

# **EDUCATALYSTS**

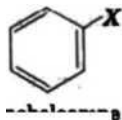
**Class(12th)**

**Introductions to Haloalkanes**

The replacement of hydrogen atom(s) in hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively.

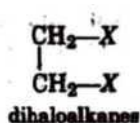
### Classification of Halogen Derivatives

On the basis of number of halogen atoms present, halogen derivatives are classified as mono, di, tri, tetra, etc., halogen derivatives, e.g.,



monohaloarene

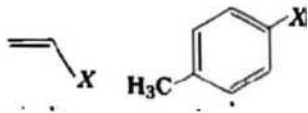
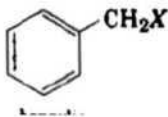
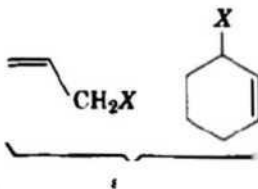
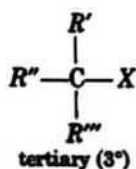
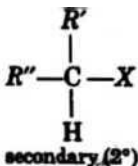
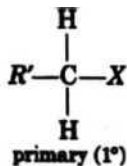
$\text{CH}_2-\text{X}$



$\text{CH}_3-\text{X}$

trihaloalkane

On the basis of the nature of the carbon to which halogen atom is attached, halogen derivatives



are classified as 1°, 2°, 3°, allylic, benzylic, vinylic and aryl derivatives, e.g.,

allylic

/

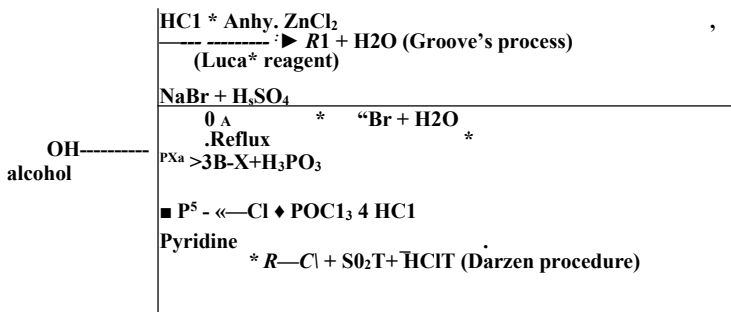
benzyl

vinylic

aryl

# General Methods of Preparation of Haloalkanes

## 1. From Alcohols

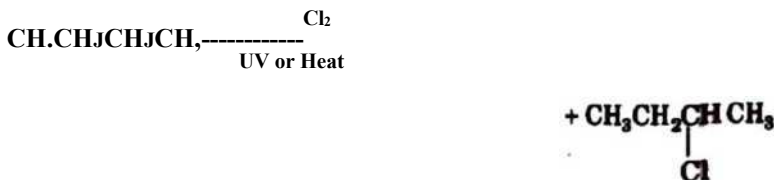


In Groove's method, ZnCh is used to weaken the C-OH bond. In case of 3° alcohols, ZnCh is not required.

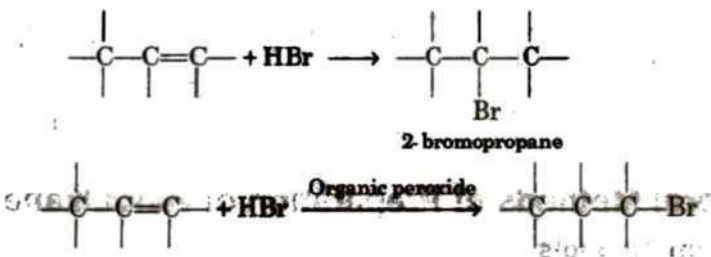
The reactivity order of halogen acids is  $\text{HI} > \text{HBr} > \text{HCl}$ .

Darzen procedure is the best method for preparing alkyl halides from alcohols since both the by products ( $\text{SO}_2$  and  $\text{HCl}$ ) are gaseous and escape easily.

## 2. Free Radical Halogenation of Alkanes



## Addition of Hydrogen Halides on Alkenes



## 1. Finkelstein Reaction



## 2. Swarts Reaction



$\text{Hg}_2\text{F}_2$ ,  $\text{COF}_2$  and  $\text{SbF}_5$  can also be used as a reagent for Swarts reaction.

## 3. Hunsdiecker Reaction

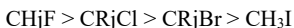


## Physical Properties of Haloalkanes

### 1. Boiling point orders

- $\text{R}-\text{I} > \text{R}-\text{Br} > \text{R}-\text{Cl} > \text{R}-\text{F}$
- $\text{CH}_3 - (\text{CH}_2)_2 - \text{CH}_2\text{Br} > (\text{CH}_3)_2\text{CHCH}_2\text{Br} > (\text{CH}_3)_3\text{CBr}$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{X} > \text{CH}_3\text{CH}_2\text{X} > \text{CH}_3\text{X}$

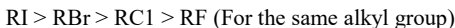
2. Bond strength of haloalkanes decreases as the size of the halogen atom increases. Thus, the order of bond strength is



3. Dipole moment decreases as the electronegativity of the halogen decreases.

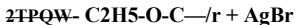
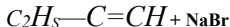
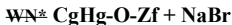
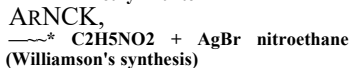
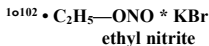
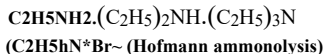
4. Haloalkanes though polar but are insoluble in water as they do not form hydrogen bonding with water.

5. Density order is



## Chemical Reactions of Haloalkanes

### 1. Nucleophilic Substitution Reactions ( $\text{S}_\text{N}$ reactions)



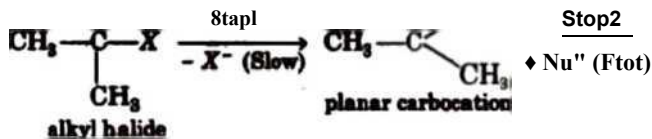
KCN is predominantly ionic and provides cyanide ions in solution, which is ambident nucleophile and bind with carbon side to form as the major product, while AgCN is covalent and form isocyanide as the major product.

Like KCN, KNO<sub>2</sub> form R-ONO while AgNCh produces R-NO<sub>2</sub> as product. Vinyl chloride is less reactive towards nucleophilic substitution reactions due to resonance.

Nucleophilic substitution reactions are of two types

(a) S<sub>N</sub>1 type (Unimolecular nucleophilic reactions proceed in two steps:

CH<sub>3</sub>,



CH<sub>3</sub>

Rate,  $r = k[\text{RX}]$ . It is a first order reaction.

Reactivity order of alkyl halide towards S<sub>N</sub>1 mechanism

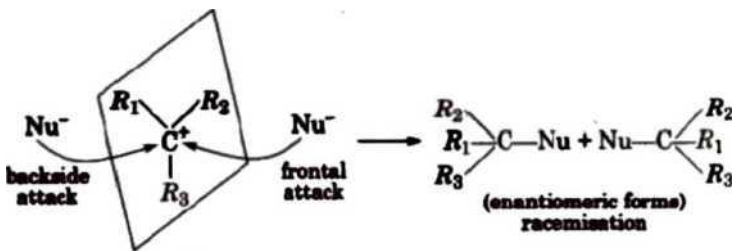
$3^\circ > 2^\circ > 1^\circ$

CH<sub>3</sub>

■ substitution product

Polar solvents, low concentration of nucleophiles and weak nucleophiles favour S<sub>N</sub>1 mechanism.

In S<sub>N</sub>1 reactions, partial racemisation occurs due to the possibility of frontal as well as backside attack

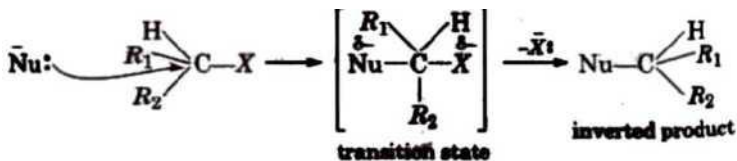


on planar carbocation.

(b) S<sub>N</sub>2 type (Bimolecular nucleophilic substitution) These reactions proceed in one step and is a second order reaction with  $r = k[\text{RX}][\text{Nu}]$ .

During S<sub>N</sub>2 reaction, inversion of configuration occurs (Walden inversion) i.e., starting with dextrorotatory halide a laevo product is obtained and vice-versa, e.g.,

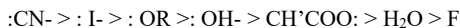
planar carbocation



Reactivity of halides towards SN2 mechanism is

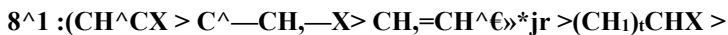


Rate of reaction in SN2 mechanism depends on the strength of the attacking nucleophile. Strength of some common nucleophiles is



Non-polar solvents, strong nucleophiles and high concentration of nucleophiles favour SN2 mechanism.

Relative rates of some alkyl halides in SN1 and SN2 reactions are in the order



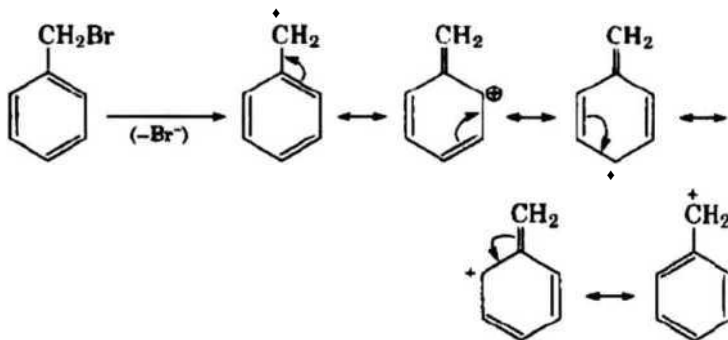
SN 2



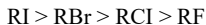
resonance stabilised



Resonating structure of benzyl carbocations are

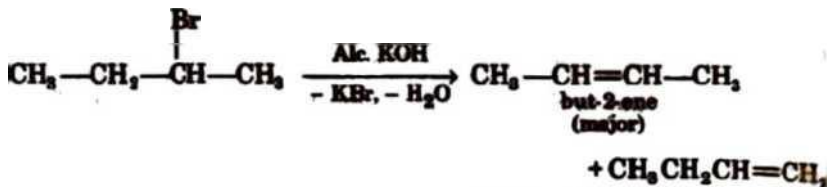


Relative reactivity of alkyl halides for same alkyl group is



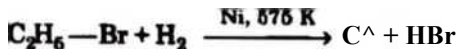
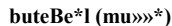
## 2. Elimination Reactions

Dehydrohalogenation is a  $\beta$ -elimination reaction in which halogen is from  $\alpha$ -carbon atom and the



hydrogen from the  $\alpha$ -carbon according to Saytzeff rule, e.g.,

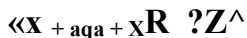
Ease of dehydrohalogenation among halides



3. Reduction

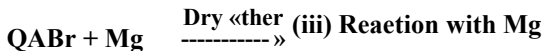
4. Reaction with Metals





(i) Wurtz reaction

Q) Wurtz-Fittig reaction



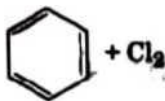
(Grignard reagent)

Grignard reagent is never isolated in the solid state as it explodes in dry state. So it is used as ethereal solution.

## 5. Isomerisation



General Methods of Preparation of Aryl Halides



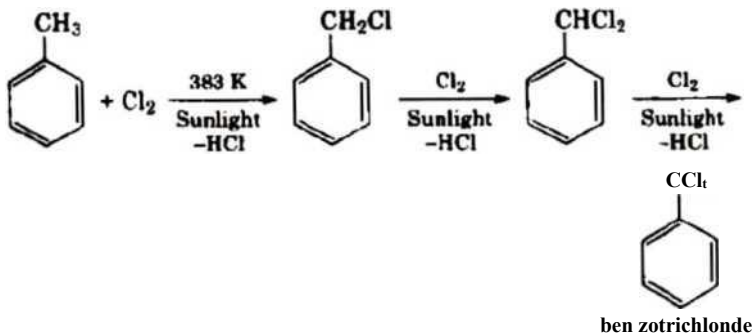
### 1. By Halogenation of Aromatic Hydrocarbons

It is an electrophilic substitution reaction.

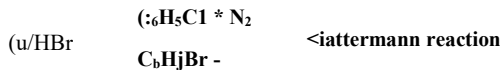
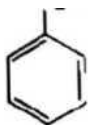
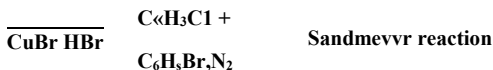
Cl

### 2. By Side Chain Halogenation



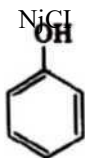
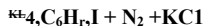


(It involves free radical mechanism.)



### 3. From Benzene Diazonium Salt

(Balz Schiemann reaction)

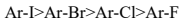


### 4. From Phenol

#### Physical Properties of Aryl Halides

1. Aryl halides are colourless liquids or colourless solids with characteristic odour.

2. Boiling point generally increases with increase in the size of aryl group or halogen atom.  
Boiling point order



3. The melting point of p-isomer is more than o- and m-isomer.

This is because of more symmetrical nature of p-isomer.

4. Due to resonance in chlorobenzene, C-Cl bond is shorter and hence, its dipole moment is less than that of cyclohexyl chloride.

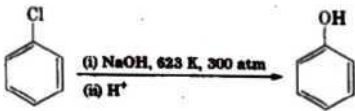
### Chemical Properties of Aryl Halides

#### 1. Nucleophilic Substitution Reaction

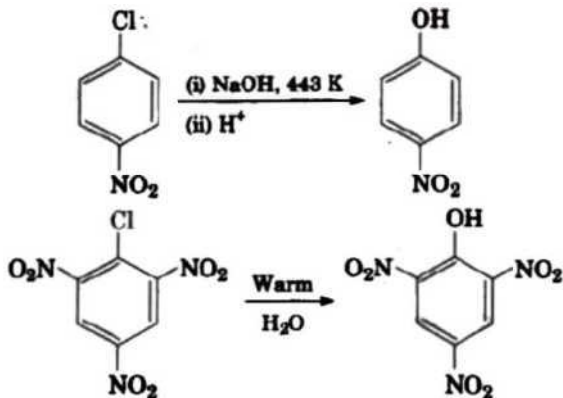
Aryl halides are less reactive towards nucleophilic substitution reaction. Their low reactivity is attributed due to the following reasons:

1. Due to resonance, C-X bond has partial double bond character.
2. Stabilisation of the molecule by delocalisation of electrons.
3. (Instability of phenyl carbocation.

However, aryl halides having electron withdrawing groups (like -NO<sub>2</sub>, -SO<sub>3</sub>H, etc.) at ortho and para positions undergo nucleophilic substitution reaction easily.

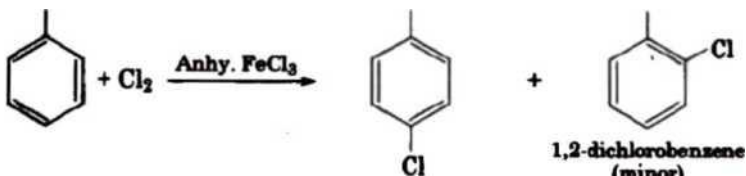


Presence of electron withdrawing group (-NO<sub>2</sub>) increases the reactivity.

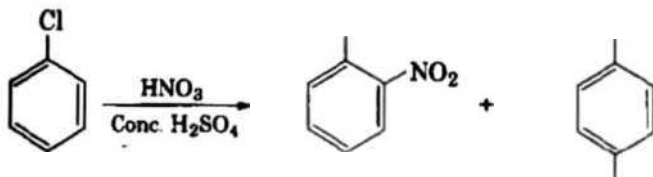


## 2. Electrophilic Substitution Reactions

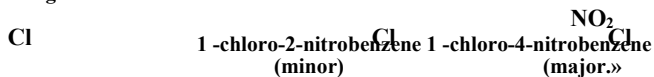
Halogens are deactivating but O, p-directing. Thus, chlorination, nitration, sulphonation and Friedel Craft's reaction give a mixture of o- and P- chloro substituted derivatives.



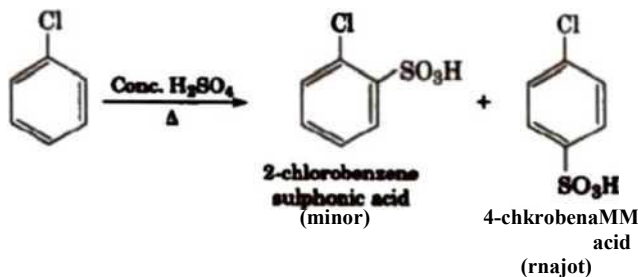
### (ii) Nitration



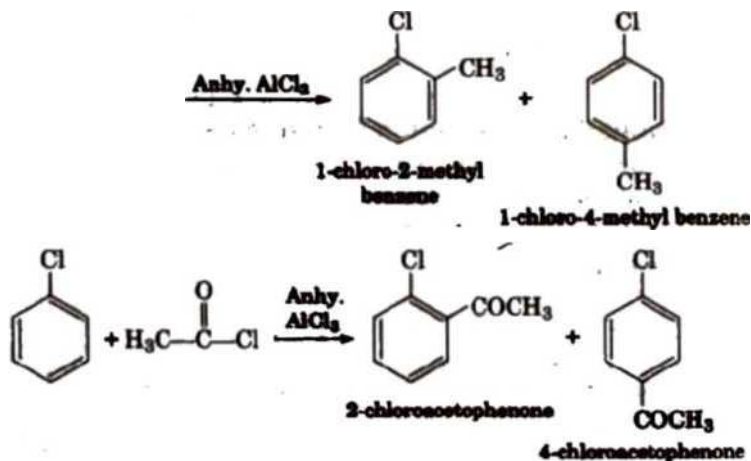
### (i) Halogenation



(iii) Sulphonation

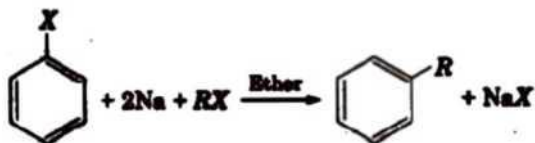


(iv) Friedel-Crafts reaction

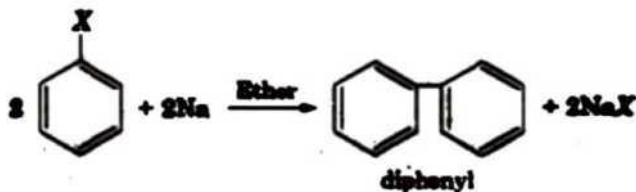


3. Reaction with Metals

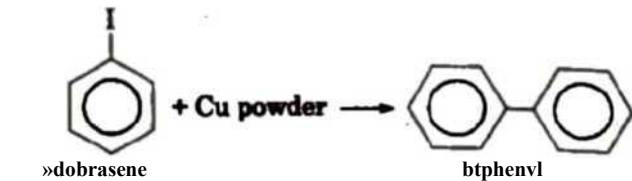
(i) Wurtz Fittig reaction



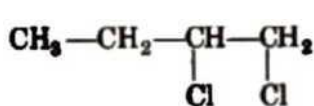
(ii) Fitting reaction



(iii) Ullmann reaction

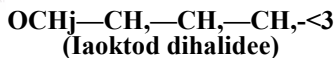


**Dihalogen Derivatives**



**(Vic or vicinal-dihalide)**

$\text{CH}_3\text{CH}_2\text{CH}_3$   
 < Geminal

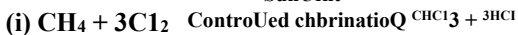


Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) is widely used as a solvent, as a propellant in aerosols. Direct contact of dichloromethane in humans causes intense burning and milk redness of the skin.

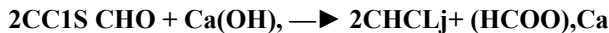
**Trihalogen Derivatives**

1. Chloroform [Trichloromethane,  $\text{CHCl}_3$ ]

**Methods of preparation**



## (ii) Haloform reaction



[Hydrolysis]

## Properties

1. Oxidation of  $\text{CHCl}_3$  gives poisonous gas phosgene (carbonyl chloride).



To avoid this oxidation  $\text{CHCl}_3$  is stored in dark brown bottles and filled to the brim. 1% ethanol is added to chloroform which converts harmful phosgene gas into diethyl carbonate.

2.  $\text{CHCl}_3$  is widely used in the production of freon refrigerant R-22.

3. On nitration, it gives tear producing insecticide substance chloropicrin.

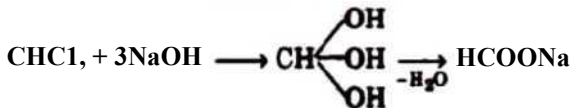


chloropicrin

4. On dehalogenation, it gives  $\text{C}^*\text{H}_3$  (acetylene).



5. When subjected to hydrolysis, it gives formate.



2. Iodoform (tri-iodomethane,  $\text{CHI}_3$ )

Iodoform is prepared by iodoform reaction.







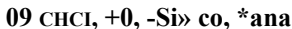
Compounds containing either  $\text{CH}_3\text{CO}-$  or  $\text{CH}_2\text{CH}(\text{OH})$  group form yellow colour iodoform with  $\text{I}_2$  and  $\text{NaOH}$ .

Iodoform when comes in contact with organic matter, decomposes easily to free iodine, an antiseptic. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

## Polyhalogen Derivatives

### 1. Tetrachloromethane (Carbon Tetrachloride, $\text{CCl}_4$ )

#### Preparation



$\text{CCl}_4$  is a colourless, non-inflammable, poisonous liquid, soluble in alcohol and ether. **Uses**

Carbon tetrachloride is used

1. as a solvent for oils, fats, resins
2. in dry cleaning
3. as fire extinguisher under the name 'pyrene'.

### 2. Freons

The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes. Carbon tetrachloride when reacts with antimony trifluoride in the presence of  $\text{SbCl}_5$  as catalyst, dichlorodifluoromethane (freon) is obtained.

### 3. DDT (p, p' -Dichlorodiphenyltrichloroethane)