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 $C_n H_{2n+1} X$, (X = F, Br, Cl, I).
- (d) In these compounds, hybridisation state of carbon is sp³.
- (e) In these compounds, geometry of carbon is tetrahedral.
- (f) Central carbon atom has a bond angle of 109° 28'.
- (g) On the basis of no. of halogen atom, these are of following types
 - (i) Monohalide They possess single halogen atom.

eg. CH₃ - CI, CH₃ - CH₂Br

(ii) Dihalide – These are of three types

eg. gem dihalide, vicinal dihalide and α, ω halide

(iii) Trihalide – They posses three halogen atoms.

eg. CHCl3, CHI3

(iv) Tetrahalide – They possess four halogen atoms.

eg. CCl4

(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.

$$R-H+X-X \xrightarrow{h_U} R-X+H-X$$

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

From Alkene (Hydrohalogenation):-

Note: From alkyne we cannot obtain monoalkylhalide.

From Alcohol: -

(a) Using dry H - X:-

$$R-OH + H-X \xrightarrow{Anhydrous ZnCl_2} R-X + H_2O$$

(dry)

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 $-3^{\circ} > 2^{\circ} > 1^{\circ} > MeOH$

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

- (b) Using $PCl_3: -3ROH + PCl_3 \longrightarrow 3R Cl + H_3PO_3$
- (c) Using PCl₅: -ROH+PCl₅ → R-Cl+HCl+POCl₃

Important Note: -

Bromine or Iodine derivatives can not be obtained from the above reaction because due to larger size of Bromine or Iodine, PBr₅ or PI₅ are unstable.

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

$$ROH + SOCl_2 \xrightarrow{Pyridine} RCI + HCI \uparrow + SO_2 \uparrow$$

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.

$$\begin{array}{c} \text{R-C-O-Ag + Br-Br} \xrightarrow{\text{CCI}_4} \text{R-Br + CO}_2 \uparrow + \text{AgBr} \downarrow \\ \text{O} \end{array}$$

Note: -

- 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:

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

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

Swarts reaction

R-Br or R-Cl
$$\xrightarrow{AgF/\Delta}$$
 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
 - CH₃F, CH₃Cl, CH₃ CH₂ F, CH₃ CH₂ 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 H₂O because they cannot form bond with H₂O.
- (d) These are completely soluble in organic solvents.
- (f) Polarity order is RF>RCI>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 H₂O due to more density of bromine than oxygen. CH₂I₃ is heavier liquid after Hg.

CHEMICAL PROPERTIES

Oxidation reaction

- 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 (CH₂)₆N₄ followed by hydrolysis.
- (iv) Reactivity α-number of α-hydrogens.

$$R - CH_2 - X \xrightarrow{DMSO \text{ or} \atop \text{(i) } (CH_2)_6N_4} R - C - H$$

$$\begin{array}{c}
X \\
| \\
R-CH-R \xrightarrow{DMSO \text{ or} \\
(i) (CH_2)_6N_4}
\end{array}$$

$$\begin{array}{c}
0 \\
| \\
R-C-R
\end{array}$$

$$\begin{array}{c} \text{O} \\ \text{II} \\ \text{C}_6\text{H}_5\text{CH}_2 - X & \xrightarrow{\text{(CH}_2)_6\text{N}_4} & \text{C}_6\text{H}_5 - \text{C} - \text{H} \end{array}$$

- Note: (1) Oxidation of Benzyl halides by (CH2)6N4 is known as sommelet aldehyde synthesis.
 - Oxidation of alkyl halide with DMSO is known as swern oxidation.

Reduction:

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

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

 By Nascent hydrogen liberated from Na/C₂H₅OH or Sn/HCl or Zn/HCl or Zn-Cu couple/ C₂H₅OH etc.

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

By hydride ion [:H^Θ] liberated from LiAlH₄ or NaBH₄. It is completed by nucleophilic substitution reaction.

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

(iii) By catalytic hydrogenation of haloalkane -

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

(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: –

$$R-X + KOH(aq.) \longrightarrow R - OH + K-X$$

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

$$R-CH_2-CH_2-X+KOH(alc.) \longrightarrow R-CH=CH_2$$

Reaction with KCN:

$$R-X+KCN \longrightarrow R-C \equiv N+KX$$

Alkane nitrile

Alkane nitrile is an important compound which gives following products.

(i)
$$R-C \equiv N$$
 $\xrightarrow{H_3O^*} R-C-O-H+NH_3$

(ii)
$$R-C \equiv N \xrightarrow{H_2O} R-C-NH_2$$

(iii)
$$R-C \equiv N \xrightarrow{\text{LiAIH}_4/\text{Reduction}} R-CH_2-NH_2$$

Reaction with AgCN:

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

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

$$R-N \equiv C$$

Reduction

 $R-N-CH_3$
 2^o -amine

Reaction with KNO,:

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

Reaction with AgNO,:

$$R-X+Ag-O-N=O \longrightarrow R-N \stackrel{O}{<_O}$$

nitro alkane

Reaction with KSH:

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

alkane thiol

Reaction with Na,S:-

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

dialkyl sulphide

Reaction with Na, SO3:

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,O:

(a) Using dry Ag₂O:

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

(b) Using moist Ag₂O:

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

Reaction with Silver Acetate:

$$\begin{array}{ccc}
R-X + Ag-O-C-CH_3 & \longrightarrow & R-O-C-CH_3 \\
\parallel & & \parallel & & \parallel \\
O & & O & & ester
\end{array}$$

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.

$$R-X+2Na+X-R$$
 Dry ether $R-R+2NaX$

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

$$R-X+X-R' \xrightarrow{\text{Dry either}} R-R+R-R'+R'-R'$$

(B) By Wurtz-Fitting Reaction

$$R-I+2Na+I-Ar \xrightarrow{Dry \text{ either}} R-Ar+2NaI$$
 $CH_3-I+2Na+I-C_6H_5 \xrightarrow{Dry \text{ either}} CH_3-C_6H_5+2NaI$

Reaction with metals:

(a) With Na: – (Wurtz reaction)

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

(b) With Mg: – (Grignard reaction)

$$R-X+Mg$$
 dry ether $R-Mg-X$

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

$$R-X+2Zn+X-R \longrightarrow R-Zn-R+ZnX_2$$

dialkyl zinc

Dialkyl zinc is known as 'Frankland - Reagent'.

(d) With Li:-

Note: Alkyl lithium is more reactive than Grignard reagent.

(e) With Na-lead alloy: –

$$4CH_3$$
- CH_2 + $4Na$ - Pb - \longrightarrow $(CH_3$ - $CH_2)_4$ Pb + $4NaCl$

TEL (tetra ethyl lead)

Note: Tetra ethyl lead is used as antiknocking agent.

Reaction with Benzene:

$$\begin{array}{c}
H \\
\bigcirc + R - X \xrightarrow{\text{AICI}_3} & \bigcirc + H - X
\end{array}$$

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): –

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

(b) From carbonyl compounds: –

$$RCHO + PCI_5 \longrightarrow \begin{matrix} R & CI \\ + POCI_3 \end{matrix}$$

(terminal dihalide)

Note: If ketone is taken internal dihalide is formed.

METHODS OF PREPARATION OF VICINAL DIHALIDES

(a) From Alkene (By halogenation):-

$$R-CH=CH_2+Cl_2 \longrightarrow R-CH-CH_2$$

$$Cl Cl$$

(b) From Vicinal glycol: –

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: –

$$R$$
 X
 $+ KOH(aq.)$
 $-KX$
 R
 C
 OH
 OH
 $-H_2O$
 H
 $C=O$

$$\begin{array}{c} \text{R-CH-X} + \text{kOH(aq.)} \xrightarrow{-\text{KX}} \begin{array}{c} \text{R-CH-OH} \\ \text{CH}_2\text{-X} \end{array}$$

(b) Reaction with alcoholic KOH: –

$$\begin{array}{c|c} H & X \\ R-C-C-H & \xrightarrow{Ak:KOH} & \xrightarrow{HX} \\ \downarrow & \downarrow \\ X & H & \end{array} \xrightarrow{Ak:KOH} R-C=C-H & \xrightarrow{NaNH_2} R-C\equiv CH$$

$$\begin{array}{c} H \ H \\ R - C - C - H \\ \downarrow \ \downarrow \ \downarrow \\ X \ X \end{array} \xrightarrow{Alc \ KOH} \begin{array}{c} R - C = C - H \\ \downarrow \ \downarrow \ \downarrow \\ -(KX + H_2O) \end{array} \xrightarrow{R - C = C - H} \begin{array}{c} NaNH_2 \\ \hline -(NaX + NH_3) \end{array} \xrightarrow{R - C = C - H} R - C \equiv CH$$

(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.

$$CH_2 - CH_2 - CH_2 + Zn \xrightarrow{\Delta} CH_2 CH_2$$

$$\downarrow X X CH_2 - CH_2 + Zn X_2 CH_2 CH_2$$

(d) Reaction with KCN:

(e) Other substitution reaction : –

$$\begin{array}{c} \text{CH}_2 - \text{X} \\ \text{I} \\ \text{CH}_2 - \text{X} \end{array} \xrightarrow{\text{NH}_3/373\text{K}} \begin{array}{c} \text{CH}_2 - \text{NH}_2 \\ \text{I} \\ \text{CH}_2 - \text{NH}_2 \end{array}$$

$$\begin{array}{c}
\text{CH}_2\text{-X} & \xrightarrow{\text{2CH}_3\text{COONa}} & \text{CH}_2\text{-OCOCH}_3 \\
\text{CH}_2\text{-X} & \text{CH}_2\text{-OCOCH}_3
\end{array} + 2\text{NaX}$$

ethylene amine

TRIHALIDES

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

TRIHALOALKANES : HALOFORM : CHX,

Preparation of Haloform

- * 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.

Example of methyl ketone:

- (i) Acetone (CH₃-CO-CH₃)
- (ii) Butanone (CH₃-CO-CH₂-CH₃)
- (iii) 2-Pentanone (CH3-CO-CH3-CH3-CH3)
- (iv) 3-Methylbutanone {CH3-CO-CH(CH3),}

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: CHCl₃

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) CH₃CH₂OH + 2Cl → CH₃CHO + 2HCl
- (iii) CH₃CHO + 6Cl → CCl₃CHO + 3HCl
- (iv) 2CCl₃CHO + Ca(OH)₂ → 2CHCl₃ + (HCOO)₂Ca

Note: (i) Chloral is an important compound and when it reacts with chlorobenzene in presence of conc. H₂SO₄, then it form an important compound DDT (Dichloro Diphenyl Trichloro ethane)

$$CI_3C-CHO+2 \bigcirc \xrightarrow{CI} \xrightarrow{Conc.} CI-C-CH$$

$$CI_3C-CHO+2 \bigcirc \xrightarrow{CI} \xrightarrow{COnc.} CI-C-CH$$

$$CI_3C-CHO+2 \bigcirc \xrightarrow{CI} \xrightarrow{COnc.} CI-C-CH$$

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:

Preparation of trihalide using 'Pyrene':

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 CHCl₃ 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.

$$\mathrm{CHCl_3} + 1/2\ \mathrm{O_2} \xrightarrow{\quad \mathrm{light} \quad} \mathrm{Cl-C-Cl} + \mathrm{HCl}$$

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.

$$COCl_2 + 2C_2H_5OH \longrightarrow O=C_2H_5$$
 + 2HCI

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 HNO3:

Reaction with Acetone:

$$\begin{array}{c} CI & CCI_3 \\ CI-C-H+CH_3-C-CH_3 & \longrightarrow CH_3-C-CH_3 \\ CI & O & OH \end{array}$$

chloretone

chloretone is used as a hypnotic agent.

Reaction with Primary amine:

$$RNH_2 + CHCl_3 + KOH (alc.) \longrightarrow R-N \equiv C + KCl + H_2O$$

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'.

Reaction with 2- Butene:

$$\begin{array}{c} \text{CH}_3\text{-CH} \\ \text{CH}_3\text{-CH} \\ \text{CH}_3\text{-CH} \\ \end{array} \\ \begin{array}{c} \text{CH}_3\text{-CH} \\ \text{CH}_3\text{-CH-CCI}_3 \\ \end{array} \\ \begin{array}{c} \text{CH}_3\text{-CH}_2 \\ \text{CH}_3\text{-CH-C} \\ \end{array} \\ \begin{array}{c} \text{CH}_3\text{-CH}_2 \\ \text{CH}_3\text{-CH-C} \\ \text{OH} \\ \end{array} \\ \begin{array}{c} \text{CH}_3\text{-CH}_2 \\ \text{CH}_3\text{-CH-CEO} \\ \text{OH} \\ \end{array} \\ \begin{array}{c} \text{CH}_3\text{-CH}_2 \\ \text{CH}_3\text{-CH-CEO} \\ \text{OH} \\ \end{array} \\ \begin{array}{c} \text{CH}_3\text{-CH-CEO} \\ \text{OH} \\ \end{array} \\ \begin{array}{c} \text{CH}_3\text{-CH-CEO} \\ \text{OH} \\ \text{OH} \\ \end{array} \\ \end{array}$$

2-methyl butanoic acid

Reaction with aq. NaOH:

$$CHCl_3 + 3NaOH(aq.) \longrightarrow H-COH + 2NaCl \longrightarrow H-COH \longrightarrow H_2O + H-COH \longrightarrow H_2$$

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Reaction with silver powder (Dehalogenation):

$$CHX_3 + 6 Ag \xrightarrow{high} CH \equiv CH + 6 AgX$$

Reduction:

CHCl₃
$$\xrightarrow{+2H}$$
 CH₂Cl₂ + HCl
CHCl₃ $\xrightarrow{+4H}$ CH₃Cl + 2HCl
CHCl₃ $\xrightarrow{-6H}$ CH₄ + 3HCl

Uses

- As an anaesthetic
- As a solvent for fat, oil and non-polar substances
- As an antiseptic
- 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
- In the manufacture of a polymer named teflon

IODOFORM CHI3

Iodoform Reaction

A yellow precipitate of CHI₃ 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**.

Na2CO3 is a strong base due to hydrolysis of CO32-ion.

TETRAHALIDE 'PYRENE'

General method of preparation:

From CS,:-

$$CS_2 + 3CI - CI \xrightarrow{\Delta 500^{\circ}C} CCI_4 + S_2CI_2$$
sulphur
monochloride

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

The reaction is used for industrial production of CCl4.

From CH4:

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

From CHCl₃:

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 H₂O or with water vapour and forms poisonous gas 'Phosgene'.
 CCl₄ + H₂O(g)
 [△] COCl₂ + 2HCl.
- (b) It reacts with aqueous or alcoholic KOH and forms inorganic salt potassium carbonate.

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

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

$$\bigcirc + CCl_4 \xrightarrow{aq.KOH} \bigcirc OH \xrightarrow{COOH}$$

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

(d) Reaction with benzene.

$$2 \bigcirc + CCl_4 \xrightarrow{anby.AlCl_3} \bigcirc Cl$$

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. CFCl₃ C - 1 = 0, H + 1 = 1, F = 1 Freon - 11

Formula	C-1	H+1	F	Name
CFCI ₃	1 - 1 = 0	0+1=1	1	Freon-11
CF ₂ Cl ₂	1 - 1 = 0	0 + 1 = 1	2	Freon-12
C ₂ F ₂ Cl ₄	2 - 1 = 1	0 + 1 = 1	2	Freon-112
C ₂ F ₃ Cl ₃	2 - 1 = 1	0 + 1 = 1	3	Freon-113
C ₂ F ₄ Cl ₂	2 - 1 = 1	0 + 1 = 1	4	Freon-114
C ₂ F ₅ Cl	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 CF₂Cl₂ = -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

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

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

$$ArX + Mg \xrightarrow{Et,O} ArMgX$$

The order of reactivity of halides with Mg is:

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

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.

$$H \xrightarrow{C} \xrightarrow{C} \xrightarrow{C} \xrightarrow{C} \xrightarrow{Ether} \xrightarrow{A} H \xrightarrow{C} \xrightarrow{C} \xrightarrow{H} MgX \xrightarrow{H_1O^\circ} H \xrightarrow{C} \xrightarrow{C} OH \xrightarrow{P} OH$$

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

$$\begin{array}{c|c} R' & \xrightarrow{Ether} & \xrightarrow{Ether} & A & R - C - O MgX \xrightarrow{H,O^{n}} & R - C - OH + Mg \\ R : MgX & & H & OH \end{array}$$

$$\begin{array}{c|c} R' & & & & & & \\ R' & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$$

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

$$R'' \xrightarrow{C = O \atop R : MgX} \xrightarrow{Ether} \xrightarrow{A} R'' \xrightarrow{C - O \atop R} H \xrightarrow{MgX} \xrightarrow{H,O^{\oplus}} R'' \xrightarrow{C - OH + Mg} \xrightarrow{N} OH$$

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:

$$\begin{array}{c}
O \\
\parallel \\
C-O-Me + 2Me \\
Methyl propanoate
\end{array}$$

$$\begin{array}{c}
Me \\
\downarrow \\
(ii) THF, \Delta \\
(ii) H,O'
\end{array}$$

$$\begin{array}{c}
C_2H, -C-OH \\
Me \\
\downarrow \\
Me
\end{array}$$

$$\begin{array}{c}
Me \\
\downarrow \\
Me
\end{array}$$

$$\begin{array}{c}
Me \\
\downarrow \\
Me
\end{array}$$

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 GR, with 1 mol of diethyl carbonate.

$$\begin{bmatrix}
O \\
|| \\
H_5C_2O - C - OC_2H_5 \text{ or } (C_2H_5O)_2 C = O
\end{bmatrix}$$

For example

Reaction with alkanoyl halide:

Two moles of G.R. reacts with acid halids
$$\begin{pmatrix} O \\ R - C - X \end{pmatrix}$$
 to give 3° alcohols.

One mole of GR. reacts with acid halids R-C-X 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 GR. After hydrolysis, the product is 3° alcohol, with two same alkyl groups that correspond to the alkyl portion of the GR.

For example:

Two moles of GR. reacts with formyl halides or methanoyl halides $\begin{pmatrix} O \\ H-C-X \end{pmatrix}$ to give 2° alcohols, with two same alkyl groups that corresponds to the alkyl portion of the GR.

$$\begin{array}{c|c}
H \\
C = O \\
X \\
R : MgX
\end{array}$$

$$\begin{array}{c|c}
Ether \\
A cid halide
\end{array}$$

$$\begin{array}{c|c}
H \\
C = O \\
X \\
R : MgX
\end{array}$$

$$\begin{array}{c|c}
H \\
R - C - O - MgX \\
X \\
Initial product ustable
\end{array}$$

$$\begin{array}{c|c}
-MgX_2 \\
Spontaneously \\
R \\
H - C = O
\end{array}$$

$$\begin{array}{c|c}
R \\
R \\
MgX
\end{array}$$

$$\begin{array}{c|c}
R \\
H - C - O | MgX \\
R \\
H | O H \\
R \\
R
\end{array}$$

$$\begin{array}{c|c}
R \\
H | O H \\
R \\
R
\end{array}$$

$$\begin{array}{c|c}
R \\
H | O H \\
R \\
R
\end{array}$$

$$\begin{array}{c|c}
R \\
R - C - O H \\
R \\
R
\end{array}$$

$$\begin{array}{c|c}
R \\
R - C - O H \\
R \\
R
\end{array}$$

$$\begin{array}{c|c}
R \\
R - C - O H \\
R \\
R
\end{array}$$

$$\begin{array}{c|c}
R \\
R - C - O H \\
R \\
R - C - O H
\end{array}$$

For example:

Reaction of dialkyl cadmium (R₂Cd) or dialkyl lithium cuprate with acid halides $\begin{pmatrix} O \\ || R - C - X \end{pmatrix}$ gives

ketones and with formyl halides $\begin{pmatrix} O \\ H-C-X \end{pmatrix}$ gives aldehydes.

(i)
$$2R - C - X + R'_{2}Cd \xrightarrow{THF, \Delta} 2R - C - R' + CdX_{2}$$

$$0 \\
\parallel \\
(iv) H - C - X + R'_{2}Cd \xrightarrow{THF, \Delta} H - C - R' + CdX_{2}$$

5. Reaction with anhydride:

Two moles of G.R. reacts with acid anhydride $\begin{pmatrix} O & O \\ \parallel & \parallel \\ R-C-O-C-R \end{pmatrix}$ to give 3° alcohol.

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

$$\begin{array}{c}
R' \\
C - O - C - R' \\
\downarrow O \\
O \end{array}
\xrightarrow{\text{Ether}}
\begin{bmatrix}
R & O \\
R' - C - O - C - R'
\end{bmatrix}$$

$$\begin{bmatrix}
R & O \\
\downarrow O \\
O & MgX
\end{bmatrix}
\xrightarrow{R} - R' - C - OMgX$$

$$\begin{array}{c}
-\delta & +\delta \\
R : MgX
\end{array}$$

$$\begin{bmatrix} R' - C - R \\ 0 \end{bmatrix} \xrightarrow{\begin{matrix} -\delta & +\delta \\ R : MgX \end{matrix}} R \xrightarrow{\begin{matrix} R' \\ -C - O \\ MgX \end{matrix}} R \xrightarrow{\begin{matrix} H' OH \\ H'OH \end{matrix}} H_{i}O^{\circ}$$

$$R'$$

$$R'$$

$$R \xrightarrow{\begin{matrix} R' \\ H'OH \end{matrix}} R$$

6. Reaction of RMgX (GR.) with oxirans (epoxides) and other cyclic ethers :

RMgX reacts with oxiranes or cyclic ethers via SN² mechanism. The R⁶ (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.

$$\begin{array}{c} +\delta & +\delta \\ \searrow \\ -\delta \end{array} + R : MgX \xrightarrow{Et,O} \xrightarrow{\Delta} \begin{array}{c} R \\ \searrow \\ M \mid OH \end{array} \xrightarrow{H,O^{\circ}} \begin{array}{c} R \\ \longrightarrow \\ OH \end{array} + Mg \xrightarrow{R} \begin{array}{c} X \\ \longrightarrow \\ OH \end{array}$$

7. Reaction with O2:

GR. react with O2 to give 1° alcohol

For example:

$$2C_2H_3MgBr + O_2 \xrightarrow{1. \text{ THF. } \Delta} 2C_2H_3OH + Mg$$
Ethanol

8. Reaction with acids:

RMgX gives alkane (R-H) on reaction with acids $R - MgX + H - X \rightarrow R - H + MgX$,

$$R-MgX + H_2O \rightarrow R - H + Mg Mg <_X^{OH}$$

9. Reaction with R-CN:

RMgX gives ketone on reaction with R-CN

$$R'-C = N + R MgX \longrightarrow R'-C = NMgX \xrightarrow{H,O'} R'-C = O$$

Ketone on further reaction with RMgX gives 3° alcohol.

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