HALOGEN DERIVATIVES

E

NEET SYLLABUS

Haloalkanes : *Nomenclature, nature of C-X bond, physical and chemical properties,* ***Haloarenes :*** *Nature of C-X bond, substitution reactions (directive influence of halogen for monosubstituted compounds only), Uses and environmental effect of dichloromethane, trichloromethane, Iodoform, freons, DDT*

OBJECTIVES

After studying this unit, we will be able to :

- Name haloalkanes and haloarenes according to the IUPAC system of nomenclature from their given structures;
- Describe the reactions involved in the preparation of haloalkanes and haloarenes and understand various reactions that they undergo;
- Correlate the structures of haloalkanes and haloarenes with various types of reactions;
- Use stereochemistry as a tool for understanding the reaction mechanism;
- Appreciate the applications of organo-metallic compounds;
- Highlight the environmental effects of polyhalogen compounds

> *"Failure will never overtake me if my*
> *determination to succeed is strong enough"*
>
> ***A.P.J. Abdul Kalam***

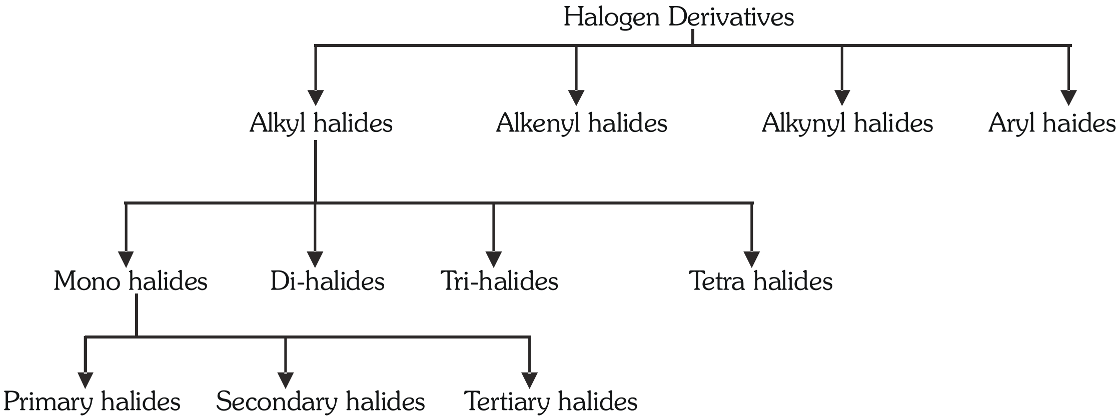
HALOGEN DERIVATIVES

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 Genreal Methods of Preparation of Monohalides

(1) By direct halogenation of alkanes :

$$R{-}H + Cl_2 \xrightarrow{\text{U.V.light}} R{-}Cl + HCl$$

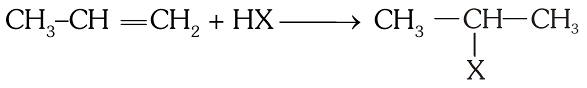
(excess)

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

$$R{-}CH{=}CHR + HX \longrightarrow RCH_2{-}CHXR$$

eg: $CH_2{=}CH_2 + HX \longrightarrow CH_3{-}CH_2X$

eg:



$$CH_3{-}CH{=}CH_2 + HX \longrightarrow CH_3{-}\underset{\displaystyle X}{\underset{|}{CH}}{-}CH_3$$

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 :

$$R{-}OH + PCl_5 \longrightarrow R{-}Cl + POCl_3 + HCl$$

$$3R{-}OH + PCl_3 \longrightarrow 3RCl + H_3PO_3$$

PBr_3 and PI_3 are less stable, thus for bromides (P + Br_2) and for iodides (P + I_2) mixture is used.

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

$$R{-}OH + SOCl_2 \xrightarrow[\text{(1 mole)}]{\text{Pyridine}} R{-}Cl + SO_2 + HCl$$

One mole One mole

Because of less stability of $SOBr_2$ and SOI_2, R—Br and RI can not be obtained by this method.

(4) Borodine – Hunsdicker's reaction :

$R{-}COOAg + X_2 \xrightarrow[\Delta]{CCl_4} R{-}X + CO_2 + AgX$

Silver salt of a fatty acid; X_2 (Cl_2 or Br_2)

(5) By halide exchange :

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

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

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 CH_3F, CH_3Cl, CH_3Br, C_2H_5Cl and C_2H_5F are gases at room temp.

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

Decreasing order of B.P. is : **R – 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 ⟶ lighter than water

R—Br and R—I ⟶ heavier than water

Decreasing order of density is : **R—I > R—Br > R—Cl > R—F**

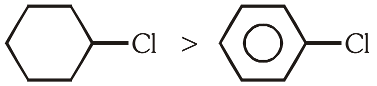
(d) R—X are polar co-valent compounds but insoluble in water because they can not form H–bonds. They dissolve in organic solvents.

(e) R—X (except R—F) burns with a green flame when interacted with Cu wire.(Beliestein test)

(f) Dipole moment order–

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

(ii)



3.3 Chemical Properties

3.3.1 Nucleophilic substitution reaction (S_N) :

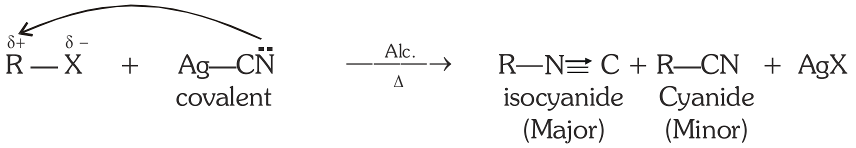
		Replacement of	Product
(a)		$\xrightarrow[\text{X by — OH}]{\text{HOH(Boil)}}$	R—OH (alcohol) + HX
(b)		$\xrightarrow[\text{X by — OH}]{\text{KOH aq.}}$	R—OH (alcohol) + KX
(c)	R—X—→	$\xrightarrow[\text{X by — OH}]{\text{moist Ag}_2\text{O}}$	R—OH (alcohol) + AgX
(d)		$\xrightarrow[\text{X by –SH}]{\text{KSH alc.}}$ (Mercapto Gp.)	R—SH + KX Alkane thiol (Mercaptane)
(e)		$\xrightarrow[\text{X by SR}]{\text{NaSR'}}$	RSR' + NaX Thioether
(f)		$\xrightarrow[\text{X by(R'COO)}]{\text{R' COOAg, }\Delta}$	R' COOR + AgX (Alkyl alkanoate) ester

(g) Reaction with KCN and AgCN :

$$\overset{\delta+}{R}—\overset{\delta-}{X} + \overset{\oplus\ \ominus}{KCN} \xrightarrow[\Delta]{Alc.} R—C\equiv N + R—NC + KX$$

Ionic — cyanide (major) — Isocyanide (minor)

- $\overset{\ominus}{:}\ddot{C}N$ ion is an ambident nucleophile.



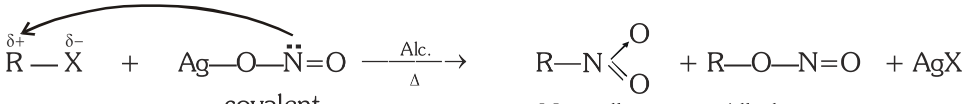
$$\overset{\delta+}{R}—\overset{\delta-}{X} + Ag—C\ddot{N} \xrightarrow[\Delta]{Alc.} R—N\equiv C + R—CN + AgX$$

covalent — isocyanide (Major) — Cyanide (Minor)

(h) Reaction with KNO_2 and $AgNO_2$:

$$\overset{\delta+}{R}—\overset{\delta-}{X} + \overset{\oplus\ \ominus}{KO}—NO \xrightarrow[\Delta]{Alc.} R—O—N=O + R—NO_2 + KX$$

Ionic — Alkyl nitrite (Major) — Nitro alkane (Minor)



$$\overset{\delta+}{R}—\overset{\delta-}{X} + Ag—O—\ddot{N}=O \xrightarrow[\Delta]{Alc.} R—NO_2 + R—O—N=O + AgX$$

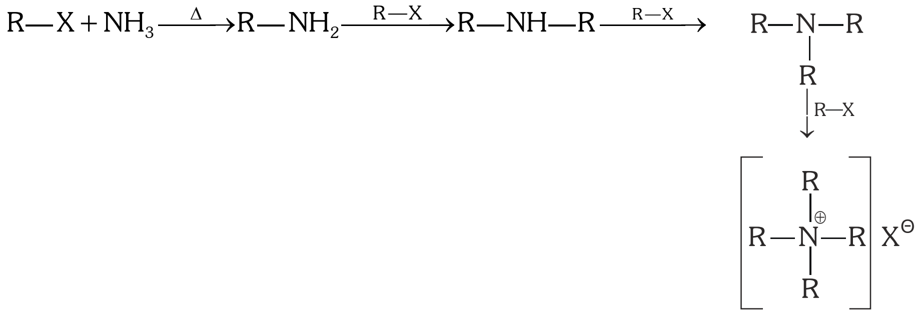
covalent — Nitroalkane (major) — Alkyl nitrite (minor)

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

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

(williamson synthesis reaction)

(j) Reaction with NH_3:

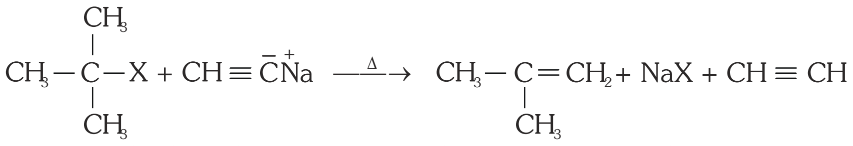


$$R—X + NH_3 \xrightarrow{\Delta} R—NH_2 \xrightarrow{R—X} R—NH—R \xrightarrow{R—X} R—\underset{R}{N}—R \xrightarrow{R—X} \left[R—\overset{R}{\underset{R}{\overset{\oplus}{N}}}—R\right]X^{\ominus}$$

(Quaternary salt)

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

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



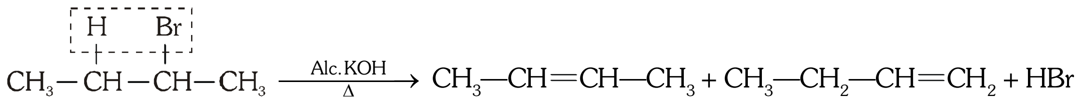
$$\text{If}\quad CH_3-\overset{CH_3}{\underset{CH_3}{C}}-X + CH\equiv\overset{-}{C}\overset{+}{Na} \xrightarrow{\Delta} CH_3-\underset{CH_3}{C}=CH_2 + NaX + CH\equiv CH$$

($3^{\underline{o}}$ halide) — (Elimination is more)

3.3.2 Dehydrohalogenation : Alkyl halides undergo β - elimination on treatment with KOH (alc.) or $NaNH_2$.

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

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



$$CH_3-\underset{}{\overset{H}{CH}}-\overset{Br}{CH}-CH_3 \xrightarrow[\Delta]{Alc.KOH} CH_3—CH{=}CH—CH_3 + CH_3—CH_2—CH{=}CH_2 + HBr$$

But-2 -ene (80%) But-1-ene (20%)

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

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

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

3.3.4 Formation of Organometallic compounds :

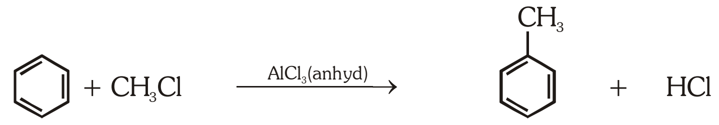
(i) $R—X + Mg \xrightarrow{\text{dry ether}} RMgX$ (Grignard reagent)

(ii) $2C_2H_5Br + 2Zn \xrightarrow{\text{dry ether}} (C_2H_5)_2\,Zn$ (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 :



Benzene Toluene

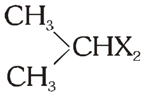
4.0 DIHALIDES

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_3CHX_2 Ethylidene dihalide (1, 1 - Dihalo ethane)



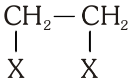
$$(CH_3)_2CHX_2$$

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.

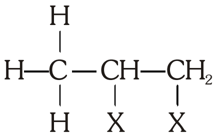
Ex.



$$\underset{X}{CH_2}-\underset{X}{CH_2}$$

Ethylene dihalide

(1,2-Dihaloethane)



$$H—\underset{H}{\overset{H}{C}}—\underset{X}{CH}—\underset{X}{CH_2}$$

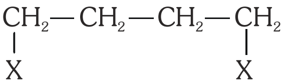
Propylene dihalide

(1,2-Dihalopropane)

Vic and Gem dihalides are position isomers.

(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.

Ex.



$$\underset{X}{CH_2}—CH_2—CH_2—\underset{X}{CH_2}$$

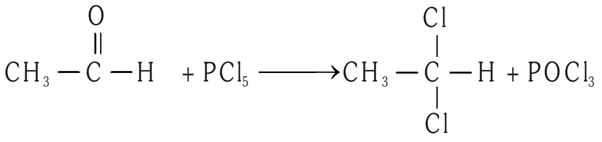
(1,4-Dihalobutane)

Tetramethylene dihalide

4.1 General Methods of Preparation

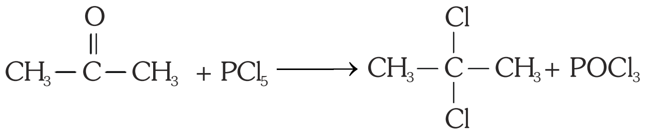
(a) Gem dihalides :

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



$$CH_3-\overset{\overset{O}{\|}}{C}-H + PCl_5 \longrightarrow CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-H + POCl_3$$

Acetaldehyde Ethylidene chloride



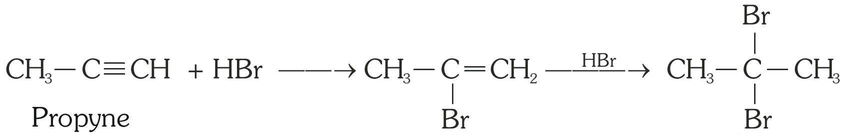
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + PCl_5 \longrightarrow CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_3 + POCl_3$$

Acetone 2, 2 - Dichloropropane

(ii) By addition of halogen acids on alkynes :

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

Vinyl bromide 1, 1 - Dibromoethane

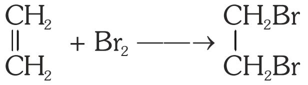


$$CH_3-C\equiv CH + HBr \longrightarrow CH_3-\underset{\underset{Br}{|}}{C}=CH_2 \xrightarrow{HBr} CH_3-\underset{\underset{Br}{|}}{\overset{\overset{Br}{|}}{C}}-CH_3$$

Propyne 2, 2 - Dibromopropane

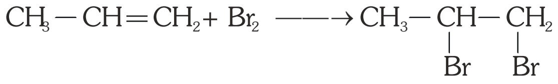
(b) Vic-dihalides :

(i) By the addition of halogens to alkenes :



$$\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + Br_2 \longrightarrow \begin{matrix}CH_2Br\\ |\\ CH_2Br\end{matrix}$$

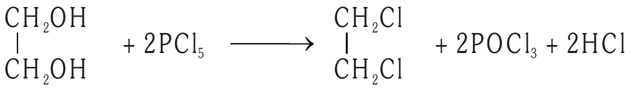
1, 2 - Dibromoethane



$$CH_3-CH=CH_2 + Br_2 \longrightarrow CH_3-\underset{\underset{Br}{|}}{CH}-\underset{\underset{Br}{|}}{CH_2}$$

1, 2 - Dibromo propane

(ii) By the action of PCl_5 on glycols :



$$\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix} + 2PCl_5 \longrightarrow \begin{matrix}CH_2Cl\\ |\\ CH_2Cl\end{matrix} + 2POCl_3 + 2HCl$$

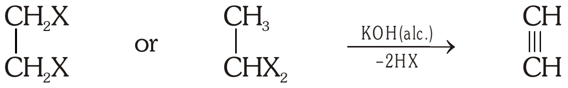
4.2 Physical Properties

(i) Lower members are colourless, oily liquids with sweet smell. Higher members are solid.

(ii) These are heavier than water.

4.3 Chemical Properties

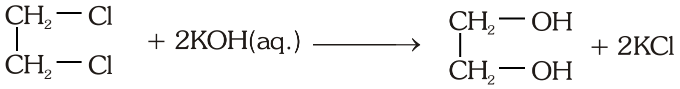
(i) Action of KOH(alc.) : (Dehydrohalogenation)



$$\begin{matrix}CH_2X\\ |\\ CH_2X\end{matrix} \text{ or } \begin{matrix}CH_3\\ |\\ CHX_2\end{matrix} \xrightarrow[-2HX]{KOH(alc.)} \begin{matrix}CH\\ |||\\ CH\end{matrix}$$

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

(a)

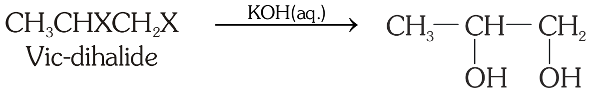


$$\begin{array}{l}CH_2-Cl\\ |\\ CH_2-Cl\end{array} + 2KOH(aq.) \longrightarrow \begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array} + 2KCl$$

Glycol

Vic-dihalide. 1, 2 - Ethanediol

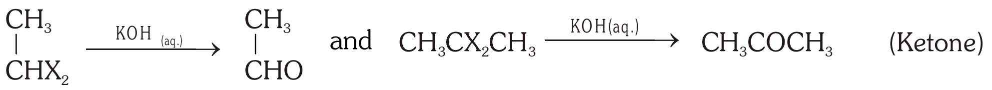
(b)



$$CH_3CHXCH_2X \xrightarrow{KOH(aq.)} \begin{array}{c}CH_3-CH-CH_2\\ \quad\ |\qquad |\\ \quad\ OH\quad OH\end{array}$$

Vic-dihalide

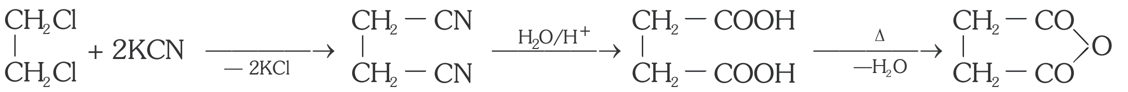
Propane - 1, 2 - diol



$$\begin{array}{l}CH_3\\ |\\ CHX_2\end{array} \xrightarrow{KOH\ (aq.)} \begin{array}{l}CH_3\\ |\\ CHO\end{array} \text{ and } CH_3CX_2CH_3 \xrightarrow{KOH(aq.)} CH_3COCH_3 \quad \text{(Ketone)}$$

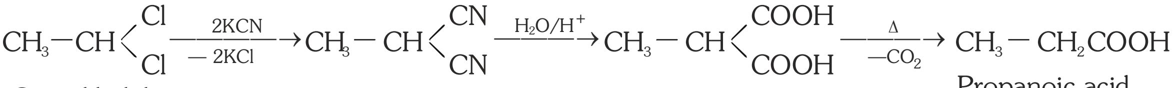
Gem-dihalides

(iii) Reaction with KCN :



$$\begin{array}{l}CH_2Cl\\ |\\ CH_2Cl\end{array} + 2KCN \xrightarrow[-\ 2KCl]{} \begin{array}{l}CH_2-CN\\ |\\ CH_2-CN\end{array} \xrightarrow{H_2O/H^+} \begin{array}{l}CH_2-COOH\\ |\\ CH_2-COOH\end{array} \xrightarrow[-H_2O]{\Delta} \begin{array}{l}CH_2-CO\\ |\qquad\quad\ \rangle O\\ CH_2-CO\end{array}$$

Vic-dihalide Succinic acid Succinic anhydride



$$CH_3-CH\langle\begin{array}{l}Cl\\ Cl\end{array} \xrightarrow[-\ 2KCl]{2KCN} CH_3-CH\langle\begin{array}{l}CN\\ CN\end{array} \xrightarrow{H_2O/H^+} CH_3-CH\langle\begin{array}{l}COOH\\ COOH\end{array} \xrightarrow[-CO_2]{\Delta} CH_3-CH_2COOH$$

Gem-dihalide Propanoic acid

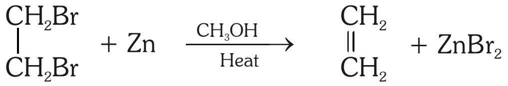
(i) – CN group on acid hydrolysis gives - COOH

(ii) Two – COOH group on one C – atom always loose CO_2 to form monocarboxylic acid on heating.

(iii) Two – COOH group on vic. C – atom loose H_2O to form cyclic anhydride on heating.

(iv) Dehalogenation :

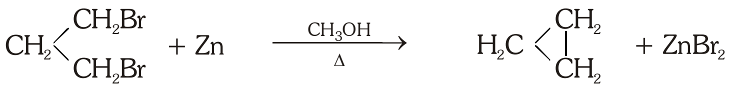
Vic.



$$\begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array} + Zn \xrightarrow[Heat]{CH_3OH} \begin{array}{l}CH_2\\ \|\\ CH_2\end{array} + ZnBr_2$$

Same Carbon Product

α – ω.



$$CH_2\langle\begin{array}{l}CH_2Br\\ CH_2Br\end{array} + Zn \xrightarrow[\Delta]{CH_3OH} H_2C\langle\begin{array}{l}CH_2\\ |\\ CH_2\end{array} + ZnBr_2$$

α, ω - dihalide. Cyclopropane

BEGINNER'S BOX-1

1. Which of the following is not organometallic compound

(1) RMgX (2) R_2Zn (3) RONa (4) R_2Hg

2. Which is Finkelstein reaction ?

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

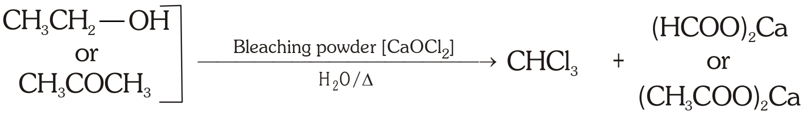
(3) $R-X + NaF \longrightarrow$ (4) $R-F + AgCl \longrightarrow$

5.0 TRI HALIDES (Haloform CHX_3)

5.1 General Method of Preparation

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

(ii) By Haloform reaction (lab method) :



$$\left.\begin{matrix} CH_3CH_2-OH \\ \text{or} \\ CH_3COCH_3 \end{matrix}\right] \xrightarrow[H_2O/\Delta]{\text{Bleaching powder } [CaOCl_2]} CHCl_3 + \begin{matrix} (HCOO)_2Ca \\ \text{or} \\ (CH_3COO)_2Ca \end{matrix}$$

Mechanism :

$$CaOCl_2 + H_2O \longrightarrow 2Cl + Ca(OH)_2$$

$$CH_3CH_2\text{–}OH + 2Cl \longrightarrow CH_3CHO + 2HCl \quad \text{(Oxidation)}$$

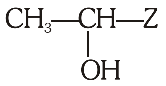
$$CH_3CHO + 6Cl \longrightarrow CCl_3CHO + 3HCl \quad \text{(Halogenation)}$$

$$CCl_3CHO + Ca(OH)_2 \longrightarrow CHCl_3 + (HCOO)_2Ca \quad \text{(Hydrolysis)}$$

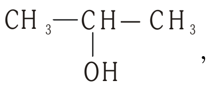
If CH_3COCH_3 is used then $CHCl_3$ is formed into 2 steps (Chlorination and Hydrolysis)

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

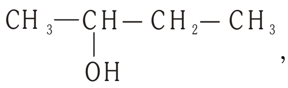
Ex. Alcohols :



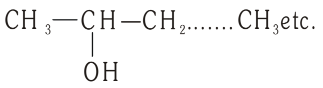
$CH_3-\underset{OH}{\underset{|}{CH}}-Z$



$CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$,

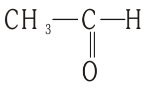


$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3$,



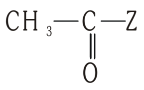
$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2 \ldots\ldots CH_3$ etc.

Aldehydes : Only acetaldehyde



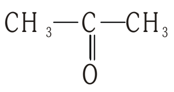
$CH_3-\underset{O}{\underset{\|}{C}}-H$

Ketones :

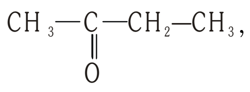


$CH_3-\underset{O}{\underset{\|}{C}}-Z$

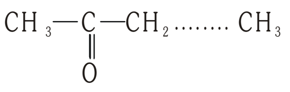
Ex .



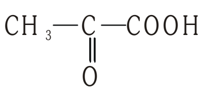
$CH_3-\underset{O}{\underset{\|}{C}}-CH_3$,



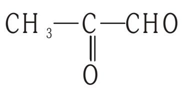
$CH_3-\underset{O}{\underset{\|}{C}}-CH_2-CH_3$,



$CH_3-\underset{O}{\underset{\|}{C}}-CH_2 \ldots\ldots CH_3$ etc. (All methyl ketones)



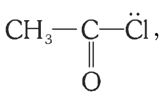
$CH_3-\underset{O}{\underset{\|}{C}}-COOH$,



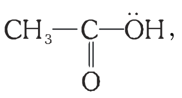
$CH_3-\underset{O}{\underset{\|}{C}}-CHO$ Also show haloform reaction.

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

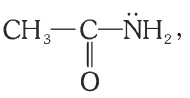
Ex.



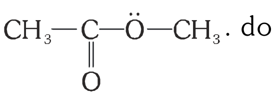
$CH_3-\underset{O}{\underset{\|}{C}}-\ddot{Cl}$,



$CH_3-\underset{O}{\underset{\|}{C}}-\ddot{O}H$,



$CH_3-\underset{O}{\underset{\|}{C}}-\ddot{N}H_2$,



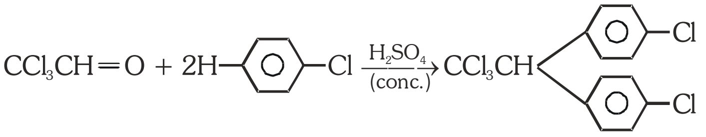
$CH_3-\underset{O}{\underset{\|}{C}}-\ddot{O}-CH_3$. do not show haloform reaction.

(iii) Preparation of pure $CHCl_3$:

$$CCl_3CHO.\ 2H_2O \xrightarrow[\Delta]{NaOH} CHCl_3 + HCOONa + 2H_2O$$

Chloral hydrate (Pure Chloroform)

Chloral can also be used in preparation of D.D.T.



Dichloro diphenyl trichloro ethane
(DDT)

(iv) Industrial preparation :

$$\begin{matrix} CH_3CH_2\text{—}OH \\ \text{or} \\ CH_3COCH_3 \end{matrix} \xrightarrow{\text{aq. NaCl/electrolysis}} CHCl_3 + \begin{matrix} HCOONa \\ \text{or} \\ CH_3COONa \end{matrix}$$

5.2 Physical Properties

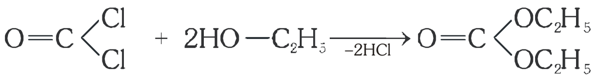
$CHCl_3$ is colourless and sweet smelling liquid. It's B.P. is 61°C and it is insoluble in H_2O and have density more than H_2O. Chloroform is used as Anaesthetic.

5.3 Chemical Properties

(i) Oxidation : $CHCl_3 + [O] \xrightarrow{\text{Air and light}} COCl_2 + HCl$

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



$$O{=}C\begin{matrix} \diagup Cl \\ \diagdown Cl \end{matrix} + 2HO{-}C_2H_5 \xrightarrow[-2HCl]{} O{=}C\begin{matrix} \diagup OC_2H_5 \\ \diagdown OC_2H_5 \end{matrix}$$

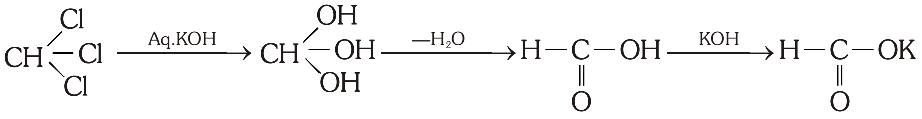
[Poisonous] Diethyl carbonate
[Non-Poisonous]

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_2SO_4	No reaction	Yellow solution

(ii) Hydrolysis :



$$CH\begin{matrix} \diagup Cl \\ -Cl \\ \diagdown Cl \end{matrix} \xrightarrow{\text{Aq.KOH}} CH\begin{matrix} \diagup OH \\ -OH \\ \diagdown OH \end{matrix} \xrightarrow{-H_2O} H-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{KOH} H-\underset{\underset{O}{\|}}{C}-OK$$

Unstable

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

Primary–Amines (Aliphatic or Aromatic) $\xrightarrow{CHCl_3 + KOH}$ Isocyanides

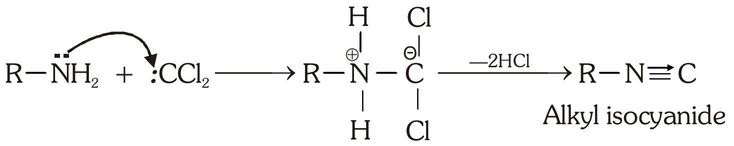
Isocyanides have unpleasant or offensive smell (Isocyanide test).

$$R\text{—}NH_2 \xrightarrow{CHCl_3 + KOH} R\text{—}NC$$

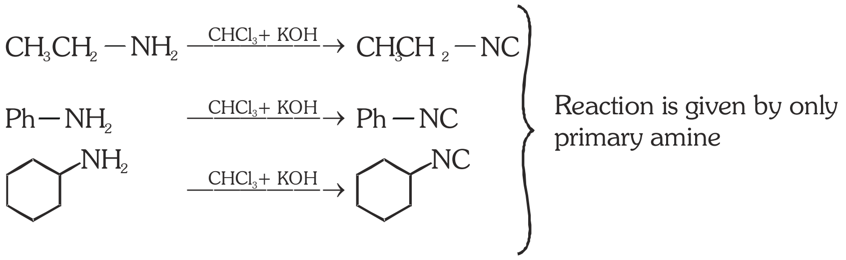
Mechanism :

$$CHCl_3 \xrightarrow{KOH} :CCl_2$$

(electrophile)

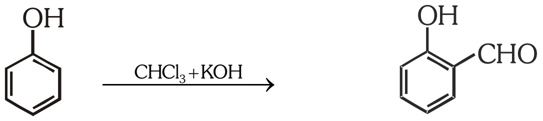


Alkyl isocyanide



Reaction is given by only primary amine

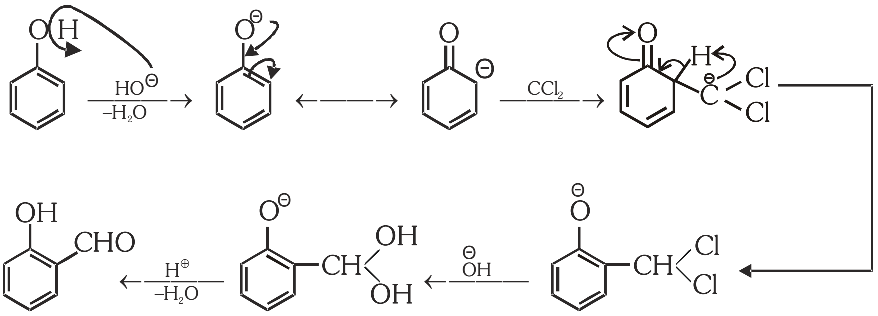
(iv) Reimer Tieman's reaction :



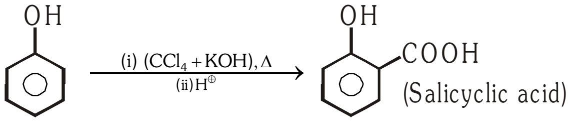
Salicylaldehyde (o–Hydroxy benzaldehyde)

Mechanism : $:CCl_2$ is neutral attacking electrophile (formed by α,α– elimination reaction)

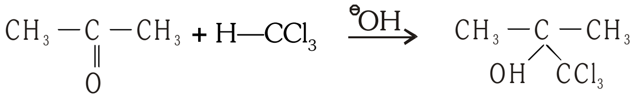
$$CHCl_3 \xrightarrow{KOH} :CCl_2$$



Note : If CCl_4 is used in place of chloroform, salicylic acid is formed as product.



(v) Reaction with CH_3COCH_3 :



Chloritone (Hypnotic)

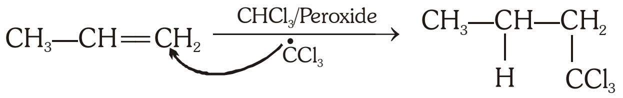
(vi) Reaction with HNO_3 :

$$CCl_3 \boxed{H + HO} NO_2 \longrightarrow CCl_3—NO_2 + H_2O$$

Chloropicrin or nitrochloroform

(Tear gas)

(vii) Reaction with $CH_3CH=CH_2$:



$$CH_3—CH=CH_2 \xrightarrow[\dot{C}Cl_3]{CHCl_3/Peroxide} CH_3—\underset{H}{\underset{|}{C}}H—\underset{CCl_3}{\underset{|}{C}}H_2$$

A free radical addition reaction

(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

$$\left.\begin{array}{c}CH_3CH_2OH\\ \text{or}\\ CH_3COCH_3\end{array}\right] \xrightarrow[\text{or } I_2 + Na_2CO_3 + H_2O]{I_2 + NaOH \text{ or } NaOI \text{ or } \overset{\ominus}{OI}} \begin{array}{c}CHI_3\\ \text{yellow crystals}\\ \text{of iodoform}\end{array}$$

- CHI_3 give yellow ppt. of AgI with $AgNO_3$ but $CHCl_3$ does not give AgCl ppt.

Reason : CHI_3 is thermally less stable than $CHCl_3$.

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

(i) CH_3CH_2OH and CH_3OH

(ii) CH_3CHO and CH_3CH_2CHO

(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 CF_2Cl_2 (Freon– 12)

Nomenclature of freons :

Freon – cba
$c = n_{c-1}$
$b = n_{H+1}$
$a = n_F$

$$CF_2Cl_2 \longrightarrow \left.\begin{array}{l} c = n_{C-1} = 1-1 = 0 \\ b = n_{H+1} = 0+1 = 1 \\ a = n_F = 2 \end{array}\right] \text{Freon–12} \qquad C_2F_4Cl_2 \longrightarrow \left.\begin{array}{l} c = n_{C-1} = 2-1 = 1 \\ b = n_{H+1} = 0+1 = 1 \\ a = n_F = 4 \end{array}\right] \text{Freon–114}$$

- 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.

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

(Grignard reagent)

(Alkyl magensium halide)

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

Ether is used to dissolve the Grignard reagent by coordination.

6.2 Chemical Reactions

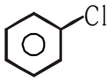
$R{-}Mg{-}X$

$\xrightarrow{\text{(i) } O_2 \text{ (ii) } H_3O^+}$	$R{-}OH$	1° Alcohol
$\xrightarrow{H_2C{=}O/H_3O^+}$	$RCH_2{-}OH$	1° Alcohol
$\xrightarrow{\overset{O}{CH_2{-}CH_2}/H_3O^+}$	$R{-}CH_2{-}CH_2{-}OH$	1° Alcohol
$\xrightarrow{RCHO/H_3O^+}$	R_2CHOH	2° Alcohol
$\xrightarrow{HCOOEt/H_3O^+}$	R_2CHOH	2° Alcohol
$\xrightarrow{RCOR/H_2O}$	$R_3C{-}OH$	3° Alcohol
$\xrightarrow{RCOOEt/H_2O\ (2:1)}$	$R_3C{-}OH$	3° Alcohol
$\xrightarrow{HCOOEt\ (1:1)}$	$RCHO$	aldehyde
$\xrightarrow{RCN/H_2O}$	$RCOR$	Ketone
$\xrightarrow{RCOOEt\ (1:1)}$	$RCOOEt$ ...	

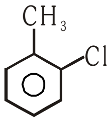
7.0 Haloarene

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

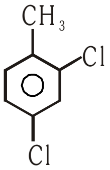
Ex.



(Chlorobenzene)



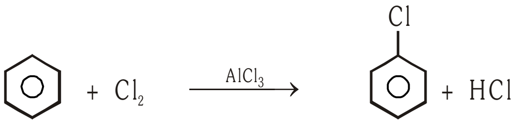
(2–Chlorotoluene)



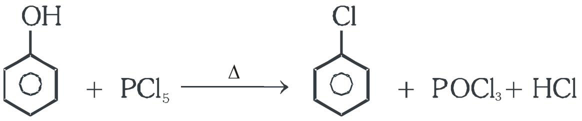
(2,4–Dichlorotoluene)

7.1 General Methods of Preparation

(1)



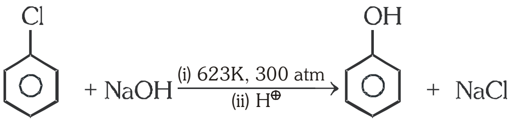
(2)



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

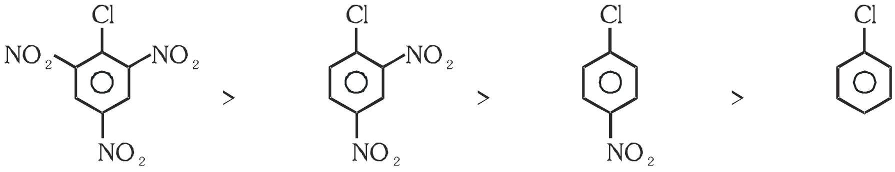
7.2 Chemical Properties

(1)

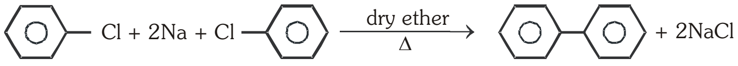


Presence of electron withdrawing group on ring makes the nucleophilic substitution easier.

Reactivity Order : (Towards nucleophilic substatitution)

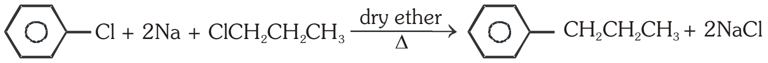


(2) Fittig reaction :



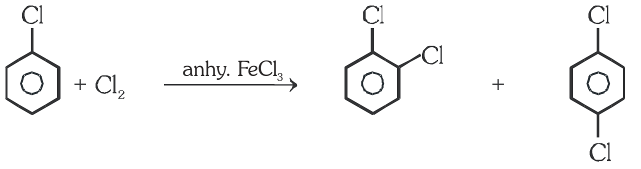
(Diphenyl)

(3) Wurtz fittig reaction :



(4) Electrophilic Substitution Reaction :

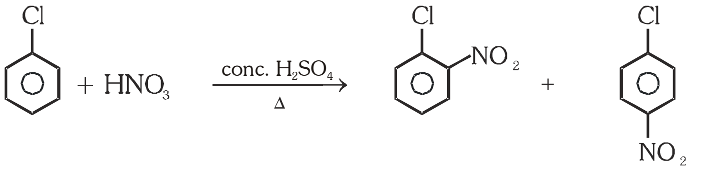
(i)



(Major)

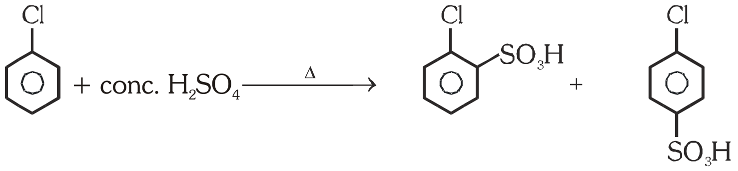
Note : Cl is o– and p– directing group.

(ii)



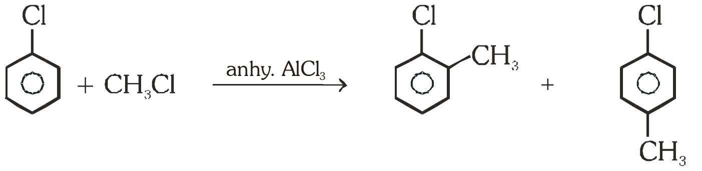
(Major)

(iii)



(Major)

(iv)



(Major)

BEGINNER'S BOX-2

1. Which can give haloform with X_2/OH^- ?

(1) CH_3OH (2) $CH_3–CH_2–CH=O$

(3) CH_3CHO (4) $CH_3CH_2CH_2OH$

2. Which of the following compounds cannot be identified by carbylamine test ?

(1) $C_6H_5–NH–C_6H_5$ (2) $CH_3CH_2NH_2$

(3) $CHCl_3$ (4) $C_6H_5–NH_2$

3. For preparation of Grignard reagent from haloalkanes which metal is used :-

(1) Na (2) Mg

(3) Ca (4) Ag

ANSWER KEY

BEGINNER'S BOX-1	**Que.**	1	2								
	Ans.	**3**	**1**								

BEGINNER'S BOX-2	**Que.**	1	2	3							
	Ans.	**3**	**1**	**2**							

EXERCISE-I (Conceptual Questions)

Build Up Your Understanding

GENERAL METHOD OF PREPARATION

1. Alkyl halides can be obtained by all methods excepts

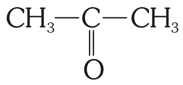
(1) $CH_3—CH_2—OH + HCl \xrightarrow{ZnCl_2}$

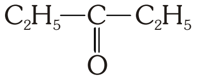
(2) $CH_2=CH—CH_3 + HBr \longrightarrow$

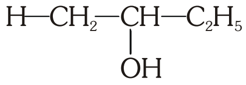
(3) $C_2H_5OH + NaCl \longrightarrow$

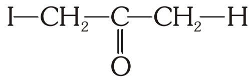
(4) $CH_3COOAg + Br_2 / CCl_4 \xrightarrow{h\nu}$

2. Which of the following will not give iodoform test

(1) 
$CH_3—\underset{\underset{O}{\|}}{C}—CH_3$

(2) 
$C_2H_5—\underset{\underset{O}{\|}}{C}—C_2H_5$

(3) 
$H—CH_2—\underset{\underset{OH}{|}}{CH}—C_2H_5$

(4) 
$I—CH_2—\underset{\underset{O}{\|}}{C}—CH_2—H$

3. Which of the following product is obtained when bleaching powder is distilled with acetone

(1) CCl_4 (2) $CHCl_3$

(3) $CH_3—CH_3$ (4) All

4. Which will give yellow ppt. with iodine and alkali

(1) Propan–2–ol (2) Benzophenone

(3) Methyl acetate (4) Acetamide

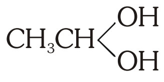
PHYSICAL PROPERTIES

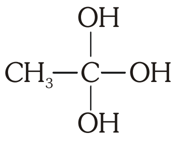
5. Which of the following has the highest boiling point

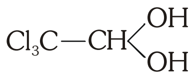
(1) CH_3CH_2I (2) CH_3Cl

(3) CH_3I (4) CH_3Br

6. A compound containing two –OH groups attached with one carbon atoms is unstable but which one of the following is stable

(1) 
$CH_3CH(OH)_2$

(2) 
$CH_3—\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}—OH$

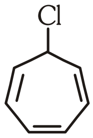
(3) 
$Cl_3C—CH(OH)_2$

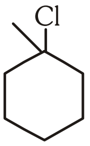
(4) All

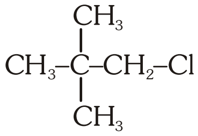
CHEMICAL PROPERTIES

7. Arrange the following compounds in decreasing order of reactivity in S_N1 reaction :-

(a) $Ph–CH_2–Cl$

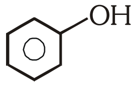
(b) 

(c) 

(d) 
$CH_3–\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}–CH_2–Cl$

(1) a > c > b > a (2) c > d > b > a

(3) a > b > c > d (4) b > a > c > d

8.  $\xrightarrow{CHCl_3+KOH}$ Product.

about above reaction the incorrect statement is

(1) The name of reaction is Reimer-Teiman's reaction

(2) The intermediate in the reaction is dichloro carbene

(3) The final product is salicylaldehyde

(4) The final product is benzyl chloride

9. The purity of $CHCl_3$ can be checked by

(1) treating $CHCl_3$ by NaOH

(2) treating $CHCl_3$ by HCl

(3) treating $CHCl_3$ with aq. $AgNO_3$

(4) treating $CHCl_3$ by $C_2H_5–OH$

10. Pure $CHCl_3$ and pure CHI_3 can be distinguished by

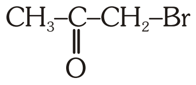
(1) treating with litmus paper

(2) treating with aq. KOH

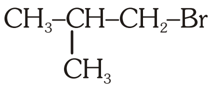
(3) treating with HCl

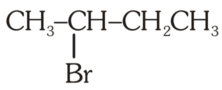
(4) treating with aq. $AgNO_3$

11. Arrange the following compound in decreasing order of reactivity in S_N2 reaction.

(a) 
$CH_3–\underset{\underset{O}{\|}}{C}–CH_2–Br$

(b) $CH_3–CH_2–CH_2–CH_2Br$

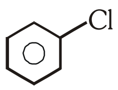
(c) 
$CH_3–\underset{\underset{CH_3}{|}}{CH}–CH_2–Br$

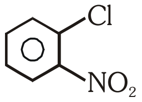
(d) 
$CH_3–\underset{\underset{Br}{|}}{CH}–CH_2CH_3$

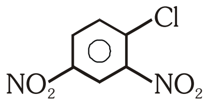
(1) b > c > d > a (2) a > b > c > d

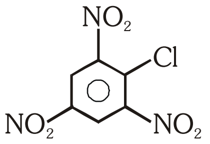
(2) b > c > a > d (4) c > a > b > d

12. Which of the following undergoes hydrolysis most easily

(1)


(2)


(3)


(4)


13. Which of the following is used as insecticide

(1) D.D.T. (2) Chloritone

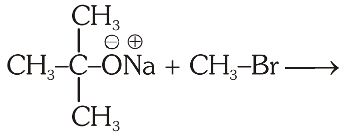
(3) $CHCl_3$ (4) All of them

14. Which of the following when heated with KOH and primary amine gives carbylamine test

(1) $CHCl_3$ (2) CH_2Cl_2

(3) CH_3OH (4) CCl_4

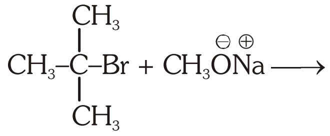
15. Which reaction gives elimination as a major product

(1)


$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\ominus\ \oplus}{ONa} + CH_3-Br \longrightarrow$

(2) $CH_3-CH_2-Br + NaCN \xrightarrow{DMSO}$

(3) $CH_3-CH_2-Br + NaI \xrightarrow{\text{Dry acetone}}$

(4)


$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br + CH_3\overset{\ominus\ \oplus}{ONa} \longrightarrow$

16. Iodoform gives a precipitate with $AgNO_3$ on heating but chloroform does not because

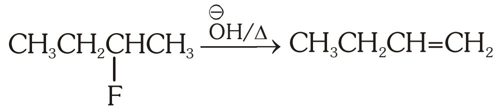
(1) Iodoform is ionic

(2) Chloroform is covalent

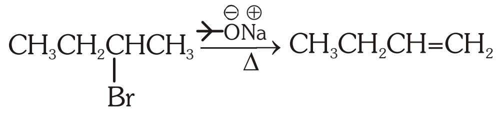
(3) C–I bond in iodoform is weak and C–Cl bond in chloroform is strong

(4) None of the above

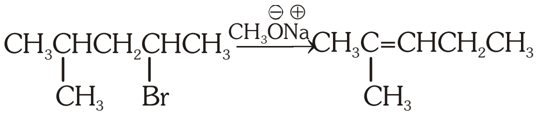
17. Which reaction product is wrong (major) product.

(1)


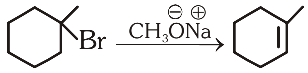
$CH_3CH_2\underset{F}{CH}CH_3 \xrightarrow{\overset{\ominus}{O}H/\Delta} CH_3CH_2CH{=}CH_2$

(2)


$CH_3CH_2\underset{Br}{CH}CH_3 \xrightarrow[\Delta]{\overset{\ominus\ \oplus}{ONa}} CH_3CH_2CH{=}CH_2$

(3)


$CH_3\underset{CH_3}{CH}CH_2\underset{Br}{CH}CH_3 \xrightarrow{CH_3\overset{\ominus\ \oplus}{ONa}} CH_3\underset{CH_3}{C}{=}CHCH_2CH_3$

(4)


18. When alkyl magnesium halide reacts with R-NH_2, the product is

(1) R—R (2) R— H

(3) R_2NH (4) R—X

19. Chloroform on reaction with acetone gives:–

(1) Acetylene (2) Chloretone

(3) Nitrochloroform (4) Chloroacetone

20. Chloroform reacts with aniline and aqueous KOH gives :-

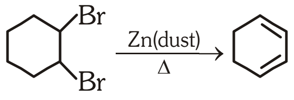
(1) $Ph - N \overset{\rightarrow}{\equiv} C$ (Phenyl isocyanide)

(2) Benzene

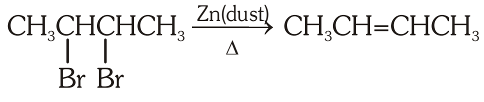
(3) Phenyl cyanide

(4) None of these

21. Which reaction product is wrong (major) product

(1)


(2) $CH_3CH_2CH_2Br \xrightarrow[\text{dry Acetone}]{NaI} CH_3CH_2CH_2I$

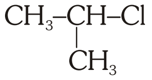
(3)


$CH_3\underset{Br}{CH}\underset{Br}{CH}CH_3 \xrightarrow[\Delta]{Zn(dust)} CH_3CH{=}CHCH_3$

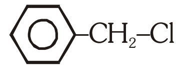
(4) $CH_3CH_2CHCl_2 \xrightarrow[\text{(ii) } H^+]{\text{(i)}NaNH_2\text{(excess)}} CH_3C{\equiv}CH$

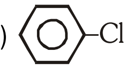
22. Which of the following undergoes nucleophilic substitution by S_N1 mechanism at fastest rate :

(1) CH_3-CH_2-Cl

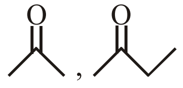
(2)


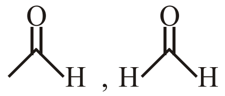
$CH_3-\underset{CH_3}{CH}-Cl$

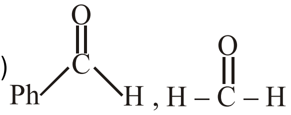
(3)


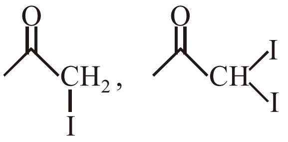
(4)


23. Which of the following pair is differentiated by iodoform test?

(1) 

(2) 

(3) 

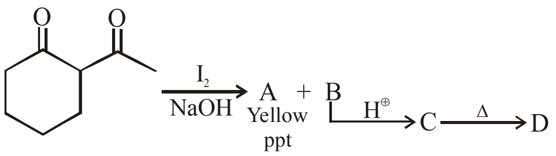
(4) 

24. Identify z in the following series

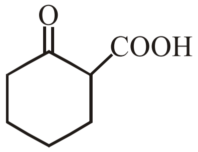
$CH_2{=}CH_2 \xrightarrow[\Delta]{HBr} x \xrightarrow{Hydrolysis} y \xrightarrow{I_2/NaOH} z$

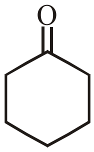
(1) C_2H_5I (2) C_2H_5OH

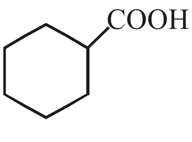
(3) CHI_3 (4) CH_3CHO

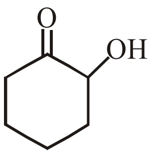
25. 

Identify D :-

(1) 

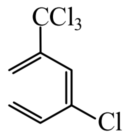
(2) 

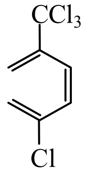
(3) 

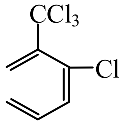
(4) 

26. $C_6H_5CCl_3 \xrightarrow[Fe]{Cl_2} X$

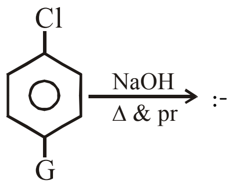
In the above reaction X is

(1) 

(2) 

(3) 

(4) None of these

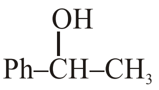
27. 

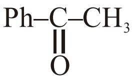
Rate of reaction is maximum if G is :-

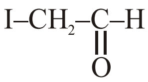
(1) $-OCH_3$ (2) $-CH_3$

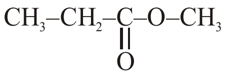
(3) $-NO_2$ (4) $-H$

28. Which does not gives iodoform test :-

(1) 
$Ph{-}\overset{OH}{\overset{|}{C}H}{-}CH_3$

(2) 
$Ph{-}\underset{O}{\underset{\|}{C}}{-}CH_3$

(3) 
$I{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}H$

(4) 
$CH_3{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}O{-}CH_3$

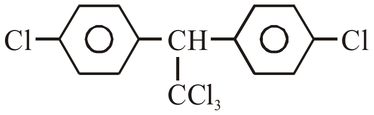
EXERCISE-I (Conceptual Questions) ANSWER KEY

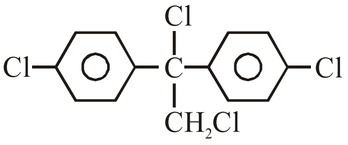
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	**3**	**2**	**2**	**1**	**1**	**3**	**4**	**4**	**3**	**4**	**2**	**4**	**1**	**1**	**4**
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28		
Ans.	**3**	**3**	**2**	**2**	**1**	**1**	**3**	**2**	**3**	**2**	**1**	**3**	**4**		

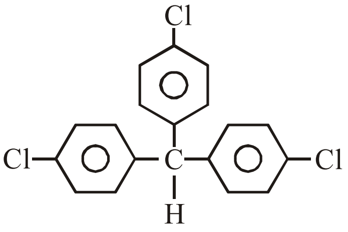
EXERCISE-II (Previous Year Questions) AIPMT/NEET & AIIMS (2006-2018)

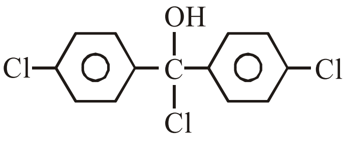
AIPMT 2009

1. Trichloroacetaldehyde, CCl_3CHO reacts with chlorobenzene in presence of sulphuric acid and produces :-

(1) 

(2) 

(3) 

(4) 

AIPMT 2010

2. In the following reaction

$C_6H_5CH_2Br \xrightarrow[2.H_3O^+]{1.Mg,\ Ether} X,$

The product 'X' is :-

(1) $C_6H_5CH_2OH$

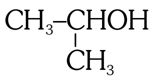
(2) $C_6H_5CH_3$

(3) $C_6H_5CH_2CH_2C_6H_5$

(4) $C_6H_5CH_2OCH_2C_6H_5$

3. Following compounds are given :

(a) CH_3CH_2OH (b) CH_3COCH_3

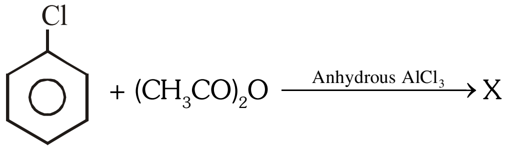
(c)  $CH_3-\underset{CH_3}{\underset{|}{C}}HOH$ (d) CH_3OH

Which of the above compound(s), on being warmed with iodine solution and NaOH, will give iodoform?

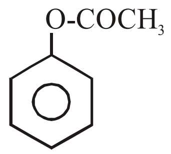
(1) Only (a) (2) (a), (b) and (c)

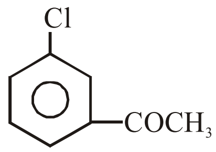
(3) (a) and (b) (4) (a), (c) and (d)

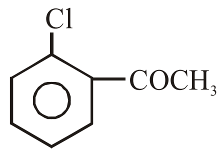
AIIMS 2010

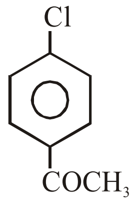
4. 

What is major product (X) :-

(1) 

(2) 

(3) 

(4) 

AIPMT Mains 2012

5. Which of the following compounds will give a yellow precipitate with iodine and alkali ?

(1) Acetamide

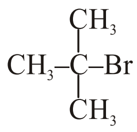
(2) Propan-2-ol

(3) Acetophenone

(4) Methyl acetate

AIIMS 2016

6. Arrange the following compounds in order of their boiling point

 $CH_3-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-Br$

(I)

 $H_3C-\underset{\underset{Br}{|}}{C}H-CH_2-CH_3$

(II)

$CH_3-CH_2-CH_2-CH_2-Br$

(III)

(1) I > II > III (2) III > II > I

(3) II > I > III (4) III > I > II

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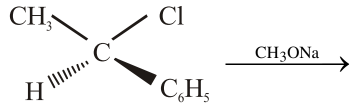
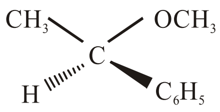
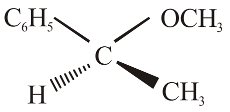
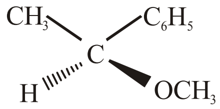
7.  Product (Major)?

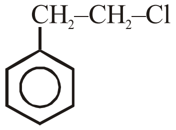
(1) 

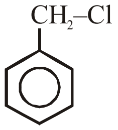
(2) 

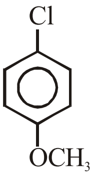
(3) 

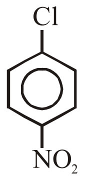
(4) $C_6H_5-CH=CH_2$

8. Correct order of reactivity towards nucleophilic substitution reaction of following is :-

(I) 

(II) 

(III) 

(IV) 

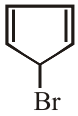
(1) II > I > IV > III

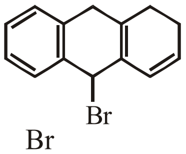
(2) III > IV > I > II

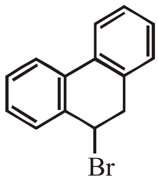
(3) II > IV > I > II

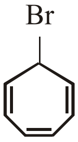
(4) IV > II > III > I

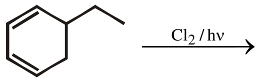
9. Which of the following react fastest with aqueous acetone.

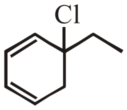
(1) 

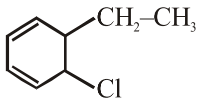
(2) 

(3) 

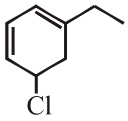
(4) 

10.  Product of reaction is -

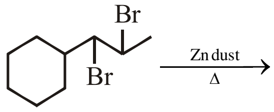
(1) 

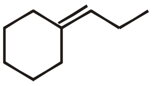
(2) 

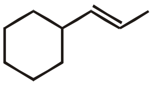
(3) 

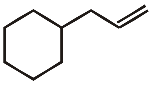
(4) 

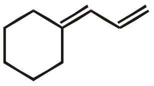
11. Product of following reaction is :-



(1) 

(2) 

(3) 

(4) 

EXERCISE-II (Previous Year Questions) **ANSWER KEY**

Que.	1	2	3	4	5	6	7	8	9	10	11
Ans.	**1**	**2**	**2**	**4**	**2,3**	**2**	**4**	**1**	**4**	**1**	**2**

EXERCISE-III (Analytical Questions)

Check Your Understanding

1. Which of the following has highest dipole moment:

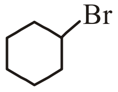
(1) CH_3Cl (2) CH_3F
(3) CH_3Br (4) CH_3I

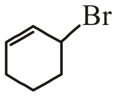
2. The final product in the reaction is

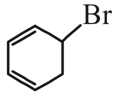
$$Ph-OH + CCl_4 \xrightarrow[(2)\ H^{\oplus}]{(1)\ KOH, \Delta} \text{product}$$

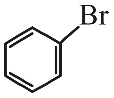
(1) Salicyl aldehyde (2) Salicylic acid
(3) Methyl salicylate (4) Benzyl chloride

3. Arrange the following in order of ease of dehydrohalogenation:

(i) 

(ii) 

(iii) 

(iv) 

(1) (iii) > (iv) > (ii) > (i)
(2) (iii) > (ii) > (i) > (iv)
(3) (ii) > (iii) > (i) > (iv)
(4) (i) > (ii) > (iii) > (iv)

4. The product in the following reaction is

$$Ph-Cl + Fe / Br_2 \longrightarrow \text{Product}$$

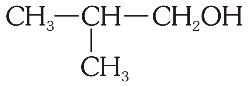
(1) o–bromo-chloro benzene

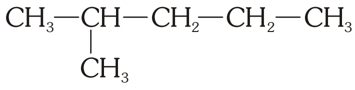
(2) p–bromo-chloro benzene

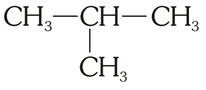
(3) both the above

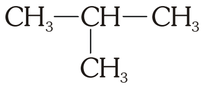
(4) 2,4,6–tribromo chloro benzene

5. Isobutyl magnesium bromide with dry ether and absolute alcohol gives

(1)  $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2OH$ and CH_3CH_2MgBr

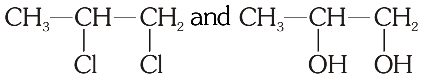
(2)  $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-CH_3$ and Mg (OH) Br

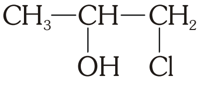
(3)  $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3$, $CH_2=CH_2$ and Mg(OH)Br

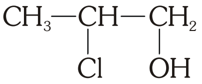
(4)  $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3$ and CH_3CH_2OMgBr

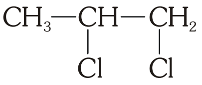
6. Identify 'Z' in the following reaction series,

$$CH_3.CH_2CH_2Br \xrightarrow{aq.NaOH} (X) \xrightarrow[Heat]{Al_2O_3} (Y) \xrightarrow{Cl_2/H_2O} (Z)$$

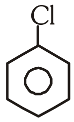
(1) Mixture of  $CH_3-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{Cl}{|}}{CH_2}$ and $CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH_2}$

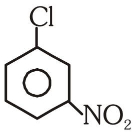
(2)  $CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{Cl}{|}}{CH_2}$

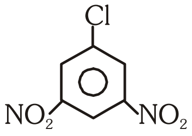
(3)  $CH_3-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{OH}{|}}{CH_2}$

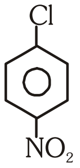
(4)  $CH_3-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{Cl}{|}}{CH_2}$

7. Arrange the following compound in increasing order of reactivity towards aromatic nucleophilic substitution reaction.

(a) 

(b) 

(c) 

(d) 

(1) c > d > b > a (2) c > b > a > d
(3) d > c > b > a (4) a > d > b > c

8. Chloroform when treated with benzene in presence of anhydrous $AlCl_3$, the product formed is

(1) Chlorobenzene
(2) Toulene
(3) Mixture of ortho and para chlorotoluene
(4) Triphenyl methane

EXERCISE-III (Analytical Questions) ANSWER KEY

Que.	1	2	3	4	5	6	7	8
Ans.	1	2	2	3	4	2	3	4

EXERCISE-IV (Assertion & Reason)

Target AIIMS

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

(A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.

(B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.

(C) If Assertion is True but the Reason is False.

(D) If both Assertion & Reason are false.

1. ***Assertion :–*** Alkyl halides are not soluble in water.
Reason :– Alkyl halide does not form H–bonds with water molecule although alkyl halide is polar in nautre.
(1) A (2) B (3) C (4) D

2. ***Assertion :–*** $CHCl_3$ is more acidic than CHF_3.
Reason :– Electronegativity of Fluorine is more than chlorine.
(1) A (2) B (3) C (4) D

3. ***Assertion :–*** Isobutanal does **not** give iodoform test.
Reason :– It does not have α-hydrogen.
(1) A (2) B (3) C (4) D

4. ***Assertion :–*** Styrene on reaction with HBr gives 1-bromo-1-phenylethane.
Reason :– Benzyl radical is more stable than alkyl radical.
(1) A (2) B (3) C (4) D

5. ***Assertion*** : Rate of alkaline hydrolysis of methyl chloride to methanol is higher in DMF than in water.
Reason : Hydrolysis of methyl chloride follows second order kinetics.
(1) A (2) B (3) C (4) D

6. ***Assertion :–*** 2-Bromo butane on reaction with alcoholic KOH mainly gives 2–butene.
Reason :– The hydrogen on C_3 carbon is more acidic than hydrogen on C_1 carbon.
(1) A (2) B (3) C (4) D

7. ***Assertion :-*** Chlorobenzene is less reactive than benzene for electrophilic substitution reaction.
Reason :- Resonance effect in chlorobenzene destabilized carbocation intermediate.
(1) A (2) B (3) C (4) D

EXERCISE-IV (Assertion & Reason) ANSWER KEY

Que.	1	2	3	4	5	6	7
Ans.	**1**	**2**	**3**	**2**	**1**	**3**	**3**