

Chemistry

# Halogen Derivatives

# Table of Content

1. General characteristics of Halo-Alkanes.
2. General methods of preparation of Alkyl Halides.
3. Properties of Alkyl Halides.
4. Preparation and properties of dihalides.
5. Tri-halides (Chloroform and iodoform).
6. Tetra-halides (Carbon tetrachloride,  $\text{CCl}_4$ ).
7. Unsaturated halides (Halo-Alkene).
8. Halo-Arenes.
9. Some more important halogen derivatives.
10. Organometallic compounds.



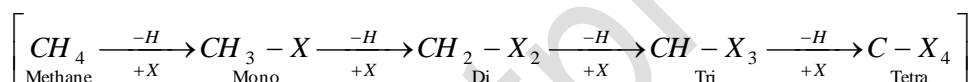
Compounds derived from hydrocarbons by the replacement of one or more hydrogen atoms by the corresponding number of halogen atoms are termed as halogen derivatives. The halogen derivatives of the hydrocarbons are broadly classified into three classes:

- Halogen derivatives of saturated hydrocarbons (Alkanes)- Halo-alkanes.
- Halogen derivatives of unsaturated hydrocarbons (Alkenes and alkynes)-Halo-alkene or alkyne.
- Halogen derivatives of aromatic hydrocarbons (Arenes)-Halo-arenes.

## 1. General characteristics of Halo-Alkanes.

(1) Organic compounds in which halogen atom ( $F, Cl, Br, I$ ) is directly linked with saturated carbon atom are known as halo-alkanes. General formula is  $C_nH_{2n+2-m}X_m$  ( $X = F, Cl, Br, I$ ) and  $m$  = no. of halogen atom;  $n$  = no. of carbon atoms.

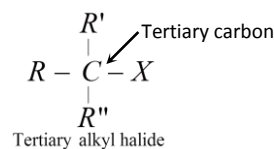
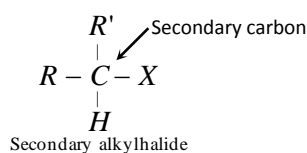
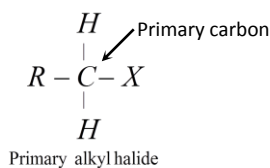
(2) Depending on the number of halogen atoms present in the halogen derivative, these are termed as mono-, di-, tri-, tetra-, and polyhalogen derivatives.



(i) Monohalogen derivatives are termed as alkyl halides.



Monohalogen derivatives or alkyl halides are classified as primary ( $1^\circ$ ), secondary ( $2^\circ$ ) or tertiary ( $3^\circ$ ) depending upon whether the halogen atom is attached to primary, secondary or tertiary carbon atoms.



(ii) The dihalogen derivatives are mainly of three types

(a) Gem-dihalides: In these derivatives both the halogen atoms are attached to the same carbon atom.

These are also called alkylidene halides.

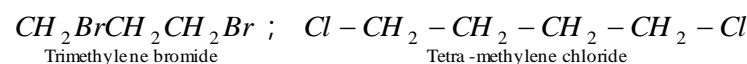


(b) Vic-dihalides: In these derivatives, the halogen atoms are attached to adjacent (Vicinal) carbon atoms.

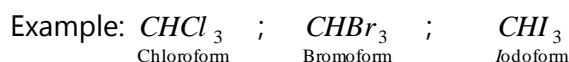
These are also termed as alkylene halides.



(c)  $\alpha$ - $\omega$  halides (Terminal dihalides): In these derivatives, the halogen atoms are attached to terminal carbon atoms. These are also called polymethylene halides.



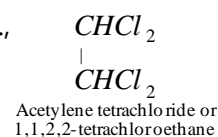
(iii) The tri-halogen derivatives are termed as halo-forms



(iv) In tetra-halogen derivatives all the four halogen atoms are attached to the same carbon atom in derivatives of methane.

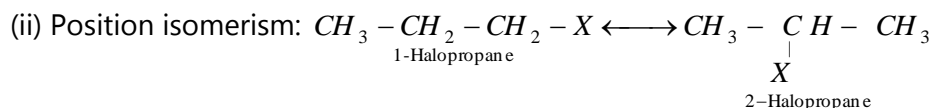


In other derivatives, the four halogen atoms are attached to different carbon atoms, e.g.,



Formula of halogen derivatives	Common name	IUPAC name
$CH_3Cl$	Methyl chloride	Chloromethane
$CH_3CH_2Br$	Ethyl bromide	Bromoethane
$CH_3CHBrCH_3$	Isopropyl bromide	2-Bromopropane
$CH_3CH_2CH_2CH_2Cl$	n-Butyl chloride	1-Chlorobutane
$\begin{array}{c} CH_3 \\   \\ CH - CH_2Br \\   \\ CH_3 \end{array} >$	Isobutyl bromide	1-Bromo -2-methylpropane
$\begin{array}{c} CH_3 \\   \\ CH_3 - C - CH_3 \\   \\ Br \end{array}$	Tertiary butyl bromide	2-Bromo -2-methylpropane
$\begin{array}{c} Cl \\   \\ CH_3CH \\   \\ Cl \end{array} <$	Ethylidene chloride	1,1-Dichloroethane
$CH_2Cl.CH_2Cl$	Ethylene chloride	1,2,-Dichloroethane
$CHCl_3$	Chloroform	Trichloromethane
$CHI_3$	Iodoform	Tri-iodomethane
$CCl_4$	Carbon tetrachloride	Tetrachloromethane

(4) Higher members of alkyl halides show following types of isomerism,



(iii) Optical isomerism: This is due to the presence of asymmetric carbon atom in secondary butyl halide.



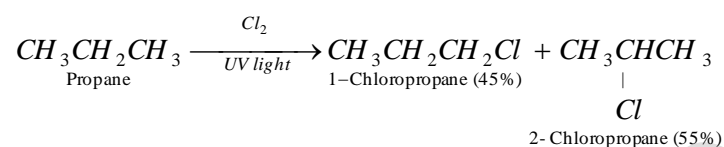
The total number of isomers in alkyl halides are: Propyl ( $C_3H_7 - X$ ) has two isomers, Butyl ( $C_4H_9 - X$ ) has four isomers, and Pentyl ( $C_5H_{11} - X$ ) has eight isomers.

(5) Halo-alkanes contain  $sp^3$  hybridised carbon atom bonded to halogen atom or atoms.

## 2. General methods of preparation of Alkyl Halides.

(1) From alkanes

(i) By halogenation:  $C_2H_6$  (Excess) +  $Cl_2 \xrightarrow{h\nu} C_2H_5Cl + HCl$   
Ethane Ethylchloride (Major product)



This reaction proceeds through free radical mechanism.

Note: Order of reactivity of  $X_2$  for a given alkane is,  $F_2 > Cl_2 > Br_2 > I_2$ .

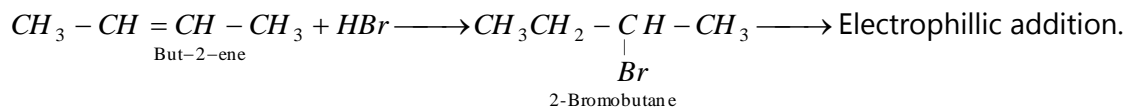
The reactivity of the alkanes follows the order:  $3^\circ\text{alkane} > 2^\circ\text{alkane} > 1^\circ\text{alkane}$ .

(ii) With sulphuryl chloride:  $R-H + SO_2Cl_2 \xrightarrow[Organic\ peroxide(R'CO_2)_2]{h\nu} R-Cl + SO_2 + HCl$

Note: In presence of light and trace of an organic peroxide the reaction is fast.



## (2) From alkenes (Hydrohalogenation)



Note: Addition of HBr to alkene in the presence of organic peroxide take place due to peroxide effect or Kharasch's effect.

This addition take place by two mechanism,

Peroxide initiates free radical mechanism.

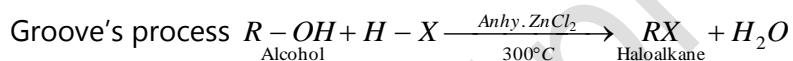
Markownikoff's addition by electrophilic mechanism.

From alkyne we cannot obtain mono alkyl halide.

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

## (3) From alcohols

### (i) By the action of halogen acids



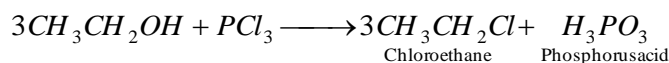
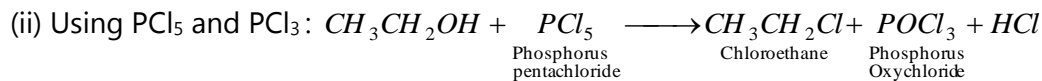
Note: The reactivity order of  $\text{HX}$  in the above reaction is :  $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$ .

Reactivity order of alcohols  $3^\circ > 2^\circ > 1^\circ > \text{MeOH}$ .

$2^\circ$  and  $3^\circ$  alcohols undergo  $\text{SN}^1$ ; where as  $1^\circ$  and MeOH undergo  $\text{SN}^2$  mechanism.

Concentrated HCl + anhy.  $\text{ZnCl}_2$  is known as lucas reagent.





Note: Bromine and iodine derivatives cannot be obtained from the above reaction, because  $\text{PBr}_5$  or  $\text{PI}_5$  are unstable.

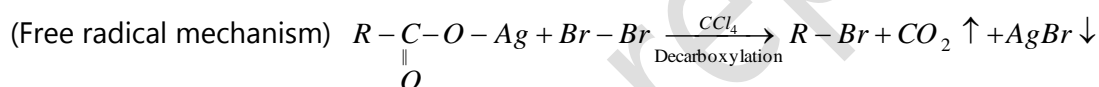
This method gives good yield of primary alkyl halides but poor yields of secondary and tertiary alkyl halides.

(iii) By the action of thionyl chloride



Note: Reaction takes place through  $\text{SN}^2$  mechanism.

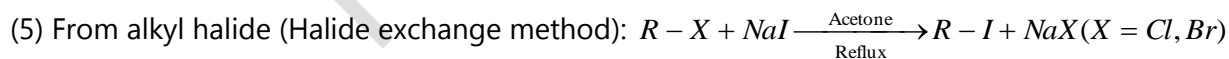
(4) From silver salt of carboxylic acids (Hunsdiecker reaction, Decarboxylation)



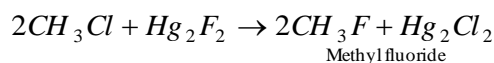
Note: The reactivity of alkyl group is  $1^\circ > 2^\circ > 3^\circ$

Not suitable for chlorination because yield is poor.

In this reaction iodine forms ester instead of alkyl halide and the reaction is called Birnbaum-Simonini reaction,

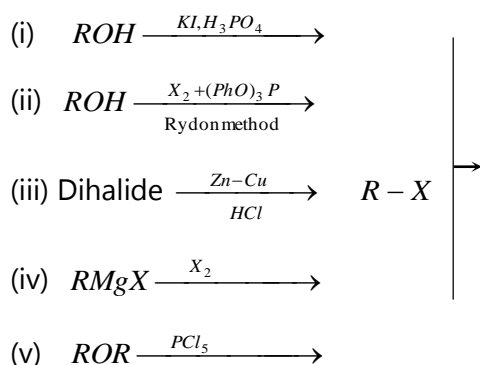


Note: Alkyl fluorides cannot be prepared by this method. They can be obtained from corresponding chlorides by the action of  $\text{Hg}_2\text{F}_2$  or antimony trifluoride.





### (6) Other method



## 3. Properties of Alkyl Halides.

### (1) Physical properties

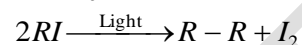
(i)  $CH_3F$ ,  $CH_3Cl$ ,  $CH_3Br$  and  $C_2H_5Cl$  are gases at room temperature. The alkyl halides upto  $C_{18}$  are colourless liquids while higher members are colourless solids.

(ii) Alkyl halides are insoluble in water but soluble in organic solvents.

(iii) They burn on copper wire with green edged flame (Beilstein test for halogens).

(iv) Alkyl bromides and iodides are heavier than water. Alkyl chlorides and fluorides are lighter than water.

(v) Alkyl iodides become violet or brown in colour on exposure as they decompose in light.



(vi) For a given alkyl group, the boiling points of alkyl halides are in the order  $RI > RBr > RCl > RF$  and for a given halogen the boiling points of alkyl halides increase with the increase of the size of the alkyl group.

(vii) Alkyl halides are in general toxic compounds and bring unconsciousness when inhaled in large amounts.

(2) Chemical properties: The alkyl halides are highly reactive, the order of reactivity is,

Iodide > Bromide > Chloride (Nature of the halogen atom)

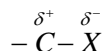
Tertiary > Secondary > Primary (Type of the halogen atom)

Amongst the primary alkyl halide, the order of reactivity is :  $CH_3X > C_2H_5X > C_3H_7X$ , etc.

The high reactivity of alkyl halides can be explained in terms of the nature of  $C-X$  bond which is highly polarised covalent bond due to large difference in the electronegativities of carbon and halogen atoms.



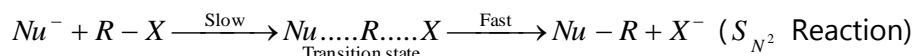
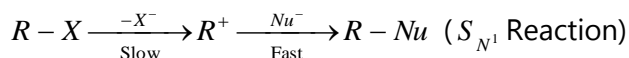
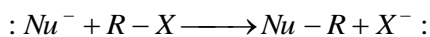
The halogen is far more electronegative than carbon and tends to pull the electrons away from carbon, i.e., halogen acquires a small negative charge and carbon a small positive charge.



This polarity gives rise to two types of reactions,

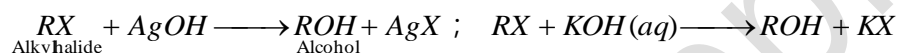
(i) Nucleophilic substitution reactions (ii) Elimination reactions

(i) Nucleophilic substitution reactions: The  $C^{\delta+}$  site is susceptible to attack by nucleophiles (An electron rich species).

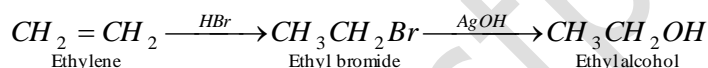


Examples of  $S_N$  reactions,

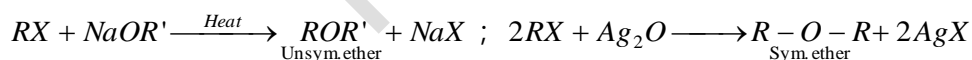
(a) Hydrolysis: Alkyl halides are hydrolyzed to corresponding alcohols by moist silver oxide ( $AgOH$ ) or by boiling with aqueous alkali solution ( $NaOH$  or  $KOH$ ). The attacking nucleophile is  $OH^-$ .



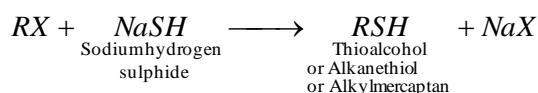
Note: With the help of this reaction an alkene can be converted into alcohol. Alkene is first reacted with  $HBr$  to form alkyl bromide and then hydrolysis is done.



(b) Reaction with alkoxides or dry silver oxide: Ethers are formed by heating alkyl halides with sodium or potassium alkoxides or dry silver oxide. The attacking nucleophile is  $OR^-$  (Williamson's synthesis).

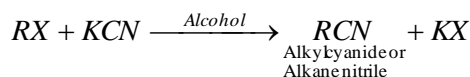


(c) Reaction with sodium or potassium hydrogen sulphide: Alkyl halides form thioalcohols with aqueous alcoholic sodium hydrogen sulphide or potassium hydrogen sulphide. The nucleophile is  $SH^-$ .

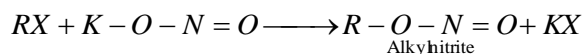


(d) Reaction with alcoholic potassium cyanide and silver cyanide: Alkyl cyanides are formed as the main product when alkyl halides are heated with alcoholic potassium cyanide. The nucleophile is  $CN^-$ .

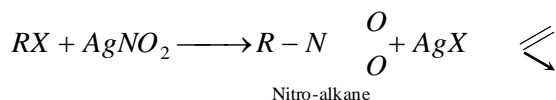




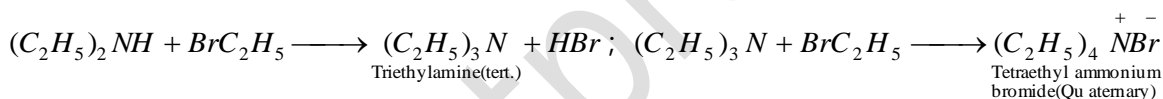
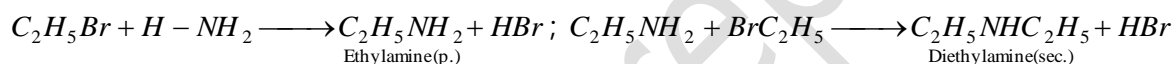
(e) Reaction with potassium nitrite or silver nitrite: On heating an alkyl halide with potassium nitrite in an aqueous ethanolic solution, alkyl nitrite is obtained as the main product though some nitro alkane is also formed. The nucleophile is  $NO_2^-$ .



However, when alkyl halide is heated with silver nitrite in an aqueous ethanolic solution, nitro-alkane is the main product. Some alkyl nitrite is also obtained.



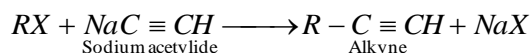
(f) Reaction with ammonia: On heating with aqueous or alcoholic solution of ammonia in a sealed tube at  $100^\circ\text{C}$ , alkyl halides yield a mixture of amines and quaternary ammonium salt. The nucleophile is  $NH_2^-$  in the first reaction.



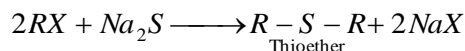
(g) Reaction with silver salts of fatty acids: On heating with silver salts of fatty acids in alcoholic solution, alkyl halides yield esters. The nucleophile is  $R'COO^-$ .



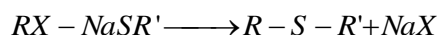
(h) Reaction with sodium acetylide: Alkyl halides react with sodium acetylide to form higher alkynes. The nucleophile is  $CH \equiv C^-$ .

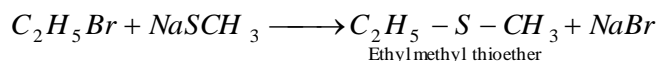


(i) Reaction with sodium or potassium sulphide: Alkyl halides react with sodium or potassium sulphide in alcoholic solution to form thioethers.

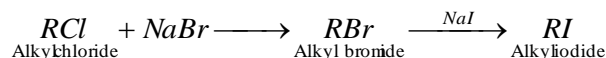


Thioethers can also be obtained by heating alkyl halides with alcoholic solution of sodium mecaptide ( $NaSR'$ ), i.e., metallic derivative of a thioalcohol.

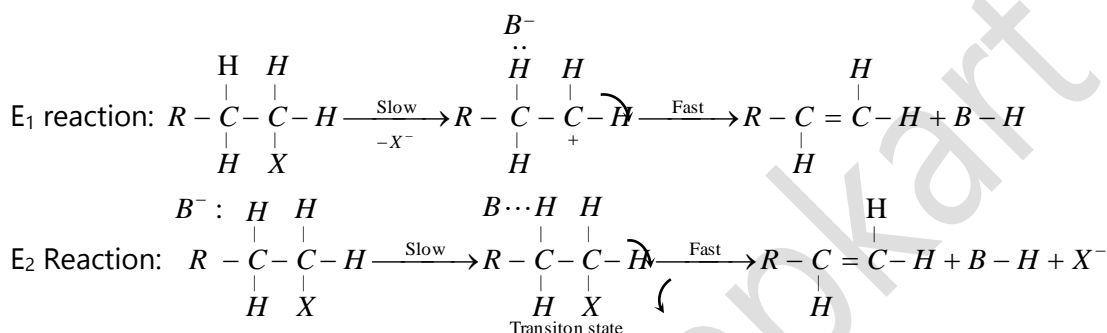




(j) Reaction with halides: Alkyl chlorides react with sodium bromide or sodium iodide to form alkyl bromide or alkyl iodide. Similarly, alkyl bromides react with sodium iodide in acetone or methanol to form alkyl iodides.



(ii) Elimination reactions: The positive charge on carbon is propagated to the neighboring carbon atoms by inductive effect. When approached by a strongest base (B), it tends to lose a proton usually from the  $\beta$ -carbon atom. Such reactions are termed elimination reactions. They are also  $E_1$  and  $E_2$  reactions.

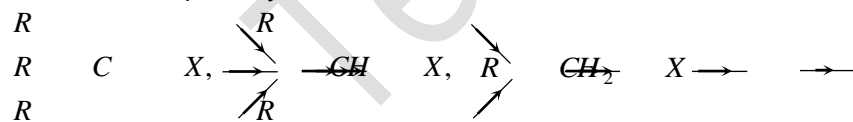


As the above reactions involve leaving of  $X^-$ , the reactivity of alkyl halides (Same alkyl group, different halogens) should be limited with  $C-X$  bond strength.

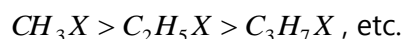
Type of bond	$C-I$	$C-Br$	$C-Cl$
Bond strength (kcal/mol)	45.5	54	66.5
			Bond strength increases $\longrightarrow$

The breaking of the bond becomes more and more difficult and thus, the reactivity decrease.

The order of reactivity (Tertiary > Secondary > Primary) is due to +I effect of the alkyl groups which increases the polarity of  $C-X$  bond.

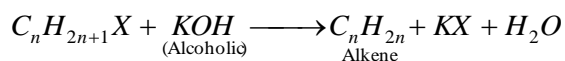


The primary alkyl halides undergo reactions either by  $S_N2$  or  $E_2$  mechanisms which involve the formation of transition state. The bulky groups cause steric hinderance in the formation of transition state. Therefore, higher homologues are less reactive than lower homologues.

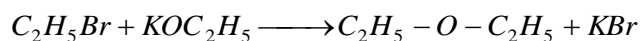


### Example of elimination reaction

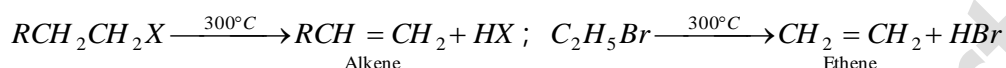
(a) Dehydrohalogenation: When alkyl halides are boiled with alcoholic potassium hydroxide, alkenes are formed.



In this reactions, ether is a by-product as potassium ethoxide is always present in small quantity.



(b) Action of heat: Alkyl halides when heated above 300°C, tend to lose a molecule of hydrogen halide forming alkenes.



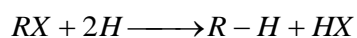
The decomposition follows the following order,

Iodide > Bromide > Chloride (When same alkyl group is present) and

Tertiary > Secondary > Primary (When same halogen is present).

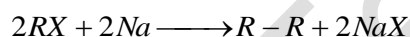
### (iii) Miscellaneous reactions

(a) Reduction: Alkanes are formed when alkyl halides are reduced with nascent hydrogen obtained by  $Zn/HCl$  or sodium and alcohol or Zn/Cu couple or  $LiAlH_4$ .

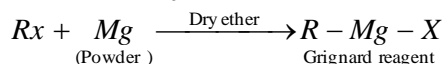


Reaction is used for the preparation of pure alkanes

(b) Wurtz reaction: An ether solution of an alkyl halide (Preferably bromide or iodide) gives an alkane when heated with metallic sodium.



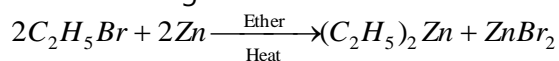
(c) Reaction with magnesium: Alkyl halides form Grignard reagent when treated with dry magnesium powder in dry ether.



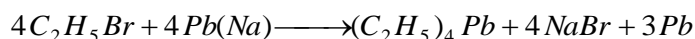
Grignard reagents are used for making a very large number of organic compounds.

(d) Reaction with other metals: Organometallic compounds are formed.

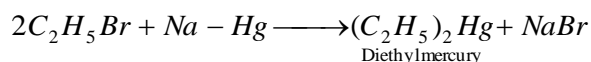
□ When heated with zinc powder in ether, alkyl halides form dialkyl zinc compounds. These are called Frankland reagents.



❑ When heated with lead-sodium alloy, ethyl bromide gives tetra ethyl lead which is used as an antiknock compound in petrol.



❑ Alkyl halides form dialkyl mercury compounds when treated with sodium amalgam.

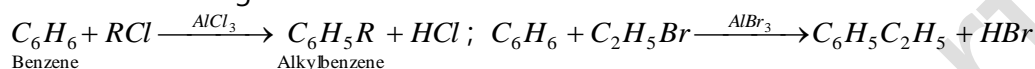


❑ Reaction with lithium: Alkyl halides react with lithium in dry ether to form alkyl lithiums.

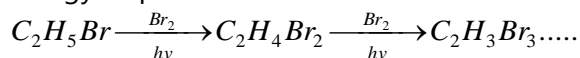


Alkyl lithiums are similar in properties with Grignard reagents. These are reactive reagents also.

(e) Friedel-Craft's reaction: Alkyl halides react with benzene in presence of anhydrous aluminium halides to form a homologue of benzene.



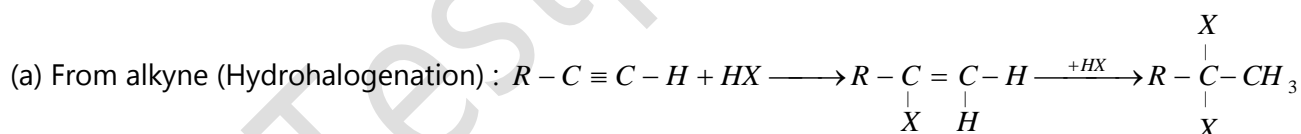
(f) Substitution (Halogenation): Alkyl halides undergo further halogenation in presence of sunlight, heat energy or peroxide.



## 4. Preparations and properties of Dihalides.

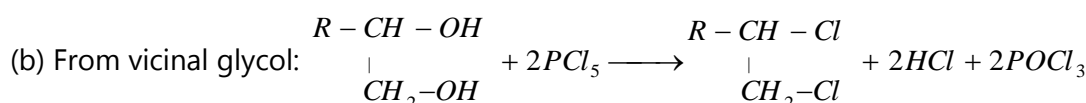
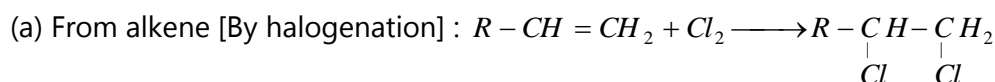
(1) Methods of preparation of dihalides

(i) Methods of preparation of gemdihalide



Note: If ketone is taken internal dihalide formed.

(ii) Methods of preparation of vicinal dihalide



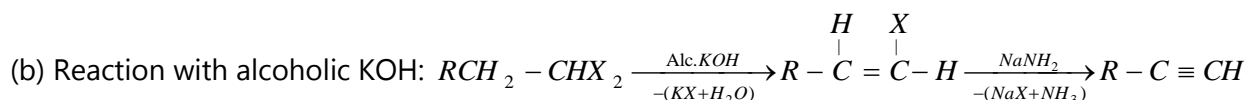
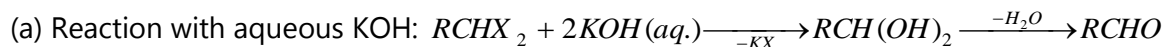


(2) Properties of dihalides

(i) Physical properties

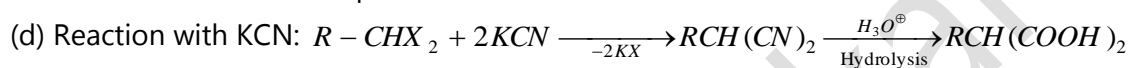
- (a) Dihalide are colourless with pleasant smell liquid. Insoluble in water, soluble in organic solvent.
- (b) M.P and B.P  $\propto$  -molecular mass.
- (c) Reactivity of vicinal dihalides > Gem dihalide.

(ii) Chemical properties of dihalide

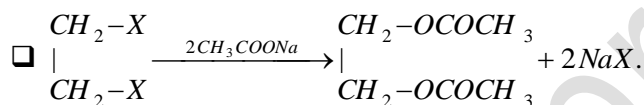
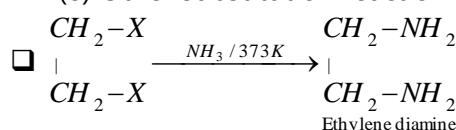


(c) Reaction with Zn dust

- Gem halide (di) form higher symmetrical alkene.
- Vicinal dihalide form respective alkene.



(e) Other substitution reaction



## 5. Tri-halides (Chloroform and iodoform).

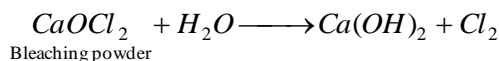
Chloroform or trichloromethane,  $CHCl_3$

It is an important trihalogen derivative of methane. It was discovered by Liebig in 1831 and its name chloroform was proposed by Dumas as it gave formic acid on hydrolysis. In the past, it was extensively used as anaesthetic for surgery but now it is rarely used as it causes liver damage.

(1) Preparation

- (i) Chloroform is prepared both in the laboratory and on large scale by distilling ethyl alcohol or acetone with bleaching powder and water. The yield is about 40%. The available chlorine of bleaching powder serves both as oxidising as well as chlorinating agent.



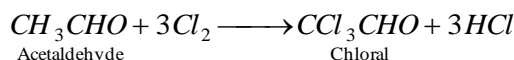


(a) From alcohol

Alcohol is first oxidised to acetaldehyde by chlorine.

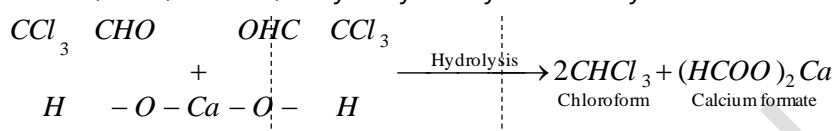


Acetaldehyde then reacts with chlorine to form chloral (Trichloro acetaldehyde).

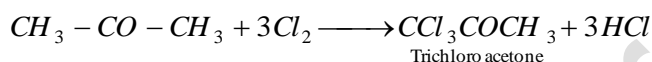


[So  $Cl_2$  acts both as an oxidising and chlorinating agent]

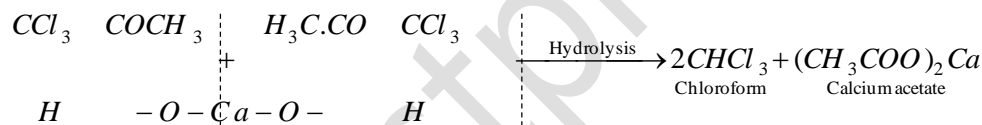
Chloral, thus, formed, is hydrolysed by calcium hydroxide.



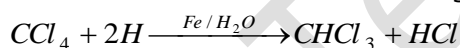
(b) From acetone: Acetone first reacts with chlorine to form trichloro acetone.



Trichloro acetone is then hydrolysed by calcium hydroxide.

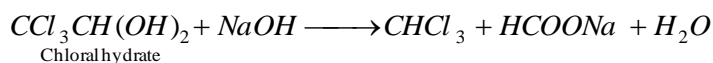


(ii) From carbon tetrachloride: Now-a-days, chloroform is obtained on a large scale by the reduction of carbon tetrachloride with iron fillings and water. This method is used in countries like U.S.A.

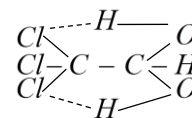


This chloroform is not pure and used mainly as a solvent.

(iii) Pure Chloroform is obtained by distilling chloral hydrate with concentrated sodium hydroxide solution.



Note: Chloral hydrate is a stable compound inspite of the fact that two  $-OH$  groups are linked to the same carbon atom. This is due to the fact that intramolecular hydrogen bonding exists in the molecule between chlorine and hydrogen atom of  $-OH$  group.



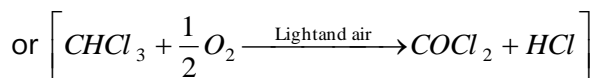
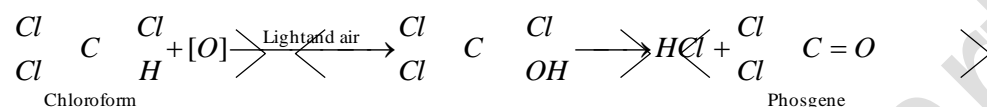


## (2) Physical properties

- (i) It is a sweet smelling colorless liquid.
- (ii) It is heavy liquid. Its density is 1.485. It boils at 61°C.
- (iii) It is practically insoluble in water but dissolves in organic solvents such as alcohol, ether, etc.
- (iv) It is non-inflammable but its vapours may burn with green flame.
- (v) It brings temporary unconsciousness when vapours are inhaled for sufficient time.

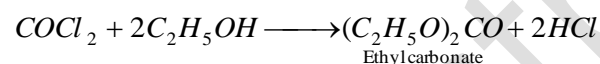
## (3) Chemical properties

(i) Oxidation: When exposed to sunlight and air, it slowly decomposes into phosgene and hydrogen chloride.

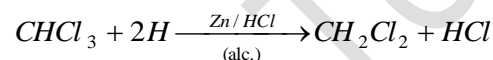


Phosgene is extremely poisonous gas. To use chloroform as an anaesthetic agent, it is necessary to prevent the above reaction. The following two precautions are taken when chloroform is stored.

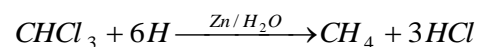
- (a) It is stored in dark blue or brown coloured bottles, which are filled upto the brim.
- (b) 1% ethyl alcohol is added. This retards the oxidation and converts the phosgene formed into harmless ethyl carbonate.



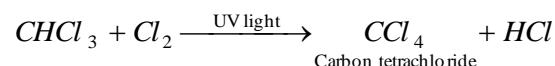
(ii) Reduction: When reduced with zinc and hydrochloric acid in presence of ethyl alcohol, it forms methylene chloride.



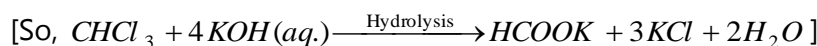
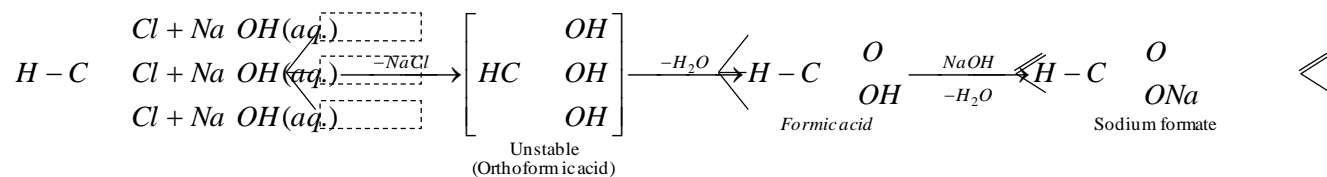
When reduced with zinc dust and water, methane is the main product.



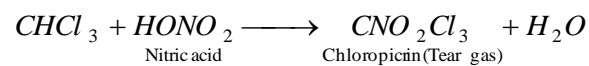
(iii) Chlorination: Chloroform reacts with chlorine in presence of diffused sunlight or UV light to form carbon tetrachloride.



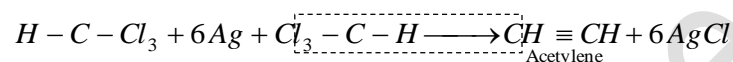
(iv) Hydrolysis: Chloroform is hydrolysed when treated with hot aqueous solution of sodium hydroxide or potassium hydroxide. The final product is sodium or potassium salt of formic acid.



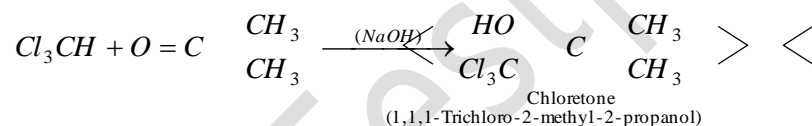
(v) Nitration: The hydrogen of the chloroform is replaced by nitro group when it is treated with concentrated nitric acid. The product formed is chloropicrin or trichloronitro methane or nitro chloroform. It is a liquid, poisonous and used as an insecticide and a war gas.



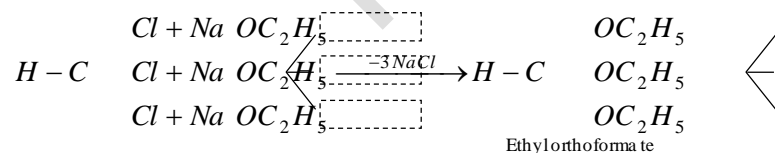
(vi) Heating with silver powder: Acetylene is formed when chloroform is heated at high temperature with silver powder.



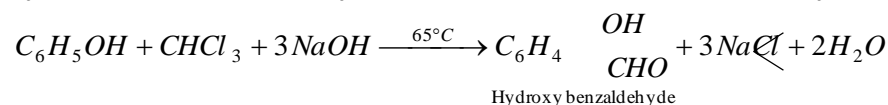
(vii) Condensation with acetone: Chloroform condenses with acetone on heating in presence of caustic alkalies. The product formed is a colourless crystalline solid called chloretone and is used as hypnotic in medicine.



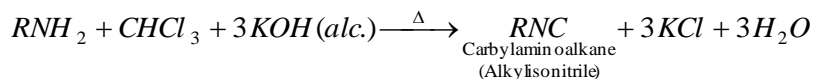
(viii) Reaction with sodium ethoxide: When heated with sodium ethoxide, ethyl orthoformate is formed.



(ix) **Reimer-Tiemann reaction:** Chloroform reacts with phenol when heated in presence of sodium hydroxide or potassium hydroxide. The product formed is salicylaldehyde.



(x) **Carbylamine reaction** (Isocyanide test): This reaction is actually the test of primary amines. Chloroform, when heated with primary amine in presence of alcoholic potassium hydroxide forms a derivative called isocyanide which has a very offensive smell.



This reaction is also used for the test of chloroform.

#### (4) Uses

- It is used as a solvent for fats, waxes, rubber, resins, iodine, etc.
- It is used for the preparation of chloretone (a drug) and chloropicrin (Insecticide).
- It is used in laboratory for the test of primary amines, iodides and bromides.
- It can be used as **anaesthetic** but due to harmful effects it is not used these days for this purpose.
- It may be used to prevent putrefaction of organic materials, i.e., in the preservation of anatomical species.

#### (5) Tests of chloroform

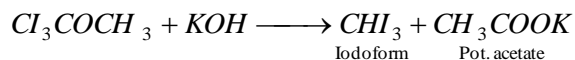
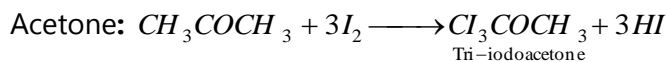
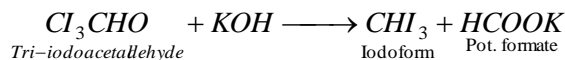
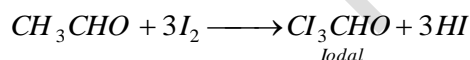
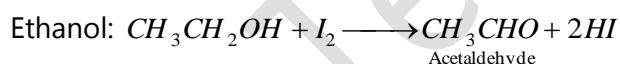
- It gives isocyanide test (Carbylamine test).
- It forms silver mirror with Tollen's reagent.
- Pure Chloroform does not give white precipitate with silver nitrate.

#### Iodoform or tri-iodomethane, $CHI_3$

Iodoform resembles chloroform in the methods of preparation and properties.

##### (1) Preparation

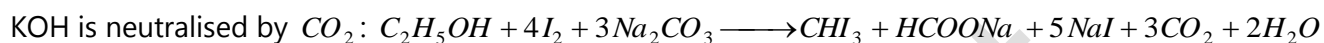
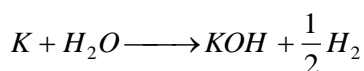
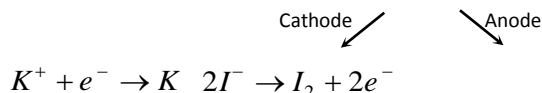
(i) **Laboratory preparation:** Iodoform is prepared in the laboratory by heating ethanol or acetone with iodine and alkali.



Sodium carbonate can be used in place of KOH or NaOH. These reactions are called iodoform reactions.



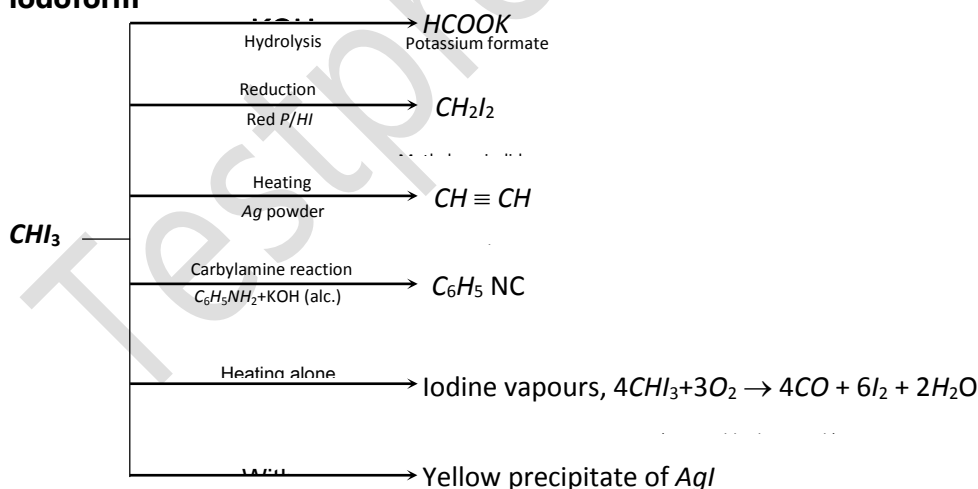
(ii) **Industrial preparation:** Iodoform is prepared on large scale by electrolysis of a solution containing ethanol, sodium carbonate and potassium iodide. The iodine set free, combine with ethanol in presence of alkali to form iodoform. The electrolysis carried out in presence of  $CO_2$  and the temperature is maintained at 60-70°C.



## (2) Properties

- (i) It is a yellow crystalline solid.
- (ii) It has a pungent characteristic odour.
- (iii) It is insoluble in water but soluble in organic solvents such as alcohol, ether, etc.
- (iv) It has melting point 119°C. It is steam volatile.

## (3) Reactions of iodoform



(4) **Uses:** Iodoform is extensively used as an **antiseptic** for dressing of wounds; but the antiseptic action is due to the liberation of free iodine and not due to iodoform itself. When it comes in contact with organic matter, iodine is liberated which is responsible for antiseptic properties.



### (5) Tests of iodoform

(i) **With  $\text{AgNO}_3$**  :  $\text{CHI}_3$  gives a yellow precipitate of  $\text{AgI}$ .

(ii) **Carbylamine reaction**:  $\text{CHI}_3$  on heating with primary amine and alcoholic KOH solution, gives an offensive smell of isocyanide (Carbylamine).

(iii) **Iodoform reaction** : With  $\text{I}_2$  and  $\text{NaOH}$  or  $\text{I}_2$  and  $\text{Na}_2\text{CO}_3$ , the iodoform test is mainly given by

ethyl alcohol ( $\text{CH}_3\text{CH}_2\text{OH}$ ), acetaldehyde ( $\text{CH}_3-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{H}$ ),  $\alpha$ -methyl ketone or 2-one ( $-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{CH}_3$ ), secondary alcohols or 2-ol ( $-\text{CHOH} \cdot \text{CH}_3$ ) and secondary alkyl halide at  $\text{C}_2(-\text{CHClCH}_3)$ . Also lactic

acid ( $\text{CH}_3-\text{CHOH}-\text{COOH}$ ), Pyruvic acid ( $\text{CH}_3-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{COOH}$ ) and methyl phenyl ketone

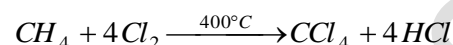
( $\text{C}_6\text{H}_5-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{CH}_3$ ) give this test.

## 6. Tetra-halides (Carbon tetrachloride or tetrachloromethane, $\text{CCl}_4$ ).

It is the most important tetrahalogen derivative of methane.

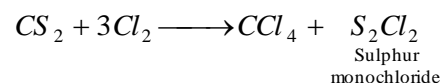
### (1) Manufacture

(i) **From methane**: Chlorination of methane with excess of chlorine at  $400^\circ\text{C}$  yields impure carbon tetrachloride.

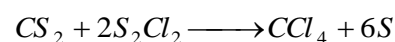


Methane used in this process is obtained from natural gas.

(ii) **From carbon disulphide**: Chlorine reacts with carbon disulphide in presence of catalysts like iron, iodine, aluminium chloride or antimony pentachloride.



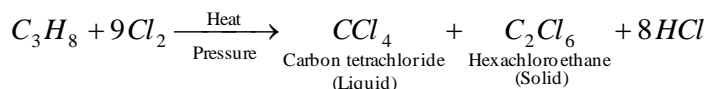
$\text{S}_2\text{Cl}_2$  further reacts with  $\text{CS}_2$  to form more of carbon tetrachloride.



Carbon tetrachloride is obtained by fractional distillation. It is washed with sodium hydroxide and then distilled to get a pure sample.



(iii) **From propane:** Propane is reacted with chlorine at about 400°C and at a pressure of 70-100 atmosphere.

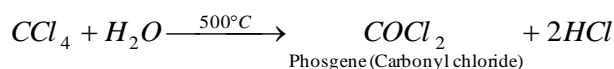


## (2) Physical properties

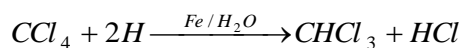
- (i) It is a colorless liquid having characteristic smell.
- (ii) It is non-inflammable and poisonous. It has boiling point 77°C.
- (iii) It is insoluble in water but soluble in organic solvents.
- (iv) It is an excellent solvent for oils, fats, waxes and greases.

(3) **Chemical properties:** Carbon tetrachloride is less reactive and inert to most organic reagents. However, the following reactions are observed.

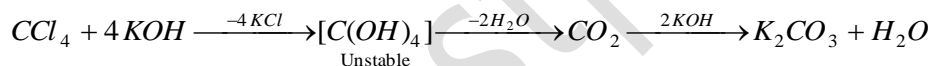
(i) **Reaction with steam (Oxidation):** Carbon tetrachloride vapours react with steam above 500°C to form phosgene, a poisonous gas.



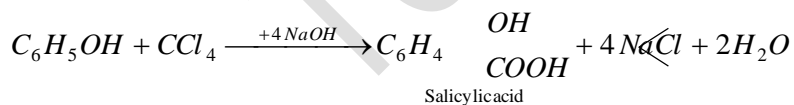
(ii) **Reduction:** It is reduced by moist iron filling into chloroform.



(iii) **Hydrolysis:** On heating with aqueous potassium hydroxide it forms carbon dioxide which combines with potassium hydroxide to give KCl and potassium carbonate (Inorganic salts).



(iv) **Reaction with phenol (Reimer-tiemann reaction) :** It combines with phenol in presence of sodium hydroxide to form salicylic acid.



## (4) Uses

- (i) It is used as a fire extinguisher under the name **pyrene**. The dense vapours form a protective layer on the burning objects and prevent the oxygen or air to come in contact with the burning objects.
- (ii) It is used as a solvent for fats, oils, waxes and greases, resins, iodine etc.
- (iii) It finds use in medicine as **helmenthicide** for elimination of hook worms.



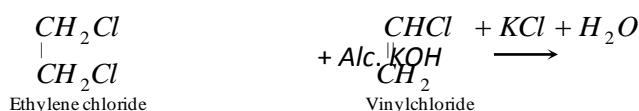


## 7. Unsaturated halides (Halo-alkene).

### Vinyl chloride or chloroethene, $\text{CH}_2=\text{CHCl}$

(1) **Synthesis:** Vinyl chloride can be synthesized by a number of methods described below:

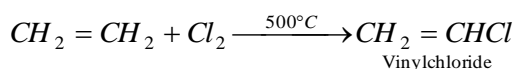
(i) **From ethylene chloride:** It is easily prepared in the laboratory by the action of dilute alcoholic solution of potassium hydroxide on ethylene chloride.



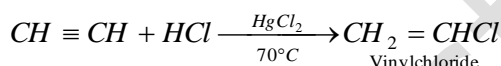
Vinyl chloride can also be obtained from ethylene chloride by thermal decomposition at 600-650°C.



(ii) **From ethylene:** Free radical chlorination of ethylene at 500°C yields vinyl chloride.



(iii) **From acetylene:** Vinyl chloride is obtained by controlled addition of HCl on acetylene. Acetylene is passed through dilute hydrochloric acid at about 70°C in presence of  $\text{HgCl}_2$  as a catalyst to form vinyl chloride. This method is also used for its manufacture.



(2) **Properties:** It is a colorless gas at room temperature. Its boiling point is  $-13^\circ\text{C}$ . The halogen atom in vinyl chloride is not reactive as in other alkyl halides. However,  $\text{C}=\text{C}$  bond of vinyl chloride gives the usual addition reactions.

The non-reactivity of chlorine atom is due to resonance stabilization. The lone pair on chlorine can participate in delocalization (Resonance) to give two structures.



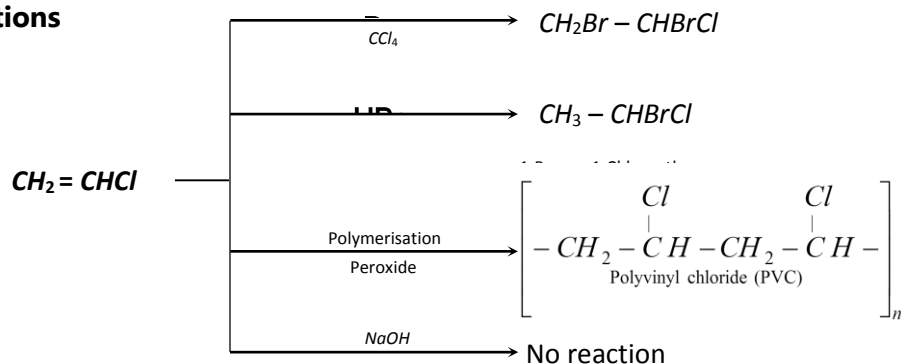
The following two effects are observed due to resonance stabilization.

(i) Carbon-chlorine bond in vinyl chloride has some double bond character and is, therefore, stronger than a pure single bond.

(ii) Carbon atom is  $sp^2$  hybridized and  $\text{C}-\text{Cl}$  bond length is shorter ( $1.69\text{\AA}$ ) and stronger than in alkyl halides ( $1.80\text{\AA}$ ) due to  $sp^3$  hybridization of the carbon atom.



### Addition reactions

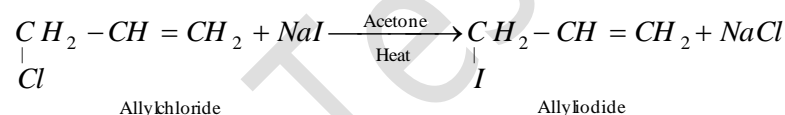
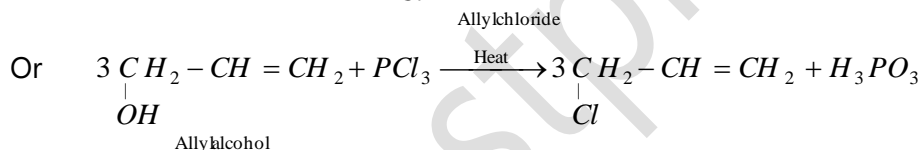
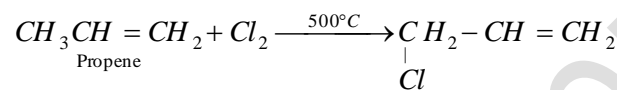


(3) **Uses:** The main use of vinyl chloride is in the manufacture of polyvinyl chloride (**PVC**) plastic which is employed these days for making synthetic leather goods, rain coats, pipes, floor tiles, gramophone records, packaging materials, etc.

### Allyl iodide or 3-iodopropene-1, $\text{ICH}_2\text{CH} = \text{CH}_2$

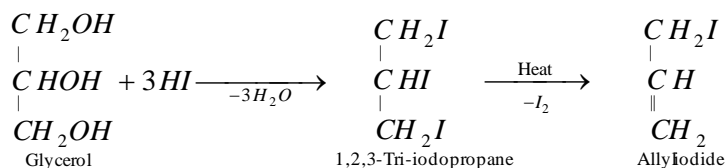
(1) **Synthesis:** It is obtained,

(i) By heating allyl chloride with sodium iodide in acetone. Allyl chloride required in the reactions is prepared either by chlorination of propene at  $500^\circ\text{C}$  or by action of  $\text{PCl}_3$  on allyl alcohol.



This is halogen- exchange reaction and is called **Finkelstein reaction**.

(ii) By heating glycerol with HI.

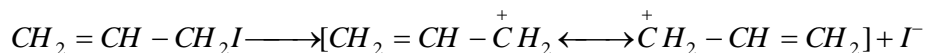


(2) **Properties:** It is a colorless liquid. It boils at  $103.1^\circ\text{C}$ . The halogen atom in allyl iodide is quite reactive. The p-orbital of the halogen atom does not interact with  $\pi$ -molecular orbital of the double bond

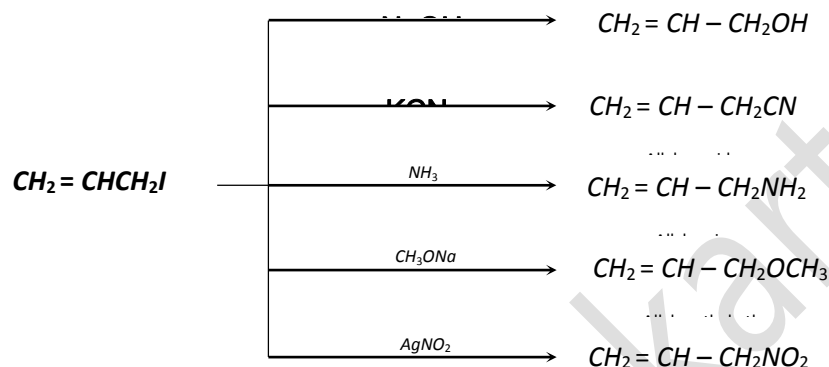




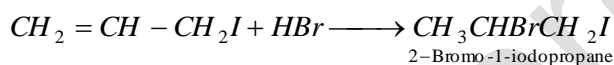
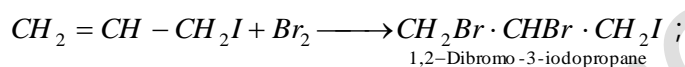
because these are separated by a saturated  $sp^3$ -hybridized carbon atom. Thus, the halogen atom in allyl halides can be easily replaced and the reactions of allyl halides are similar to the reaction of alkyl halides. In terms of valence bond approach, the reactivity of halogen atom is due to ionisation to yield a carbonium ion which can stabilize by resonance as shown below,



**Substitution reactions:** Nucleophilic substitution reactions occur,



**Addition reactions:** Electrophilic addition reactions take place in accordance to Markownikoff's rule.



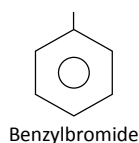
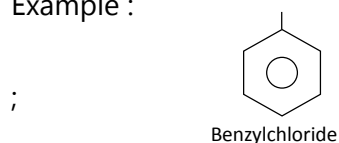
Allyl iodide is widely used in organic synthesis.

## 8. Halo-arenes.

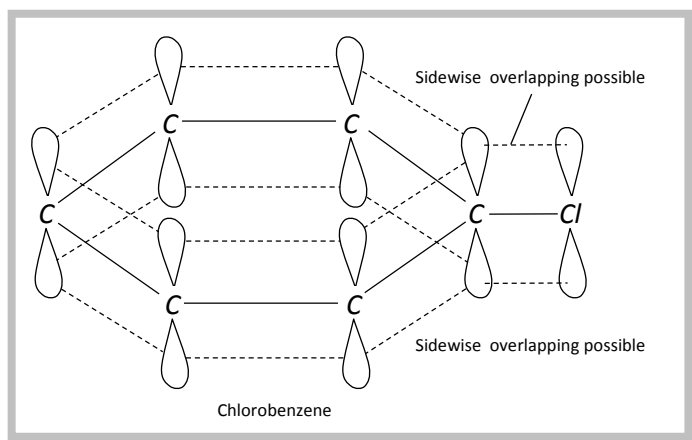
In these compounds the halogen is linked directly to the carbon of the benzene nucleus.

(1) **Nomenclature:** Common name is aryl halide IUPAC name is halo-arene.

Example :

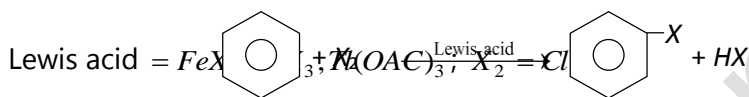


## (2) Structure

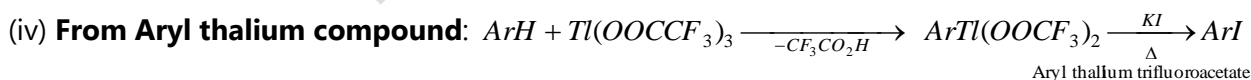
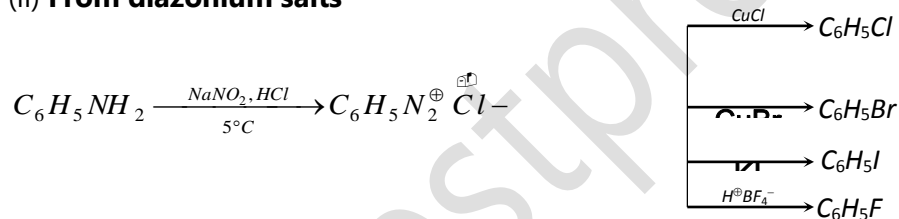


## (3) Methods of preparation

### (i) By direct halogenation of benzene ring



### (ii) From diazonium salts



## (4) Physical properties

(i) **Physical state:** Haloarenes are colourless liquid or crystalline solid.

(ii) **Solubility:** They are insoluble in water, but dissolve readily in organic solvents. Insolubility is due to inability to break hydrogen bonding in water. Para isomer is less soluble than ortho isomer.

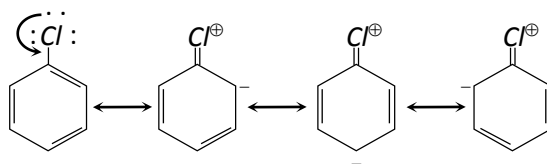
(iii) Halo-arenes are heavier than water.

(iv) B.P. of halo-arenes follow the trend. Iodo arene > Bromo arene > Chloro arene.



## (5) Chemical properties

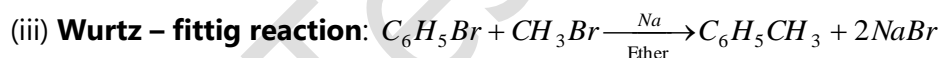
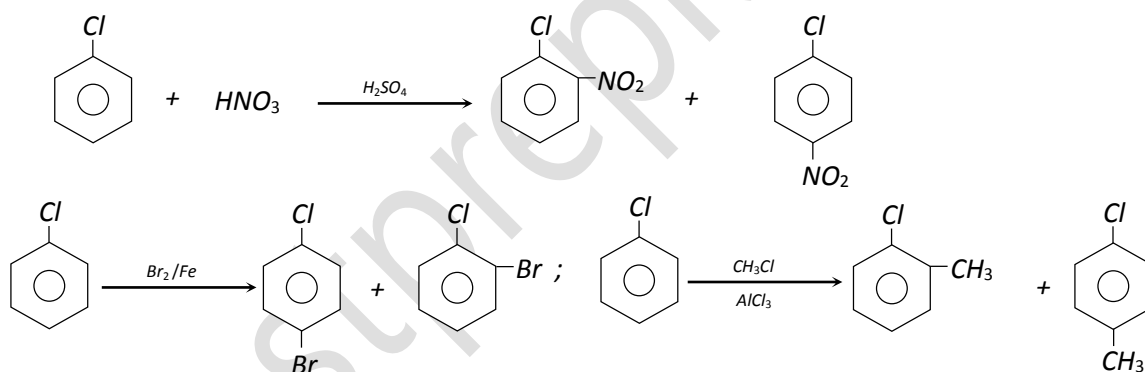
**Inert nature of chlorobenzene:** Aryl halides are unreactive as compared to alkyl halides as the halogen atom in these compounds is firmly attached and cannot be replaced by nucleophiles. Such as  $\text{OH}^-$ ,  $\text{NH}_2^-$ ,  $\text{CN}^-$  etc.



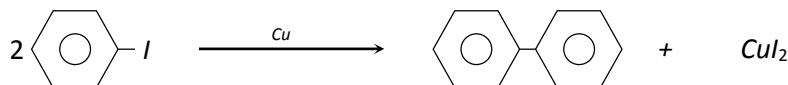
Thus delocalization of electrons by resonance in aryl halides, brings extra stability and double bond character between  $\text{C} - \text{X}$  bonds. This makes the bond stronger and shorter than pure single bond. However under vigorous conditions the following nucleophilic substitution reactions are observed,



## (ii) Electrophilic aromatic substitution



## (v) Ullmann reaction

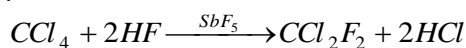


## 9. Some more important halogen derivatives.

(1) **Freons:** The chloro fluoro derivatives of methane and ethane are called freons. Some of the derivatives are:  $\text{CHF}_2\text{Cl}$  (monochlorodifluoromethane),  $\text{CF}_2\text{Cl}_2$  (dichlorodifluoromethane),  $\text{HCF}_2\text{CHCl}_2$  (1,1-dichloro-2,2-difluoroethane). These derivatives are non-inflammable, colourless, non-toxic, low boiling liquids. These are stable upto  $550^\circ\text{C}$ . The most important and useful derivative is  $\text{CF}_2\text{Cl}_2$  which is commonly known as **freon** and **freon-12**.

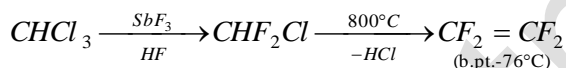
Freon or freon-12 ( $\text{CF}_2\text{Cl}_2$ ) is prepared by treating carbon tetrachloride with antimony trifluoride in the presence of antimony pentachloride as a catalyst.  $3\text{CCl}_4 + 2\text{SbF}_3 \xrightarrow[\text{Catalyst}]{\text{SbCl}_5} 3\text{CF}_2\text{Cl}_2 + 2\text{SbCl}_3$

Or it can be obtained by reacting carbon tetrachloride with hydrofluoric acid in presence of antimony pentafluoride.

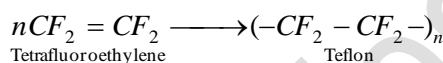


Under ordinary conditions freon is a gas. Its boiling point is  $-29.8^\circ\text{C}$ . It can easily be liquified. It is chemically inert. It is used in air-conditioning and in domestic refrigerators for cooling purposes (As refrigerant). It causes depletion of ozone layer.

(2) **Teflon:** It is plastic like substance produced by the polymerisation of tetrafluoroethylene ( $\text{CF}_2 = \text{CF}_2$ ). Tetrafluoroethylene is formed when chloroform is treated with antimony trifluoride and hydrofluoric acid.

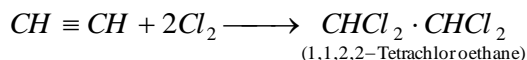


On polymerisation tetrafluoroethylene forms a plastic-like material which is called **teflon**.



Teflon is chemically inert substance. It is not affected by strong acids and even by boiling aqua-regia. It is stable at high temperatures. It is, thus, used for electrical insulation, preparation of gasket materials and non-sticking frying pans.

(3) **Acetylene tetrachloride (Westron),  $\text{CHCl}_2 \cdot \text{CHCl}_2$ :** Acetylene tetrachloride is also known as sym. tetrachloroethane. It is prepared by the action of chlorine on acetylene in presence of a catalyst such as ferric chloride, aluminium chloride, iron, quartz or kieselguhr.

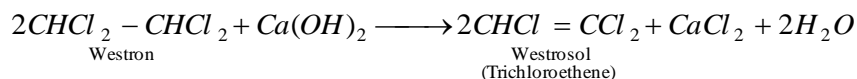


In absence of catalyst, the reaction between chlorine and acetylene is highly explosive producing carbon and HCl. The reaction is less violent in presence of a catalyst.

It is a heavy, non-inflammable liquid. It boils at  $146^\circ\text{C}$ . It is highly toxic in nature. Its smell is similar to chloroform. It is insoluble in water but soluble in organic solvents.



On further chlorination, it forms penta and hexachloroethane. On heating with lime (Calcium hydroxide), it is converted to useful product **westrosol** ( $\text{CCl}_2 = \text{CHCl}$ ).



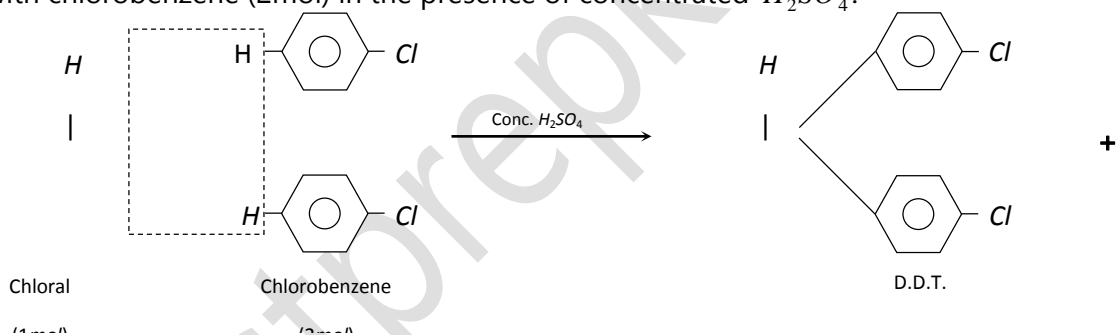
Both westron and westrosol are used as solvents for oils, fats, waxes, resins, varnishes and paints, etc.

(4) **p-Dichlorobenzene:** It is prepared by chlorination of benzene.

It is a white, volatile solid having melting point of 325 K, which readily sublimes. It resembles chlorobenzene in their properties.

It is used as general insecticides, germicide, soil fumigant deodorant. It is used as a larvicide for cloth moth and peach tree borer.

(5) **DDT; 2, 2-bis (p-Chlorophenyl) –1,1,1-trichloroethane** : It is synthesised by heating a mixture of chloral (1mol) with chlorobenzene (2mol) in the presence of concentrated  $\text{H}_2\text{SO}_4$ .

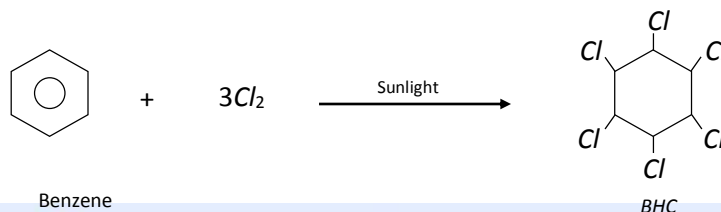


### Properties and uses of D.D.T.

- (i) D.D.T. is almost insoluble in water but it is moderately soluble in polar solvents.
- (ii) D.D.T. is a powerful insecticide. It is widely used as an insecticide for killing mosquitoes and other insects.

**Side Effects of D.D.T.:** D.D.T. is not biodegradable. Its residues accumulate in environment and its long term effects could be highly dangerous. It has been proved to be toxic to living beings. Therefore, its use has been abandoned in many western countries. However, in spite of its dangerous side effects, D.D.T. is still being widely used in India due to non-availability of other cheaper insecticides.

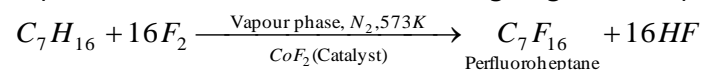
(6) **BHC (Benzene hexachloride),  $\text{C}_6\text{H}_6\text{Cl}_6$ :** It is prepared by chlorination of benzene in the presence of sunlight.



**Uses:** It is an important agricultural pesticide mainly used for exterminating white ants, leaf hopper, termite, etc. It is also known by the common name gamma-xene or lindane or 666.

**Note:** sssss conformation of  $C_6H_6Cl_6$  is most powerful insecticide.

(7) **Perfluorocarbons (PFCs):** Perfluorocarbons ( $C_nF_{2n+2}$ ) are obtained by controlled fluorination of vapourized alkanes diluted with nitrogen gas in the presence of a catalyst.



These are colorless, odorless, non-toxic, non-corrosive, non-flammable, non-polar, extremely stable and unreactive gases, liquids and solids. These are stable to ultraviolet radiations and other ionising radiations and therefore, they do not deplete the ozone layer like freons.

These are good electrical insulators. These have many important uses such as :

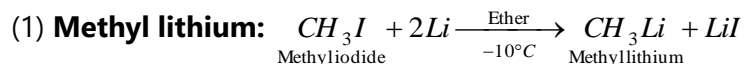
- (i) These are used as lubricants, surface coatings and dielectrics.
- (ii) These are used as heat transfer media in high voltage electrical equipment.
- (iii) These are used for vapour phase soldering, gross leak detection of sealed microchips etc. in electronic industry.
- (iv) These are also used in health care and medicine such as skin care cosmetics, wound healing, liquid ventilation, carbon monoxide poisoning and many medical diagnosis.

## 10. Organometallic compounds.

Organic compounds in which a metal atom is directly linked to carbon or organic compounds which contain at least one carbon-metal bond are called organometallic compounds.

Example : Methyl lithium  $\longrightarrow CH_3Li$ ; Dialkyl zinc  $\longrightarrow R_2Zn$ ; Alkyl magnesium halide

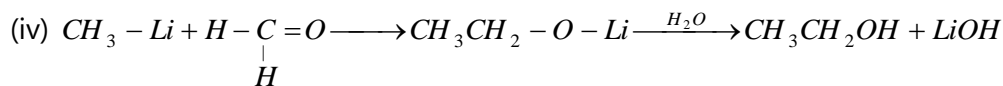
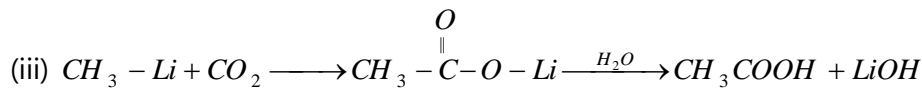
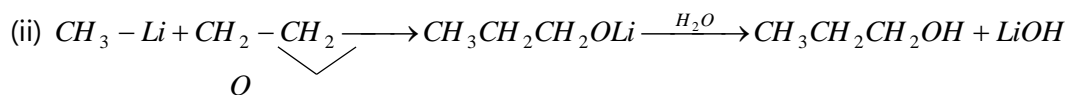
$\longrightarrow R - Mg - X$



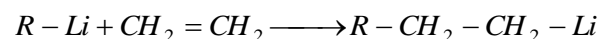
**Note:** High reactivity of  $CH_3Li$  over grignard reagent is due to greater polar character of  $C - Li$  bond in comparison to  $C - Mg$  bond.



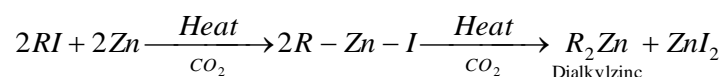
## Chemical properties



Note: Unlike grignard reagents, alkyl lithium can add to an alkenic double bond.



(2) **Dialkyl zinc:** First organometallic compound discovered by Frankland in 1849.

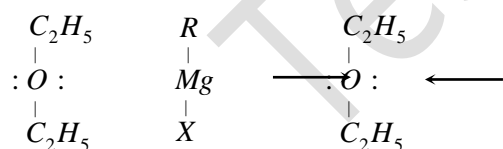


## Chemical properties



(3) **Grignard reagent:** Grignard reagent are prepared by the action of alkyl halide on dry burn magnesium in presence of alcohol free dry ether.

Dry ether dissolves the grignard reagent through solvolysis.



Grignard reagents are never isolated in free state on account of their explosive nature.

Note: For given alkyl radical the ease of formation of a grignard reagent is, Iodide > Bromide > Chloride

Usually alkyl bromides are used.

For a given halogen, the ease of formation of grignard reagent is,  $CH_3X > C_2H_5X > C_3H_7X \dots\dots\dots$

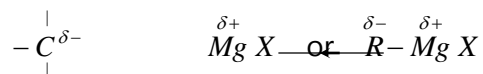
Since tertiary alkyl iodides eliminate HI to form an alkene, tertiary alkyl chlorides are used in their place.

Grignard reagent cannot be prepared from a compound which consists in addition to halogen, some reactive group such as  $-OH$  because it will react rapidly with the grignard reagent.



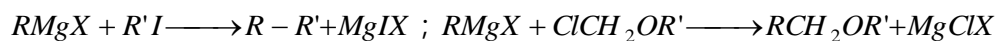
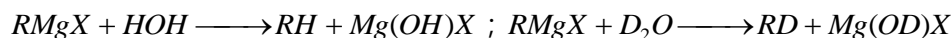


The  $C - Mg$  bond in grignard reagent is somewhat covalent but highly polar.



The alkyl group acts as carbanion. The majority of reaction of grignard reagent fall into two groups:

(i) Double decomposition with compound containing active hydrogen atom or reactive halogen atom



(ii) Addition reaction with compounds containing  $\overset{\curvearrowright}{C} \geq O$  ;  $-C \equiv N$ ,  $\overset{\curvearrowright}{C} \geq S$  etc.

