



NATIONAL TESTING AGENCY

Chemistry

Organic Chemistry



NEET - UG

S.NO.	CONTENT	Page					
ORGANIC CHEMISTRY							
1.	Haloalkanes and Haloarenes	1					
2.	Alcohols, Phenols and Ethers	15					
3.	Organic Chemistry – Some Basic Principles and Techniques	41					
4.	Aldehydes, Ketones and Carboxylic Acids	86					
5.	Hydrocarbons and Petroleum	129					
6.	Amines	159					
7.	Biomolecules	182					
8.	Polymers	207					
9.	Chemistry in Everyday Life	219					

Dear Aspirant, Thank you for making the right decision by choosing ToppersNotes. To use the QR codes in the book, Please follow the below steps :-



Click on Scan QR

Choose the **QR from book**

1

CHAPTER

Haloalkanes and Haloarenes

Chlorobenzene

CHAPTER OUTLINE

- Haloalkanes
- Teflon (– CF₂ CF₂ –)_n

HALOALKANES

 Haloalkanes are the halogen derivatives of hydrocarbons, and their structure is determined by the number of hydrogen atoms they contain.

Classification

On the basis of No. of Halogen Atoms

- A. Monohalides (R-X)
 - As alkyl halides, monohalides are the monohalogen derivatives of alkanes with
 - the general formula $C_nH_{2n+1}X$.
 - R X may be of three types:
 - 1. Primary R CH₂X
 - 2. Secondary R₂. CH.X
 - 3. Tertiary R₃.C.X
- B. Dihalides $(C_nH_{2n}X_2)$
 - Dihalides are alkanes' di-halogen derivatives and come in geminal and vicinal forms.

Geminal





CH₃CHBr₂ Ethylidine dibromide BrCH₂CH₂Br Ethylene dibromide

Example:

 $BrCH_2 - CH_2 - CH_2 - CH_2Br$ 1, 4-dibromobutane

- C. Trihalides $(C_nH_{2n-1}X_3)$ or haloforms (CHX₃)
 - Trihalides are alkane-derived tri-halogen compounds.

D. Tetrahalides $(CX_4 \text{ or } CX_2Y_2)$

CCl₄ Or Pyrene (Carbon-tetra-Chloride)

• Tetrahalides are the tetra-halogen derivatives of alkanes.

On the basis of Nature of C-X Bond

(i) Compounds containing sp^3 hybridised C – X bond

(a) Alkyl halides or halo alkanes RCH₂X R₂CHX R₂CX

$$H_2X R_2CHX R_3CX$$

 $1^\circ 2^\circ 3^\circ$

(b) Allylic halides: Halogen atom is linked to an sp^3 hybridised carbon atom which has a C = C bond attached to it.



(c) Benzylic halides: The tetrahedral carbon involved in C - X bond is linked to an aromatic ring.



- (ii) <u>Compounds containing sp² hybridised C X</u> bond
 - (a) Vinylic halides
 - The halogen atom is linked to the C=C bond's sp² hybridised carbon atom.



- (b) Aryl Halides
 - Halogen atom is linked to the carbon atom of the benzene ring.





Monohalides

- Haloalkanes are monohalides; for instance, the IUPAC name for C₂H₅Br is bromoethane.
- These molecules may exhibit chain, position, and optical isomerisms.

Methods of preparation

By direct halogenation of alkanes

 $R-H+X-X \xrightarrow{hv} R-X+HX$

Example:

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

The reactivity order is
 F₂ > Cl₂ > Br₂ > l₂
 R₃CH > R₂CH₂ > RCH₃ > CH₄

t s From alcohols

• $R - OH + PCl_5 \rightarrow R - Cl + POCl_3 + HCl$

р

- $3R OH + PCI_3 \rightarrow 3R CI + H_3PO_3$
- $R OH + SOCI_2 \xrightarrow{Pyridine} R CI + SO_2 + HCI$

It is called **Darzen's process.** Here, pyridine is used to reflux gaseous by-products.

•
$$R-H+SO_2Cl_2 \xrightarrow{Pyridine} R-Cl+HCl+SO_2$$

Here, Pyridine also reacts with HCl



By Groove's method

• $R - OH + HX \xrightarrow{Anhy. ZnCl_2} R - X + H_2O$

•
$$R - OH \xrightarrow{H^+} R - OH \xrightarrow{H^+} R + H_2O$$

$$R^{+} \xrightarrow{X^{-}}_{fast} R - X(S_{N}1)$$

or $R - \overset{+}{O}H_{2} \xrightarrow{X^{-}}_{Slow} R - X + H_{2}O S_{N}^{-}$

- The order of reactivity of HX with alcohols is HI > HBr > HCl
- The order of reactivity of alcohols towards HX is tertiary (t) > secondary (s) > primary (p).

Example:

 $(CH_3)_3 C - OH + HCI \longrightarrow (CH_3)_3 C - CI + H_2O$ Tert. butyl alcohol Tert. butyl chloride

• In case of tertiary alcohols, the reaction may take place even in the absence of ZnCl₂.

 The function of ZnCl₂ is make cleavage of -C - O- bond by co-ordination with Oatom.

Bromoalkanes

 $C_2H_5OH + KBr + H_2SO_4 \rightarrow C_2H_5Br + KHSO_4 + H_2O$

Facts to Remember

Conc. ${}^{n}H_{2}SO_{4}$ must not be used in case of s°, t^{o} , and neo alcohols as they undergo dehydration with it.



<u>Iodoalkanes</u>

 $CH_{3}CH_{2}OH \xrightarrow{KI/H_{2}SO_{4}} CH_{3}CH_{2}I + KHSO_{4} + H_{2}O$ $CH_{3} - CH_{2}OH + HI \xrightarrow{H_{3}PO_{4}} CH_{3} - CH_{2}I + H_{2}O$ $C_{2}H_{5}OH + KI + H_{3}PO_{4} \longrightarrow C_{2}H_{5}I + KH_{2}PO_{4} + H_{2}O$ Here 57% HI can also be used in place of KI.

Reaction of R - OH with $P + I_2$ or Br_2 $6R - OH + 2P + 3I_2 \rightarrow 6R - I + 2H_3PO_3$ $6C_2H_5OH + 2P + 3Br_2 \rightarrow 6C_2H_5Br + H_3PO_3$ $3C_2H_5OH + PBr_3 \xrightarrow{OR} 3C_2H_5Br + H_3PO_3$ By finkelstein reaction It is specially used for iodo alkanes preparation using $S_N 2$ mechanism. $CH_3 - CH_2Br + NaI \rightarrow CH_3CH_2I + NaBr$ As NaCl, NaBr are insoluble in Acetone so they are removed by filteration.

Fluoroalkane

 $CH_3Cl + AgF \rightarrow CH_3F + AgCl$ $2CH_3Cl + Hg_2F_2 \rightarrow 2CH_3F + Hg_2Cl_2$ $3CH_3Cl + AsF_3 \rightarrow 3CH_3F + AsCl_3$ This reaction is called **Swart reaction**.

Borodine-Hunsdiecker reaction: It is used mainly for preparing bromoalkanes from silver salts of acids:

 $\text{RCOOAg} + X_2 \xrightarrow{\text{CCl}_4} \text{R} - \text{X} + \text{CO}_2 + \text{AgX}$



- Follows a free radical mechanism and reduces one C atom number.
- The yield of R − X decreases: 1° > 2° > 3°.
- In case of iodine, an ester is formed and the reaction is called **Birnbaum-Simonini reaction**.

 $\label{eq:RCOOAg} 2\text{RCOOAg} + \text{I}_2 \longrightarrow \text{R} - \text{COOR} + 2\text{CO}_2 + 2\text{Ag}_2\text{I}$ From ethers

 $R - O - R + PCl_5 \rightarrow 2R - Cl + POCl_3$

 $R - O - R' + PCl_5 \longrightarrow R - Cl + R' - Cl + POCl_3$

From alkenes: HX reacts with alkenes in accordance with Markovnikov's or anti- Markovnikov's to produce haloalkanes in the following manner:

• According to Markovnikov's rule:-

$$CH_3 - CH_7 = CH_7 + HBr \longrightarrow CH_3 - CH - CH_3$$

In the event that the carbocation formed is less stable, a one-time rearrangement via 1,2-shift of hydride or methyl is performed.

Example:



• According to Anti-Markovnikov's rule:- $CH_3 - CH = CH_2 + HBr \xrightarrow{Benzoylperoxide}$

 $CH_3 - CH_2 - CH_2Br$

From primary amines

 $\begin{array}{c} \mathsf{R}-\mathsf{NH}_2+\mathsf{NOCI}\longrightarrow \mathsf{R}-\mathsf{CI}+\mathsf{N}_2+\mathsf{H}_2\mathsf{O}\\ \text{Nitrosyl}\\ \text{chloride} \end{array}$

Physical properties of monohalides

- Lower members (CH₃X, C₂H₅X) are colourless gases, whereas higher members (C₁₈ and higher) are colorless liquids.
- The boiling point and density of a substance increase as its molecular weight increases.
 C₄H₉Cl > C₃H₇Cl > C₂H₅Cl > CH₃Cl RI > RBr > RCl > RF ...

Like in alkanes branching also decrease B.P.



- The trend followed for the dipole moment of various compounds is $\mathbf{RCl} > \mathbf{RF} > \mathbf{RBr} > \mathbf{RI}$ $CH_3Cl > CH_3F > CH_3Br > CH_3I$ $\mu \rightarrow 1.86D \quad 1.847D \quad 1.83D \quad 1.636D$
- The stability of compounds vary in the following sequence as bond length increases and bond energy decreases.

RF > RBr > RCl > RI

Solubility

- These are less soluble in water because less energy is released when new attractions are established between the haloalkane and the mater molecules, because these new attractions are not as strong as the original H-bonds in water.
- Their solubility in organic solvents is quite good due to interactions that are nearly identical.
- Solubilities $\propto \frac{1}{\text{Mol. wt.}}$

 $CH_3X > C_2H_5X > C_3H_7X > C_4H_9X$

Chemical properties of monohalides

- Since the C-X is polar, these are reactive compounds.
- The reactivity order is as follows: RI > RBr > RCl $R_3CX > R_2CHX > RCH_2X$ $CH_3X > C_2H_5HX > C_3H_7X > \cdots$

Nucleophilic substitution reactions: Alkyl halides undergo nucleophilic substitution reactions as:

$$+\delta - \delta$$

 $R - X + Z^- \longrightarrow R - Z + X^-$
Strong
nucleophile

This reactions occurs by either $S_{\rm N} 1$ or $S_{\rm N} 2$ mechanism.



Examples:

- $R X \xrightarrow{Aq. KOH} R OH + HX$
- $R X \xrightarrow{AgOH} R OH + AgX$
- R−X → R−CN+KX
 R−CN is the major product as KCN being ionic, provides CN⁻ions. Therefore, the attack occurs from the carbon atom side.
- $R X \xrightarrow{AgCN} R NC + AgX$

The major product is R - NC as AgCN being covalent cannot furnish CN^- ions. Therefore, the attack occurs from nitrogen atom (Ip e⁻ side) to give R - NC.

- $R X \xrightarrow{AgNO_2} R NO_2 + AgX$ Nitroalkane
- $R-X \xrightarrow{KNO_2} R-O-N=O+KX$ Alkyl nitrite
- $R X \xrightarrow{NaN_3} R N_3 + NaX$ Azides
- $R X \xrightarrow{NASH} R SH + NaX$ Thiols
- $R X \xrightarrow{R'COOAg} R'COOH + AgX$
- R-X → R'-O-R+NaX
 The above reaction is called Williamson synthesis (Method to prepare all kind of ethers. (R X must be p° or s° halide).
- $R X \xrightarrow{R'SNa} R' S R + NaX$ Thioether
- $R-X \xrightarrow{Na_2S} R-S-R+2NaX$
- $R X \xrightarrow{C_6H_6} C_6H_5 R + HX$

The above reaction is called **Friedel-Crafts** reaction.

 $R - X \xrightarrow{Moist Ag_2O} R - OH$

- $2R X + Ag_2O \longrightarrow R O R + 2AgX$ Dry Ether
- $R-X+NaC \equiv CR' \longrightarrow R-C \equiv C-R'+NaX$ Alkyne

$$R - X \xrightarrow{NH_3} R - NH_2 \xrightarrow{X-R} P^\circ$$

 $NH \xrightarrow{X-R}_{-HX} R_3 N \xrightarrow{X-R}_{4} NX \xrightarrow{+}_{7} R_4 NX$ Quarternary
ammoniumhalide

Dehydrohalogenation: It involves α , β elimination following E_1 and E_2 mechanisms. Here, the following, α , β -elimination reaction takes place:

 In the case of t°and s° halides, elimination predominates over substitution, whereas substitution predominates in the case of p° halides. In addition to high temperature and solvent polarity, the strength of the base also favours elimination over substitution.

$$\begin{array}{c} \begin{array}{c} R-CH-CH_{3} \xrightarrow{aq} KOH & R-CH-CH_{3} \\ | & | \\ X & OH \end{array} \end{array} Major product \\ R-CH-CH_{3} \xrightarrow{\Delta KOH} R-CH = CH_{2} \end{array} Major product \\ | \\ X \\ \beta & \alpha \\ R-CH-CH_{2} \longrightarrow R-CH = CH_{2} + HX \\ | & | \\ H & X \end{array} \\ \begin{array}{c} R-CH-CH_{2} & R-CH = CH_{2} + HX \\ | & | \\ H & X \end{array}$$

Saytzeff's Rule

According to Saytzeff's rule, the removal of β -H-atoms from β -carbon atoms with a greater number of alkyl groups results in the formation of a more stable alkene.

Example:

$$CH_{3} - CH - CH_{2} - CH_{3} \xrightarrow{\Delta} CH_{3} - CH = CH - CH_{3}$$

$$| But 2 - ene major$$

$$CI$$

$$CH_{2} = CH - CH_{2} - CH_{3}$$

minor



In the case of a fluoro-alkane or other s^o halide reacting with a very strong base, such as $(CH_3)_3COK$ or C_2H_5ONa , the predominant product (Alkene) is determined by the Hoffmann Rule. According to this theory, β -Hatom is eliminated from β -C-atom with less Hatom or less acidic β -H-atom, resulting in less stable alkene.



$$CH_{3} - CH - CH_{2} - CH_{3} \xrightarrow[Hoffmann]{KOH}{Always} CH_{2} = CH - CH_{2} - CH_{3}$$

$$\downarrow \\
F \qquad + CH_{3} - CH = CH - CH_{3}$$

$$CH_{3} - CH - CH_{2} - CH_{3} \xrightarrow[(CH_{3})_{3}COK]{COK} CH_{2} = CH - CH_{2} - CH_{3}$$

$$\downarrow \\
X \qquad + CH_{3} - CH = CH - CH_{3}$$

$$H_{3} - CH = CH - CH_{3}$$

Reaction with Metals

- (a) Reaction with Na (Wurtz reaction) $R-X+2Na+X-R \xrightarrow{Dry ether} R-R+2NaX$
- (b) Reaction with Zn (Frankland reaction) $R - X + Zn + X - R \xrightarrow{\Delta} R - R + ZnX_2$
- (c) Reaction with Mg $R - X + Mg \xrightarrow{\text{Dry ether}} R - Mg - X$ Grignard reagent

R may be CH_3 , C_2H_5 , C_6H_5 etc. Reactivity order for R - MgX can be given as R - I > R - Br > R - Cl $CH_3X > C_2H_5X > C_3H_7X >$

- Alkene is the main product of R₃CX only in the case of iodide.
- Here, ether molecules coordinate with ether as crystallisation ether.
- (d) Reaction with lead sodium alloy $4C_2H_5Br + 4Pb(Na) \rightarrow (C_2H_5)_APb + 4NaBr + 3Pb$ Tetraethyl lead
- Tetraethyl lead (TEL) is an anti-knocking substance used in petrol to avoid knocking.

(e) Reaction with lithium

 $R-X+2Li \xrightarrow{Ether} R-Li+LiX$

Reduction

 $R - X + 2[H] \xrightarrow{\text{Li AlH}_4} R - H + HX$ $R - X + 2HI \longrightarrow R - H + LiX$

Heating effect

 $R - CH_2 - CH_2 \xrightarrow{560^{\circ}C} R - CH = CH_2 + HX$

Isomerination



Dihalides

Gem or geminal halide or alkylidene halides



Methods of preparation of geminal halides

1. From aldehyde or ketone





2. From alkyne

HC=CH
$$\xrightarrow{\text{HBr}}$$
 CH₂ = CH $\xrightarrow{\text{HBr}}$ CH₃-CHBr₂
Br

Br



Chemical properties of geminal halides (Alkylidene halides)

Br

These are less reactive than alkyl halides because the presence of a single X-atom (E.W.G) makes the replacement of additional X-atoms slightly hard.

1. Reaction with alcoholic KOH

$$\begin{array}{c} \text{CH. H}_2 \\ | \\ \text{CH.Cl}_2 \end{array} + 2\text{KOH} \xrightarrow{\text{C}_2\text{H}_5\text{OH}} \text{CH} = \text{CH} \\ + 2\text{KCl} \\ + 2\text{H.O} \end{array}$$

2. Reaction with aqueous KOH Here, R-CHO, R-CO-R are formed $_{\rm CH_3-CH} < \stackrel{\rm Cl}{\underset{\rm Cl}{\overset{\rm Aq. 2KOH}{\longrightarrow}}} _{\rm CH_3-CH} < \stackrel{\rm OH}{\underset{\rm OH}{\longleftarrow}} -$ СН,-СНО 🗲 $\begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \end{array} \sim \begin{array}{c} Cl \\ Cl \\ CH_{3} \\ \end{array} \xrightarrow{Cl} \begin{array}{c} Aq. 2KOH \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ \end{array} \sim \begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \end{array} \rightarrow \begin{array}{c} CH_{3} \\ CH$ ⊢н,о CH,COCH,



3. <u>Reaction with KCN</u>

$$CH_{3}-CH \underbrace{\overset{Br}{\underset{-2KBr}{\xrightarrow{-2KBr}}} CH_{3}-CH \underbrace{\overset{CN}{\underset{-2KBr}{\xrightarrow{-2KBr}}} CH_{3}-CH \underbrace{\overset{CN}{\underset{-CN}{\xrightarrow{-CO_{2}}}}$$

4.
$$\xrightarrow{\text{CH}}_{\text{Br}}$$
 + Zn $\xrightarrow{\Lambda}_{\text{CH}_{3}\text{OH}}$ $\xrightarrow{\text{CH}}_{\text{CH}_{2}}$ + ZnBr₂

Vic or vicinal dihalide or alkylene halides



Methods of preparation of vicinal dihalides

1. From diols like glycol

 $\begin{array}{c} CH_2Br \\ 3| \\ CH_2Br \\ CH_2Br \\ \end{array} + 3H_3PO_3 \longrightarrow 3| \\ CH_2Br \\ CH_2Br \\ \end{array} + 3H_3PO_3 \\ CH_2Br \\ CH_2Br \\ \end{array}$

2. <u>From alkenes</u> CH_2 Br CH_2Br $|| + | \longrightarrow |$ CH_3 Br CH_3Br

Chemical properties of vicinal dihalides

1. <u>Reaction with KOH</u>

 $\begin{array}{c} \mathsf{CH}_2 - \mathsf{CI} \\ | & +2\mathsf{KOH} \xrightarrow{\Delta} \mathsf{HC} \equiv \mathsf{CH} + \mathsf{H}_2\mathsf{O} + 2\mathsf{KCI} \\ \mathsf{CH}_2 - \mathsf{CI} \\ \\ \mathsf{CH}_2\mathsf{Br} & \mathsf{CH}_2\mathsf{OH} \\ | & +2\mathsf{KOH} \xrightarrow{\Delta} | \\ \mathsf{CH}_2\mathsf{OH} & \mathsf{CH}_2\mathsf{OH} \\ & \mathsf{Glycerol} \end{array}$

2. <u>Reaction with KCN</u> $\begin{array}{c} CH_2Br \\ CH_2-Br \end{array} \xrightarrow{2KCN} CH_2CN \\ CH_2-Br \end{array}
\begin{array}{c} H_2O \\ H_2O \end{array}$



3. Br Br
$$\frac{d^{\Delta}}{CH_3OH}$$
 $CH_2 = CH_2 + ZnBr_2$

Trihalides or Haloforms (CHX₃)

$Chloroform (CHCl_3)$

- Chloroform was discovered by Justus von Liebig and named by Jean-Baptiste Dumas.
- Its anaesthetic nature was discovered by James Young Simpson.

Methods of preparation

1. From chloral

 $CCl_3CHO + NaOH \xrightarrow{\Delta} CHCl_3 + HCOONa$

2. From ethyl alcohol or acetone Ethyl alcohol or acetone reacts with bleaching powder to give chloroform: $CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$ $H_2O + Cl_2 \longrightarrow HCl + [O]$ $CH_3CH_2OH \xrightarrow{[O]} CH_3CHO + H_2O$ $CH_3CHO \xrightarrow{3Cl_2} - CCl_3CHO + H_2O$ $CH_3CHO \xrightarrow{3Cl_2} - CCl_3CHO + H_2O$

$$CH_{3}COCH_{3} \xrightarrow{2} -HCl \xrightarrow{2 \text{ moles}} 2CH_{3}COCH_{3}$$

$$2CHCl_{3} + (CH_{3}COO)_{2}Ca \xrightarrow{4} CCl_{3}CHO \xrightarrow{\Delta} 2CHCl_{3}$$

$$Ca(OH)_{2} + 2CCl_{3}CHO \xrightarrow{\Delta} 2CHCl_{3}$$

$$HCOO \xrightarrow{4} CCl_{3}COCH_{3}$$

- HCOO ^{>Ca}
- 3. From CCl₄ CCl₄ + 2[H] $\xrightarrow{Fe/H_2O}$ CHCl₃ + HCl
- 4. From chloral hydrate $CCl_3 - CH \xrightarrow{OH} + NaOH \longrightarrow CHCl_3 + HCOONa + H_2O$
- Chloral hydrate is stable due to intramolecular hydrogen bonding in it (butterfly-like structure).



5. Haloform reaction

(A) It is given by >C = O having −COCH₃ group.For example,



 CH_3





Does not show

• CH₃CHO is the only aldehyde to show the reaction.

For example,

$$\begin{array}{c} O \\ -C \\ -C \\ -C \\ H \\ H \end{array} + 3X - X + 3OH^{-\frac{3X^{-}}{-3H_{2}O}} OH^{-1} \\ CHX_{3} + HCOO^{-1} \end{array}$$

- $CH_3CHO + 3I_2 + 4NaOH \rightarrow CHI_3 \downarrow + HCOONa + 3NaX + 3H_2O$
- $CH_3COCH_3 + 3I_2 + 4NaOH \rightarrow CHI_3 \downarrow + CH_3COONa + 3NaX + 3H_2O$
- (B) Alcohol having $CH_3 CH OH$ group shows

haloform reaction.

Example:

CH3-CH2-OH

Shows

$$CH_3 > CH - CH_2OH C$$

Does not show

$$CH_3 \xrightarrow{H} CH_3 OH$$

CH3 OH

Shows

Does not show

Shows

For example,

 $CH_3 - CH_2 - OH + 4I_2 + 6NaOH → CHI_3 ↓ + HCOONa + 5NaX$

CHCl₃

• It is a colourless liquid with sweet smell.

CH

• Its boiling point is 61°C.

• This substance is insoluble in water, but soluble in organic solvents. Additionally, it is a useful solvent for lipids, resins, etc.

CHBr₃

 It is a colourless liquid and its boiling point is 149.5°C.

CHI₃

- It occurs as yellow, hexagonal plate like crystats.
- Its melting point is 119°C.
- It can be used as an antiseptic (due to the liberation of free I₂).

Test of Purity of CHCl₃

No precipitate is produced when chloroform and silver nitrate react. Due to the fact that $CHCl_3$ is covalent, it cannot provide Cl^-ions .

Chemical properties of chloroform (CHCl₃)

1. Nitration

 $CHCl_3 + HO - NO_2 \longrightarrow CCl_3 \cdot NO_2 + H_2O$ Chloropicrin (insecticide)

• It is used in the manufacture of tear gas $[C_6H_5COCH_2 Cl]$, phenacyl chloride.

$$CHCl_{3} \xrightarrow{6[H]Zn+H_{2}O} CH_{4} + 3HCl$$
$$CHCl_{3} \xrightarrow{2[H]Zn/HCl} CH_{2}Cl_{3} + HCl$$

$$CHCl_{3} + 4(H) \xrightarrow{Zn} CH_{3}Cl + 2HCl$$

3. Oxidation

$$CHCl_3 + \frac{1}{2}O_2 \xrightarrow{hv} COCl_2 + HCl$$

Phosgene
(poisonous)

- To prevent oxidation or the formation of phosgene, chloroform is stored in a dark, completely filled, securely sealed bottle with a small amount of ethyl alcohol (a negative catalyst).
- Phosgene is converted to non-poisonous diethyl carbonate by ethyl alcohol.

$$O = C < Cl + 2HOC_2H_5 \longrightarrow O = C < OC_2H_5 + 2HCl OC_2H_5 + 2HCl Diethyl carbonate$$



00.11

4. <u>Reaction with hot NaOH</u>

$$\begin{array}{c} H \longrightarrow C & \stackrel{Cl}{\longleftarrow} \begin{array}{c} 3NaOH \\ Cl \\ \hline Cl \\ HCOONa \\ \hline -H_2O \end{array} & HCOOH \\ \hline HCOOH \\ \hline -H_2O \end{array} \\ \begin{array}{c} OH \\ OH \\ -H_2O \end{array}$$

5. Reaction with hot C₂H₅ONa

$$H - C \leftarrow Cl_{Cl}^{Cl} + 3NaOC_{2}H_{5} \xrightarrow{-3NaCl} H - C \leftarrow OC_{2}H_{5}^{OC_{2}H_{5}} OC_{2}H_{5}^{OC_{2}H_{5}} OC_{2}H_{5}^{OC_{2}H_{5}} OC_{2}H_{5}^{OC_{2}H_{5}}$$

6. **Carbylamine reaction:** It is a test of primary amine. Here, the primary amine reacts with chloroform and base KOH, to give bad smelling isocyanide as follows:

 $R-NH_2+CHCl_3+3KOH \rightarrow R-NC+3KCl+3H_2O$

- Here, the reaction intermediate is: CCl₂, that is, dichlorocarbene.
- If ethylamine is taken, the product formed is ethyl isocyanide.

 $\label{eq:c2H5NH2} \begin{array}{l} \mathsf{C_2H_5NH_2} + \mathsf{CHCI_3} + \mathsf{3KOH} \rightarrow \mathsf{C_2H_5NH} + \mathsf{3KCI} + \\ \mathsf{3H_2O} \end{array}$

 If aniline is taken, the product formed is phenylisocyanide.

 $C_6H_5NH_2$ + CHCl₃ + 3KOH → C_6H_5NC + 3KCl + 3H₂O

- 7. <u>Reaction with Ag powder</u> CHX₃ + 6Ag + CHX₃ $\xrightarrow{\Delta}$ C₂H₂ + 6AgX
- 8. <u>Reimer-Tiemann reaction:</u>

Here reaction inter mediate is: CCI_2 .



- Chloretone is used in hypnotic medicines.

CCI₄ OR PYRENE (Carbon Tetra-Chloride)

- Tetrahedral structure
- sp³ hybridization
- Bond angle 109°28 '
- μ is zero

Methods of preparation

- 1. $CH_4 + 4Cl_2 \xrightarrow{hv} -4HCl} CCl_4$
- 2. $CH_4 + 4Cl_2 \xrightarrow{hv} CCl_4$
- 3. $CS_2 + 2S_2CI_2 \longrightarrow CCI_4 + 6'S'$

4.
$$C_3H_8 + 9Cl_2 \xrightarrow{\Delta} CCl_4 + C_2Cl_6 + 8HCl Solid$$

Physical properties of pyrene

- It is a poisonous, colourless, noncombustible liquid with a boiling point of 350K.
- It is insoluble in water but soluble in organic solvents and is an excellent fat, oil, and paraffin solvent.

Chemical properties of pyrene

1. <u>Reaction with steam</u>

$$CCl_4 \xrightarrow{H_2O} COCl_2 + 2HCl$$

- 2. <u>Hydrolysis</u> $CCl_4 \xrightarrow{\Delta} C(OH)_4 \xrightarrow{\Delta} CO$
- 3. <u>Reaction with HF</u> $CCl_4 + 2HF \xrightarrow{SbF_5} CF_2Cl_2 + 2HCl$ Freon
- Freon-12 is used in refrigerators and air conditioners as a refrigerant.
- 4. Reaction with phenol





Uses of CCl₄:

- (i) As a solvent for oils, fats, Resins etc.
- (ii) Under the pyrene it is used as a fire extinguisher.

Teflon (– $CF_2 - CF_2 -)_n$

- Teflon is a polymer of tetrafluoroethylene.
- It is a thermoplastic that is chemically inert and used for electrical insulation and gasket materials.

 $CHCl_{3} \xrightarrow{SbF_{3}} CHF_{2}Cl \xrightarrow{800^{\circ}C} -HCl} CF_{2} = CF_{2}$ $nCF_{2} = CF_{2} \longrightarrow (-CF_{2} - CF_{2} -)_{n}$ Tetrafluoroethylene Teflon

Chlorobenzene



iodination as not only the reaction is reversible but also HI being a reductant can reduce

into Benzene. But if strong oxidants like

 HNO_3 , HgO are used the reaction is possible as they oxidise HI into I_2 .

cannot be obtained as F is highly

reactive and the reaction is violent also.

Commercial method or Raschig method

$$\begin{array}{c} & & \\ & &$$

$$\bigcirc -\text{OH} + \text{PCl}_{\text{s}} \xrightarrow{\Delta} \bigcirc -\text{Cl} + \text{POCl}_{\text{s}} + \text{HCl}$$

From benzene diazonium chloride or Sand

$$\bigvee$$
 N=N-Cl $\xrightarrow{\Delta}$ Cl₂ Cl₂ Cl₂ Cl + N₂

Gatterman reaction



Physical properties of Chlorobenzene

- It is a colourless liquid with a pleasant odour and a boiling point of 132°C.
- It is heavier than water and insoluble in it.

Chemical properties of Chlorobenzene Due to benzene ring

 The Cl-atom present in the ring renders the ring inactive, but it is both o- and p-directing. Electrophilic substitution occurs at a slower rate than benzene.

Here, the electron (e⁻) density increases at the o and p positions due to resonance, but the -X atom tends to withdraw electrons from the benzene ring due to the -I effect. It indicates that the rate of electrophilic substitution decreases due to ring deactivation.





ortho, para dichlorobenzene



ortho, para nitrochlorobenzene



• <u>Sulphonation</u>



ortho, para-chlorobenzene sulphonic acid

• <u>Friedel Crafts Alkylation</u>



ortho, para-methyl chlorobenzene

<u>Acylation</u>

arenes.



Here para product is major in all these cases.

Reactions due to chlorine

 Reactivity of chlorine atom in chlorobenzene Cl⁻atom in chlorobenzene is much less reactive than R-X because C-Cl bond in chlorobenzene has a double bond character and is resonance stabilised, requiring more energy to break a double bond than a single bond.



• Substitution by-OH group



When a strong Electron Withdrawing Group (E.W.G) group, such as -NO₂, is present at the o, p position, the substitution of -X becomes considerably easier and a reaction takes place.



• Substitution by NH₂ group







DDT is produced when chloral is heated with chlorobenzene in the presence of concentrated H₂SO₄ (p, p-dichlorodiphenyl trichloroethane). Due to the fact that both Cl-atoms are linked to the benzene ring, it is not biodegradable.



1, 1, 1 trichloro ethane

Uses and Effects of Polyhalogen Compounds on Environment and Human Health

(i) Chloroform

- It is used primarily in the production of the R-22 Freon refrigerant and as a solvent for lipids, alkaloids, iodine, etc.
- It results in dizziness, headache, and fatigue.
- Chronic chloroform exposure can result in liver and kidney injury.

(ii) Iodoform

- It is primarily employed as an antiseptic because it releases free iodine.
- However, it is no longer used due to its foul odour.

(iii) Freon

- Freon is used as a refrigerant in refrigerators and air conditioning units.
- However, its use has been discontinued because it depletes the ozone layer.

(iv) DDT

- DDT, a popular pesticide consisting of an off-white crystalline substance, is exceedingly toxic to fish.
- It is not swiftly metabolised by animals; instead, it is deposited and retained in fatty tissues.
- Since its residues are nonbiodegradable, they accumulate in the environment and are toxic to mammals, etc.

(v) Carbon tetrachloride

- CCl₄ or carbon tetrachloride is primarily employed in the synthesis of chloroflourocarbons.
- It may induce human liver cancer.
- It may result in migraines, nausea, and nerve injury.
- It may contribute to the depletion of the ozone layer.



(vi) Benzene Hexachloride (B.H.C)

 It is commonly called as Gammexene or γ-Lindane or 6,6,6[C₆H₆Cl₆].

It is a popular pesticide for killing of Thermites (white ants) from soil.

Facts to Remember

- As a treatment for hookworms, CCl₄ is used as a medication.
- 2. CFCl₃ is freon-11, while CF₄ is freon-14, CF₃Cl is freon-13 and CF₂Cl₂ is freon-12.
- 3. Perfluorocarbons have a standard chemical formula- $C_n F_{2n+2}$.

 $C_6H_{14} + 14F_2 \xrightarrow{573K, COF_2} C_6F_{14} + 14HF$

- Halothane (CF₃CHClBr) is employed as an inhalational anaesthetic.
- 5. Chloretone is a substance that induces hypnosis or sleep.
- 6. Westron is composed of tetrachloroethane while Westrosol is trichloroethylene.

 $\begin{pmatrix} \mathsf{CHCl}_2 \\ \mathsf{I} \\ \mathsf{CHCl}_2 \end{pmatrix}$ Westron

(CCl₂ || CHCl) Westrosol

7. The boiling point have the following order:

Alkyl iodides > alkyl bromides > alkyl chlorides > alkyl fluorides

R - I > R - Br > R - Cl > R - F

- 8. The volatility has the following order: R - Cl > R - Br > R - I
- 9. **Dipole moment** has the following order: $CH_3Cl > CH_3 F > CH_3Br > CH_3I$
- 10. The order of the **boiling points** in a group of isomeric alkyl halides is Primary > Secondary > Tertiary
- 11. The order of the **densities of** alkyl halides is R - I > R - Br > R - Cl > R - F $CH_3Cl < CH_2Cl_2 < CHCl_3 < CCl_4$

12. The **order of chemical reactivity** of alkyl halides is

RI > RBr > RCl

13. The **order of reactivity** of an alkyl halides is

Tertiary > Secondary > Primary This is due to the inductive effect of alkyl groups, which increases the polarity of the C-X bond, making it more reactive.

14. Despite their higher positive ionisation energy, it has been observed that the presence of bulky groups in primary halides causes steric hindrance and makes them less reactive towards the S_N^2 mechanism.

The reactivity follows the order $CH_3X > C_2H_5X > C_3H_7X$.

- 15. Antiseptic action of \mbox{CHI}_3 is due to the liberation free $\mbox{I}_2.$
- 16. Perfluoro carbons (PFCs) have a general formula $C_n H_{2n+2}$

$$C_7H_{16} + 16F_2 \xrightarrow{\Delta 573K} C_7F_{16} + 16HF$$
Vapour Phase N₂C₀F₂ Perfluoro heptane

These substances are odourless, nonpolar, stable, and non-toxic. They are resistant to U.V and other types of radiation, so they do not deplete the U_3 layer. They can be utilised as lubricants, in skin-care medications, in medical diagnosis, etc.

17. Halogen derivatives of aromatic hydrocarbons with a halogen atom in the side chain are known as aryl alkyl halides or aralkyl halides.

Examples: $Ar - CH_2 - X$.

- 18. Bond strength and stability decreases as R F > R Cl > R Br > R I
- 19. The relative nucleophilicity order for $S_{N}\mathbf{1}$ Reaction:

 $R\overline{S} > \overline{C}N > \overline{I} > R - \overline{O} > \overline{O}H$

20. The leaving group tendency for $S_{\rm N}2$. Reaction:

 $p - CF_{3}C_{6}H_{5}SO_{3}^{-} > p - CH_{3}C_{6}H_{4}SO_{3}^{-} > I^{-} > Br^{-}$ $> CI^{-} > H_{3}^{+}O > F^{-} > CH_{3}COO^{-} > N^{+}R_{3} > R - O^{-}$ $> R_{2}N^{-} > N^{-}H_{2}$



- 21. Decreasing order of Reactivity of Nucleophilic Substitution Reaction: $O_2N \rightarrow O_2 \rightarrow$
- 22. R-Br and R-I cannot be derived using Dorzen's approach since SOBr₂ is unstable and SOI₂ does not exist.

NEET AND AIIMS ESSENTIALS

In the following questions, two statements Assertion (A) and Reason (R) are given. Mark

- (a) if A and R both are correct and R is the correct explanation of A
- (b) *if A and R both are correct but R is not the correct explanation of A*
- (c) A is true but R is false
- (d) A is false but R is true
- (e) A and R both are false
 - (A) : The effect of electron withdrawing group at ortho and para position increases the reactivity of haloarenes but at meta position
 - (R) : As at meta position negative charge can not be stabilized by such a group in any resonating structure
 - 2. (A) : Alkyl iodides darken on standing.
 - (R) : Alkyl iodides are prepared by Finkelstein reation.
 - (A) : 2-chloro-3-methylbutane on treatment with alcoholic potash gives 2-methyl-butene-2 as major product.
 - (R) : The reaction occurs according to Saytzeff rule.
 - (A) : Primary benzylic halides are more reactive than primary alkyl halides towards S_N1 reactions.

- (R) : Reactivity depends upon the nature of the nucleophile and the solvent.
- 5. (A) : Isopropyl chloride is more reactive than CH_3Br in S_N2 reactions.
 - (R): S_N2 reactions are always accompanied by inversion of configuration.
- (A) : o-dichloro benzene has higher metlting point than p-dichlorobenzene.
 - (R) : Stronger the Van der Waal's forces of attraction, higher is the melting point.
- 7. (A) : Addition of Br_2 to cis-but-2-ene is stereoselective.
 - $(R): S_N 2 \mbox{ reactions are stereospecific as } \\ \mbox{ well as stereoselective.}$
- (A): S_N2 reaction of an optically activealkyl halide with an aqueous solution of KOH gives an alcohol with opposite sign of rotation.
 - $(R): S_N 2 \quad reactions \quad proceed \quad with \\ inversion of configuration.$
- 9. (A) : Benzyl chloride is more reactive than p-chlorotoluene towards aqueous NaOH.
 - (R) : The C Cl bond in benzyl chloride is more polar than C - Cl bond in pchlorotoluene.
- (A) : Tertiary haloalkanes are more reactive than primary haloalkanes towards elimination reactions.
 - (R) : The +I-effect of the alkyl gropus weakens the C X bond.
- 11. (A) : Rate of reaction is dependent only on the concentration of nucloephile in $S_N 1$ reactions.
 - (R) : Polar solvent favours S_N1 reaction.
- 12. (A) : The carbon halogen bond in an aryl halide is shorter than the carbon halogen bond in an alkyl halide.



- (R) : A bond formed of an sp^3 orbital should be shorter than the corresponding bond involving an sp^2 orbital.
- 13. (A) : $S_N 2$ reaction of $CH_3 Br$ is faster in DMSO than in H_2O .
 - (R) : DMSO has greater capability to solvate nucleophile.
- 14. (A) : In $S_N 1$ mechanism, the product with inversion of configuration is obtained in higher amount compared to the product with the retention of configuration.

- (R) : Front side attack of nucleophile is hindered due to the presence of leaving group in the vicinity.
- 15. (A) : Bromobenzene upon reaction with Br_2/Fe gives 1, 4-dibromobenzene as the major product.
 - (R) : In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile.

ANSWER KEY

1. 11.	(a) (d)	2. 12.	(c) (c)	3. 13.	(a) (c)	4. 14.	(b) (a)	5. 15.	(d) (c)	6.	(d)	7.	(b)	8.	(a)	9.	(a)	10.	(b)

CHAPTER

2

Alcohols, Phenols and Ethers

CHAPTER OUTLINE

- Alcohols
- Glycerol or Glycerine
- Ethers (R–O–R)

- Ethyl Glycol
- Phenols
- Epoxy Ethers

ALCOHOLS

- Alcohols are hydroxy derivatives of alkanes or alkyl derivatives of water obtained by replacing one or more H atoms by –OH group.
- General formula of the alcohol is **R OH**.

Types of Alcohols

Monohydric alcohols	Dihydric alcohols	Trihydric alcohols
Alcohols with only one -OH	Alcohols that have two-OH groups.	Alcohols having three $-OH$
group with their general		groups
formula $C_nH_{2n+1}OH$		0
Types of Monohydric Alcohol	Example:	Example:
(a) Primary alcohol (1°)	Glycol, Propan 1, 2 diol	CH ₂ OH
RCH ₂ OH	CH ₂ OH CH	$AYX 0 \Lambda$
<u>Example</u> : CH ₃ OH methyl	OH	СНОН
alcohol (Methanol)	CH ₂ OH	ADDAR IN VOU
(b) Secondary alcohol (2°)	I UNICASH LHE L	CH ₂ OH
R₂CHOH		
<u>Example</u> : $(CH_3)_2CHOH$		
isopropyl alcohol (Propan-		
2-ol)		
(c) Tertiary alcohol (3°) R ₃ C.OH		
<u>Example</u> : $(CH_3)_3COH -$		
tertiary butyl alcohol (2-		
methyl-propan-2-ol)		

Nomenclature of Alcohols

- The common names of alcohols are derived by adding the word alcohol to the common name of the alkyl group, such as CH₃OH for methyl alcohol or methanol.
- Replace 'e' in the name of alkane with 'ol' to form the IUPAC name for alcohols. Thus, it is an alkanol, such as

 $\begin{array}{ll} \mathsf{CH}_3-\mathsf{CH}_2-\mathsf{CH}_2\mathsf{OH} & \mathsf{Propanol} \\ \mathsf{CH}_3-\mathsf{CH}-\mathsf{CH}_3 & \mathsf{Propan-2-ol} \\ & | \\ & \mathsf{OH} \end{array}$