# ALKYL HALIDE

## CHARACTERISTICS

(a) These are the organic compound in which halogen is directly linked with carbon atom.

(b) These are also called as Haloalkane.

(c) Their general formula is $C_nH_{2n+1}X$ , (X = F, Br, Cl, I).

(d) In these compounds, hybridisation state of carbon is $sp^3$.

(e) In these compounds, geometry of carbon is tetrahedral.

(f) Central carbon atom has a bond angle of $109^o\,28'$.

(g) On the basis of no. of halogen atom, these are of following types –

(i) Monohalide – They possess single halogen atom.
eg. $CH_3 - Cl$, $CH_3 - CH_2Br$

(ii) Dihalide – These are of three types
eg. gem dihalide, vicinal dihalide and α, ω halide

(iii) Trihalide – They posses three halogen atoms.
eg. $CHCl_3$ , $CHI_3$

(iv) Tetrahalide – They possess four halogen atoms.
eg. $CCl_4$

(vi) Polyhalide – They possess more than four halogen atoms.

(h) Alkyl halide shows chain and position isomerism. If unsymmetrical or chiral carbon is present then it shows optical isomerism also.

## METHODS OF PREPARATION OF ALKYL HALIDES

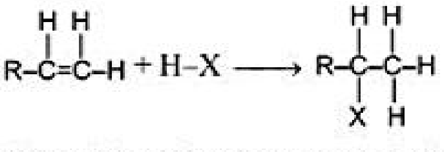
**(a) By Halogenation of Alkanes**

Halogenation of alkanes takes place by free radical mechanism.

$$R{-}H + X{-}X \xrightarrow{h\nu} R{-}X + H{-}X$$

$$R{-}H + Cl{-}SO_2{-}Cl \xrightarrow{\text{Peroxide}} R{-}Cl + SO_2 + H{-}Cl$$

**From Alkene ( Hydrohalogenation ) :–**



$$R{-}\overset{H}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}{-}H + H{-}X \longrightarrow R{-}\underset{X}{\underset{|}{\overset{H}{\overset{|}{C}}}}{-}\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}{-}H$$

**Note :** From alkyne we cannot obtain monoalkylhalide.

**From Alcohol : –**

(a) Using dry H - X : –

$$R{-}OH + \underset{\text{(dry)}}{H{-}X} \xrightarrow[\Delta,\ 300^\circ C]{\text{Anhydrous } ZnCl_2} R{-}X + H_2O$$

**Note :**

(i) The reactivity order of HX in the above reaction is – HI > HBr > HCl

(ii) The reactivity order of alcohols in the above reaction is – 3° > 2° > 1° > MeOH

The above reaction is called as '**Grove's Process**'.

(b) Using $PCl_3$ : – $3ROH + PCl_3 \longrightarrow 3R-Cl + H_3PO_3$

(c) Using $PCl_5$ : – $ROH + PCl_5 \longrightarrow R-Cl + HCl + POCl_3$

**Important Note : –**

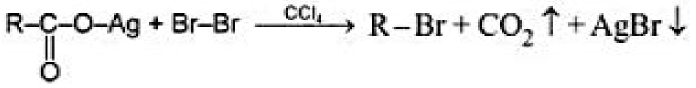
Bromine or Iodine derivatives can not be obtained from the above reaction because due to larger size of Bromine or Iodine, $PBr_5$ or $PI_5$ are unstable.

(d) Darzen's Process : – It is the best method for preparation of alkyl halide.

$$ROH + SOCl_2 \xrightarrow{\text{Pyridine}} RCl + HCl\uparrow + SO_2\uparrow$$

**From Silver Salt of Carboxylic Acid :**

The reaction is called as '**Borodiene - Hunsdiecker' reaction**. It is also a good method for obtaining alkyl halide, but from this reaction we obtain only bromo derivatives because reaction is based upon free radical mechanism.



$$R-\underset{\underset{O}{\|}}{C}-O-Ag + Br-Br \xrightarrow{CCl_4} R-Br + CO_2\uparrow + AgBr\downarrow$$

**Note : –**

(i) In the above reaction the reactivity of alkyl group is : 1° > 2° > 3°

(ii) It is also an example of decarboxylation.

**From Alkyl Halide :**

**Finkelstein Reaction :**

$$R-Br \text{ or } R-Cl + KI \xrightarrow{\text{Acetone}} R-I + KCl$$

In this reaction only exchange takes place and the reaction is called as Halogen exchange reaction or '**Finkelstein Reaction**'.

**Swarts reaction**

$$R-Br \text{ or } R-Cl \xrightarrow[\text{or } Hg_2F_2/\Delta]{AgF/\Delta} R-F$$

This reaction is called as '**Swarts reaction**'

## PHYSICAL PROPERTIES

(a) Alkyl halides are colourless with sweet smell or pleasant smell oily liquid, whereas

$CH_3F$, $CH_3Cl$, $CH_3-CH_2-F$, $CH_3-CH_2-Cl$ are gaseous in nature.

(b) Alkyl halides having 18-carbon or more than it are solid in nature.

(c) Although carbon - halogen bond is polar in nature but alkyl halides are insoluble in $H_2O$ because they cannot form bond with $H_2O$.

(d) These are completely soluble in organic solvents.

(e) M.P & B.P. $\propto$ molecular weight. For same alkyl group the order of B.P. is $RI > RBr > RCl > RF$

(f) Polarity order is $RF > RCl > RBr > RI$

(g) Reactivity order is $RI > RBr > RCl > RF$

(h) For same halide group reactivity order is 3° halide > 2° halide > 1° halide

Fluorides and Chlorides are lighter than water where as bromides and iodides are heavier than $H_2O$ due to more density of bromine than oxygen. $CH_2I_2$ is heavier liquid after Hg.

## CHEMICAL PROPERTIES

**Oxidation reaction**

(i) Only primary and secondary alkyl halides undergo oxidation. Tertiary alkyl halide does not undergo oxidation.

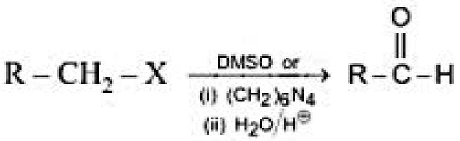
(ii) Primary alkyl halides give aldehyde where as secondary alkyl halides give ketone in this reaction.

(iii) Oxidising agent is either :

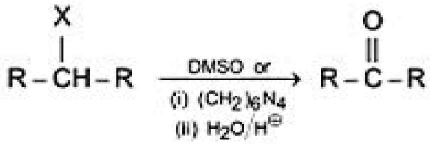
  (a) Dimethyl sulphoxide or

  (b) Reaction with $(CH_2)_6N_4$ followed by hydrolysis.

(iv) Reactivity $\propto$–number of $\alpha$–hydrogens.



$$R-CH_2-X \xrightarrow[\text{(i) }(CH_2)_6N_4 \text{ (ii) } H_2O/H^{\ominus}]{\text{DMSO or}} R-\overset{O}{\overset{\|}{C}}-H$$



$$R-\underset{}{\overset{X}{\overset{|}{C}}H}-R \xrightarrow[\text{(i) }(CH_2)_6N_4 \text{ (ii) } H_2O/H^{\ominus}]{\text{DMSO or}} R-\overset{O}{\overset{\|}{C}}-R$$

$$C_6H_5CH_2-X \xrightarrow[H_2O/H^{\oplus}]{(CH_2)_6N_4} C_6H_5-\overset{O}{\overset{\|}{C}}-H$$

**Note :** (1) Oxidation of Benzyl halides by $(CH_2)_6N_4$ is known as **sommelet aldehyde synthesis.**

(2) Oxidation of alkyl halide with DMSO is known as **swern oxidation**.

**Reduction :**

Haloalkanes on reduction produces alkanes frequently, reduction is done as follows.

$$R-X + 2H \longrightarrow R-H + HX$$

(i) By Nascent hydrogen liberated from Na/$C_2H_5OH$ or Sn / HCl or Zn / HCl or Zn-Cu couple/ $C_2H_5OH$ etc.

$$R-X+2H \longrightarrow R-H+HX$$

(ii) By hydride ion [:$H^{\ominus}$] liberated from $LiAlH_4$ or $NaBH_4$. It is completed by nucleophilic substitution reaction.

$$R-X+:H^{\ominus} \longrightarrow R-H+:X^{\ominus}$$

(iii) By catalytic hydrogenation of haloalkane -

$$R-X+H_2 \xrightarrow{\text{catalyst Pd}} R\text{-}H+HX$$

(iv) By reduction of RI with HI in presence of red P.

$$R-X+HI \xrightarrow{\text{redP / 150°C}} R-H+I_2$$

**Reaction with KOH :**

(a) With aqueous KOH : –

$$R\text{–}X+KOH(aq.) \longrightarrow R-OH+K-X$$

(b) With alcoholic KOH : – Dehydrohalogenation takes place and alkenes are formed.

$$R-CH_2-CH_2-X+KOH(alc.) \longrightarrow R\text{–}CH=CH_2$$

**Reaction with KCN :**

$$R-X+KCN \longrightarrow \underset{\text{Alkane nitrile}}{R-C\equiv N}+KX$$

Alkane nitrile is an important compound which gives following products.

(i) 

$$R\text{–}C\equiv N \xrightarrow[\text{Complete hydrolysis}]{H_3O^+} R-\underset{\underset{O}{\|}}{C}-O-H+NH_3$$

(ii) 

$$R-C\equiv N \xrightarrow[\text{Partial hydrolysis}]{H_2O} R-\underset{\underset{O}{\|}}{C}-NH_2$$

(iii) $$R-C\equiv N \xrightarrow{LiAlH_4\text{ / Reduction}} R-CH_2-NH_2$$

**Reaction with AgCN :**

$$R-X+AgCN \longrightarrow R-N\equiv C+AgX$$

$$R-N\equiv C \xrightarrow{\text{hydrolysis}} R-NH_2+HCOOH$$

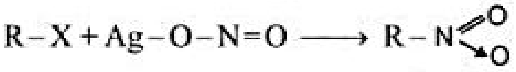
$$R-N\equiv C \xrightarrow{\text{Reduction}} R\text{–}\overset{\overset{H}{|}}{N}\text{–}CH_3$$

2°–amine

**Reaction with $KNO_2$ :**

$$R-X+\overset{+}{K}-\overset{-}{O}-N=O \longrightarrow \underset{\text{alkyl nitrite}}{R-O-N=O}$$

**Reaction with $AgNO_2$ :**



$$R-X+Ag-O-N=O \longrightarrow R-N\overset{\nearrow O}{\searrow O}$$

nitro alkane

**Reaction with KSH :**

$$R-X+K-SH \longrightarrow R-SH$$

alkane thiol

**Reaction with $Na_2S$ :–**

$$2R-X+Na_2S \longrightarrow R-S-R$$

dialkyl sulphide

**Reaction with $Na_2SO_3$ :**

$$R-X+Na_2SO_3 \longrightarrow RSO_3Na+NaX$$

alkyl sodium sulphonate

Reaction is know as **"Strecker reaction".**

**Reaction with NaOR :**

$$R-X+NaOR \longrightarrow R-O-R+NaX$$

The above reaction is called as "**Williamson ether synthesis**".

**Reaction with $Ag_2O$ :**

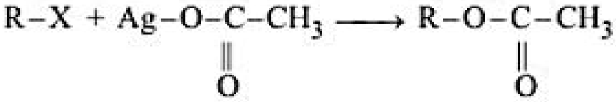
(a) Using dry $Ag_2O$ :

$$2R-X+Ag_2O \longrightarrow R-O-R+2AgX$$

(b) Using moist $Ag_2O$ :

$$2R-X+Ag_2O+H_2O \longrightarrow R-OH+2AgX$$

**Reaction with Silver Acetate :**



$$R-X+Ag-O-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow R-O-\underset{\underset{O}{\|}}{C}-CH_3$$

ester

The reaction is called as '**Esterification**'.

**Coupling Reactions**

(A) **By Wutrz Reaction :** An alkane having even number of carbon atoms can be obtained by **Wurtz Reaction.**

$$R-X+2Na+X-R \xrightarrow{\text{Dry ether}} R-R+2NaX$$

Alkane having odd number of carbon atoms can be obtained by mixed **Wurtz Reaction.**

$$R-X+X-R' \xrightarrow[\text{Na}]{\text{Dry ether}} R-R+R-R'+R'-R'$$

$$CH_3-I+CH_3-CH_2-I \xrightarrow[\text{Na}]{\text{Dry ether}} CH_3-CH_3+CH_3-CH_2-CH_3+CH_3-CH_2-CH_2-CH_3$$

(B) **By Wurtz-Fitting Reaction**

$$R-I+2Na+I-Ar \xrightarrow{\text{Dry ether}} R-Ar+2NaI$$

$$CH_3-I+2Na+I-C_6H_5 \xrightarrow{\text{Dry ether}} CH_3-C_6H_5+2NaI$$

**Reaction with metals :**

(a) With Na : – (Wurtz reaction)

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

(b) With Mg : – (Grignard reaction)

$$R-X+Mg \xrightarrow{\text{dry ether}} R-Mg-X$$

(c) With Zn dust : – (**Frankland reaction**)

$$R-X+2Zn+X-R \longrightarrow \underset{\text{dialkyl zinc}}{R-Zn-R}+ZnX_2$$

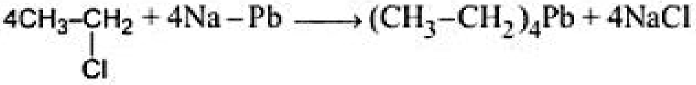
Dialkyl zinc is known as '**Frankland - Reagent**'.

(d) With Li : –

$$R-Cl+2Li \xrightarrow{\text{dry ether}} \underset{\text{alkyl lithium}}{RLi}+LiCl$$

**Note :** Alkyl lithium is more reactive than Grignard reagent.

(e) With Na-lead alloy : –

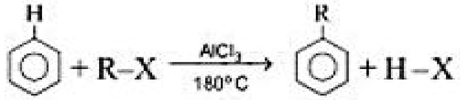


$$4CH_3-\underset{\underset{Cl}{|}}{CH_2}+4Na-Pb \longrightarrow (CH_3-CH_2)_4Pb+4NaCl$$

TEL (tetra ethyl lead)

**Note :** Tetra ethyl lead is used as antiknocking agent.

**Reaction with Benzene :**



The reaction is called as '**Friedel-craft Reaction**'.

**Important Note :–** Alkyl halide shows electrophilic substitution reaction in the above reaction, which is exception in alkyl halide

**Uses of Alkyl Halides**

**(i)** Alkyl halides are used as **weak refrigerants**, but more suitable **freons** are now being used in place of alkyl halides.

**(ii)** Synthesis of **detergents** is carried out from alkyl halides by Strecker's reaction.

**(iii)** Synthesis of **antiknock compounds**.

**(iv)** Alkyl halides, especially alkyl bromides and alkyl iodides are used for the synthesis of other organic compounds of almost all classes, in laboratory and in industry.

**(v)** Alkyl halides are generally used as starting substances for the manufacture of **alcohols**, **ethers** and **esters**.

**(vii)** Synthesis of important organometallic compounds, like Grignard's reagents. Frankland's reagents, etc., is carried out from alkyl halides.

## TYPES OF DIHALIDES

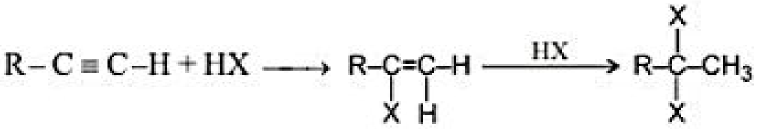
Dihalides are of two types : –

(a) **Gem dihalide :** These are the halides in which two identical halogen atoms are attached on same carbon.

(b) **Vicinal dihalide :** In these halides two identical halogen atoms are attached on adjacent carbon atoms.

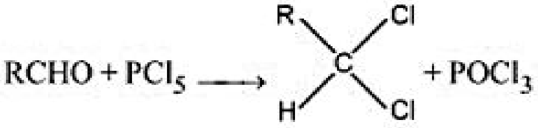
## METHODS OF PREPARATION OF GEM DIHALIDES

(a) From Alkyne (By hydrohalogenation) : –



$$R-C\equiv C-H + HX \longrightarrow R-\underset{X}{C}=\underset{H}{C}-H \xrightarrow{HX} R-\overset{X}{\underset{X}{C}}-CH_3$$

(b) From carbonyl compounds : –

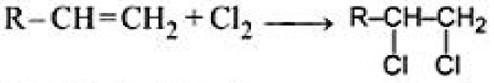


(terminal dihalide)

**Note :** If ketone is taken internal dihalide is formed.

## METHODS OF PREPARATION OF VICINAL DIHALIDES

(a) From Alkene (By halogenation) :–



$$R-CH=CH_2 + Cl_2 \longrightarrow R-\underset{Cl}{CH}-\underset{Cl}{CH_2}$$

(b) From Vicinal glycol : –

$$\begin{array}{l} R-CH-OH \\ \quad\ | \\ \quad CH_2-OH \end{array} + \begin{array}{c} PCl_5 \\ PCl_5 \end{array} \longrightarrow \begin{array}{l} R-CH-Cl \\ \quad\ | \\ \quad CH_2-Cl \end{array} + 2HCl + 2POCl_3$$

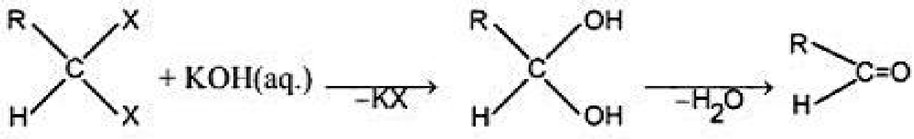
## PHYSICAL PROPERTIES OF DIHALIDES

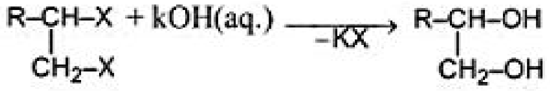
(a) Dihalides are colourless with pleasant smell liquid, Insoluble in water, soluble in organic solvent.

(b) Melting point and boiling points are directly proportional to molecular mass but boiling point of vicinal dihalides are more than gem dihalides. Also, reactivity of vicinal dihalide is more than gemdihalide, but these are less reactive than monohalide.

## CHEMICAL PROPERTIES OF DIHALIDES

(a) Reaction with aqueous KOH : –

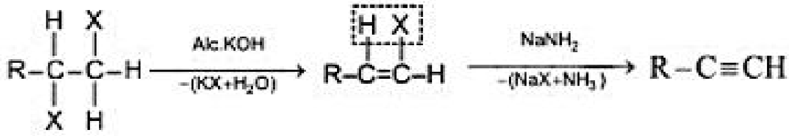




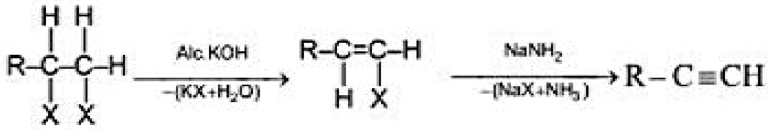
$$R-\underset{CH_2-X}{\underset{|}{CH}}-X + KOH(aq.) \xrightarrow{-KX} R-\underset{CH_2-OH}{\underset{|}{CH}}-OH$$

glycol

(b) Reaction with alcoholic KOH :–



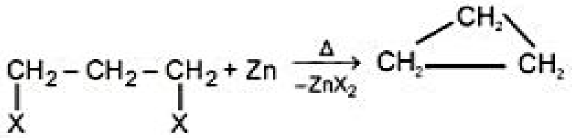
$$R-\underset{X}{\overset{H}{C}}-\underset{H}{\overset{X}{C}}-H \xrightarrow[-(KX+H_2O)]{Alc.KOH} R-\overset{H}{C}=\overset{X}{C}-H \xrightarrow[-(NaX+NH_3)]{NaNH_2} R-C\equiv CH$$



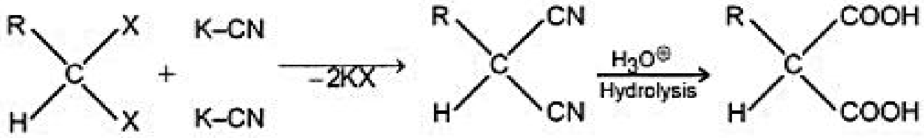
$$R-\underset{X}{\overset{H}{C}}-\underset{X}{\overset{H}{C}}-H \xrightarrow[-(KX+H_2O)]{Alc.KOH} R-\underset{H}{C}=\underset{X}{C}-H \xrightarrow[-(NaX+NH_3)]{NaNH_2} R-C\equiv CH$$

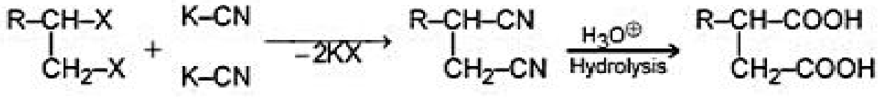
(c) **Reaction with zinc dust :** Gem dihalide reacts with Zn dust to form higher symmetrical alkene while vicinal dihalide reacts with Zn dust to form respective alkene.

**Note** – α , ω dihalide form cyclic alkane.



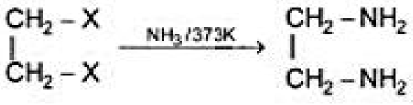
(d) Reaction with KCN :





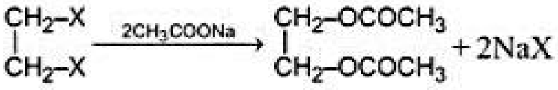
$$R-\underset{CH_2-X}{\underset{|}{CH}}-X + \begin{matrix}K-CN\\K-CN\end{matrix} \xrightarrow{-2KX} R-\underset{CH_2-CN}{\underset{|}{CH}}-CN \xrightarrow[Hydrolysis]{H_3O^{\oplus}} R-\underset{CH_2-COOH}{\underset{|}{CH}}-COOH$$

(e) Other substitution reaction :–



$$\begin{matrix}CH_2-X\\|\\CH_2-X\end{matrix} \xrightarrow{NH_3/373K} \begin{matrix}CH_2-NH_2\\|\\CH_2-NH_2\end{matrix}$$

ethylene amine



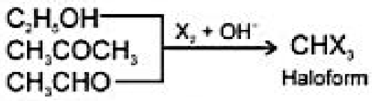
$$\begin{matrix}CH_2-X\\|\\CH_2-X\end{matrix} \xrightarrow{2CH_3COONa} \begin{matrix}CH_2-OCOCH_3\\|\\CH_2-OCOCH_3\end{matrix} + 2NaX$$

## TRIHALIDES

Trihalo derivatives of alkanes are known as trihalides. Reaction of method of preparation of trihalides is known as haloform reaction.

## TRIHALOALKANES : HALOFORM : $CHX_3$

**Preparation of Haloform**

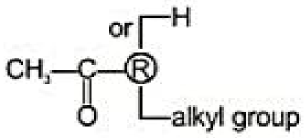


$$\left.\begin{array}{l}C_2H_5OH\\CH_3COCH_3\\CH_3CHO\end{array}\right]\xrightarrow{X_2\,+\,OH^-}\underset{\text{Haloform}}{CHX_3}$$

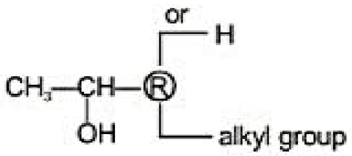
* The following compound give haloform reaction.

* Acetaldehyde, all methyl ketones, acetone, ethylalcohol, all 2-alkanols etc.

When the following compounds are heated with alkali and halogen haloform is obtained.



$\boxed{CH_3CO\text{ — group}}$



$\boxed{CH_3CH(OH)\text{— group}}$

**Example of methyl ketone :**

(i) Acetone ($CH_3$–CO–$CH_3$)

(ii) Butanone ($CH_3$–CO–$CH_2$–$CH_3$)

(iii) 2-Pentanone ($CH_3$–CO–$CH_2$–$CH_2$–$CH_3$)

(iv) 3-Methylbutanone {$CH_3$–CO–$CH(CH_3)_2$}

**Haloform Reaction**

$$C_2H_5OH + 4X_2 + 6NaOH \longrightarrow CHX_3 + 5NaX + 5H_2O + HCOONa$$

$$CH_3COCH_3 + 3X_2 + 4NaOH \longrightarrow CHX_3 + 3NaX + CH_3COONa + 3H_2O$$

**(i)** **Chloroform : $CHCl_3$**

**Preparation of Chloroform**

**1.** **Laboratory Methods – Chloroform Reaction**

On heating ethyl alcohol with bleaching powder, the reaction occurs in the followings steps :

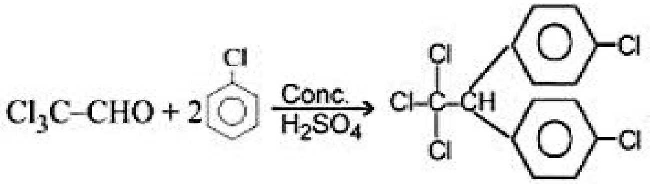
**(i)** $CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + 2Cl$

**(ii)** $CH_3CH_2OH + 2Cl \rightarrow CH_3CHO + 2HCl$

**(iii)** $CH_3CHO + 6Cl \rightarrow \underset{\text{Chloral}}{CCl_3CHO} + 3HCl$

**(iv)** $2CCl_3CHO + Ca(OH)_2 \rightarrow 2CHCl_3 + (HCOO)_2Ca$

**Note :** (i) Chloral is an important compound and when it reacts with chlorobenzene in presence of conc. $H_2SO_4$, then it form an important compound DDT (Dichloro Diphenyl Trichloro ethane )



DDT [1,1,1-trichloro-2,2-bis (parachloro phenyl) ethane]

(ii) Preparation of pure Chloroform – Alkaline solution of chlorohydrate is used in the formation of chloroform. Which on distillation gives pure chloroform as follows :

$$Cl-\overset{Cl}{\underset{Cl}{C}}-\overset{OH}{\underset{OH}{C}}-H \xrightarrow[\text{distillation}]{NaOH} CHCl_3 + HCOONa + H_2O$$

chloral hydrate

**Preparation of trihalide using 'Pyrene' :**

$$CCl_4 + 2H \xrightarrow{Fe/H_2O\ \text{reduction}} CHCl_3 + HCl$$

## PHYSICAL PROPERTIES

(a) Chloroform is colourless with pleasant smell.

(b) Insoluble in water and soluble in organic solvent. Vapours of chloroform are poisonous in nature.

(c) It cause temporary unconsciousness, so used as an anaesthetic agent.

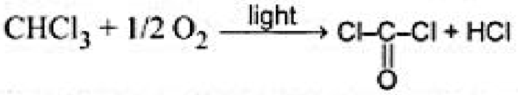
(d) Boiling point of $CHCl_3$ is 61° C.

(e) It is best solvent for fats, oil and wax.

(f) Iodoform is yellow crystalline solid. It has melting point 119 °C.

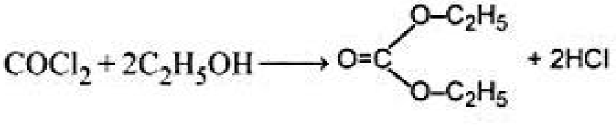
## CHEMICAL PROPERTIES

**Oxidation :** In presence of light it forms poisonous gas phosgene with atmospheric oxygen or with air.



$$CHCl_3 + 1/2\ O_2 \xrightarrow{\text{light}} Cl-\underset{\underset{O}{\|}}{C}-Cl + HCl$$

For protection it is kept into dark room in coloured bottle filling completely. For removal of phosgene we can use 0.5 to 1% ethanol solution which converts poisonous phosgene into non-poisonous salt diethyl carbonate.



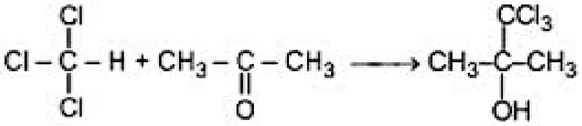
**Note :** We use silver nitrate solution to check the impurity of phosgene in solution which will form white ppt. of AgCl with HCl

**Reaction with $HNO_3$ :**

$$\mathrm{Cl{-}\overset{Cl}{\underset{Cl}{C}}{-}H{-}O{-}NO_2 \xrightarrow{\Delta} Cl{-}\overset{Cl}{\underset{Cl}{C}}{-}NO_2}$$

tear gas
(chloropicrin)

**Reaction with Acetone :**



$$\mathrm{Cl-\overset{Cl}{\underset{Cl}{C}}-H + CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow CH_3-\overset{CCl_3}{\underset{OH}{C}}-CH_3}$$

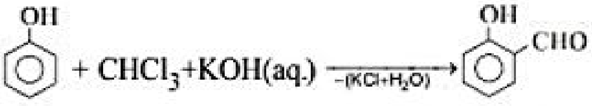
chloretone
chloretone is used as a hypnotic agent.

**Reaction with Primary amine :**

$R\ddot{N}H_2 + CHCl_3 + KOH\ (alc.) \longrightarrow R-N \equiv C + KCl + H_2O$

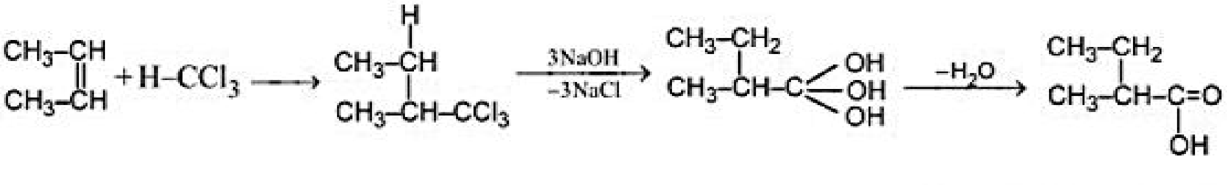
The reaction is called as 'Hoffman-carbylamine Reaction' or 'Isocyanide-test'. These isocyanides (product) has offensive smell. So, the reaction is used to test 1° amine. Reacting species of reaction is dichloro carbene.

**Reaction with Phenol :** The reaction is called as '**Reimer-tiemann Formylation**'.



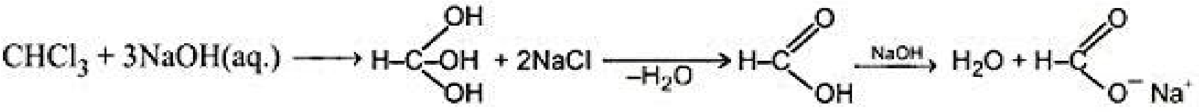
salicylaldehyde
or
(o-hydroxy benzaldehyde)

**Reaction with 2- Butene :**



2-methyl butanoic acid

**Reaction with aq. NaOH :**



$$\mathrm{CHCl_3 + 3NaOH(aq.) \longrightarrow H-\overset{OH}{\underset{OH}{C}}-OH + 2NaCl \xrightarrow[-H_2O]{} H-C\overset{\nearrow O}{\searrow OH} \xrightarrow{NaOH} H_2O + H-C\overset{\nearrow O}{\searrow O^- Na^+}}$$

Unstable

**Reaction with silver powder (Dehalogenation) :**

$$CHX_3 + 6\,Ag \xrightarrow[\text{temp}]{\text{high}} CH \equiv CH + 6\,AgX$$

**Reduction :**

$$CHCl_3 \xrightarrow[Zn/HCl]{+2H} CH_2Cl_2 + HCl$$

$$CHCl_3 \xrightarrow[Zn/HCl]{+4H} CH_3Cl + 2HCl$$

$$CHCl_3 \xrightarrow[Zn/H_2O]{+6H} CH_4 + 3HCl$$

**Uses**

1. As an anaesthetic
2. As a solvent for fat, oil and non-polar substances
3. As an antiseptic
4. In the manufacture of a hypnotic drug named chloretone
5. In the manufacture of a war gas named chloropicrin
6. In the manufacture of triphenylmethane dyes
7. In the manufacture of a polymer named teflon

## IODOFORM $CHI_3$

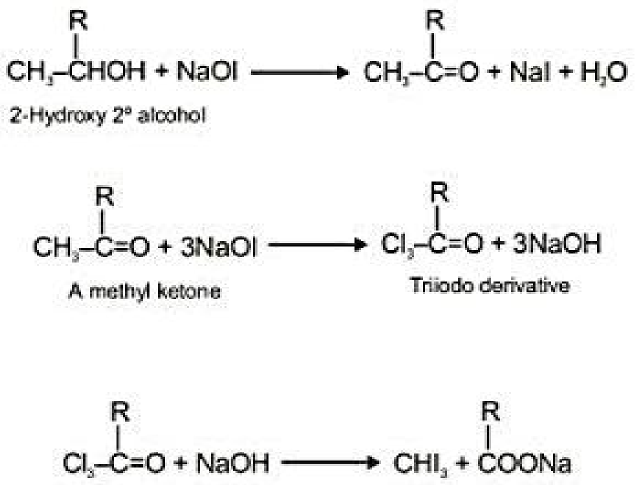
Iodoform Reaction

A yellow precipitate of $CHI_3$ is obtained on mixing saturated solution of sodium carbonate in the compound that gives haloform reaction, and heating the solution with adding iodine pinch by pinch. This reaction is called **iodoform test.**

$Na_2CO_3$ is a strong base due to hydrolysis of $CO_3^{2-}$ ion.

$$CO_3^{2-} + H_2O \longrightarrow HCO_3^- + OH^-$$

$$2OH^- + I_2 \longrightarrow I^- + IO^- + H_2O$$



$$\underset{\text{2-Hydroxy 2° alcohol}}{CH_3-\overset{\overset{R}{|}}{C}HOH} + NaOI \longrightarrow CH_3-\overset{\overset{R}{|}}{C}=O + NaI + H_2O$$

$$\underset{\text{A methyl ketone}}{CH_3-\overset{\overset{R}{|}}{C}=O} + 3NaOI \longrightarrow \underset{\text{Triiodo derivative}}{CI_3-\overset{\overset{R}{|}}{C}=O} + 3NaOH$$

$$CI_3-\overset{\overset{R}{|}}{C}=O + NaOH \longrightarrow CHI_3 + \overset{\overset{R}{|}}{C}OONa$$

## TETRAHALIDE 'PYRENE'

**General method of preparation :**

**From $CS_2$ : –**

$$CS_2 + 3Cl-Cl \xrightarrow[\text{Fe dust}+I_2]{\Delta\, 500°C} CCl_4 + \underset{\text{sulphur monochloride}}{S_2Cl_2}$$

$$2S_2Cl_2 + CS_2 \longrightarrow CCl_4 + 6S\downarrow$$

The reaction is used for industrial production of $CCl_4$.

**From $CH_4$ :**

$$CH_4 + Cl_2 \longrightarrow CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

**From $CHCl_3$ :**

$$CHCl_3 + Cl-Cl \xrightarrow{\text{ultra violet light}} CCl_4 + HCl$$

**Physical Properties :**

(a) It is colourless liquid with specific smell. It is insoluble in water and soluble in organic solvent.

(b) It is the only organic solvent which is non-combustible. So used as fire-extinguisher called as '**Pyrene**'.

**Chemical Properties :**

(a) It reacts with hot $H_2O$ or with water vapour and forms poisonous gas '**Phosgene**'.

$$CCl_4 + H_2O(g) \xrightarrow{\Delta} COCl_2 + 2HCl.$$

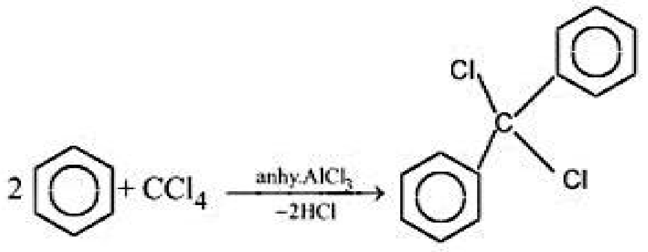
(b) It reacts with aqueous or alcoholic KOH and forms inorganic salt potassium carbonate.

$$CCl_4 + 4KOH\,(aq.) \xrightarrow[-4KCl]{} \underset{\text{(unstable)}}{C(OH)_4} \xrightarrow[-2H_2O]{} CO_2 \xrightarrow{+2KOH} K_2CO_3 + H_2O$$

(c) It reacts with phenol and forms salicylic acid.

The reaction is called as '**Riemer-Tieman Carboxylation**'.

(d) Reaction with benzene.



dichloro diphenyl methane

## FREONS

These are poly chlorofluoro derivative of alkane.

**Preparation of freons :**

$$CCl_4 + HF \xrightarrow{SbCl_5} CCl_3F + HCl$$

$$C_2Cl_6 + 2HF \xrightarrow{SbCl_5} C_2F_2Cl_4 + 2HCl$$

hexachloro ethane        freons–112

**Nomenclature of Freons :**

The common name of freons is Freon - cba or freon C - 1, H + 1, F, where

c = no. of carbon atom –1, b = no. hydrogen atom + 1, a = total no. of atoms of fluorine

eg. $CFCl_3$        C – 1 = 0, H + 1 = 1, F = 1 Freon - 11

| Formula | C-1 | H + 1 | F | Name |
|---|---|---|---|---|
| $CFCl_3$ | 1 – 1 = 0 | 0 + 1 = 1 | 1 | Freon-11 |
| $CF_2Cl_2$ | 1 - 1 = 0 | 0 + 1 = 1 | 2 | Freon-12 |
| $C_2F_2Cl_4$ | 2 - 1 = 1 | 0 + 1 = 1 | 2 | Freon-112 |
| $C_2F_3Cl_3$ | 2 - 1 = 1 | 0 + 1 = 1 | 3 | Freon-113 |
| $C_2F_4Cl_2$ | 2 - 1 = 1 | 0 + 1 = 1 | 4 | Freon-114 |
| $C_2F_5Cl$ | 2 - 1 = 1 | 0 + 1 = 1 | 5 | Freon-115 |

**Properties & uses of freons : –**

(a) Freons are colourless, odourless, unreactive & non-combustible liquids.

(b) Having very low boiling points (e.g $CF_2Cl_2$ = – 29.8°C).They easily converted from gaseous state to liquid state, therefore they are used as a coolant in A.C. & Refrigerator.

(c) Used as a aerosole propellant in aeroplane & rockets.

(d) Also used as a solvent.

**Note :** CFC is the main cause of Ozone layer decay (CFC – chlorofluoro carbon)

# GRIGNARD REAGENTS

Organomagnesium halides were discovered by **French chemist Victor Grignard** in 1900.

## PREPARATION OF GRIGNARD REAGENTS

G.R. are prepared by the reaction of organic halide (RX) with Mg in dry either solvent.

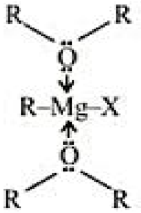
$$RX + Mg \xrightarrow[\Delta]{\text{Diethyl ether}} RMgX$$

$$ArX + Mg \xrightarrow[\Delta]{Et_2O} ArMgX$$

**The order of reactivity of halides with Mg is :**

$$RI > RBr > RCl$$

G.R. form a complex with ether solvent and formation of this complex imparts stability to G.R.



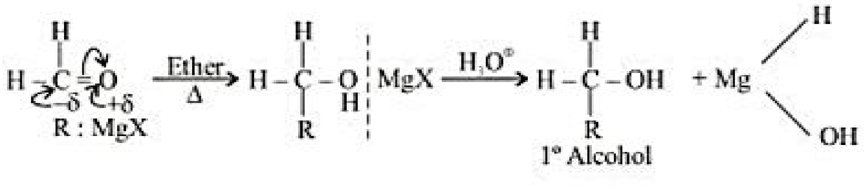
The method (which can be used for 1°, 2° and 3° alcohols) is little used in practice, since an alkyl halide can be converted into the corresponding alcohols.

## REACTIONS OF GRIGNARD REAGENTS

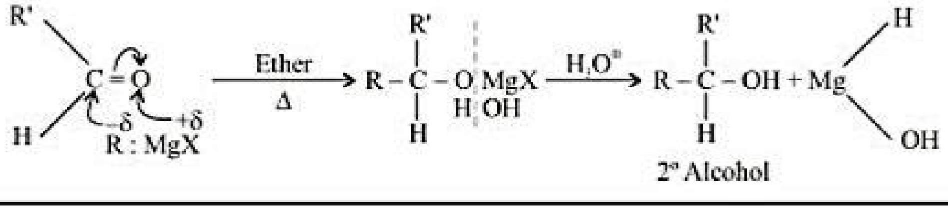
1. **Reaction with carbonyl compounds :**

GR react with carbonyl compounds to give 1°, 2° and 3° alcohols.

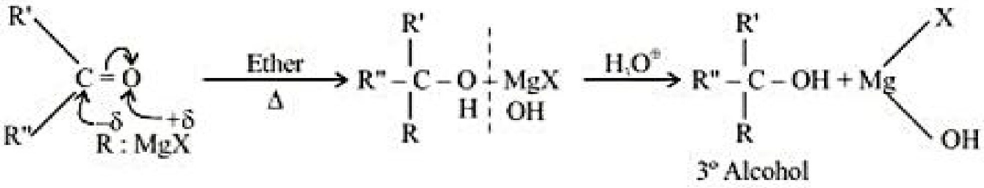
**(a)** G.R. react with formaldehyde (methanal, HCHO) to gives 1° alcohol.



**(b)** G.R. react with all other aldehydes to given 2° alcohols.

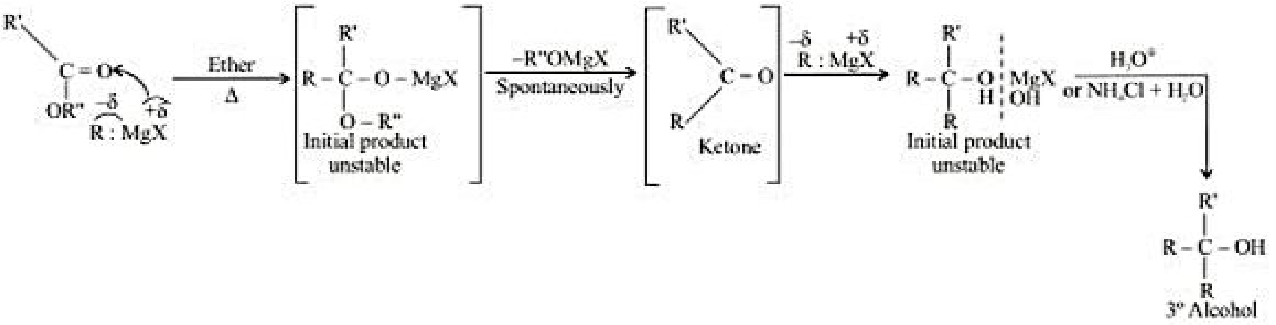


**(c)** G.R. react with ketones to give 3° alcohols.

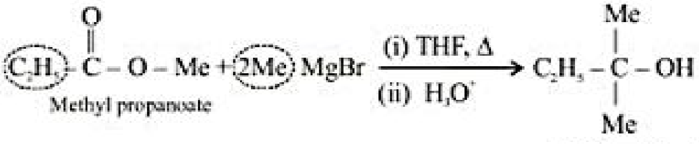


2. **Reaction with ester :**

Two moles of G.R. reacts with esters to give 3° alcohols. One mole of G.R. reacts with esters to form ketones. Ketones are more reactive towards G.R. than esters. Therefore, as soon as a molecule of the ketone is formed in the mixture, it reacts with a second molecule of G.R. After hydrolysis, the product is 3° alcohol, with two same alkyl groups that correspond to the alkyl portion of the G.R.



**For example :**



$$C_2H_5-\overset{\overset{O}{\|}}{C}-O-Me + 2Me\,MgBr \xrightarrow[(ii)\ H_3O^+]{(i)\ THF,\ \Delta} C_2H_5-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{C}}-OH$$

2-Methyl-2-ol

3. **Reaction with dialkyl carbonate :**

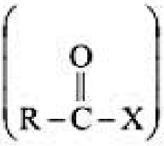
Preparation of 3° alcohol containing three identical alkyl groups :

This may be prepared by the reaction between 3 mol of G.R. with 1 mol of diethyl carbonate .

$$\left[H_5C_2O-\overset{\overset{O}{\|}}{C}-OC_2H_5 \text{ or } (C_2H_5O)_2\,C=O\right]$$

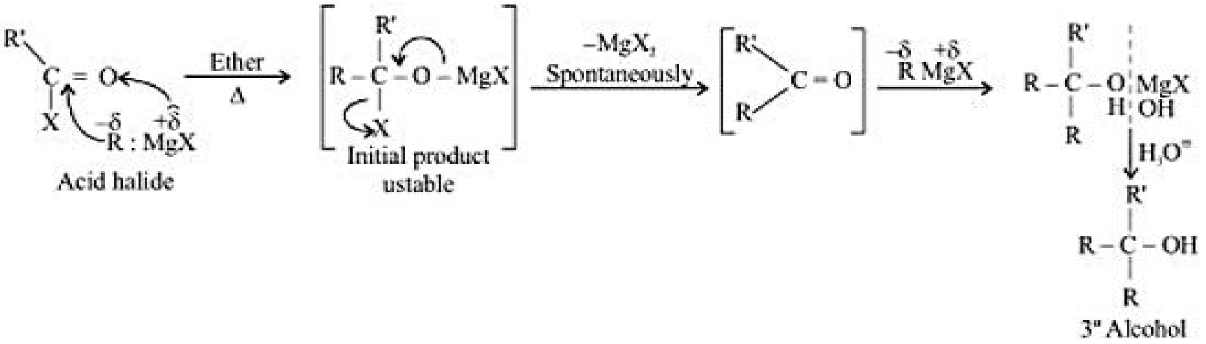
For example

4. **Reaction with alkanoyl halide :**

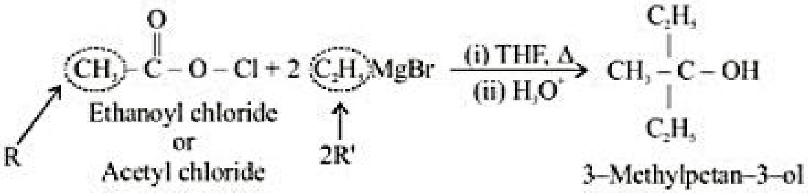


Two moles of G.R. reacts with acid halids $\left(R-\overset{\overset{O}{\|}}{C}-X\right)$ to give 3° alcohols.

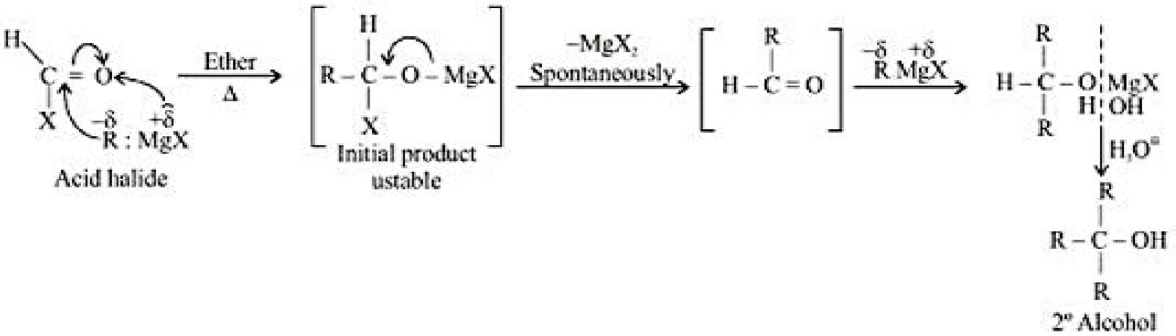
One mole of G.R. reacts with acid halids $\left(R-\overset{O}{\overset{\|}{C}}-X\right)$ to form ketones. Ketones are more reactive than acid halides. Therefore, as soon as a molecule of ketone is formed in the mixture, it reacts with a second molecule of G.R. After hydrolysis, the product is 3° alcohol, with two same alkyl groups that correspond to the alkyl portion of the G.R.



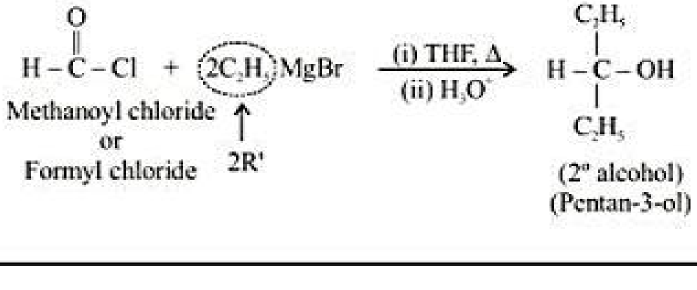
**For example :**



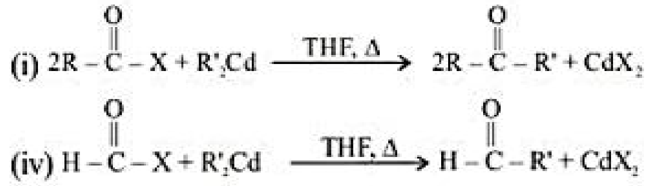
Two moles of G.R. reacts with formyl halides or methanoyl halides $\left(H-\overset{O}{\overset{\|}{C}}-X\right)$ to give 2° alcohols, with two same alkyl groups that corresponds to the alkyl portion of the G.R.



**For example :**



Reaction of dialkyl cadmium ($R_2Cd$) or dialkyl lithium cuprate with acid halides $\left(R-\overset{\overset{\displaystyle O}{\|}}{C}-X\right)$ gives ketones and with formyl halides $\left(H-\overset{\overset{\displaystyle O}{\|}}{C}-X\right)$ gives aldehydes.



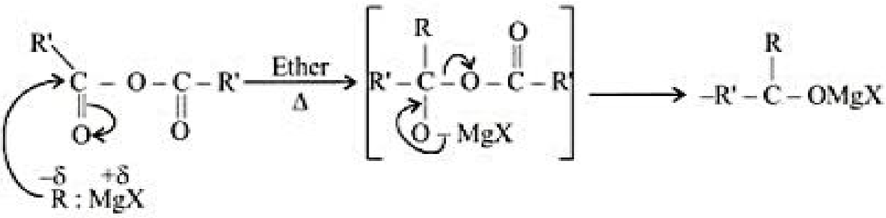
$$\text{(i) } 2R-\overset{\overset{\displaystyle O}{\|}}{C}-X+R'_2Cd \xrightarrow{THF,\ \Delta} 2R-\overset{\overset{\displaystyle O}{\|}}{C}-R'+CdX_2$$

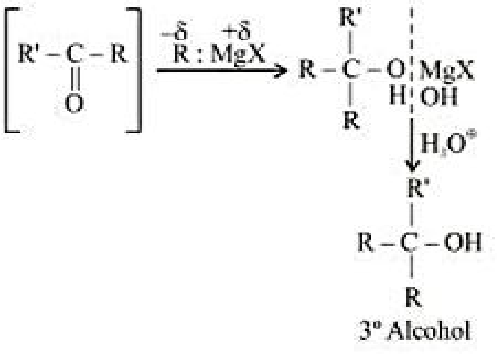
$$\text{(iv) } H-\overset{\overset{\displaystyle O}{\|}}{C}-X+R'_2Cd \xrightarrow{THF,\ \Delta} H-\overset{\overset{\displaystyle O}{\|}}{C}-R'+CdX_2$$

## 5. Reaction with anhydride :

Two moles of G.R. reacts with acid anhydride $\left(R-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-R\right)$ to give 3° alcohol.

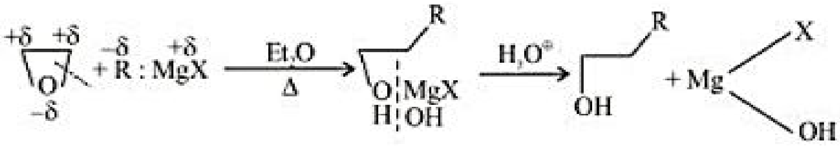
Acid anhydrides react in the same way as ester, and acid halides react with RMgX.

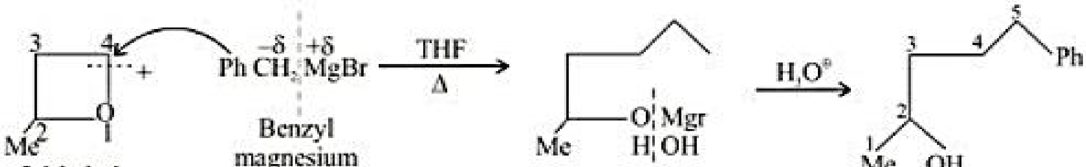




## 6. Reaction of RMgX (G.R.) with oxirans (epoxides) and other cyclic ethers :

RMgX reacts with oxiranes or cyclic ethers via $SN^2$ mechanism. The $R^{\ominus}$ (nucleophile) of RMgX attacks the partially charged C atom of oxirane ring. Since it is highly strained, the ring opens and forms a salt of 1°C alcohol, which gives alcohol on acidification.





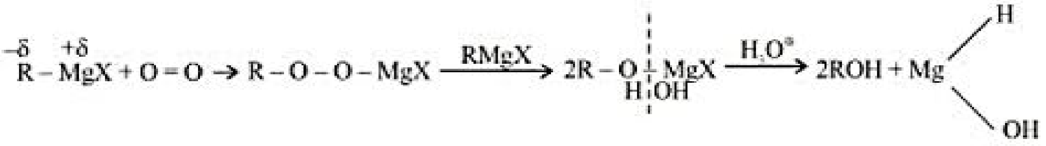
2-Methyl oxetane

Benzyl magnesium bromide

5-Phenyl pentan-2-ol

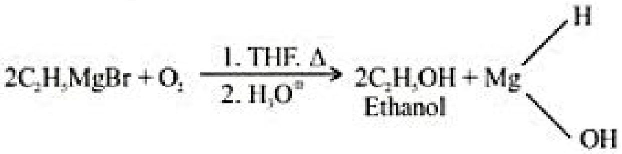
## 7. Reaction with $O_2$ :

G.R. react with $O_2$ to give 1° alcohol



$$\overset{-\delta}{R} - \overset{+\delta}{MgX} + O = O \rightarrow R - O - O - MgX \xrightarrow{RMgX} 2R - O \vdots MgX \xrightarrow{H_3O^{\oplus}} 2ROH + Mg\langle^{H}_{OH}$$

**For example :**



$$2C_2H_5MgBr + O_2 \xrightarrow[2.\ H_3O^{\oplus}]{1.\ THF.\ \Delta} \underset{\text{Ethanol}}{2C_2H_5OH} + Mg\langle^{H}_{OH}$$

## 8. Reaction with acids :

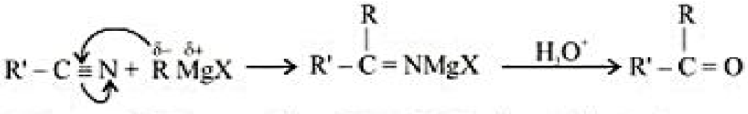
RMgX gives alkane (R–H) on reaction with acids

$R - MgX + H - X \rightarrow R - H + MgX_2$

$R{-}MgX + H_2O \rightarrow R - H + Mg\ Mg\langle^{OH}_{X}$

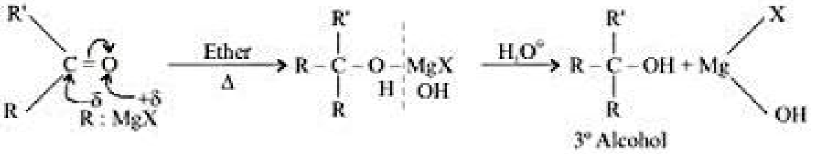
## 9. Reaction with R–CN :

RMgX gives ketone on reaction with R–CN



$$R' - C \equiv N + \overset{\delta-\ \delta+}{R\ MgX} \longrightarrow R' - \overset{R}{\overset{|}{C}} = NMgX \xrightarrow{H_3O^{+}} R' - \overset{R}{\overset{|}{C}} = O$$

Ketone on further reaction with RMgX gives 3° alcohol.



3° Alcohol