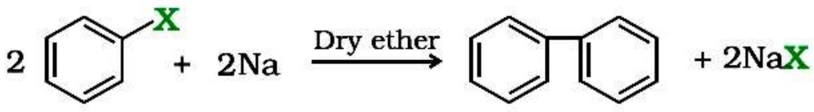
2. WURTZ FITTIG REACTION

- A mixture of alkyl halide and an aryl halide when treated with sodium in dry ether gives an alkyl arene.



3. FITTIG REACTION

- When aryl halides are heated with sodium in dry ether, the two aryl groups are joined together to form diphenyl.



Diphenyl

POLY HALOGEN COMPOUNDS

1. DICHLOROMETHANE OR METHYLENE CHLORIDE [CH_2Cl_2]

- It is used
- as solvent, as paint remover, as propellant, as process solvent in the manufacture of drugs.
- As metal cleaning and finishing solvent.
- Exposure to lower levels of methylene chloride in air can lead to slightly impaired hearing and vision.
- Higher levels of methylene chloride in air cause dizziness, nausea, tingling and numbness in the fingers and toe.
- In humans, direct skin contacts cause intense burning and mild redness of the skin.
- Direct contact with eyes can burn the cornea.

2. TRICHLORO METHANE OR CHLOROFORM [$CHCl_3$]

- Chloroform is used as a solvent.
- It is used for the production of Freon refrigerant (R-22).
- It was used as a general anesthetic in surgery.
- Inhaling chloroform vapours depresses the central nervous system.
- Breathing chloroform can cause dizziness, fatigue and headache.
- Chronic exposure to chloroform may cause damage to liver and kidneys.
- Chloroform is slowly oxidized by air in the presence of light to an extremely poisonous gas, carbonyl chloride known as phosgene.
- It is therefore stored in closed dark coloured bottles, completely filled so that air is kept out.

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

3. TRIIODOMETHANE OR IODOFORM [CHI_3]

- It was used earlier as an antiseptic.
- It is due to the liberation of free iodine due to tis objectionable smell.
- It has been replaced by other formulation containing iodine.
- Any compound containing CH_3CO- or $CH_3CH(OH)-$ group, when heated with iodine and aqueous NaOH gives yellow precipitate of iodoform.
- The reaction is known as iodoform reaction.

4. TETRACHLOROMETHANE [CCl_4]

- Used for the manufacture of refrigerants and propellants.
- Used for the synthesis of chlorofluorocarbons and other chemicals and pharmaceuticals and as general solvents.
- Used as a cleaning fluid, as a spot remover, and as a fire extinguisher.
- Exposure to CCl_4 causes liver cancer in humans.
- It may cause dizziness, Nausea and vomiting.

- Exposure to CCl_4 can make the heart beat irregular or stop.
- It can cause ozone layer depletion.

5. FREONS

- CFC's of methane and ethane are collectively known as Freons.
- They are extremely stable, unreactive, non-toxic, and easily liquefiable gases.
- Freon-12 is one of the most common Freon of industrial use.
- Freon-12 is manufactured from tetrachloromethane by Swartz Reaction.
- Used for aerosol propellants, refrigeration and air conditioning purposes.

6. P,P'-DICHLORO DIPHENYL TRICHLORO ETHANE

- The IUPAC name of DDT is 1,1,1-trichloro-2,2-bis (p-chlorophenyl)ethane.
- First chlorinated organic insecticide.
- Highly toxic and chemically stable.
- Paul Muller was awarded Nobel prize for its discovery.
- Prepared by heating chloral with chlorobenzene in the presence of Conc. H_2SO_4