

Halogen Derivatives Part 1

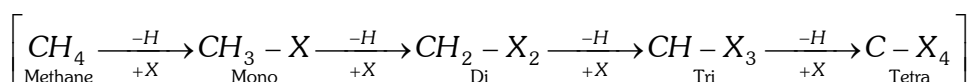
Compounds derived from hydrocarbons by the replacement of one or more hydrogen atoms by the corresponding number of halogen atoms are termed as halogen derivatives. The halogen derivatives of the hydrocarbons are broadly classified into three classes:

- 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.

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 $m = \text{no. of halogen atom}$; $n = \text{no. of carbon atoms}$.

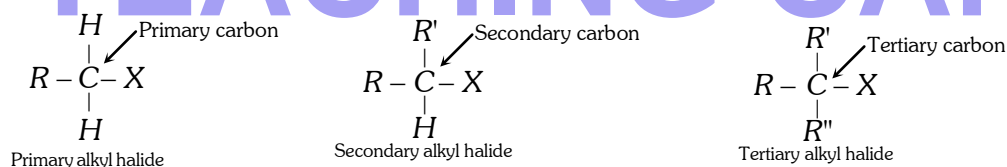
(2) Depending on the number of halogen atoms present in the halogen derivative, these are termed as mono-, di-, tri-, tetra-, and polyhalogen derivatives.



(i) **Monohalogen derivatives** are termed as alkyl halides.

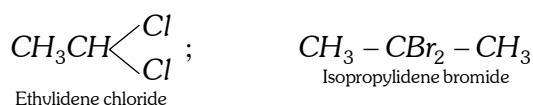


Monohalogen derivatives or alkyl halides are classified as primary (1°), secondary (2°) or tertiary (3°) depending upon whether the halogen atom is attached to primary, secondary or tertiary carbon atoms.



(ii) **The dihalogen derivatives are mainly of three types**

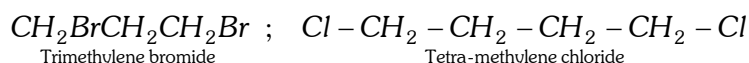
(a) **Gem-dihalides** : In these derivatives both the halogen atoms are attached to the same carbon atom. These are also called alkyldiene halides.



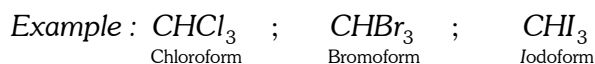
(b) **Vic-dihalides** : In these derivatives, the halogen atoms are attached to adjacent (Vicinal) carbon atoms. These are also termed as alkylene halides.



(c) α - ω 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**

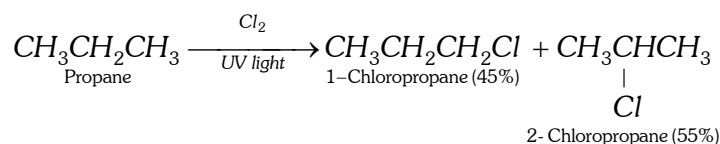
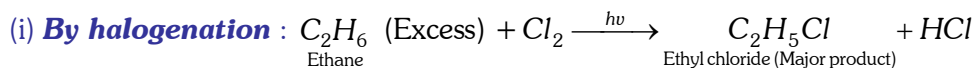


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(5) Halo-alkanes contain sp^3 hybridised carbon atom bonded to halogen atom or atoms.

General methods of preparation of Alkyl Halides.

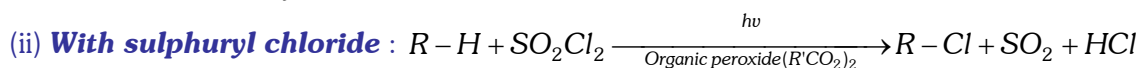
(1) From alkanes



This reaction proceed through free radical mechanism.

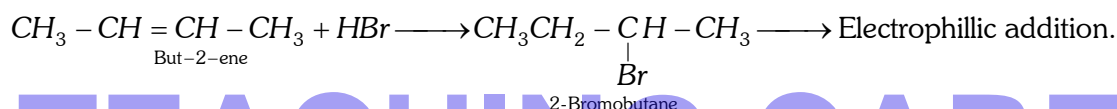
Note : * Order of reactivity of X_2 for a given alkane is, $F_2 > Cl_2 > Br_2 > I_2$.

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



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.

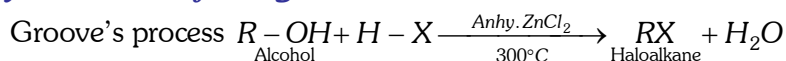
Markownikoff's addition by electrophilic mechanism.

* From alkyne we cannot obtain mono alkyl halide.

* The order of reactivity of halogen acids is, $HI > HBr > HCl$.

(3) From alcohols

(i) By the action of halogen acids

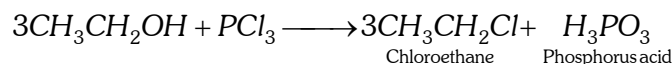
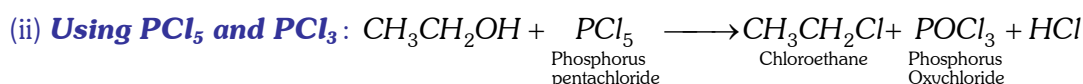


Note : * The reactivity order of HX in the above reaction is : $HI > HBr > HCl > HF$.

* Reactivity order of alcohols $3^\circ > 2^\circ > 1^\circ > MeOH$.

* 2° and 3° alcohols undergo SN^1 ; where as 1° and $MeOH$ undergo SN^2 mechanism.

* Concentrated $HCl + anhy. ZnCl_2$ is known as lucas reagent.



Note : * Bromine and iodine derivatives cannot be obtain from the above reaction, because PBr_5 or PI_5 are unstable.

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

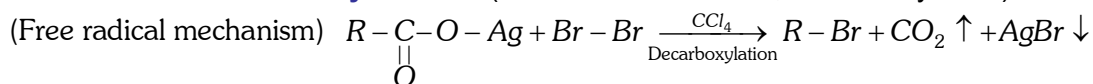
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(iii) By the action of thionyl chloride



Note : * Reaction takes place through SN^2 mechanism.

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



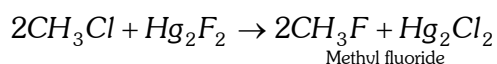
Note : * The reactivity of alkyl group is $1^\circ > 2^\circ > 3^\circ$

* Not suitable for chlorination because yield is poor.

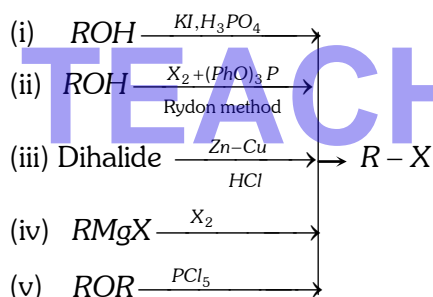
* In this reaction iodine forms ester instead of alkyl halide and the reaction is called Birbourn-Simonini reaction, $2\text{R}-\text{COOAg} + \text{I}_2 \longrightarrow \text{RCOOR}' + 2\text{CO}_2 + 2\text{AgI}$.

(5) From alkyl halide (Halide exchange method) : $\text{R}-\text{X} + \text{NaI} \xrightarrow[\text{Reflux}]{\text{Acetone}} \text{R}-\text{I} + \text{NaX} (\text{X} = \text{Cl}, \text{Br})$

Note : * Alkyl fluorides can not be prepared by this method. They can be obtained from corresponding chlorides by the action of Hg_2F_2 or antimony trifluoride.



(6) Other method



Properties of Alkyl Halides.

(1) Physical properties

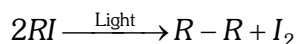
(i) $\text{CH}_3\text{F}, \text{CH}_3\text{Cl}, \text{CH}_3\text{Br}$ and $\text{C}_2\text{H}_5\text{Cl}$ are gases at room temperature. The alkyl halides upto C_{18} are colourless liquids while higher members are colourless solids.

(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 $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$ 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,

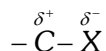
Iodide > Bromide > Chloride (Nature of the halogen atom)

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

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

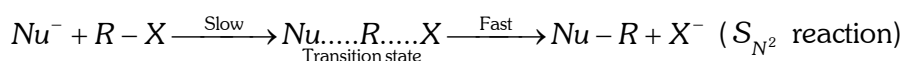
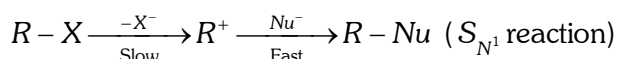
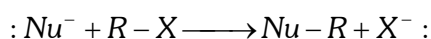
The high reactivity of alkyl halides can be explained in terms of the nature of $C-X$ bond which is highly polarised covalent bond due to large difference in the electronegativities of carbon and halogen atoms. The halogen is far more electronegative than carbon and tends to pull the electrons away from carbon, i.e., halogen acquires a small negative charge and carbon a small positive charge.



This polarity gives rise to two types of reactions,

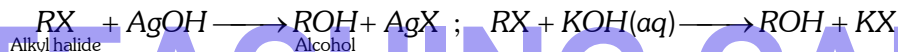
(i) Nucleophilic substitution reactions (ii) Elimination reactions

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

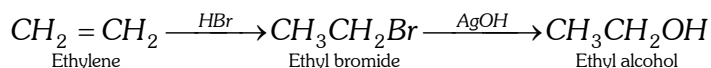


Examples of S_N reactions,

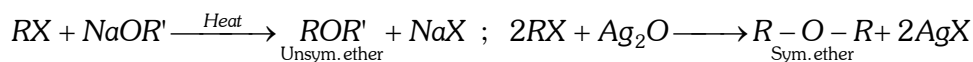
(a) **Hydrolysis** : Alkyl halides are hydrolysed to corresponding alcohols by moist silver oxide ($AgOH$) or by boiling with aqueous alkali solution ($NaOH$ or KOH). The attacking nucleophile is OH^- .



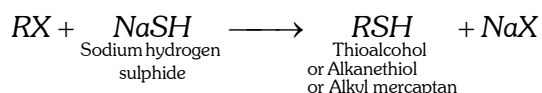
Note : * With the help of this reaction an alkene can be converted into alcohol. Alkene is first reacted with HBr to form alkyl bromide and then hydrolysis is done.



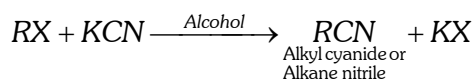
(b) **Reaction with alkoxides or dry silver oxide** : Ethers are formed by heating alkyl halides with sodium or potassium alkoxides or dry silver oxide. The attacking nucleophile is OR^- (Williamson's synthesis).



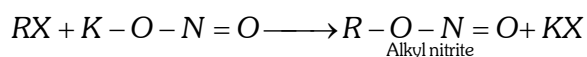
(c) **Reaction with sodium or potassium hydrogen sulphide** : Alkyl halides form thioalcohols with aqueous alcoholic sodium hydrogen sulphide or potassium hydrogen sulphide. The nucleophile is SH^- .



(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^- .

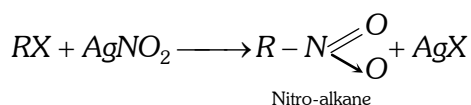


(e) **Reaction with potassium nitrite or silver nitrite** : On heating an alkyl halide with potassium nitrite in an aqueous ethanolic solution, alkyl nitrite is obtained as the main product though some nitro alkane is also formed. The nucleophile is NO_2^- .

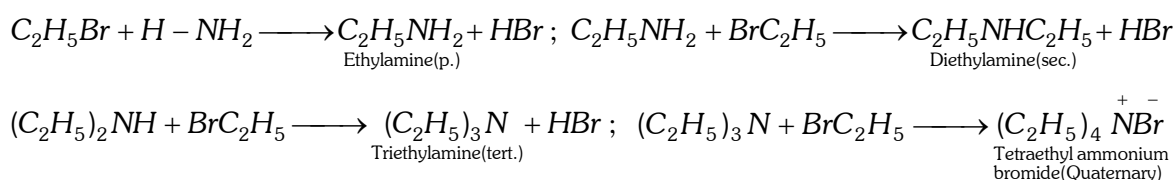


Halogen Derivatives Part 1

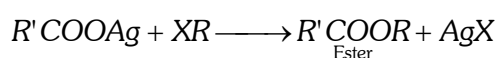
However, when alkyl halide is heated with silver nitrite in an aqueous ethanolic solution, nitro-alkane is the main product. Some alkyl nitrite is also obtained.



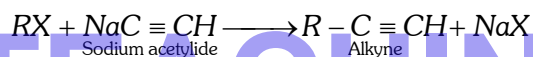
(f) *Reaction with ammonia* : On heating with aqueous or alcoholic solution of ammonia in a sealed tube at 100°C, alkyl halides yield a mixture of amines and quaternary ammonium salt. The nucleophile is NH_2^- in the first reaction.



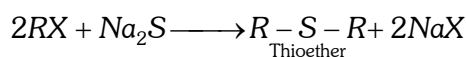
(g) *Reaction with silver salts of fatty acids* : On heating with silver salts of fatty acids in alcoholic solution, alkyl halides yield esters. The nucleophile is $R'COO^-$.



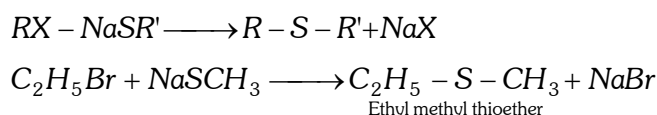
(h) *Reaction with sodium acetylide* : Alkyl halides react with sodium acetylide to form higher alkynes. The nucleophile is $CH \equiv C^-$.



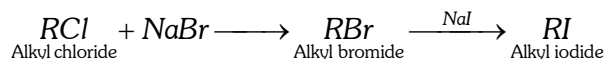
(i) *Reaction with sodium or potassium sulphide* : Alkyl halides react with sodium or potassium sulphide in alcoholic solution to form thioethers.



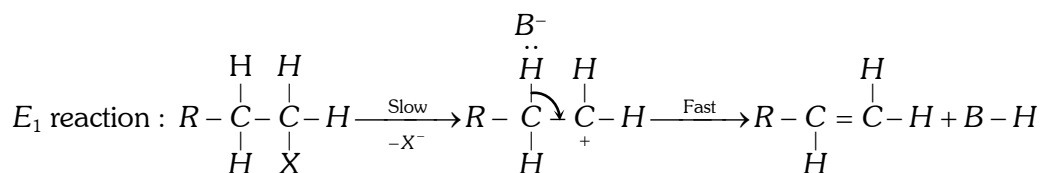
Thioethers can also be obtained by heating alkyl halides with alcoholic solution of sodium mecapside ($NaSR'$), i.e., metallic derivative of a thioalcohol.



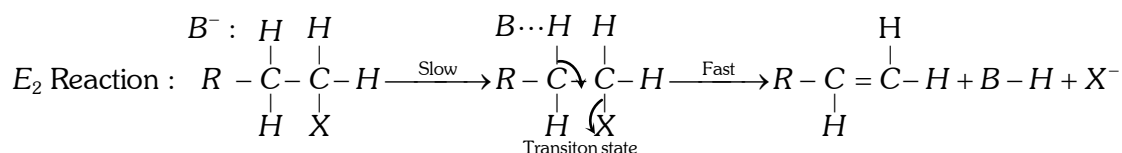
(j) *Reaction with halides* : Alkyl chlorides react with sodium bromide or sodium iodide to form alkyl bromide or alkyl iodide. Similarly, alkyl bromides react with sodium iodide in acetone or methanol to form alkyl iodides.



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



Halogen Derivatives Part 1

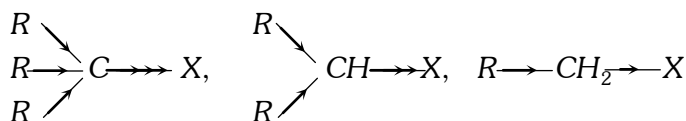


As the above reactions involve leaving of X^- , the reactivity of alkyl halides (Same alkyl group, different halogens) should be limited with $C - X$ bond strength.

Type of bond	$C - I$	$C - Br$	$C - Cl$
Bond strength (kcal/mol)	45.5	54	66.5
	$\xrightarrow{\hspace{10em}}$ Bond strength increases		

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

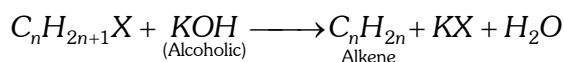
The order of reactivity (Tertiary > Secondary > Primary) is due to +I effect of the alkyl groups which increases the polarity of $C - X$ bond.



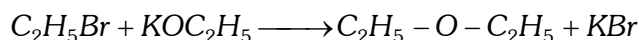
The primary alkyl halides undergo reactions either by S_N2 or E_2 mechanisms which involve the formation of transition state. The bulky groups cause steric hinderance in the formation of transition state. Therefore, higher homologues are less reactive than lower homologues. $CH_3X > C_2H_5X > C_3H_7X$, etc.

Example of elimination reaction

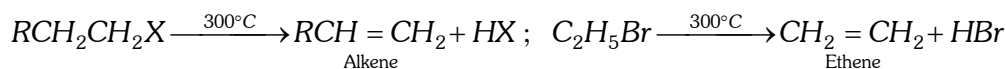
(a) *Dehydrohalogenation* : When alkyl halides are boiled with alcoholic potassium hydroxide, alkenes are formed.



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 $300^\circ C$, tend to lose a molecule of hydrogen halide forming alkenes.



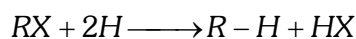
The decomposition follows the following order,

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

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

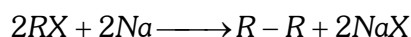
(iii) Miscellaneous reactions

(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 $LiAlH_4$.



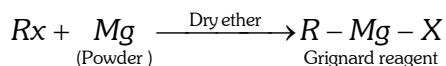
Reaction is used for the preparation of pure alkanes

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



Halogen Derivatives Part 1

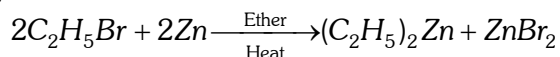
(c) *Reaction with magnesium* : Alkyl halides form Grignard reagent when treated with dry magnesium powder in dry ether.



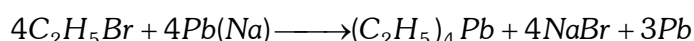
Grignard reagents are used for making a very large number of organic compounds.

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

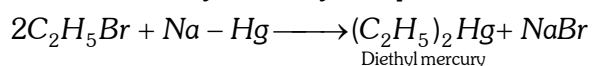
✱ When heated with zinc powder in ether, alkyl halides form dialkyl zinc compounds. These are called Frankland reagents.



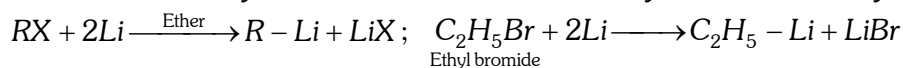
✱ When heated with lead-sodium alloy, ethyl bromide gives tetra ethyl lead which is used as an antiknock compound in petrol.



✱ 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.

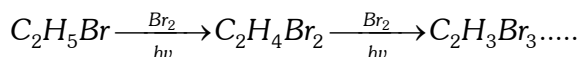


Alkyl lithiums are similar in properties with Grignard reagents. These are reactive reagents also.

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



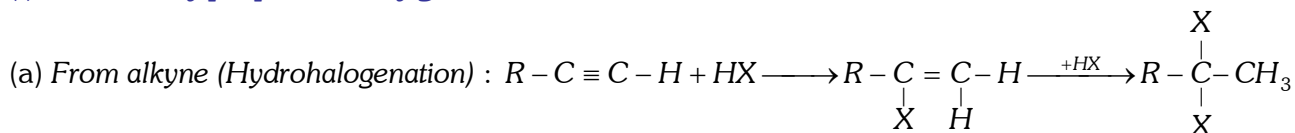
(f) *Substitution (Halogenation)* : Alkyl halides undergo further halogenation in presence of sunlight, heat energy or peroxide.



Preparations and properties of Dihalides.

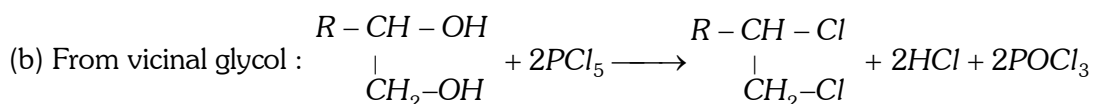
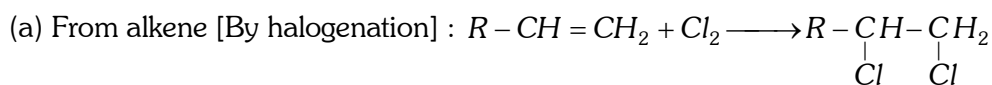
(1) Methods of preparation of dihalides

(i) Methods of preparation of gemdihalide



Note : ✱ If ketone is taken internal dihalide formed.

(ii) Methods of preparation of vicinal dihalide



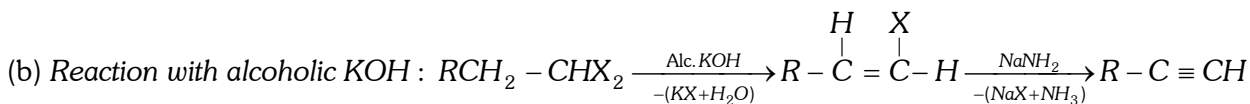
Halogen Derivatives Part 1

(2) Properties of dihalides

(i) Physical properties

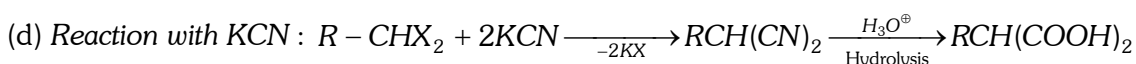
- (a) Dihalide are colourless with pleasant smell liquid. Insoluble in water, soluble in organic solvent.
- (b) *M.P* and *B.P* \propto -molecular mass.
- (c) Reactivity of vicinal dihalides > Gem dihalide.

(ii) Chemical properties of dihalide

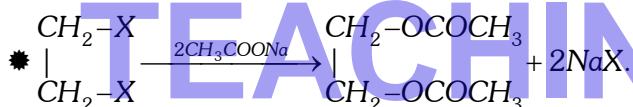
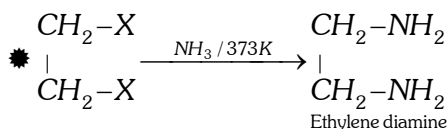


(c) Reaction with Zn dust

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



(e) Other substitution reaction



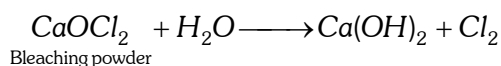
Tri-halides (Chloroform and iodoform).

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.

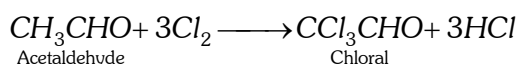


(a) From alcohol

- ✱ Alcohol is first oxidised to acetaldehyde by chlorine.



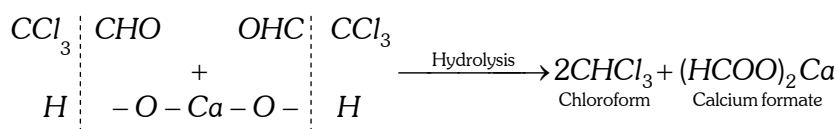
- ✱ Acetaldehyde then reacts with chlorine to form chloral (Trichloro acetaldehyde).



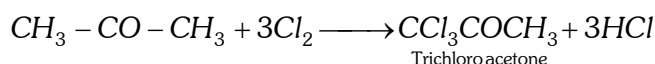
[So Cl_2 acts both as an oxidising and chlorinating agent]

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

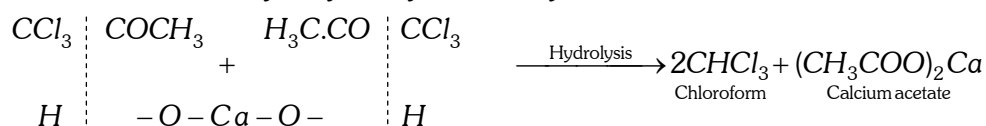
Halogen Derivatives Part 1



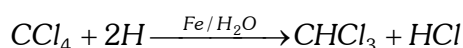
(b) *From acetone* : Acetone first reacts with chlorine to form trichloro acetone.



✱ Trichloro acetone is then hydrolysed by calcium hydroxide.

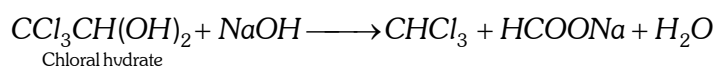


(ii) **From carbon tetrachloride** : Now-a-days, chloroform is obtained on a large scale by the reduction of carbon tetrachloride with iron filings and water. This method is used in countries like U.S.A.

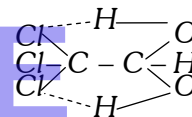


This chloroform is not pure and used mainly as a solvent.

(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 $-\text{OH}$ 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 $-\text{OH}$ group.

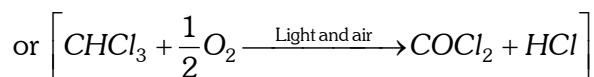
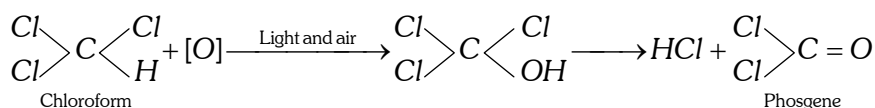


(2) Physical properties

- (i) It is a sweet smelling colourless 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

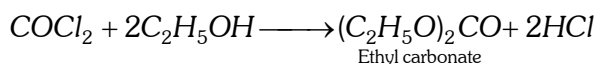
(i) **Oxidation** : When exposed to sunlight and air, it slowly decomposes into phosgene and hydrogen chloride.



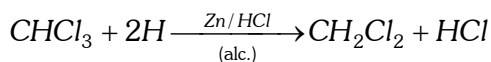
Phosgene is extremely poisonous gas. To use chloroform as an anaesthetic agent, it is necessary to prevent the above reaction. The following two precautions are taken when chloroform is stored.

- (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.

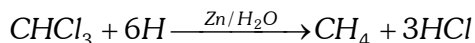
Halogen Derivatives Part 1



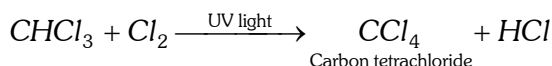
(ii) **Reduction** : When reduced with zinc and hydrochloric acid in presence of ethyl alcohol, it forms methylene chloride.



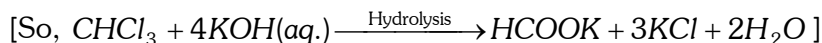
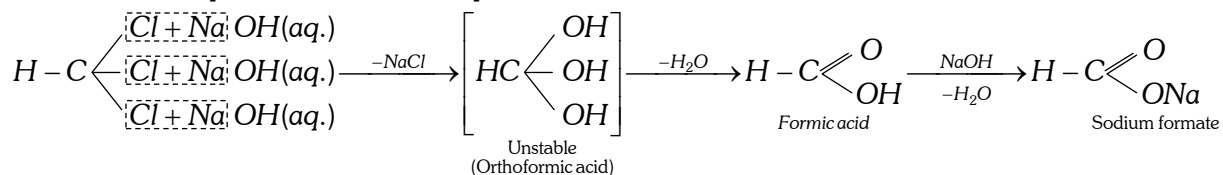
When reduced with zinc dust and water, methane is the main product.



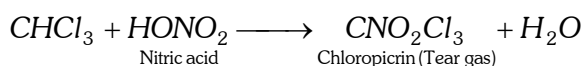
(iii) **Chlorination** : Chloroform reacts with chlorine in presence of diffused sunlight or UV light to form carbon tetrachloride.



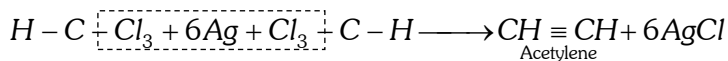
(iv) **Hydrolysis** : Chloroform is hydrolysed when treated with hot aqueous solution of sodium hydroxide or potassium hydroxide. The final product is sodium or potassium salt of formic acid.



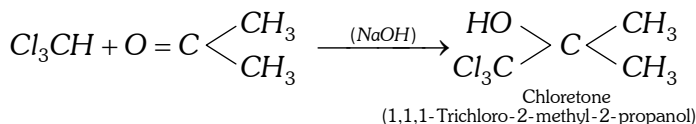
(v) **Nitration** : The hydrogen of the chloroform is replaced by nitro group when it is treated with concentrated nitric acid. The product formed is chloropicrin or trichloronitro methane or nitro chloroform. It is a liquid, poisonous and used as an insecticide and a war gas.



(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.

