Haloalkanes and Haloarenes

Classification and Nomenclature

Classification

- Based on number of halogen atoms
- Monohalogen
- Dihalogen
- Polyhalogen (tri-, tetra-, penta- etc.)
- Examples of haloalkanes:

CH_3X

Monohaloalkane

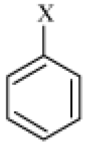
CH_2X-CH_2X

Dihaloalkane

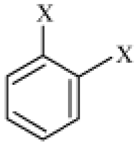
$CH_2X-CHX-CH_2X$

Trihaloalkane

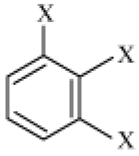
- Examples of haloarenes:



Monohaloarene



Dihaloarene



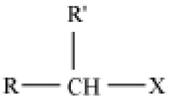
Trihaloarene

- Based on the hybridisation of C−atom of C−X bond of **monohalocompounds**
- Compounds containing sp^3 C−X bond (X = F, Cl, Br, I)

(i) Alkyl halides or haloalkanes (R−X) → They form homologous series of general formula $C_nH_{2n+1}X$. They are further classified into primary, secondary, and tertiary.

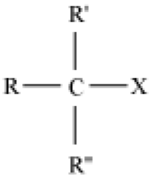
$R-CH_2-X$

Primary (1°)



$R-CH(R')-X$

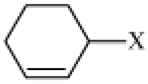
Secondary (2°)



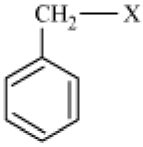
$R-C(R')(R'')-X$

Tertiary (3°)

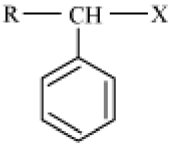
(ii) Allylic halides → Compounds containing halogen atom bonded to an allylic carbon



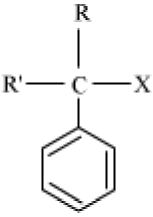
(iii) Benzylic halides → Compounds containing halogen atom bonded to an sp^3 hybridised carbon atom next to an aromatic ring



Primary (1°)



Secondary (2°)

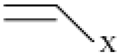


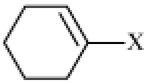
Tertiary (3°)

To test your knowledge of this concept, solve the following puzzle.

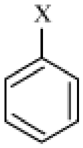
- Compounds containing sp^2 C−X bond (X = F, Cl, Br, I)

(i) Vinylic halides → Compounds containing halogen atom bonded to a vinylic carbon





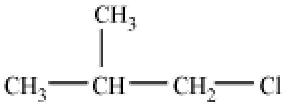
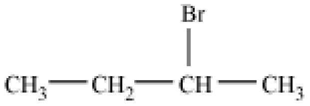
(ii) Aryl halides → Compounds containing halogen atom bonded to an sp^2 hybridised carbon atom of an aromatic ring



Nomenclature

- For haloalkanes
- Common name → Name of alkyl group followed by name of the halide
- IUPAC name → Named as halo-substituted hydrocarbon in IUPAC
- Examples:

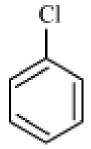
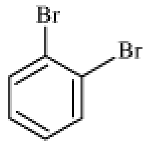
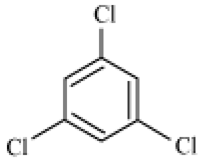
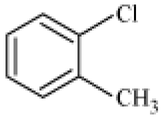
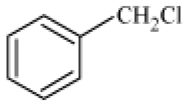
Structure	Common Name	IUPAC Name

$CH_3CH_2CH_2CH_2Br$	*n*–Butyl bromide	1-Bromobutane
 $CH_3-CH(CH_3)-CH_2-Cl$	Isobutyl chloride	1-Chloro-2-methyl-propane
 $CH_3-CH_2-CH(Br)-CH_3$	*sec*-butyl bromide	2-Bromobutane
$CH_3CH_2CH(Cl)CH_3$	*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_2Cl_2	Methylene chloride	Dichloromethane

- For haloarenes
- Named as halo-substituted hydrocarbon (for both common and IUPAC name)
- For dihalogen derivatives:

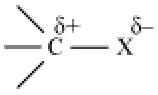
  In common names → prefixes *o*-, *m*-, *p*- are used

  In IUPAC names → numerals 1, 2; 1, 3; 1, 4 are used
- Examples:

Structure	Common name	IUPAC name
	Chlorobenzene	Chlorobenzene
	*o*-Dibromobenzene	1,2-Dibromobenzene
	*sym*-Trichlorobenzene	1,3,5-Trichlorobenzene
	*o*-Chlorotoluene	1-Chloro-2-methylbenzene or 2-Chlorotoluene
	Benzyl chloride	Chlorophenylmethane

Nature of C−X bond

- C-atom bears partial positive charge and X-atom bears partial negative charge.



- C−X bond length increases down the group.
- Reason − Size of halogen atom increases down the group.

Methods of Preparation

From Alcohols

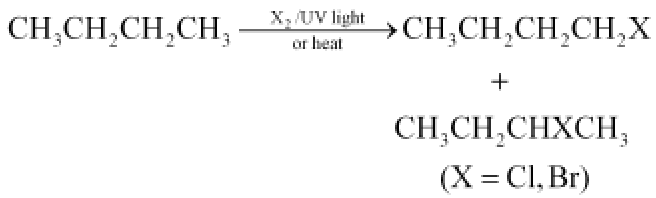
- $3R - OH + PX_3 \longrightarrow 3R - X + H_3PO_3$ (X = Cl, Br)
- $R - OH + PCl_5 \longrightarrow R - Cl + POCl_3 + HCl$
- $R - OH \xrightarrow[X_2 = Br_2, I_2]{\text{red } P/X_2} R - X$
- $R - OH + SOCl_2 \longrightarrow R - Cl + SO_2 + HCl$
- $R - OH + NaCl + H_2SO_4 \longrightarrow R - Cl + NaHSO_4 + H_2O$
- $R - OH + HX \xrightarrow{ZnCl_2} R - X + H_2O$
- For this reaction, the increasing order of reactivity of alcohols is

  1° < 2° < 3°
- This reaction cannot be applied to produce aryl halides.

  Reason − It is difficult to break carbon-oxygen bond in phenols as it possesses a partial double bond character.

From Hydrocarbons

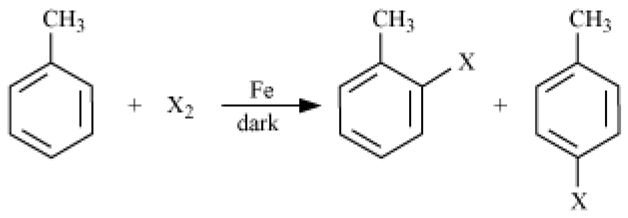
- **Free radical halogenation**
- Gives a complex mixture of isomeric mono- and poly- haloalkanes This method is not of much practical use as it is difficult to separate the complex mixture.
- When only mono-substitution is carried out



$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{X_2/\text{UV light}} CH_3CH_2CH_2CH_2X + CH_3CH_2CHXCH_3$$

$(X = Cl, Br)$

- **Electrophilic Substitution**

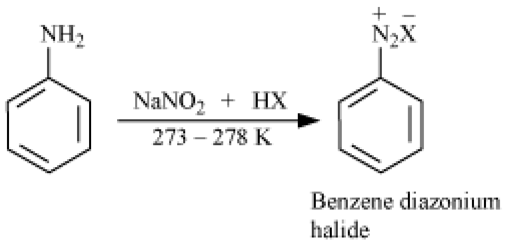


$(X = Cl, Br)$

- However, iodination is a reversible reaction. Oxidising agent such as HNO_3 or HIO_4 is required to oxidise HI formed during the reaction.

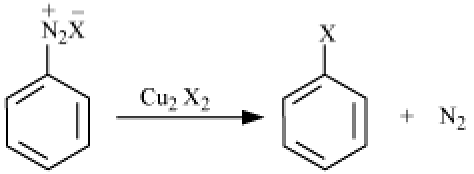
- **Sandmeyer's Reaction:** The Cl , Br and CN nucleophiles can easily be introduced in the benzene ring of benzene diazonium salt in the presence of Cu(I) ion. This reaction is called Sandmeyer reaction. It is applicable to primary aromatic amine.

Step I: Preparation of diazonium salt

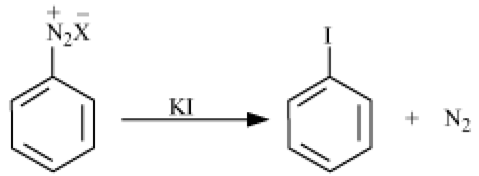


Step II: Formation of haloarene with release of nitrogen gas

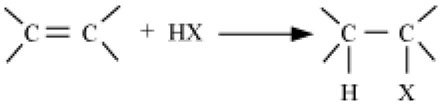
For Cl and Br:



For I:



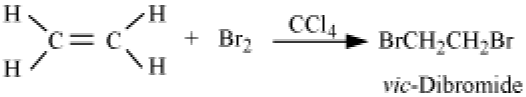
- **From Alkenes**
- By adding hydrogen halides



(X = Cl, Br, I)

$$\underset{\text{(According to Markovnikov's rule)}}{CH_3CH=CH_2 + HI \longrightarrow \underset{\text{(Minor)}}{CH_3CH_2CH_2I} + \underset{\text{(Major)}}{CH_3CHICH_3}}$$

- By adding halogens



vic-Dibromide

This method is used to detect double bond in a molecule as reddish brown colour of bromine is discharged during the reaction.

Halogen Exchange

- **Finkelstein Reaction**

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

- This reaction in forward direction can be favoured by precipitating NaX formed in dry acetone (according to Le Chatelier’s principle).
- **Swarts Reaction**
- Preparation of alkyl fluoride
- Requires metallic fluoride such as AgF, Hg_2F_2, CoF_2, or SbF_3

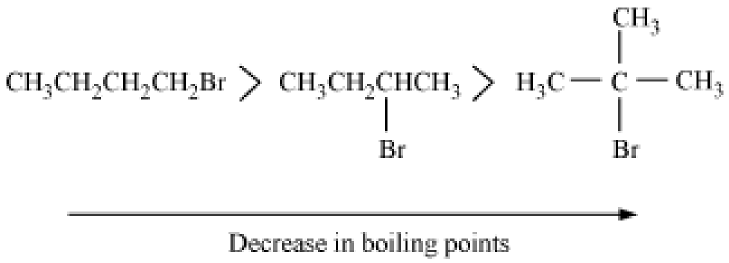
$$H_3C{-}X + AgF \longrightarrow H_3C - F + AgX$$
$$(X = Cl, Br)$$

Physical Properties

- Pure alkylhalides are colourless. However, in the presence of light, bromides and iodides become coloured.
- Some halides are sweet in smell.

Melting and Boiling Points

- Chlorides, bromides, and iodides have higher boiling points than hydrocarbons of comparable molecular mass.
- Reason – Chlorides, bromides, and iodides are polar in nature whereas hydrocarbons are non-polar. Therefore, these halides have greater intermolecular forces of attraction (dipole – dipole) than their parent hydrocarbons and hence, have higher boiling points.
- $\xrightarrow[\text{Increase in boiling points}]{RF < RCl < RBr < RI}$
- Reason – Vander Waals forces increase with increase in size and mass of halogen atoms and hence, boiling point also increases.
- Boiling points of isomeric haloalkanes decrease with increase in branching.
- For example,



$$CH_3CH_2CH_2CH_2Br > CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 > H_3C - \underset{\displaystyle Br}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} - CH_3$$

Decrease in boiling points

- The boiling points of isomeric dihalobenzenes are nearly the same.
- However, the melting point of para-isomer is higher than those of ortho- and meta- isomers.

Reason – Better fit of para-isomer in crystal lattice due to its symmetry

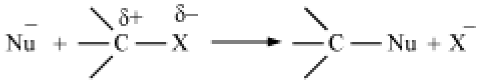
- Lower members (such as CH_3Cl, CH_3Br, C_2H_5Cl) are gases whereas higher members are liquids or solids at room temperature.

Density

- Increases with the increase in
- number of carbon atoms
- number of halogen atoms
- atomic mass of the halogen atoms
- Very slightly soluble in water, but soluble in organic solvents
- Reason – The energy required to overcome the intermolecular attraction between the haloalkane molecules is greater than the energy released during dissolution in water.

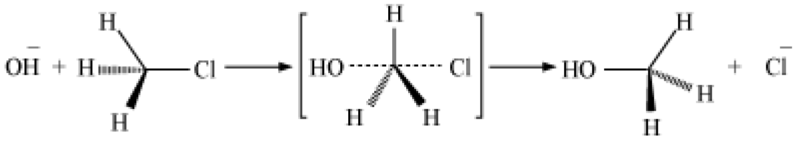
Reactions of Haloalkanes

Nucleophilic Substitution Reactions



Mechanism

- **Substitution nucleophilic bimolecular (S_N2)**

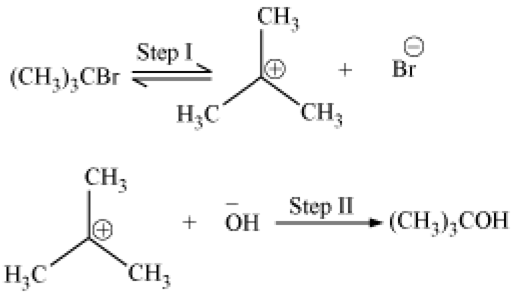


- Inversion of configuration takes place.
- The increasing order of reactivity is

  3° halide < 2° halide < 1° halide

  Reason – Due to the presence of bulky substituents in 3° and 2° halides, nucleophile cannot approach.

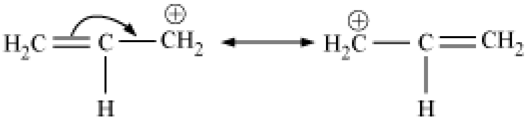
- **Substitution nucleophilic unimolecular (S_N1)**

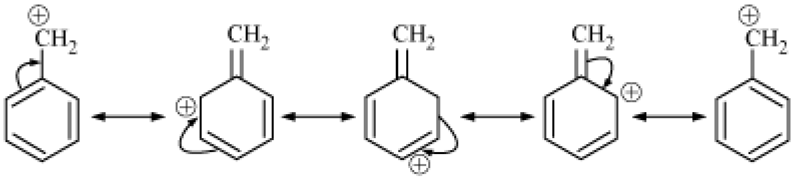


- Carried out in polar protic solvents such as water, alcohol, acetic acid, etc.
- The increasing order of reactivity is

  1° halide < 2° halide < 3° halide

  Reason – Greater the stability of carbocation, more easily the alkyl halide is formed and hence, faster is the reaction rate. The increasing order of stability of carbocation is 1° < 2° < 3°. Since 1° halide forms 1° carbocation, 2° halide forms 2° carbocation, and 3° halide forms 3° carbocation. Therefore, the increasing order of reactivity is 1° halide < 2° halide < 3° halide.
- Allylic and benzylic halides are very reactive towards S_N1 reaction because of stabilisation of their carbocations through resonance.





- For both S_N1 and S_N2 reaction, the order of reactivity of halides is

  R–F << R–Cl < R–Br < R–I

  Stereochemical Aspects of Nucleophilic Substitution
- In S_N2 reaction, complete stereochemical inversion takes place.
- In S_N1 reaction, racemisation takes place.

Some Stereochemical Terms:

Compounds that rotate the plane polarised light are called optically active compounds.

Angle of rotation of plane polarised light is measured by an instrument called polarimeter.

Dextrorotatory or *d*-form – Compounds that rotate plane polarised light to right

Laevorotatory or *l*-form – Compounds that rotate plane polarised light to left

d- and *l*- forms of a compound are called optical isomers and the phenomenon is called optical isomerism.

Asymmetric carbon or stereocentre – Carbon atom with all the four substituents attached to it are different.

The objects which are non-superimposable on their mirror images are known as chiral and the property is known as chirality.

The objects which are superimposable on their mirror images are known as achiral.

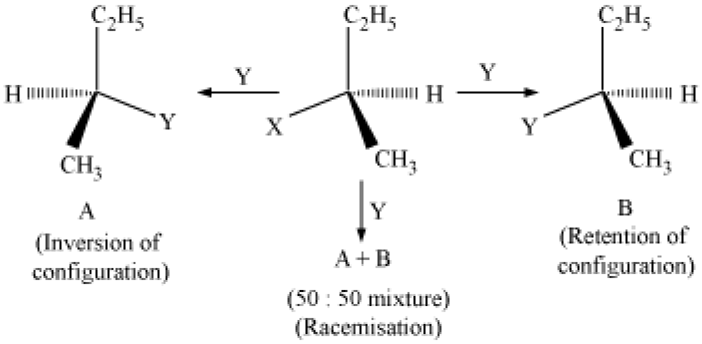
Enantiomers are stereoisomers which are non-superimposable mirror images.

There are three outcomes for a reaction at an asymmetric carbon atom.

Inversion

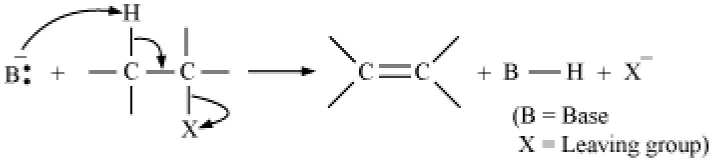
Retention

Racemisation

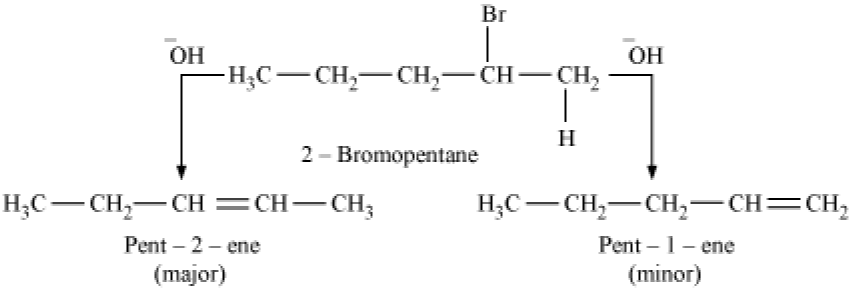


Elimination Reactions

- On heating a haloalkane containing β-hydrogen atom with alcoholic KOH solution, elimination of H from β carbon and a halogen from α takes place.



- Also called β-elimination as β-hydrogen is eliminated
- In case of more than one product:
- Saytzeff’s rule − In dehydrohalogenation reactions, the alkene with the greater number of alkyl groups attached to the doubly bonded carbon atoms is preferably formed.



Reaction with Metals

- Chlorides, bromides, and iodides react with certain metals to form organo-metallic compounds such as Grignard reagents.

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

Grignard reagent

- Wurtz Reaction

$2RX + 2Na \xrightarrow{\text{dry ether}} R{-}R + 2NaX$

- Hydrocarbon containing double the number of carbon atoms present in the halide is formed.

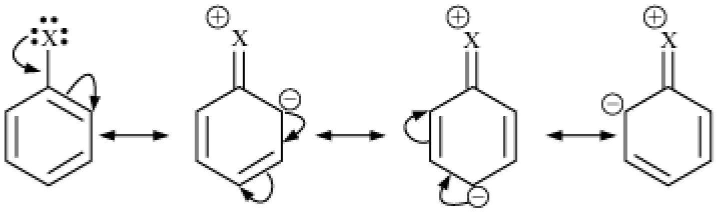
Reactions of Haloarenes

The aryl and vinyl halides are much less reactive than the alkyl halides. Let us undersatnd this by means of the following video.

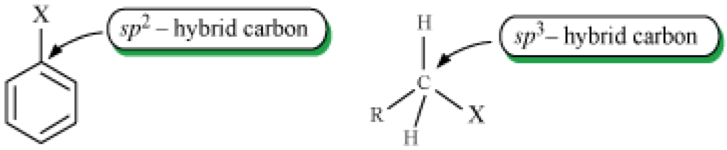
Nucleophilic Substitution Reactions

- Haloarenes are much less reactive towards nucleophilic substitution reactions due to the following reasons:

- In haloarenes, the benzene ring undergoes resonance and as a result, the C−X bond acquires a partial double bond character. Therefore, it becomes difficult to break the C−X bond.



- In haloalkanes, the halogen atom is attached to an sp^3 hybridised carbon atom while in haloarenes, it is attached to an sp^2 hybridised carbon atom. Since an sp^2 hybridised carbon has more *s*-character than sp^3 hybridised carbon, the former is more electronegative than the latter. As a result, the electron pair of C−X bond is held by carbon atom more tightly in haloarenes than haloalkanes. Therefore, the C−X bond becomes shorter in haloarenes and hence, becomes stronger.



- The phenyl cation formed by the self ionisation is unstable and hence, S_N1 mechanism is avoided.

- Electron-rich nucleophile cannot approach electron-rich arenes due to repulsion.

- Replacement by hydroxyl group

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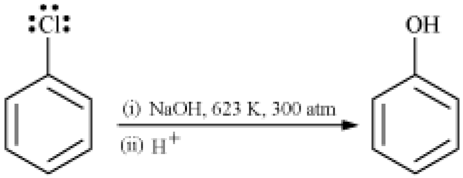
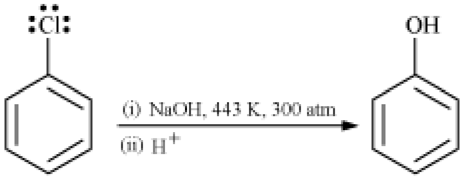
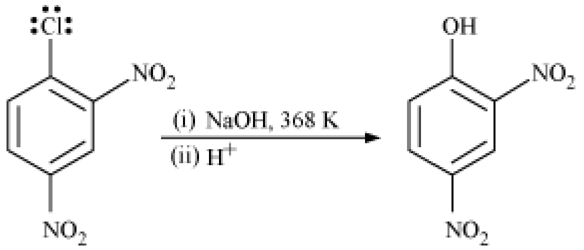
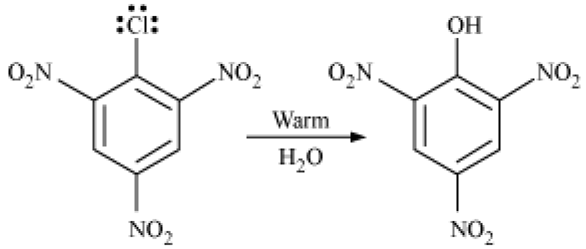


- Reactivity increases if an electron withdrawing group ($-NO_2$) is present at ortho- and para-positions. This can be observed as the temperature required to carry out the reaction decreases in the presence of $-NO_2$ group at *o*-and *p*-positions.

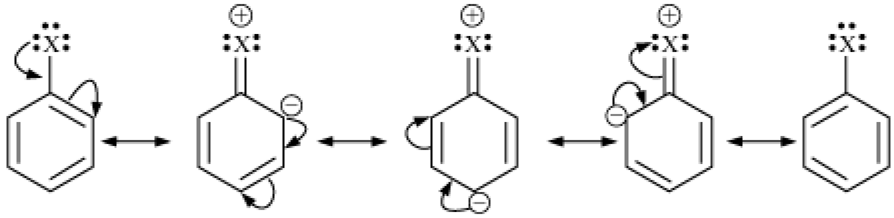




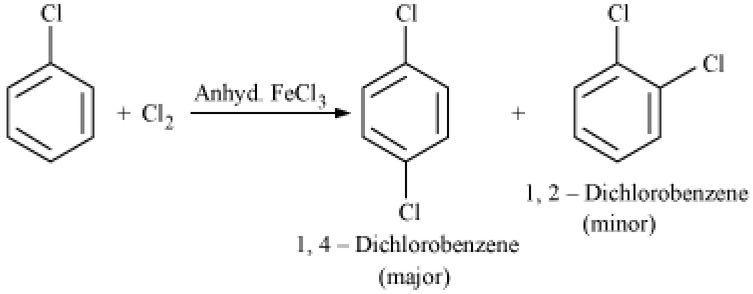


Electrophilic Substitution Reactions

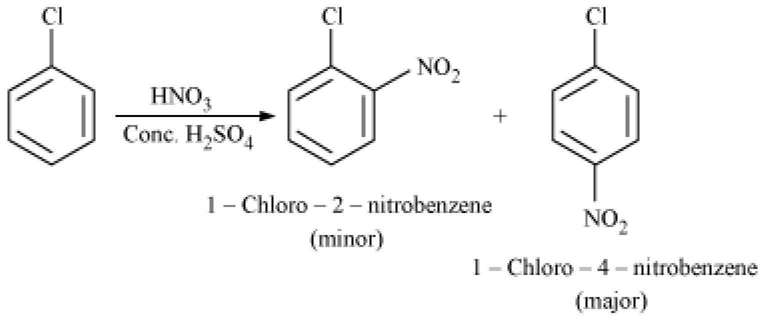
- Substitution occurs at *o*- and *p*-direction due to availability of electrons at these positions because of resonance.



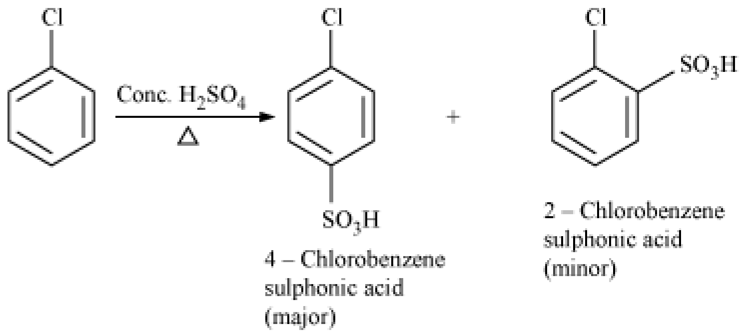
- Halogenation



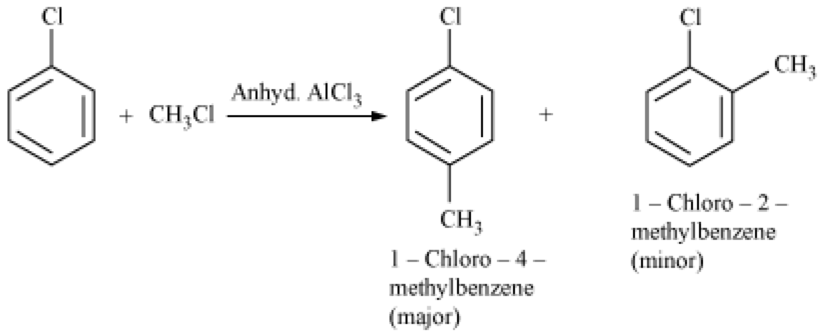
- Nitration



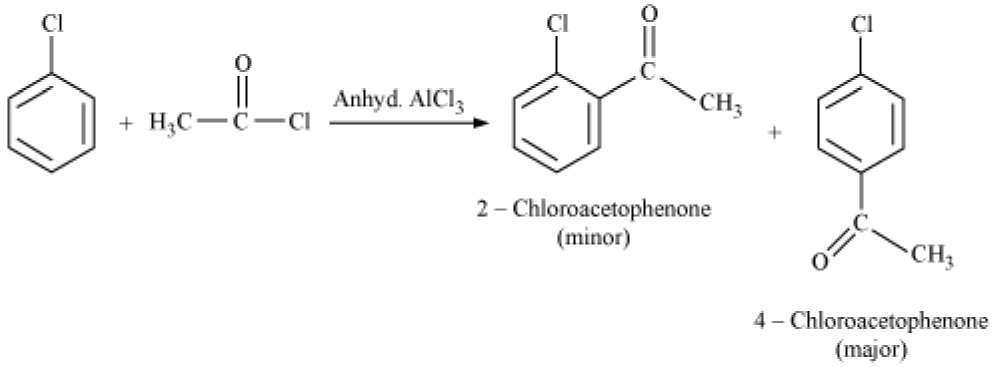
- Sulphonation



- Friedel–Crafts Alkylation

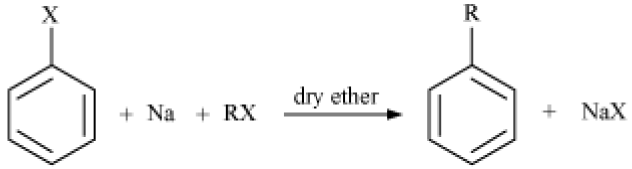


- Friedel-Crafts Acylation

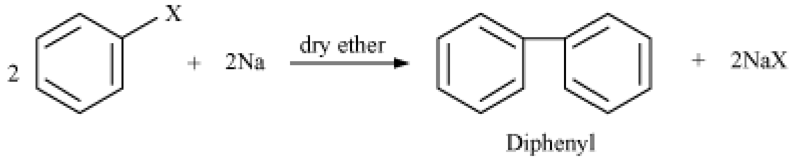


Reaction with Metals

- Wurtz–Fittig Reaction



- Fittig reaction



Polyhalogen Compounds

- Polyhalogen compounds are carbon compounds containing more than one halogen atom.

Dichloromethane or Methylene Chloride (CH_2Cl_2)

- **Uses**
- As propellant in aerosols
- As metal finishing and cleaning solvent
- As a process solvent in the manufacture of drugs
- **Toxicity**

- Harms the human central nervous system
- Lower levels of CH_2Cl_2 in air can lead to slightly impaired hearing and vision.
- Higher levels of CH_2Cl_2 in air can cause dizziness, nausea, tingling and numbness in the fingers and toes.
- Direct skin contact causes intense burning and mild redness of the skin.

Trichloromethane or Chloroform ($CHCl_3$)

- **Uses**
- As a solvent for fats, alkaloids, iodine, and other substances
- In the production of the freon refrigerant R-22
- Earlier used as anaesthetic, but has been replaced due its toxicity
- **Toxicity**
- Inhaling of $CHCl_3$ vapours can cause depression of the central nervous system, dizziness, fatigue, and headache.
- Chronic chloroform exposure may lead to damage of the liver and kidneys.
- Immersion of skin in $CHCl_3$ leads to development of sores.
- $CHCl_3$ is oxidised to an extremely poisonous gas phosgene ($COCl_2$) in the presence of light.

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

That is why chloroform is stored in closed dark-coloured bottles completely filled so that no air is left inside the bottles.

Triiodomethane or Iodoform (CHI_3)

Uses

- Earlier used as an antiseptic, but has been replaced due to its objectionable smell
- Its antiseptic properties are not due to iodoform itself, but due to the liberation of free iodine.

Tetrachloromethane or Carbon Tetrachloride (CCl_4)

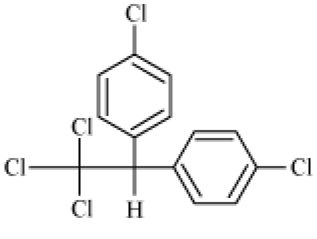
- **Uses**

- In the manufacture of refrigerants and aerosol propellants
- As feedstock in the synthesis of chlorofluorocarbons
- In pharmaceutical manufacturing
- As industrial solvent
- As cleaning fluid
- As fire extinguisher
- **Toxicity**
- Causes lives cancer, dizziness, light headedness, nausea, vomiting These effects may lead to stupor, coma, unconsciousness, or death.
- Leads to irregularity in heart beat or even stop
- Causes irritation of eyes on contact
- Causes depletion of ozone layer, leading to increase in skin cancer, eye diseases

Freons

- Chlorofluorocarbon compounds of methane and ethane are collectively called freons.
- Physical properties:
- Stable and unreactive
- Non-toxic and non-corrosive
- Easily liquefiable gas
- **Uses**
- In aerosol propellants, refrigeration, and air conditioning purposes
- **Toxicity**
- Upsets the natural ozone balance
- Freon 12 (CCl_2F_2) is one of the most common freons that have industrial use.

p,p' **-Dichlorodiphenyltrichloroethane (DDT)**



DDT

- **First Chlorinated Organic Insecticide**
- Effective against mosquitoes that spread malaria and lice that carry typhus
- **Toxicity**
- DDT is highly stable and is not metabolised very rapidly by animals. Rather it is deposited and stored in the fatty tissues. It is proved to be toxic to living beings. It is banned in many countries due to its toxicity.