

ORGANIC CHEMISTRY

ENTHUSIAST | LEADER | ACHIEVER



STUDY MATERIAL

Halogen Derivatives

ENGLISH MEDIUM





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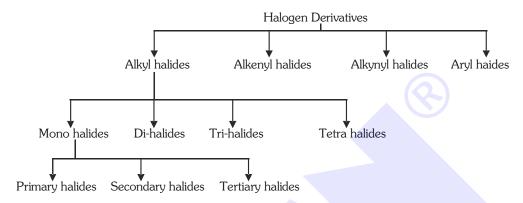
HALOGEN DERIVATIVES

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:



3.0 MONOHALIDES:

3.1 General Methods of Preparation of Monohalides

(1) By direct halogenation of alkanes:

(2) By the addition of H—X on alkenes:

$$R - CH = CHR + HX \longrightarrow RCH_{2} - CHXR$$

$$eg: CH_{2} = CH_{2} + HX \longrightarrow CH_{3} - CH_{2}X$$

$$eg: CH_{3} - CH = CH_{2} + HX \longrightarrow CH_{3} - CH - CH_{3}$$

Isopropyl halide

(3) By Alcohols:

(a) By the action of hydrogen halides:

$$R-CH_2-OH \xrightarrow{H-X} RCH_2-X$$

(b) By the action of phosphorous halides:

 PBr_3 and PI_3 are usually generated in site (Produced in reaction mixture) by the reaction of red phosphorous with bromine and iodine, respectively.

(c) By reaction with thionyl chloride (Darzen's procedure):

$$R$$
—OH + $SOCl_2$ — Pyridine R —Cl + SO_2 + HCl

One mole One mole

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



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(4) Borodine - Hunsdicker's reaction:

$$R$$
—COOAg + $X_2 \xrightarrow{CCl_4} R$ — $X + CO_2 + AgX$

Silver salt of $(Cl_2 \text{ or } Br_2)$

a fatty acid

(5) By halide exchange:

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

$$2CH_{3}Cl \ + Hg_{2}F_{2} \xrightarrow{\quad Water \quad} 2CH_{3}\text{--}F \ + \ Hg_{2}Cl_{2} \text{ (Swart reaction)}$$

 $oldsymbol{Note}$: Finkelstein 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: R-I > R-Br > R-CI > R-F

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

R—Br and R—I \longrightarrow heavier than water

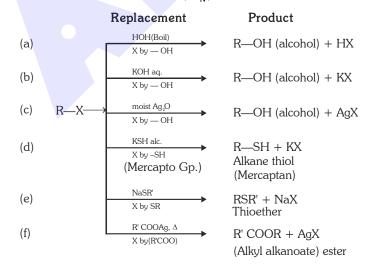
Decreasing order of density is : R-I > R-Br > R-CI > R-F

- (d) R—X are polar co-valent compounds 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. (Beilstein test)
- (f) Dipole moment order-

(i)
$$CH_3Cl > CH_3F > CH_3Br > CH_3I$$
 (ii) $Cl > Cl > Cl$

3.3 Chemical Properties

3.3.1 Nucleophilic substitution reaction (S_N):





(g) Reaction with KCN and AgCN:

 \bullet : $\overset{\odot}{C}\overset{\cdot}{N}$ ion is an ambident nucleophile.

(h) Reaction with KNO₂ and AgNO₂:

$$\stackrel{\delta^{+}}{R} \stackrel{\delta^{-}}{X} + \stackrel{\$}{K} \stackrel{\circ}{O} \longrightarrow NO \xrightarrow{\stackrel{Alc.}{\Delta}} R \longrightarrow NO \longrightarrow N= O + R \longrightarrow NO_{2} + KX$$

$$\stackrel{Ionic}{Ionic} \stackrel{Alc.}{\longrightarrow} R \longrightarrow NO \longrightarrow N= O + R \longrightarrow NO_{2} + KX$$

$$\stackrel{Alkyl \ nitrite}{\longrightarrow} Nitro \ alkane$$

$$(Major) \qquad (Minor)$$

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

$$R$$
— X + $NaOR'$ — — R — OR' + NaX

(williamson synthesis reaction)

(j) Reaction with NH₃:

(k) Reaction with $CH \equiv CNa$:

$$R - X + CH \equiv CNa \xrightarrow{\Delta} R - C \equiv CH + NaX$$

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

$$R - \overset{\beta}{C}H_2 - \overset{\alpha}{C}H_2 - X + KOH(alc.) \xrightarrow{\Delta} R - CH = CH_2 + HX$$

$$CH_3 - CH_2 - CH_2 - CH_2 - Br + KOH(alc.) \xrightarrow{\Delta} CH_3 - CH_2 - CH = CH_2 + HBr$$

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

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

3.3.4 Formation of Organometallic compounds:

(i)
$$R-X + Mg \xrightarrow{Dry \ ether} RMgX$$
 (Grignard reagent)

(ii)
$$2C_2H_5Br + 2Zn \xrightarrow{Dry \text{ ether}} (C_2H_5)_2 Zn \text{ (Frankland reagent)} + ZnBr_2$$

(iii)
$$4C_2H_5Cl + 4Na / Pb \longrightarrow (C_2H_5)_4 Pb + 4NaCl + 3Pb$$

Sodium lead Alloy Tetra ethyl lead (used as antiknocking agent)

3.3.5 Friedel - Crafts reaction:

4.0 **DIHALIDES**

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

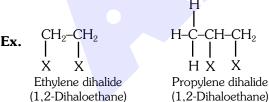
(a) **Gem dihalide**: The term Gem is derived from geminal means - same position.

Two similar halogen atoms are attached to same C - atom

$$CH_3$$
 CX_2 Isopropylidene dihalide (2, 2 - Dihalo propane)

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

Two halogen atoms are attached on adjacent carbon atom.



Ethylene dihalide Propylene dihalide

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

(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 polymethylene halides.

Vic and Gem dihalides are position isomers.

$$\begin{array}{c|cccc} \textbf{Ex.} & CH_2-CH_2-CH_2-CH_2 & (1,4\text{-Dihalobutane}) \\ & & & & \text{Tetramethylene dihalide} \\ & & & & X & & X \\ \end{array}$$



General Methods of Preparation 4.1

(a) Gem dihalides:

By the reaction of PCl₅ on carbonyl compound.

O
$$Cl$$
 $CH_3 - C - H + PCl_5 \longrightarrow CH_3 - C - H + POCl_3$
 Cl
 Cl

Acetaldehyde Ethylidene chloride

CCH₃ - C - CH₃ + PCl₅
$$\longrightarrow$$
 CH₃ - C - CH₃ + POCl₃ $\stackrel{|}{\underset{Cl}{|}}$

Acetone

2, 2 - Dichloropropane

By addition of halogen acids on alkynes: (ii)

$$CH \equiv CH + HBr \longrightarrow CH_2 = CHBr \xrightarrow{HBr} CH_3 CHBr_2$$

$$Vinyl \ bromide \qquad 1, \ 1 - Dibromoethane$$

$$CH_3 - C \equiv CH + HBr \longrightarrow CH_3 - C = CH_2 \xrightarrow{HBr} CH_3 - C - CH_3$$

$$Propyne \qquad Br \qquad 2, \ 2 - Dibromopropane$$

(b) Vic-dihalides:

By the addition of halogens to alkenes:

$$\begin{array}{cccc} \text{CH}_2 & \text{CH}_2\text{-Br} \\ \parallel & + & \text{Br}_2 \longrightarrow & \mid \\ \text{CH}_2 & \text{CH}_2\text{-Br} \\ & 1,2\text{-Dibromoethane} \\ \\ \text{CH}_3\text{-CH=CH}_2\text{+Br}_2 \longrightarrow & \text{CH}_3\text{-CH-CH}_2 \\ & & \mid & \mid \\ & & \text{Br} & \text{Br} \\ & 1,2\text{-Dibromo propane} \end{array}$$

(ii) By the action of PCl₅ on glycols:

$$\begin{array}{ccc} \text{CH}_2\text{OH} & & \text{CH}_2\text{CI} \\ | & + & 2\text{PCl}_5 & \longrightarrow & | & +2\text{POCl}_3 + 2\text{HCl} \\ \text{CH}_2\text{OH} & & \text{CH}_2\text{CI} & \end{array}$$

Physical Properties

- Lower members are colourless, oily liquids with sweet smell. Higher members are solid.
- They are heavier than water.

Chemical Properties 4.3

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

$$\begin{array}{ccccc} CH_2X & CH_3 & KOH(alc.) & CH \\ & \text{Or} & CHX_2 & -2HX & CH \end{array}$$

TG: @Chalnaayaaar

Chemistry: Halogen Derivatives

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(ii) Action of KOH(aq.): (Hydrolysis) It is a distinction test for gem - and vic - dihalides.

$$\begin{array}{c|cccc} & CH_2\text{-}Cl & & CH_2\text{-}OH \\ & & & & & & & & & & \\ \text{(a)} & CH_2\text{-}Cl & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\$$

(b)
$$CH_3CHXCH_2X$$
 $\xrightarrow{KOH(aq.)}$ $CH_3-CH-CH_2$ \downarrow \downarrow \downarrow OH OH Propane-1, 2-diol

(iii) Reaction with KCN:

$$\begin{array}{c} \text{CH}_2\text{Cl} \\ \mid \\ \text{CH}_2\text{Cl} \end{array} + 2\text{KCN} \xrightarrow{-2\text{KCl}} \begin{array}{c} \text{CH}_2\text{-CN} \\ \mid \\ \text{CH}_2\text{-CN} \end{array} \xrightarrow{\text{H}_2\text{O}/\text{H}^+} \begin{array}{c} \text{CH}_2\text{-COOH} \\ \mid \\ \text{CH}_2\text{-COOH} \end{array} \xrightarrow{\text{CH}_2\text{-CO}} \begin{array}{c} \text{CH}_2\text{-CO} \\ \text{CH}_2\text{-COOH} \end{array}$$

- (i) CN group on acid hydrolysis gives COOH
- (ii) Two COOH group on one C atom always loose CO2 to form monocarboxylic acid on heating.
- (iii) Two COOH group on vic. C atom loose H₂O to form cyclic anhydride on heating.

(iv) Dehalogenation:

BEGINNER'S BOX-1

1. Which of the following is not organometallic compound

(1) RMgX (2) R₂Zn

(3) RONa (4) R_2Hg

2. Which is Finkelstein reaction?

(1) $R-X + NaI \xrightarrow{acetone}$ (2) $R-X + AgF \longrightarrow$

 $(3) R-X + NaF \longrightarrow (4) R-F + AgCl \longrightarrow$



5.0 TRI HALIDES (Haloform CHX₃)

5.1 General Method of Preparation

(i) From CH₄:
$$CH_4 + 3Cl_2 \xrightarrow{hv} CHCl_3 + 3HCl$$

(ii) By Haloform reaction (lab method):

$$\begin{array}{c} \text{CH}_3\text{CH}_2\text{-OH} \\ \text{or} \\ \text{CH}_3\text{COCH}_3 \end{array} \right] \quad \begin{array}{c} \text{Bleaching power [CaOCl}_2] \\ \hline H_2\text{O}/\Delta \end{array} \quad \text{CHCl}_3 + \\ \text{(CH}_3\text{COO)}_2\text{Ca} \end{array}$$

Mechanism:

If CH₃COCH₃ is used then CHCl₃ is formed into 2 steps (Chlorination and Hydrolysis)

(+) ve haloform reaction: Reaction which gives haloform with alkali and X_2 is called as (+) ve haloform reaction.

Aldehydes : Only acetaldehyde CH_3 –C–H

$$\begin{array}{cccc} CH_3-C-COOH & CH_3-C-CHO & Also show haloform reaction. \\ \parallel & , & \parallel \\ O & O \end{array}$$

(-) ve haloform reaction : Reaction in which haloforms are not formed with X_2 and alkali.



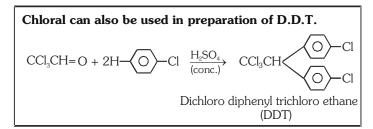
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(iii) Preparation of pure CHCl₃:

$$CCl_{3}CHO. \ 2H_{2}O \ \xrightarrow{ \ \ NaOH \ \ \ \ } \ CHCl_{3} + HCOONa + 2H_{2}O$$

Chloral hydrate

(Pure Chloroform)



(iv) Industrial preparation:

5.2 Physical Properties

CHCl₃ 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:
$$CHCl_3 + [O]$$
 Air and light $COCl_2 + HCl$

Phosgene gas or Carbonyl Chloride (Poisonous gas)

 $CHCl_3$ 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

$$\begin{array}{c} \text{Cl} \\ \text{O=C} \\ \text{Cl} \\ \text{[Poisonous]} \end{array} + 2\text{HO} - \text{C}_2\text{H}_5 \xrightarrow{-2\text{HCl}} \begin{array}{c} \text{OC}_2\text{H}_5 \\ \text{O=C} \\ \text{OC}_2\text{H}_5 \\ \text{Diethyl carbonate} \\ \text{[Non-Poisonous]} \end{array}$$

GOLDEN KEY POINTS

Test of CHCl,

Reagent Pure CHCl₃ Impure CHCl₃ (COCl₂ +HCl)
 Blue litmus No Change turns into red
 AgNO₃ No reaction White ppt of AgCl

(ii) Hydrolysis :
$$CH \xrightarrow{Cl} \xrightarrow{Aq.KOH} CH \xrightarrow{OH} \xrightarrow{-H_2O} H - C - OH \xrightarrow{KOH} H - C - OK OH$$

Unstable



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

(iv) Reimer Tiemann's reaction:

Mechanism: :CCl₂ is neutral attacking electrophile (formed by α, α – elimination reaction)

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



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(v) Reaction with CH₃COCH₃:

(vi) Reaction with HNO_3 :

$$CCl_3$$
 $\overline{\{H + HO\}}$ NO_2 \longrightarrow $CCl_3 - NO_2 + H_2O$ Chloropicrin or nitrochloroform (Tear gas)

(vii) Reaction with $CH_3CH=CH_2$:

$$CH_3 - CH = CH_2 \xrightarrow{CHCl_3/Peroxide} CH_3 - CH - CH_2 \\ CCl_3 & H CCl_3 \\ A \text{ free radical addition}$$

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

(ix) FCR: $3Ph - H + CHCl_3 \xrightarrow{AlCl_3} Ph_3CH$ Triphenyl methane

GOLDEN KEY POINTS

Iodoform Test

$$\begin{array}{c} \text{CH}_3\text{CH}_2\text{OH} \\ \text{or} \\ \text{CH}_3\text{COCH}_3 \end{array} \xrightarrow{I_2 + \text{NaOH or NaOI or OI}} \begin{array}{c} \overset{\text{\scriptsize 0}}{\text{OI}} \\ \text{or } I_2 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \end{array} \xrightarrow{\text{\scriptsize vellow crystals}} \\ \text{of iodoform}$$

ullet CHI $_3$ give yellow ppt. of AgI with AgNO $_3$ but CHCl $_3$ does not give AgCl ppt.

Reason: CHI₃ is thermally less stable than CHCl₃.

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

- (i) CH₂CH₂OH and CH₂OH
- (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.

CF₂Cl₂ – (dichloro difluoro methane)

C₂F₂Cl₄ – (Tetrachloro difluoroethane)

Most useful is CF₂Cl₂ (Freon-12)

ALLEN® Pro-Modical

Nomenclature of freons:

Freon - cba

$$\begin{array}{l} c = n_{c-1} \\ b = n_{H+1} \\ a = n_{F} \end{array}$$

$$\begin{array}{l} c = n_{c-1} = 1 - 1 = 0 \\ b = n_{H+1} = 0 + 1 = 1 \\ a = n_{F} = 2 \end{array} \\ \end{array} \quad \begin{array}{l} c = n_{c-1} = 2 - 1 = 1 \\ b = n_{H+1} = 0 + 1 = 1 \\ a = n_{F} = 4 \end{array} \\ \end{array} \quad \begin{array}{l} Freon-114 \\ a = n_{F} = 4 \end{array}$$

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

6.0 Grignard Reagent

6.1 General Method of Preparation

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{dry} $R - Mg - X$

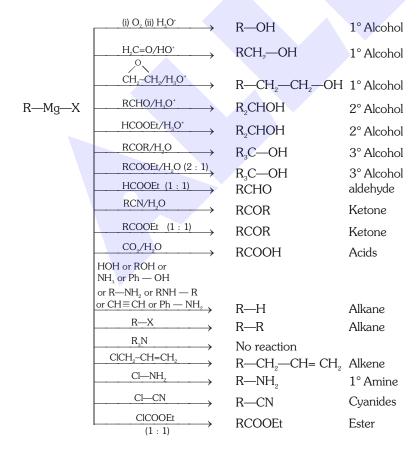
(Grignard reagent)

(Alkyl magnesium halide)

The ease of formation of Grignard reagent is in the order RI > RBr > RCI

Ether is used to stablised the Grignard reagent.

6.2 Chemical Reactions





7.0 Haloarene

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

Ex.

(Chlorobenzene) (2-Chlorotoluene) (2,4-<u>Dic</u>hlorotoluene)

7.1 General Methods of Preparation

(1)
$$\bigcirc$$
 + $\text{Cl}_2 \xrightarrow{\text{AlCl}_3} \bigcirc$ + HCl

(2)
$$OH$$

$$+ PCl_5 \xrightarrow{\Delta} O$$

$$+ POCl_3 + HCl$$

$$3C_6H_5OH + POCl_3 \longrightarrow (C_6H_5)_3 PO_4 + 3HCl_3$$

7.2 Chemical Properties

(1)
$$Cl$$
 + NaOH (i) 623K, 300 atm (ii) H^{\oplus} + NaCl

Presence of electron withdrawing group on ring makes the nucleophilic substitution easier.

Reactivity Order: (Towards nucleophilic substitution)

(2) Fittig reaction:

(3) Wurtz fittig reaction:

$$Cl + 2Na + ClCH_2CH_2CH_3 \xrightarrow{dry \ ether} CH_2CH_2CH_3 + 2NaCl$$



(4) Electrophilic Substitution Reaction:

(i)
$$\bigcirc$$
 + \bigcirc + \bigcirc Anhy. FeCl₃ + \bigcirc Cl + \bigcirc Cl (Major)

Note: Cl is o- and p- directing group.

(iii)
$$Cl$$
 + conc. H_2SO_4 Δ Cl SO_3H + SO_3H (Major)

(iv)
$$Cl$$
 + CH_3Cl anhy. $AlCl_3$ + CH_3 + CH_3 (Major)

BEGINNER'S BOX-2

- **1.** Which can give haloform with X_2/OH^- ?
 - (1) CH₃OH

(2) CH₃-CH₂-CH=O

(3) CH₃CHO

- (4) CH₃CH₂CH₂OH
- 2. Which of the following compounds cannot be identified by carbylamine test?
 - (1) $C_6H_5-NH-C_6H_5$

(2) CH₃CH₂NH₂

(3) CHCl₃

- $(4) C_6 H_5 NH_2$
- 3. Which metal is used for preparation of Grignard reagent from haloalkanes:-
 - (1) Na

(2) Mg

(3) Ca

(4) Ag

ANSWER'S KEY					
BEGINNER'S BOX-1	Que.	1	2		
	Ans.	3	1		
BEGINNER'S BOX-2	Que.	1	2	3	
	Ans.	3	1	2	