HALOGEN DERIVATIVES

1.0 HALOGEN DERIVATIVES

Compounds derived from hydrocarbons by replacement of one or more H-atoms by corresponding no. of halogen atoms are known as halogen derivatives.

2.0 CLASSIFICATION

On the basis of nature of hydrocarbon from which they are obtained, halogen derivatives can be classified as :



Because of less stability of SOBr2 and SOI2, R-Br and RI can not be obtained by this method .

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 $\begin{array}{ccc} R - COOAg & + & X_2 & \xrightarrow{CCl_4} R - X + CO_2 + AgX \\ \begin{array}{c} \text{Silver salt of} \\ a \text{ fatty acid} \end{array} & \begin{array}{c} (Cl_2 \text{ or } Br_2) & \Delta \end{array} \end{array}$

(5) By halide exchange :

 $R-Cl \text{ or } R-Br + KI \xrightarrow{Acetone} R-I + KCl \text{ or } KBr (Conant fiilkelstein reaction)$

 $2CH_3Cl + Hg_2F_2 \xrightarrow{Water} 2CH_3 - F + Hg_2Cl_2$ (Swart reaction)

Note : Fmkelstein reaction can only be used to prepare R-I and swart's reaction can only be used to prepare R–F

3.2 Physical Properties

(a) The lower members CH₃F, CH₃Cl, .CH₃Br, C₂H₅Cl and C₂H₅F are gases at room temp.

(b) Higher B.P. than parent alkanes.

Decreasing order of B.P. is : B-I > R-Br > R-Cl > R-F

among isomeric R-X, decreasing order of B.P; is : Primary > Secondary > tertiary

(c) R–F and R–Cl \longrightarrow lighter than water R–Br and R–l \longrightarrow heavier than water

Decreasing order of density Is: R-I > R - Br > R - Cl > R - F

- (d) R-X are polar co-valent compound but insoluble in water because they can not form H-bonds. They dissolve in organic solvents.
- (e) R-X (except R-F} burns with a green flame when interacted with Cu wire.(Beliestein test}

(ii)

- (f) Dipole moment order-
 - (i) $CH_3Cl > CH_3F > CH_3Br > CH_3I$

3.3 Chemical Properties

3.3.1 Nucleophili¢ substitution reaction



(g) Reaction with KCN and AgCN :

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+ AgX

(minor)

| $\overset{\delta_{+}}{R} - \overset{\delta_{-}}{X} + \overset{\bigoplus}{KCN} \xrightarrow{Alc.} \overset{Alc.}{\longrightarrow}$ | RC≡N | + RNC + KX |
|---|---------|------------|
| Ionic | cyanide | Isocyanide |
| | (major) | (minor) |

• :CN ion is an ambident nucleophile .

$$\delta^{+}$$
 δ^{-} $R \rightarrow X$ + Ag $-CN$ $\rightarrow R \rightarrow R \rightarrow R \rightarrow C + R \rightarrow CN + AgX$
covalent isocyanide Cyanide (Major) (Minor)

(h) Reaction with KNO_2 and $AgNO_2$

$$\overset{\delta^{+}}{R} \xrightarrow{\delta^{-}} X + \overset{\delta^{-}}{K} \overset{O}{\overset{-}} NO \xrightarrow{Alc.}{\Delta} \xrightarrow{} R \xrightarrow{-} O \xrightarrow{-} N = O + R \xrightarrow{-} NO_{2} + KX$$
Ionic
$$\overset{\delta_{+}}{Alkyl nitrite} Nitro alkane
(Major)
(Minor)$$

$$\overset{\delta_{+}}{\delta^{-}} \xrightarrow{\delta^{-}} X + Ag \xrightarrow{-} O \xrightarrow{-} \overset{N}{N} = O \xrightarrow{-} \overset{Alc.}{\Delta} \xrightarrow{} R \xrightarrow{-} N \overset{O}{\underset{O}{\overset{-}}} + R \xrightarrow{-} O \xrightarrow{-} N = O$$
Nitroalkane
Alkyl nitrite

(i) Reaction with NaOR' (Sodium alkoxide) :

 $R - X + NaOR' \longrightarrow R - OR' + NaX$

(williamson synthesis reaction)

(major)

(j) Reaction with NH₃:

$$R - X + NH_{3} \xrightarrow{\Delta} R - NH_{2} \xrightarrow{R-X} R - NH - R \xrightarrow{R-X} R - N - R$$

$$\downarrow R - X$$

$$\begin{bmatrix} R \\ R - N - R \\ R \end{bmatrix} X^{\Theta}$$
(Outperpendicular)

(k) Reaction with CH=CNa:

 $R \rightarrow X + CH \equiv CNa \rightarrow R \rightarrow C \equiv CH + NaX$

If
$$CH_{3} \rightarrow CH_{3} \rightarrow CH_{3} \rightarrow CH_{2} + NaX + CH \equiv CH_{3}$$

 $CH_{3} \rightarrow CH_{3} - C = CH_{2} + NaX + CH \equiv CH_{3}$
 $CH_{3} \rightarrow CH_{3} \rightarrow CH_{3} - C = CH_{2} + NaX + CH \equiv CH_{3}$
 $CH_{3} \rightarrow CH_{3} \rightarrow$

3.3.2 Dehydrohalogenation : Alkyl halides undergo β -elimination on treatment with KOH(alc.) or NaNH₂.

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$$R - \overset{p}{C}H_{2} - \overset{\alpha}{C}H_{2} - X + KOH (alc.) \xrightarrow{A} R - CH = CH_{2} + HX$$

$$CH_{3} - CH_{2} - CH_{2} - CH_{2} - Br + KOH (alc.) \xrightarrow{A} CH_{3} - CH_{2} - CH = CH_{2} + HBr$$

$$\begin{bmatrix} H & Br \\ -+--++ \\ -+--++ \end{bmatrix}$$

$$CH_{3} - CH - CH_{-}CH_{3} \xrightarrow{Alc.KOH} CH_{3} - CH = CH - CH_{3} + CH_{3} - CH_{2} - CH = CH_{2} + HBr$$

$$But-2 - ene (80\%) \qquad But-1 - ene (20\%)$$

3.3.3 Wurtz Reaction : $2RX + 2Na \xrightarrow{Dry ether} R-R + 2NaX$

When a mixture of different alkyl halides, $(R_1 - X)$ and $(R_2 - X)$ is used a mixture of alkane is formed

 $R_1 - X + 2 Na + X - R_2 \xrightarrow{\text{Dry ether} \Delta} R_1 - R_2 + R_1 - R_1 + R_2 - R_2 + NaX$

3.3.4 Formation of Organometallic compounds :

| (i) R–X + | Mg — | $\xrightarrow{\text{try ether}} RM_{2}$ | gX (Grigna | rd reage | nt) | | | |
|---|-------|---|-----------------------------|-------------------------|----------|--------|----------|-----------------|
| (ii) 2C ₂ H ₅ Br | + | 2Zn — dry eth | $\xrightarrow{er} (C_2H_5)$ |) ₂ Zn (Fr | ankland | reagen | t) + Znl | Br ₂ |
| (iii) 4C ₂ H ₅ Cl | + | 4 Na/Pb — | $\rightarrow (C_2H_5)_4P$ | ² b + 4N | aCl + 3P | 'b | | |
| Sodium lead | Alloy | Tetra ethyl | lead (used a | as an <mark>tikn</mark> | ocking a | gent) | | |

3.3.5 Friedel – Crafts reaction :

0



4.0 DIHAUDES

General formula $C_nH_{2n}X_2$. Two H - atom of alkanes, replaced by two halogen atoms to form dihalides. Dihalides are classified as :

(a) Gem dihalide : The term Gem is derived from geminal means - same position.

Two similar halogen atoms are attached to same C - atom

| Ex. | CH ₃ CHX ₂ | Ethylidene dihalide | (1, 1 - Dihalo ethane) |
|-----|----------------------------------|---|-------------------------|
| | СН | Selation de la company de Esta de la company de la com | |
| | | Isopropylidene dihalide | (2, 2 - Dihalo propane) |
| | CH ₃ | | |

(b) Vic dihalides : Vic term from - Vicinal means adjacent C - atoms

Two halogen atoms are attached on adjacent carbon atom

Ex.
$$CH_2 - CH_2$$

 $\downarrow \qquad H - C - CH - CH_2$
 $\downarrow \qquad I \qquad H - X \qquad H \qquad X \qquad X$
Ethylene dihalide Propylene dihalide V

Vic and Gem dihalides are positive isomers.

(1,2-Dihaloethane) (1,2-Dihalopropane)

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(c) α , ω dihalides: Halogen atoms are attached with terminal C- atom. They are separated by 3 or more C - atoms. They are also known as polyroethylene halides.

Ex.
$$CH_2 - CH_2 - CH_2 - CH_2$$
 (1,4-Dihalobutane)
 X Tetramethylene dihalide

4.1 General Methods of Preparation

(a) Gem dihalides :

(i) By the reaction of PCl_5 on carbonyl compound.

$$\begin{array}{c} O & Cl \\ H \\ CH_{3} - C - H + PCl_{5} \longrightarrow CH_{3} - C - H + POCl_{3} \\ Cl \\ \end{array}$$
Acetaldehyde Ethylidene chloride
$$\begin{array}{c} O \\ H \\ \end{array}$$

$$CH_{3} - \overset{\parallel}{C} - CH_{3} + PCL_{5} \longrightarrow CH_{3} - \overset{\downarrow}{C} - CH_{3} + POCL_{5}$$

Acetone

2, 2 - Dichloropropane

(ii) By addition of halogen acids on alkynes :

(b) Vic-dihalides :

(i) By the addition of halogens to alkenes :

$$\begin{array}{c} CH_2 \\ \parallel \\ CH_2 \end{array} + Br_2 \longrightarrow \begin{array}{c} CH_2Br \\ \parallel \\ CH_2Br \\ 1, 2 \text{ - Dibromoethane} \end{array}$$

$$CH_{3} - CH = CH_{2} + Br_{2} \longrightarrow CH_{3} - CH - CH_{1}$$

1, 2 - Dibromo propane

(ii) By the action of PCl₅, on glycols :

 $\begin{array}{c} CH_2OH \\ I \\ CH_2OH \end{array} + 2PCI_{\$} \longrightarrow \begin{array}{c} CH_2CI \\ I \\ CH_2CI \end{array} + 2POCI_{\$} + 2HCI \end{array}$

4.2 Physical Properties

- (i) Lower members are colourless, oily liquids with sweet smell. Higher members are solid,
- (ii) These are heavier than water.

4.3 Chemical Properties

(i) Action of KOH(alc.) : (Dehydrohalogenation)

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5.0 TRI HALIDES ·(Haloform CHX₃)

5.1 General Method of Preparation

- (i) From $CH_4 : CH_4 + 3Cl_2 \xrightarrow{hv} CHC1_3 + 3HCI$
- (ii) By Halofonn reaction (lab method) :

| CH₃CH₂—OH | Planshing neurolay (CoOC) | (HCOO) ₂ Ca |
|-----------------------------------|---|---------------------------------------|
| or | $\xrightarrow{\text{Bieaching powder [CaOCI_2]}} \text{CHCl}_3$ | + or |
| CH ₃ COCH ₃ | H ₂ 0/Δ | (CH ₃ COO) ₂ Ca |

Mechanism:

 $\begin{array}{l} CaOCl_2 + H_2O \longrightarrow 2CI + Ca \ (OH)_2 \\ CH_3CH_2 - 0H + 2Cl \longrightarrow CH_3CHO + 2HCI \ (Oxidation) \\ CH_3CHO + 6CI \longrightarrow CC1_3CHO + 3HCI \ (Halogenation) \\ CC1_3CHO + Ca(OH)_2 \longrightarrow CHCl_3 + (HCOO)_2Ca \ (Hydrolysis) \\ \end{array}$ If CH_3COCH_3 is used then CHCl_3is formed into 2 steps (Chlorination and Hydrolysis)

(+)**ve haloform reaction:** Reaction which gives haloform with alkali and Xi is called as(+) ve haloform reaction.

Ex. Alcohols : CH_{3} - $CH_{-}Z$ OH CH_{3} - $CH_{-}CH_{3}$ OH OHOH

(-) ve haloform reaction : Reaction in which haloforms are not formed With X_2 and alkali. Ex. $CH_3 - C - CI$, $CH_3 - C - OH$, $CH_3 - C - NH_2$, $CH_3 - C - O - CH_3 \cdot do$ not show haloform reaction.

(iii) Preparation of pure CHCl₃:

 $\text{CCl}_3\text{CHO.2H}_2\text{O} \xrightarrow[]{\text{NaOH}} \text{CHCl}_3 + \text{HCOONa} + 2\text{H}_2\text{O}$

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(iv) Industrial preparation :



5.2 Physical Properties

 $CHCl_3$ is colourless and sweet smelling liquid. It's B.P. is 61° C and it is insoluble in H₂O and have density more than H₂O. Chloroform is used as Anaesthetic.

5.3 Chemical Properties

(i) Oxidation : $CHCl_3 + [O]$ __Airandlight \rightarrow $COCl_2 + HCl_3$

Phosgene gas or Carbonyl Chloride (Poisonous gas)

CHCl₃ is stored in dark coloured bottles which are filled upto the brim to prevent oxidation of $CHCl_3$ into $COCl_2$ and 1% ethanol is also added to chloroform

$$O = C \left\langle \begin{array}{c} Cl \\ Cl \end{array} + 2HO - C_2H_3 \xrightarrow{-2HC} O = C \left\langle \begin{array}{c} OC_2H \\ OC_2H \end{array} \right\rangle$$

[Poisonous]

Diethyl carbonate [Non-Poisonous]

GOLDEN KEY POINTS

| | | Test | of CHCl ₃ |
|-----|--------------------------------------|--|---|
| | Reagent | Pure CHCl ₃ | Impure CHCl ₃ (COCl ₂ + HCl) |
| • | Blue litmus | No Change | turns into red |
| • | AgNO ₃ | No reaction | White ppt of AgCl |
| • | Conc. H ₂ SO ₄ | No Change | Yellow solution |
| (ii |) Hydrolysis: CH Ca | $\xrightarrow{Aq.KOH} CH \begin{pmatrix} OH \\ -H \\ OH \end{pmatrix}$ | $ \begin{array}{c} \overset{0}{\longrightarrow} H - \overset{0}{C} - OH \xrightarrow{KOH} H - \overset{0}{C} - OK \\ \overset{1}{\longrightarrow} O & O \end{array} $ |
| | | Unstable | |

(iii)Carbyl amine reaction or isocyanide test: (Hoffman's carbylamines reaction:-

Primary-Amines (Aliphatic or Aromatic) $\xrightarrow{\text{CHCl}_3+\text{KOH}}$ Isocyanides

Isocyanides have unpleasant or offensive smell (Isocyanide test).

$$R - NH_2 \xrightarrow{CHCl_3 + KOH} R - NC$$

Mechanism:

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 $CHCl_3 \xrightarrow{KOH} :CCl_2$



Note: If CCl₄ is used in place of chloroform, salicylic acid is formed as product.



(v) Reaction with CH₃COCH₃:

$$CH_{3} - C - CH_{3} + H - CCI_{3} \xrightarrow{\circ} OH CH_{3} - C - CH_{3}$$

(vi) Reaction with HNO₃:

$$CCl_3 - H + HO - NO_2 - CCl_3 - NO_2 + H_2O$$

Chloropicrin or nitrochloroform

(Tear gas)

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(vii) Reaction with CH₃CH=CH₂:

$$CH_{3}-CH = CH_{2} \xrightarrow{CHCl_{3}/Peroxide} \xrightarrow{CH_{3}-CH-CH_{2}} | |_{H CCl_{3}}$$

A free radical addition reaction

(viii) Reaction with Ag: $CHCl_3 \xrightarrow{Ag} CH=CH$

(ix) FCR : $3Ph - H + CHCl_3 \xrightarrow{AgCl_3} Ph_3CH$

Triphenyl methane

GOLDEN KEY POINTS

Iodoform Test

| CH ₃ CH ₂ OH | I2+ NaOH or NaOI or OI |
|------------------------------------|---|
| CH ₃ COCH ₃ | or I ₂ + Na ₂ CO ₃ + H ₂ O yellow crystals |
| | of iodoform |

• CHI_3 give yellow ppt. of AgI with AgNO₃ but $CHCl_3$ does not give AgCl ppt.

Reason : CHI₃ is thermally less stable than CHCl₃.

Iodofonm test can be used to distinguish the following pairs of compounds.

- (i) CH₃CH₂OH and CH₃OH
- (ii) CH₃CHO and CH₃CH₂CHO
- (iii) 2-Pentanol and 3-Pentanol
- (iv) Acetophenone and benzophenone
- (v) 2-Propanol and 1-Propanol

Freons

The chlorofluoro derivatives of methane and ethane are called freons.

 CF_2Cl_2 – (dichloro difluoro methane)

 $C_2F_2Cl_4$ – (Tetrachloro difluoroethane)

Most useful is CF₂Cl₂(Freon-12)

Nomenclature of freons:

Freon-cha

 $c = n_{c-1}$ $b = n_{U+1}$

$$0 - \Pi_{H+I}$$

 $a = n_F$

| | $c = n_{C-1} = 1 - 1 = 0$ | | | $c=n_{c-1}=2-1=1$ | |
|----------------------------|-------------------------------|----------|------------------------------|---------------------|-----------|
| $CF_2Cl_2 \longrightarrow$ | $b = n_{\rm H+1} = 0 + 1 = 1$ | Freon-12 | $C_2F_4Cl_2 \longrightarrow$ | $b=n_{H+1}=0+1=1$ | Freon-114 |
| | a=n _F =2 | | | a=n _F =4 | |

• Excess use of Freons is harmful for Ozone layer (depletion of Ozone layer).

6.0 Grignard Reagent

6.1 General Method of Preparation

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Grignard reagents are prepared. in the laboratory by the action of alkyl halides on magnesium metal in the presence of dry ether.

 $R - X + Mg \xrightarrow[ether]{dry} R - Mg - X$ (Grignard reagent)(Alkyl magnesium halide)

The ease of formation of Grignard reagent is in the order $Rl > RBr > RCl \cdot$ Ether is used to dissolve the Grignard reagent by coordination.

6.2 Chemical Reactions

| | $\xrightarrow{(i) O_2 (ii) H_5O^*} \rightarrow$ | R—OH | 1° Alcohol |
|---------------------------------|---|----------------------|------------|
| | $H_2C=0/H_3O^*$ | RCH _z -OH | 1° Alcohol |
| | CH₂-CH₄∕H₃O* | R-CH2-CH2-OH | 1° Alcohol |
| R—Mg—X | RCHO/H₃O ⁺ → | R₂CHOH | 2° Alcohol |
| 가 가 가 다 가지. 이 가 다 가 가 가 가 다. | HCOOEt/H₃O ⁺ → | R,CHOH | 2° Alcohol |
| | RCOR/H₂O → | - R₃C—OH | 3° Alcohol |
| | RCOOEt/H₂O (2 : 1) → | R ₂ C—OH | 3° Alcohol |
| | HCOOEt (1:1) | RCHO | aldehyde |
| | RCN/H ₂ O | RCOR | Ketone |
| | RCOOEt (1 : 1) | RCOR | Ketone |
| | CO₂/H₂O → | RCOOH | Acids |
| | HOH or ROH or NH, or Ph — OH | | |
| | or $CH \equiv CH$ or $Ph - NH_2$ | R—H | Alkane |
| | R—X → | R—R | Alkane |
| | R₃N → | No reaction | |
| | $CICH_2-CH=CH_2$ | R-CH-CH = CH | Alkene |
| | | R—NH, | 1° Amine |
| | | R—CN | Cyanides |
| | CICOOEt | RCOOEt | Ester |

7.0 Haloarene

If halogen atom is directly attached to the benzene ring, then compound is called as Haloarene.



7.1 General Methods of Preparation

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(2)
$$\bigcirc$$
 + PCl₅ \longrightarrow \bigcirc + POCl₃+ HCl

$$3C_6H_5OH + POCl_3 \longrightarrow (C_6H_5)_3PO_4 + 3HCl$$

7.2 Chemical Properties

(ii)

(1)
$$(1) \xrightarrow{\text{CI}} + \text{NaOH} \xrightarrow{(i) 623K, 300 \text{ atm}} (i) H^{\oplus} + \text{NaCI}$$

Presence of electron withdrawing group on ring makes the nucleophilic substitution easier. **Reactivity Order :** (Towards nucleophilic substation)



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NO₂

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- $\begin{array}{cccc}
 (1) C_{6}H_{5}-NH-C_{6}H_{5} & (2) CH_{3}CH_{2}NH_{2} \\
 (3) CHC1_{3} & (4) C_{6}H_{5}-NH_{2}
 \end{array}$
- 3. For preparation of Grignard reagent from haloalkanes which metal is used :- . (1) Na (2) Mg (3) Ca (4) Ag

| | | A | NS | WE | <u>s</u> Kl | EY | | 1. 1. 1 . | | |
|------------------|------|---|----|----|-------------|----------|--------|---------------------|--------|----|
| RECINNER'S ROV 1 | Que. | 1 | 2 | | | . Steres | | 1100 | | |
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