ALKYL HALIDE (HALOGEN DERIVATIVES)

Preface

Organic compound in which halogen is linked directly with carbon is halo alkane/ halogen derivative of alkane or alkyl halide. Polyhalogen derivatives of alkane is most useful in daily life. This topic deals with preparation of alkyl halide from various organic compound, its physical properties, its various chemical properties, SN^1 and SN^2 mechanism of reactions as well as difference between this To study the chapter you are suggested to study alkane, alkene and reaction mechanism before this chapter, differentiation Gem and vicinal dihalide with their preparation and properties.

This book consists of theoritical & practical explanations of all the concepts involved in the chapter. Each article followed by a ladder of illustration. At the end of the theory part, there are miscellaneous solved examples which involve the application of multiple concepts of this chapter.

Students are advised to go through all these solved examples in order to develope bettter understanding of the chapter and to have better grasping level in the class.

Total number of Questions in **ALKYL HALIDE** are :–
(i) In chapter Examples 22
(ii) Solved Examples 31

Total no. of question 53

1. INTRODUCTION ⁚⁚

(a) These are the organic compound in which halogen is directly linked with carbon atom.

(b) These are also called as Haloalkane.

(c) Their general formula is $C_nH_{2n+1}X$, (X = F, Br, Cl, I).

(d) In these compounds, hybridisation state of carbon is sp^3.

(e) In these compounds, geomerty of carbon is tetrahedral.

(f) Central carbon atom has a bond angle of 109° 28'.

(g) On the basis of no. of halogen atom, these are of following types –

(i) Monohalide – They possess single halogen atom.
eg. CH_3 - Cl, CH_3 - CH_2Br

(ii) Dihalide – These are of three types
eg. gem dihalide, vicinal dihalide and α, ω halide

(iii) Trihalide – They posses three halogen atoms.
eg. $CHCl_3$ / CHI_3

(iv) Tetrahalide – They possess four halogen atoms.
eg. CCl_4

(vi) Polyhalide – They possess more than four halogen atoms.

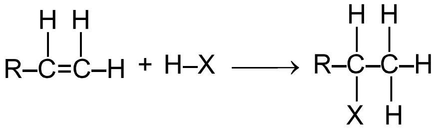
(h) Alkyl halide shows chain and position isomerism. If unsymmetrical or chiral carbon is present then it showsoptical isomerism also.

2. METHODS OF PREPARATION OF ALKYL HALIDES ⁚⁚

2.1 From Alkane (Halogenation) : –

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

2.2 From Alkene (Hydrohalogenation) :–



$$R-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H + H-X \longrightarrow R-\underset{X}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-H$$

Note : From alkyne we cannot obtain monoalkylhalide.

2.3 From Alcohol : –

(a) Using dry H - X : –

$$R - OH + \underset{\text{dry}}{H - X} \xrightarrow[\Delta\,300^\circ]{\text{Anhydrous } ZnCl_2} R - X + H_2O$$

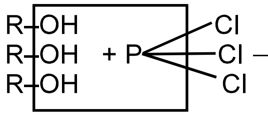
Note :

(i) The reactivity order of HX in the above reaction is –
HI > HBr > HCl < HF

(ii) The reactivity order of alcohols in the above reaction is –
3° > 2° > 1° > MeOH

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

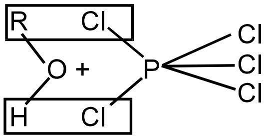
(b) Using PCl_3 : –



$$\longrightarrow 3R - Cl + H_3PO_3$$

phosphorous acid

(c) Using PCl_5 : –

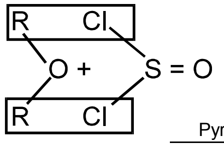


$$\longrightarrow R - Cl + HCl + POCl_3$$

Important Note : –

Bromine or Iodine derivatives can not be obtained from the above reaction becaues due to larger size of Bromine or Iodine, PBr_5 or PI_5 are unstable.

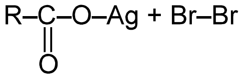
(d) Darzen's Process : – It is the best method for preparation of alkyl halide.



$$\xrightarrow{\text{Pyridine}} RCl + HCl + SO_2\uparrow$$

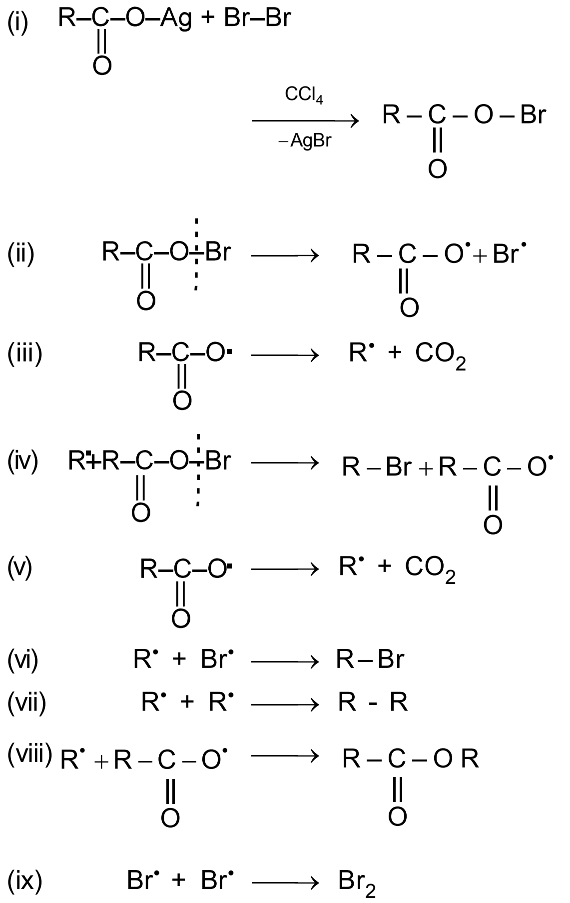
2.4 From Silver Salt of Carboxylic Acid : –

The reaction is called as '**Borodiene - Hunsdiecker**'reaction. It is also a good method for obtaining alkyl halide, but from this reaction we obtain only bromo derivatives because reaction is based upon free radical mechanism.



$$R-\underset{O}{\underset{\|}{C}}-O-Ag + Br-Br \xrightarrow{CCl_4} R-Br + CO_2\uparrow + AgBr\downarrow$$

Mechanism : –



(i) $R-\underset{\underset{O}{\|}}{C}-O-Ag + Br-Br \xrightarrow[-AgBr]{CCl_4} R-\underset{\underset{O}{\|}}{C}-O-Br$

(ii) $R-\underset{\underset{O}{\|}}{C}-O\vdots Br \longrightarrow R-\underset{\underset{O}{\|}}{C}-O^{\bullet} + Br^{\bullet}$

(iii) $R-\underset{\underset{O}{\|}}{C}-O^{\bullet} \longrightarrow R^{\bullet} + CO_2$

(iv) $R^{\bullet} + R-\underset{\underset{O}{\|}}{C}-O\vdots Br \longrightarrow R-Br + R-\underset{\underset{O}{\|}}{C}-O^{\bullet}$

(v) $R-\underset{\underset{O}{\|}}{C}-O^{\bullet} \longrightarrow R^{\bullet} + CO_2$

(vi) $R^{\bullet} + Br^{\bullet} \longrightarrow R-Br$

(vii) $R^{\bullet} + R^{\bullet} \longrightarrow R - R$

(viii) $R^{\bullet} + R-\underset{\underset{O}{\|}}{C}-O^{\bullet} \longrightarrow R-\underset{\underset{O}{\|}}{C}-O\,R$

(ix) $Br^{\bullet} + Br^{\bullet} \longrightarrow Br_2$

Note : –

(i) In the above reaction the reactivity of alkyl group is :

$1^o > 2^o > 3^o$

(ii) It is also an example of decarboxylation.

2.5 From Alkyl Halide : –

2.5.1 Finkelstein Reaction : –

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

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

2.5.2 Swars reaction : –

$$R\text{–Br or } R-Cl \xrightarrow[\text{or}\,Hg_2F_2/\Delta]{AgF/\Delta} R-F$$

In this reaction is called as **'Swarts reaction'**

Examples based on Preparation of Alkyl Halide

Ex.1 In Hunsdiecker reaction -

(A) Number of carbon atoms decrease

(B) Number of carbon atoms increase

(C) Number of carbon atoms remain same

(D) None of the above

Ans.(A)

Sol. Hunsdiecker reaction is a decarboxylation reaction.

Ex.2 Alkyl halides can be obtained by all methods except -

(A) $CH_3CH_2OH + HX/ZnCl_2$

(B) $CH_2 = CH - CH_3 + HBr$

(C) $C_2H_5OH + NaCl$

(D) $CH_3COOAg + Br_2 / CCl_4$

Ans.(C)

Sol. Alkyl halide can not be formed by the reaction between $C_2H_5OH + NaCl$.

$C_2H_5OH + NaCl \longrightarrow C_2H_5ONa + HCl$

Ex.3 Finkelstein reaction is -

(A) $2CH_3CH_2Cl + Ag_2O$ (dry) $\longrightarrow CH_3CH_2OCH_2CH_3 + 2AgCl$

(B) $CH_3CH_2Br + NaI \xrightarrow{\text{acetone}} CH_3CH_2I + NaBr$

(C) $CH_3CH_2Br + Ag_2O$ (moist) $\longrightarrow CH_3CH_2OH + AgBr$

(D) $CH_3CH_2Cl + NaOCH_3 \longrightarrow CH_3CH_2OCH_3 + NaCl$

Ans.(B)

Sol. The formation of alkyl iodide from alkyl bromide and alkyl chloride is known as Finkelstein reaction (Halogen exchange reaction).

3. PHYSICAL PROPERTIES

(a) Alkyl halides are colourless with sweet smell or pleasant smell oily liquid, whereas CH_3F, CH_3Cl, $CH_3 - CH_2 - F$, $CH_3 - CH_2 - Cl$ are gaseous in nature.

(b) Alkyl halides having 18-carbon or more than it are solid in nature.

(c) Although carbon - halogen bond is polar in nature but alkyl halides are insoluble in H_2O because they cannot form bond with H_2O.

(d) These are completely soluble in organic solvents.

(e) M.P & B.P. ∝ molecular weight. For same alkyl group the order of B.P. is

RI > RBr > RCl > RF

(f) Polarity order is RF > RCl > RBr > RI

(g) Reactivity order is RI > RBr > RCl > RF

(h) For same halide group reactivity order is

3° halide > 2° halide > 1° halide

(i) Fluorides and Chlorides are lighter than water whereas bromides and iodides are heavier than H_2O due to more density of bromine than oxygen. CH_2I_2 is heavier liquid after Hg.

Examples based on Physical properties of Alkyl Halide

Ex. 4 Which of the following has the highest boiling point : –

(A) CH_3CH_2I (B) CH_3Cl

(C) CH_3I (D) CH_3Br

Ans. (A)

Sol. Boiling point ∝ molecular weight.

Ex. 5 Ethyl chloride is soluble in : –

(A) C_2H_5OH (B) H_2O

(C) Both (A)& (B) (D) None **Ans. (A)**

Sol. Alkyl halides are soluble in organic solvents.

4. CHEMICAL PROPERTIES

Main reaction of alkyl halides are nucleophilic substitution reaction. These are of two types –

4.1 $S_N{}^1$ Reactions (Nucleophilic Unimolecular Substitution Reactions) : –

(a) These reaction completes in two step.

(b) In first step a carbocation is formed from alkyl halide molecule.

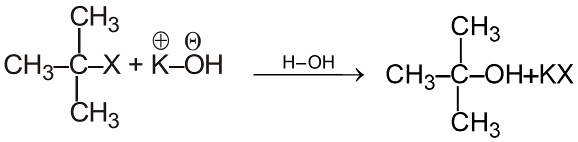
(c) It is slow step so it is also rate determining step.

(d) In second step an attacking nucleophile attacks on this carbocation and form a final product.

(e) In this reaction rate of reaction is dependent on the concentration of alkyl halide molecule only, not on the concentration of nucleophile. So the reaction is called as unimolecular substitution reaction.

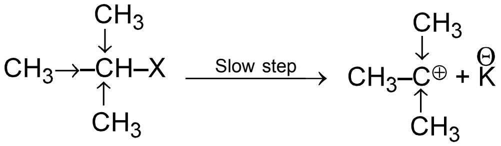
(f) Polar Medium is necessary for the reaction.

(g) All tertiary halides and sometimes secondary halides show this type of reaction.eg.

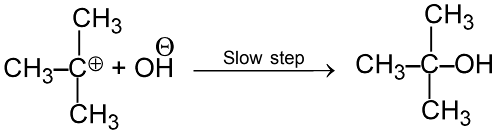


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-X + \overset{\oplus}{K}-\overset{\ominus}{OH} \xrightarrow{H-OH} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH+KX$$

Mechanism : –

(i) 

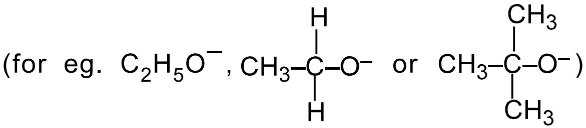
$$CH_3\rightarrow-\underset{\uparrow\ CH_3}{\overset{CH_3\ \downarrow}{C}}H-X \xrightarrow{\text{Slow step}} CH_3-\underset{\uparrow\ CH_3}{\overset{CH_3\ \downarrow}{C}}{}^{\oplus} + \overset{\ominus}{K}$$

(ii) 

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}{}^{\oplus} + \overset{\ominus}{OH} \xrightarrow{\text{Slow step}} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$$

Important Note : –

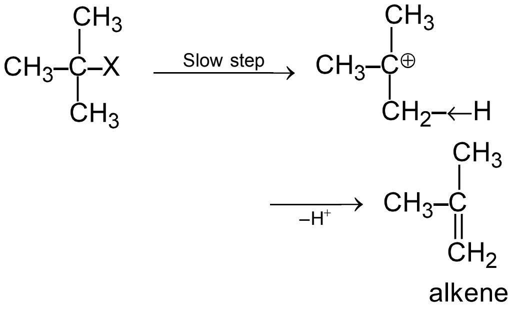
If nucleophile is bulky group



$$(\text{for eg. } C_2H_5O^{-}, CH_3-\underset{H}{\overset{H}{C}}-O^{-} \text{ or } CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O^{-})$$

polar medium is absent then reaction follows elimination reaction and is called '**Nucleophilic unimolecular elimination reaction**($E_N{}^1$)'

eg.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-X \xrightarrow{\text{Slow step}} CH_3-\underset{CH_2\leftarrow H}{\overset{CH_3}{C}}{}^{\oplus} \xrightarrow[-H^{+}]{} CH_3-\underset{\underset{\text{alkene}}{CH_2}}{\overset{CH_3}{C}}\!\!{\scriptstyle\|}$$

4.2 $S_N{}^2$ Reactions (Nucleophilic Bimolecular Substitution actions) : –

(a) These reaction completes in single step.

(b) In these reactions an attacking nucleophile attacks from back side of the central carbon atom of alkyl halide. This back side attack is called as '**Walden Inversion**'

(c) When nucleophile attacks on central atom then a transition state is formed in which attacking nucleophile and halogen atom both are linked with half bond with central atom. This stage is unstable stage, after sometime halogen atom attract bonded electrons towards itself and releases in the form of halide ion while attacking nucleophile forms complete bond with central carbon.

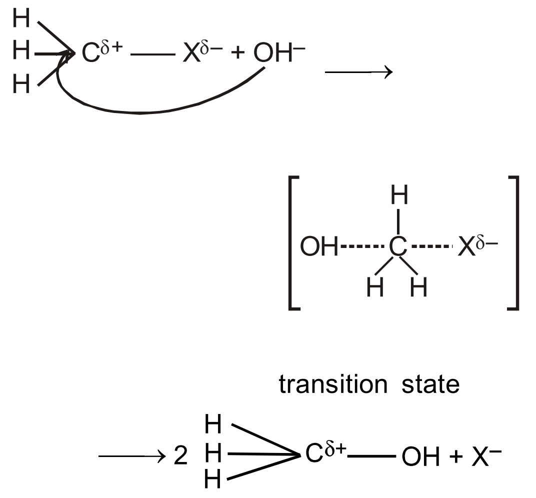
(d) In this reaction, bond breaking and bond forming process both can take place simultaneously and rate of reaction is dependent on the concentration of alkyl halide and concentration of attacking nucleophile both. So the reaction is called as biomolecular substitution reaction.

(e) Molecularity of reaction is two and the order of reaction is also two.

(f) In this reaction product is 100% opposite rotatory than reagent.

(g) Polar medium is not necessary for this type of reaction. All primary halides and sometimes 2° halide shows this type of reaction.

eg.$CH_3 - X + K - OH \longrightarrow CH_3 - OH + KX$



(i) Rate of reaction α [CH_3 X] [OH^-]

(h) Energy releases from the transition state.

Examples based on Chemical properties

Ex.6 What would be the product when tert. butyl chloride reacts with sodium ethoxide : -

(A) Tert. butyl alcohol

(B) Tert. butyl ethyl ether

(C) Iso butyl ethyl ether

(D) Isobutylene **Ans. (D)**

Sol. In the reaction halide is 3° and the nucleophile is bulky, reaction will be elimination E_N^1 and the product would be alkene.

Ex.7 What would be the product when sodium ethoxide reacts with isobutyl chloride : -

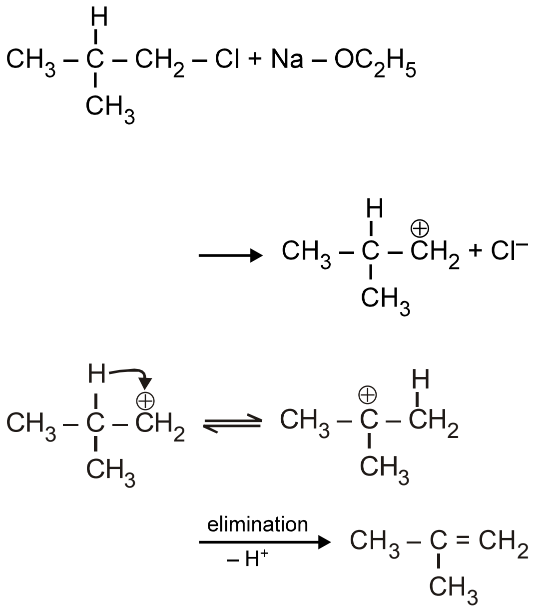
(A) Tert. butyl alcohol

(B) Tert. butyl ethyl ether

(C) Iso butyl ethyl ether

(D) Isobutylene **Ans. (D)**

Sol.



$$CH_3-\underset{CH_3}{\overset{H}{C}}-CH_2-Cl + Na-OC_2H_5 \longrightarrow CH_3-\underset{CH_3}{\overset{H}{C}}-\overset{\oplus}{C}H_2 + Cl^-$$

$$CH_3-\underset{CH_3}{\overset{H}{C}}-\overset{\oplus}{C}H_2 \rightleftharpoons CH_3-\underset{CH_3}{\overset{\oplus}{C}}-\overset{H}{C}H_2 \xrightarrow[-H^+]{\text{elimination}} CH_3-\underset{CH_3}{C}=CH_2$$

5. CHEMICAL REACTION

5.1 Reduction : –

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

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

(i) By Nascent hydrogen liberated from Na/C_2H_5OH or Sn / HCl or Zn / HCl or Zn-Cu couple/C_2H_5OH etc.

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

(ii) By hydride ion [:$H^{\ominus}$] liberated from $LiAlH_4$ or $NaBH_4$. It is completed by nucleophilic substitution reaction.

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

(iii) By catalytic hydrogenation of haloalkane -

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

(iv) By reduction of RI with HI in presence of red P.

$$R-X + HI \xrightarrow{\text{redP / 150°C}} R-H + I_2$$

5.2 Reaction with KOH : –

(a) With aqueous KOH : –

$$R–X + K–OH \longrightarrow R - OH + K–X$$

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

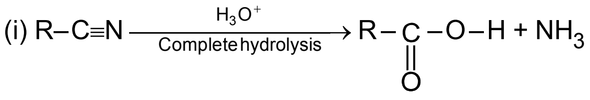
$$R–CH_2–CH_2–X + KOH(alc.) \longrightarrow R\text{-}CH{=}CH_2$$

5.3 Reaction with KCN : –

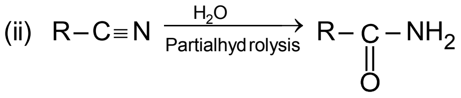
$$R–X + KCN \longrightarrow R–C{\equiv}N + KX$$

Alkane nitrile

Alkane nitrile is an important compound which gives following products.



$$\text{(i) } R–C{\equiv}N \xrightarrow[\text{Complete hydrolysis}]{H_3O^+} R–\underset{\underset{O}{\|}}{C}–O–H + NH_3$$



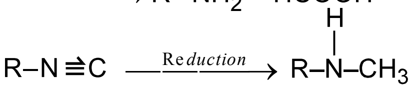
$$\text{(ii) } R–C{\equiv}N \xrightarrow[\text{Partial hydrolysis}]{H_2O} R–\underset{\underset{O}{\|}}{C}–NH_2$$

$$\text{(iii) } R–C{\equiv}N \xrightarrow{LiAlH_4\,/\,Reduction} R–CH_2–NH_2$$

5.4 Reaction with AgCN : —

$$R–X + AgCN \longrightarrow R–N \overset{\rightarrow}{=} C + AgX$$

$$R–N \overset{\rightarrow}{=} C \xrightarrow{\text{hydrolysis}} R–NH_2 + HCOOH$$



$$R–N \overset{\rightarrow}{=} C \xrightarrow{Reduction} R–\overset{\overset{H}{|}}{N}–CH_3$$

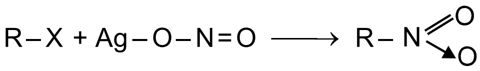
2°- amine

5.5 Reaction with KNO_2 : –

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

alkyl nitrite

5.6 Reaction with $AgNO_2$: –



$$R–X + Ag–O–N{=}O \longrightarrow R–N\genfrac{}{}{0pt}{}{\nearrow\!\!\!\!=O}{\searrow O}$$

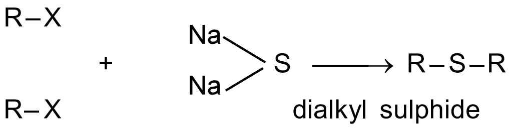
nitro alkane

5.7 Reaction with KSH : –

$$R–X + K–SH \longrightarrow R - SH$$

alkane thiol

5.8 Reaction with Na_2S :–



$$\begin{matrix} R–X \\ \quad + \\ R–X \end{matrix} \begin{matrix} Na \searrow \\ \\ Na \nearrow \end{matrix} S \longrightarrow R–S–R$$

dialkyl sulphide

5.9 Reaction with Na_2SO_3 : –

$$R–X + Na_2SO_3 \longrightarrow RSO_3Na + NaX$$

alkyl sodium sulphonate

Reaction is know as **"Strecker reaction".**

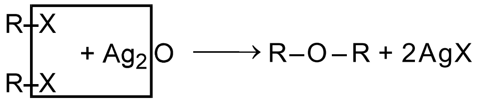
5.10 Reaction with NaOR : –

$$R–X + NaOR \longrightarrow R–O–R + NaX$$

The above reaction is called as "**Williamson ether synthesis**".

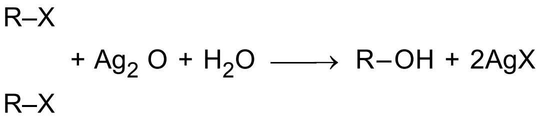
5.11 Reaction with Ag_2O : –

(a) Using dry Ag_2O : –



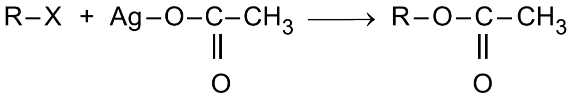
$$\begin{matrix} R– \\ \\ R– \end{matrix}\boxed{\begin{matrix} X & & \\ & + Ag_2 & \\ X & & \end{matrix}} O \longrightarrow R–O–R + 2AgX$$

(b) Using moist Ag_2O : –



$$\begin{matrix} R–X \\ \\ R–X \end{matrix} + Ag_2O + H_2O \longrightarrow R–OH + 2AgX$$

5.12 Reaction with Silver Acetate : –



$$R–X + Ag–O–\underset{\underset{O}{\|}}{C}–CH_3 \longrightarrow R–O–\underset{\underset{O}{\|}}{C}–CH_3$$

ester

The reaction is called as '**Esterification**'.

5.13 Reaction with metals : –

(a) With Na : – (Wurtz reaction)

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

(b) With Mg : – (Grignard reaction)

$$R–X + Mg \xrightarrow{\text{dry ether}} R–Mg–X$$

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

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

dialkyl zinc

Dialkyl zinc is known as '**Frankland - Reagent**'.

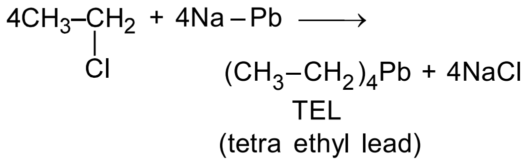
(d) With Li : –

$$R–Cl + 2Li \xrightarrow{\text{dry ether}} RLi + LiCl$$

alkyl lithium

Note : Alkyl lithium is more reactive than Grignard reagent.

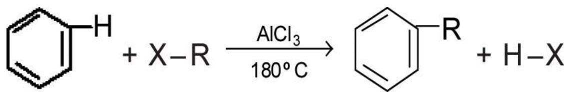
(e) With Na-lead alloy : –



$$4CH_3-\underset{\displaystyle Cl}{\underset{|}{C}}H_2 + 4Na-Pb \longrightarrow \underset{\text{(tetra ethyl lead)}}{\underset{\text{TEL}}{(CH_3-CH_2)_4Pb}} + 4NaCl$$

Note : Tetra ethyl lead is used as antiknocking agent.

5.14 Reaction with Benzene : –



The reaction is called as '**Friedel-craft Reaction**'.

Important Note :– Alkyl halide shows electrophilic substitution reaction in the above reaction, which is exception in alkyl halide

Examples based on Chemical Reaction of Mono Haloalkane

Ex.8 Reduction of alkyl halide by $LiAlH_4$ is the type of reaction –

(A) Nueleophilic substitution reaction

(B) Electrophilic substitution reaction

(C) Electrophilic Addition reaction

(D) None of these **Ans. (A)**

Sol. $LiAlH_4$, provdies $:H^{\ominus}$ ion there fore this reaction is of Nucleophilic substitution reaction.

Ex.9 Alkyl halide with alcoholic KOH gives –

(A) Alkane	(B) Acoholic salt
(C) Alkene	(D) Alcohol

Ans. (C)

Sol. Alkyl halide with alcoholic KOH by elimination reaction gives alkene due to alkoxide reaction species.

Ex.10 Reduction of alkane nitrile gives –

(A) Primary amine

(B) Secondary amine

(C) Acid

(D) Nitro alkane **Ans. (A)**

Sol. By $LiAlH_4$ or any other reductant from alkane nitrile, primary amine is formed.

Ex.11 Tetra ethyl lead is used as an antiknocking agent, can be prepared by reacting ethyl chloride with –

(A) Sodium

(B) Sodium lead alloy

(C) lead

(D) Lead oxide **Ans. (B)**

Sol. TEL (tetra ethyl lead) is easily prepared by the reaction of ethyl chloride and Na-Pb alloy.

6. TYPES OF DIHALIDES

Dihalides are of two types : –

(a) Gem dihalide : –

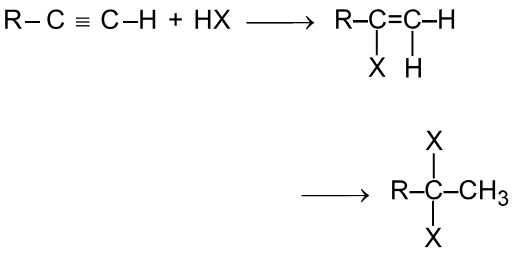
These are the halides in which two identical halogen atoms are attached on same carbon.

(b) Vicinal dihalide : –

In these halides two identical halogen atoms are attatched on adjacent carbon atoms.

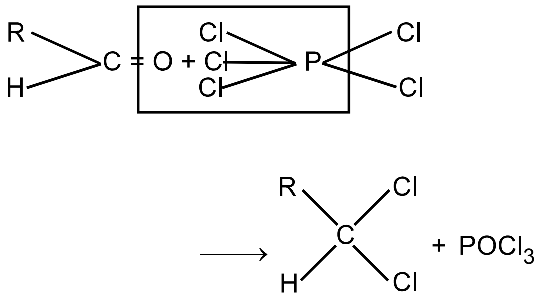
6.1 Methods of Preparation of Gem dihalides : –

(a) From Alkyne (By hydrohalogenation) : –



$$R-C\equiv C-H + HX \longrightarrow R-\underset{X}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-H \longrightarrow R-\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}-CH_3$$

(b) From carbonyl compounds : –

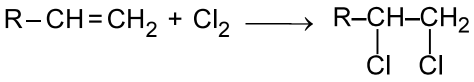


(terminal dihalide)

Note : If ketone is taken internal dihalide is formed.

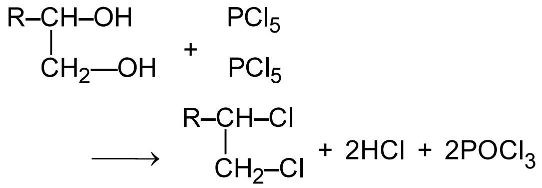
6.2 Methods of preparation of Vicinal dihalides :–

(a) From Alkene (By halogenation) :–



$$R-CH=CH_2 + Cl_2 \longrightarrow R-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$$

(b) From Vicinal glycol : –



$$\begin{array}{l}R-CH-OH\\ \quad |\\ \quad CH_2-OH\end{array} + \begin{array}{c}PCl_5\\ PCl_5\end{array} \longrightarrow \begin{array}{l}R-CH-Cl\\ \quad |\\ \quad CH_2-Cl\end{array} + 2HCl + 2POCl_3$$

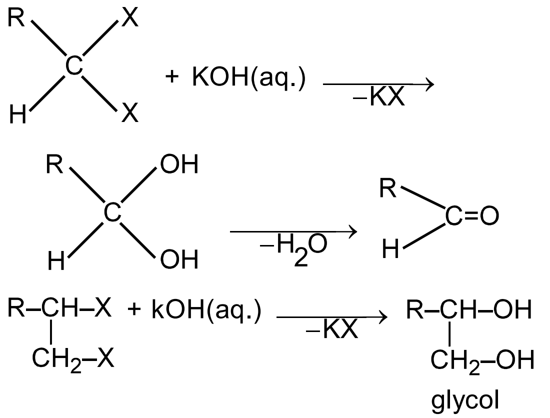
6.3 Physical properties of dihalides : –

(a) Dihalides are colourless with pleasant smell liquid. Insoluble in water, soluble in organic solvent.

(b) Melting point and boiling points are directly proportional to molecular mass but boiling point of vicinal dihalides are more than gem dihalides. Also, reactivity of vicinal dihalide is more than gemdihalide, but these are less reactive than monohalide.

6.4 Chemical Properties of dihalides : –

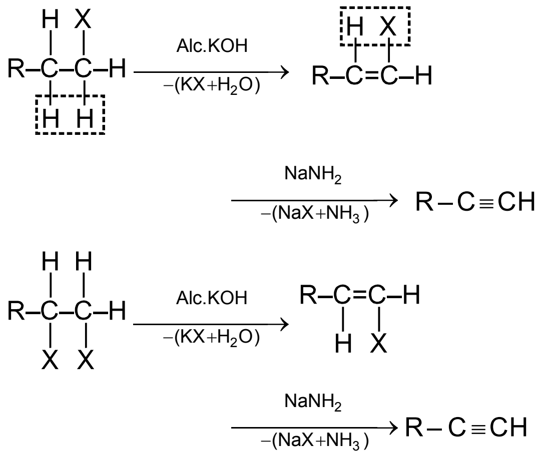
(a) Reaction with aqueous KOH : –



$$\begin{array}{l}R-CH-X\\ \quad |\\ \quad CH_2-X\end{array} + kOH(aq.) \xrightarrow[-KX]{} \begin{array}{l}R-CH-OH\\ \quad |\\ \quad CH_2-OH\end{array}$$

glycol

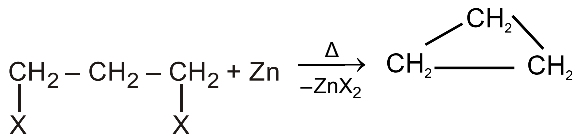
(b) Reaction with alcoholic KOH : –



(c) Reaction with zinc dust : –

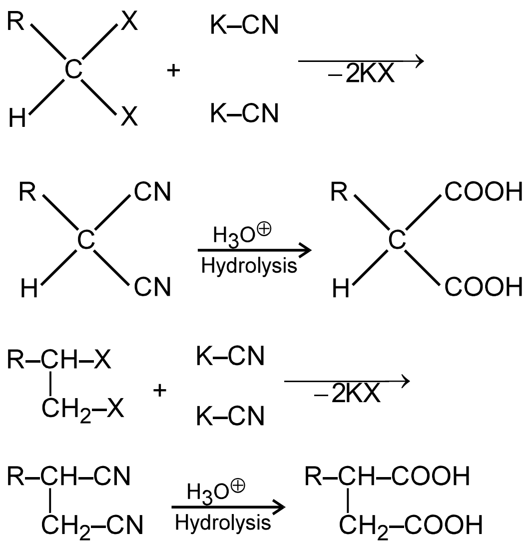
Gem dihalide reacts with Zn dust to form higher symmetrical alkene while vicinal dihalide reacts with Zn dust to form respective alkene.

Note – α , ω dihalide form cyclic alkane.



$$\underset{X}{\underset{|}{CH_2}}-CH_2-\underset{X}{\underset{|}{CH_2}} + Zn \xrightarrow[-ZnX_2]{\Delta}$$

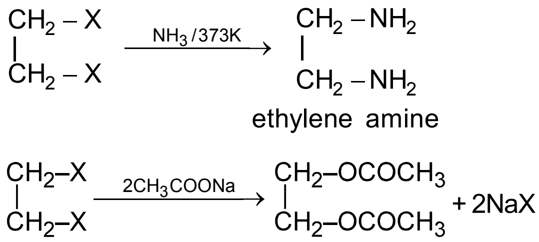
(d) Reaction with KCN : –



$$\begin{array}{l}R-CH-X\\ \quad |\\ \quad CH_2-X\end{array} + \begin{array}{c}K-CN\\ K-CN\end{array} \xrightarrow[-2KX]{}$$

$$\begin{array}{l}R-CH-CN\\ \quad |\\ \quad CH_2-CN\end{array} \xrightarrow[Hydrolysis]{H_3O^{\oplus}} \begin{array}{l}R-CH-COOH\\ \quad |\\ \quad CH_2-COOH\end{array}$$

(e) Other substitution reaction : –



$$\begin{array}{l}CH_2-X\\ |\\ CH_2-X\end{array} \xrightarrow{NH_3/373K} \begin{array}{l}CH_2-NH_2\\ |\\ CH_2-NH_2\end{array}$$

ethylene amine

$$\begin{array}{l}CH_2-X\\ |\\ CH_2-X\end{array} \xrightarrow{2CH_3COONa} \begin{array}{l}CH_2-OCOCH_3\\ |\\ CH_2-OCOCH_3\end{array} + 2NaX$$

Examples based on Dihalide

Ex.12 Ethylene glycol with PCl_5 gives –

(A) Ethylene chloride

(B) Ethyl chloride

(C) 1, 1–Dichloro ethane

(D) Oxyrane **(Ans. A)**

Sol. PCl_5 , replace-OH group by Cl to give chloroderivative., Here ethylene chloride is the product.

Ex.13 To form Malonic acid, we have to starts a reaction from –

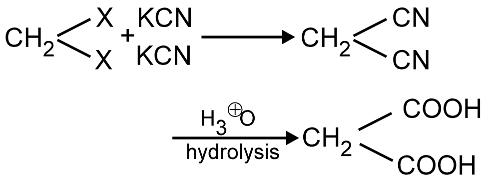
(A) Ethylidine chloride

(B) Methyl chloride

(C) Methylene chloride

(D) Chloro ethane **(Ans.C)**

Sol.



$$CH_2X_2 + 2KCN \longrightarrow CH_2(CN)_2 \xrightarrow[\text{hydrolysis}]{H_3^{\oplus}O} CH_2(COOH)_2$$

7. TRIHALIDES

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

7.1 Haloform Reaction : –

If any compound contains $CH_3-\underset{\underset{O}{\|}}{C}-H$ or $CH_3-\underset{\underset{O}{\|}}{C}-R$ group, (or may be oxidises in this group). When reacts with halogen and conc. alkali, trihalides are produced. Reaction is called as haloform reaction.

(a) $CaCl_2 + H_2O \longrightarrow Ca(OH)_2 + 2Cl^{\bullet}$

(b) $CH_3-CH_2-OH + 2Cl^{\bullet} \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-H + 2H-Cl$

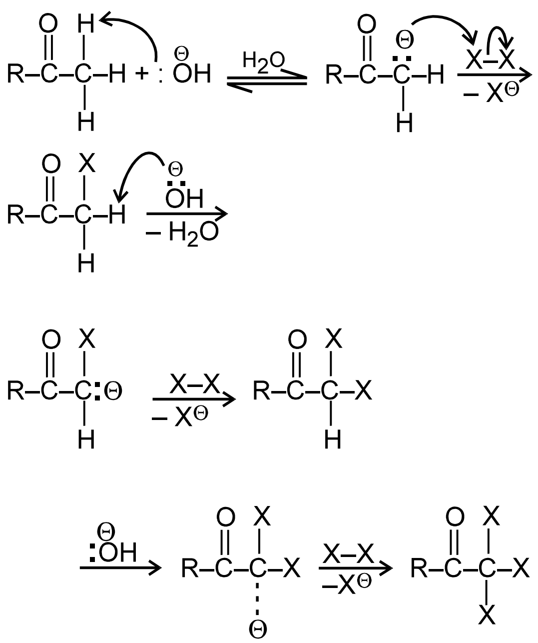
(c) $CH_3-\underset{\underset{O}{|}}{C}-H + 6Cl^{\bullet} \longrightarrow CCl_3-\underset{\underset{O}{\|}}{C}-H + 6HCl$

chloral

(d) $2CCl_3-\underset{\underset{O}{\|}}{C}-H + Ca(OH)_2 \longrightarrow 2CHCl_3 + (HCOO)_2Ca$

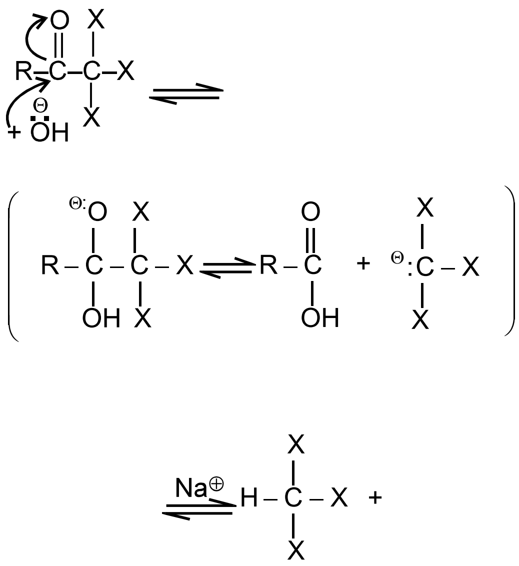
Mechanism of haloform reaction

(A) When methyl ketone reacts with halogen in the presence of aqueous base then acidic hydrogen of methyl group is substituted by halogen as follows:



tri haloketone

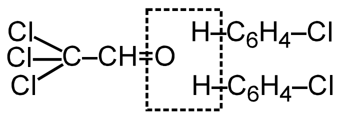
(B) Hydroxide ion of NaOH attacks on carbonyl group of trihaloketone and add, at last with breaking of C – C bond haloform is formed.

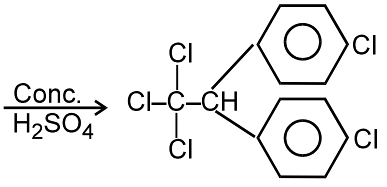


haloform

Note : –

(i) Chloral is an important compound and when it reacts with chlorobenzene in presence of conc. H_2SO_4, then it form an important compound DDT (Dichloro Diphenyl Trichloro ethane)

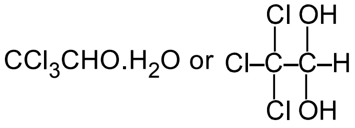




DDT

[1,1,1-trichloro-2,2-bis (parachloro phenyl) ethane]

(ii) Preparation of pure Chloroform – Alkaline solution of chlorohydrate is used in the formation of chloroform. Which on distillation gives pure chloroform as follows :



$CCl_3CHO.H_2O$ or $Cl-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-H$

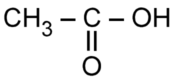
chloro hydrate

$\xrightarrow[\text{distillation}]{\text{NaOH}} CHCl_3 + HCOONa + H_2O$

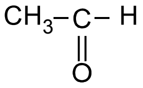
Examples based on

Haloform Reaction

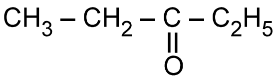
Ex.14 Which of the following shows haloform reaction : -

(A) 

$CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-OH$

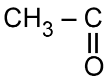
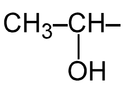
(B) 

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

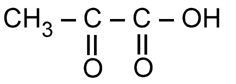
(C) 

$CH_3-CH_2-\underset{\underset{\displaystyle O}{\|}}{C}-C_2H_5$

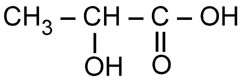
(D) None **(Ans. B)**

Sol. The compound containing  $CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-$ group or  $CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-$ group will show the haloform reaction.

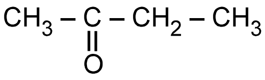
Ex.15 Which of the following shows haloform reaction : -

(A) 

$CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle O}{\|}}{C}-OH$

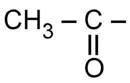
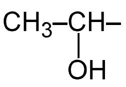
(B) 

$CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-\underset{\underset{\displaystyle O}{\|}}{C}-OH$

(C) 

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

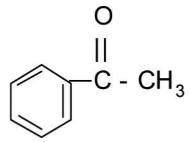
(D) All of above **Ans. (D)**

Sol. All of the above compounds contain  $CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-$ group or  $CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-$ group.

Ex.16 Which of the follwoing shows haloform reaction : -

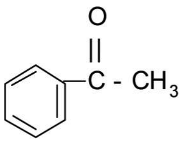
(A) CH_3 - OH

(B) CH_3 - COOH

(C) 

(D) None of these

Ans. (C)

Sol. The compound shows 

haloform reaction but in acetic acid typical > C = O group is absent due to resonance. So it will not show haloform reaction.

7.2 Preparation of trihalide using 'Pyrene' : –

$$CCl_4 + 2H \xrightarrow{\text{Fe/H}_2\text{O reduction}} CHCl_3 + HCl$$

7.3 Physical Properties : –

(a) Chloroform is colourless with pleasant smell. Insoluble in water and soluble in organic solvent. Vapours of chloroform are poisonous in nature. It cause temporary unconsciousness, so used as an anasthetic agent.

(b) Boiling point of $CHCl_3$ is 61° C.

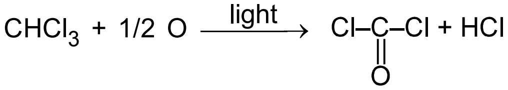
(c) It is best solvent for fats, oil and wax.

(d) Iodoform is yellow crystalline solid. It has melting point 119 °C.

7.4 Chemical Properties : –

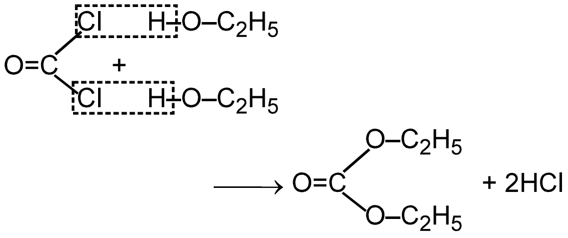
7.4.1 Oxidation : –

In presence of light it forms poisonous gas phosgene with atmospheric oxygen or with air.



$$\mathrm{CHCl_3 + 1/2\ O \xrightarrow{light} Cl-\underset{\underset{O}{\|}}{C}-Cl + HCl}$$

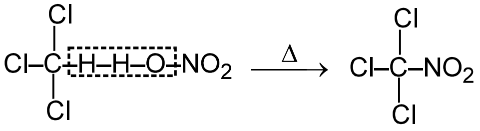
For protection it is kept into dark room in coloured bottle filling completely. For removal of phosgene we can use 0.5 to 1% ethanol solution which converts poisonous phosgene into non-poisonous salt diethyl carbonate.



Note :

We use silver nitrate solution to check the impurity of phosgene in solution which will form white ppt. of AgCl with HCl

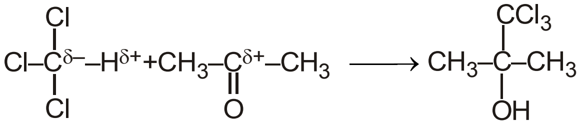
7.4.2 Reaction with HNO_3 : –



$$\mathrm{Cl-\overset{Cl}{\underset{Cl}{C}}-\boxed{H-H-O}-NO_2 \xrightarrow{\Delta} Cl-\overset{Cl}{\underset{Cl}{C}}-NO_2}$$

tear gas
(chloropicrin)

7.4.3 Reaction with Acetone : –



$$\mathrm{Cl-\overset{Cl}{\underset{Cl}{C^{\delta-}}}-H^{\delta+}+CH_3-\underset{\underset{O}{\|}}{C^{\delta+}}-CH_3 \longrightarrow CH_3-\overset{CCl_3}{\underset{OH}{C}}-CH_3}$$

chloretone

chloretone is used as a hypnotic agent.

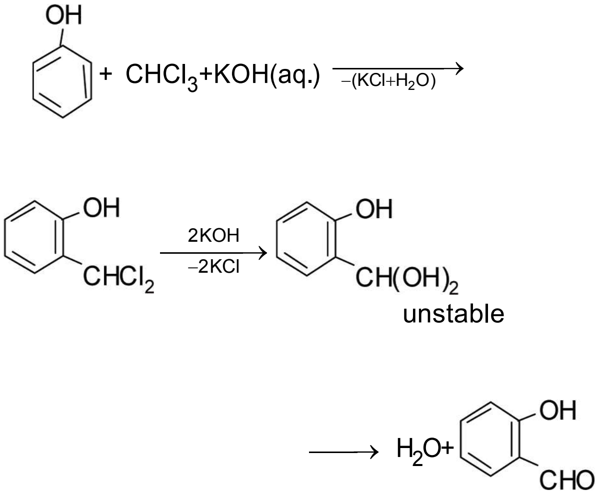
7.4.4 Reaction with Primary amine : –

$$\mathrm{R\ddot{N}H_2 + CHCl_3 + KOH\ (alc.) \longrightarrow R-N \overset{\rightarrow}{\equiv} C + KCl + H_2O}$$

The reaction is called as 'Hoffman-carbylamine Reaction' or 'Isocyanide-test'. These isocyanides (product) has offensive smell. So, the reaction is used to test 1° amine. Reacting species of reaction is dichloro carbene.

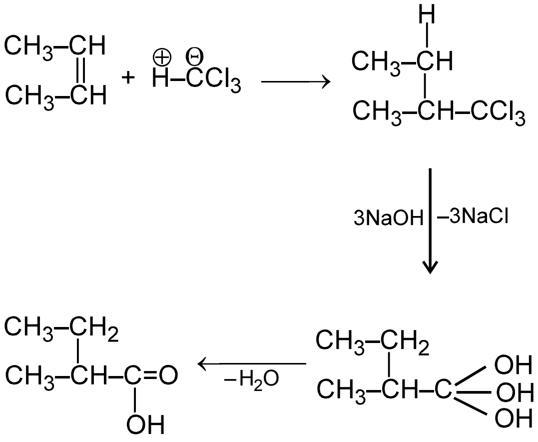
7.4..5 Reaction with Phenol : –

The reaction is called as '**Reimer-tiemann Formylation**'.



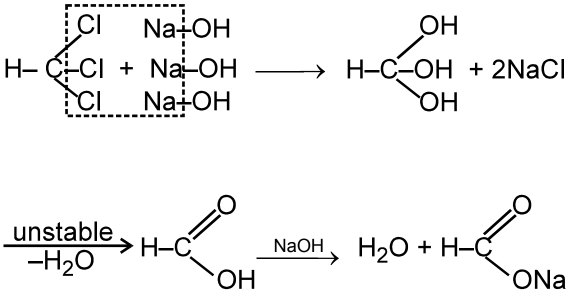
salicylaldehyde
or
(o-hydroxy benzaldehyde)

7.4.6 Reaction with 2- Butene : –



2–methyl butanoic acid

7.4.7 Reaction with Alcoholic KOH : –



7.4.8 Reaction with silver powder (Dehalogenation) : –

$$CHX_3 + 6\,Ag + X_3CH \xrightarrow[\text{temp}]{\text{high}} CH \equiv CH + 6\,AgX$$

7.4.9 Reduction : –

$$CHCl_3 \xrightarrow[\text{Zn/HCl(alc.)}]{+2H} CH_2Cl_2 + HCl$$

$$CHCl_3 \xrightarrow[\text{Zn/HCl(aq.)}]{+4H} CH_3Cl + 2HCl$$

$$CHCl_3 \xrightarrow[\text{Zn/}H_2O]{+6H} CH_4 + 3HCl$$

Examples based on Trihalide

Ex.17 Carbyl amine reaction is used for the test of–

(A) Primary aliphatic amine

(B) Primary aromatic amine

(C) Both of these

(D) Secondary amine aliphatic

Ans. (C)

Sol. In Hoffamann–Carbyl amine reaction, an offensive smell compound isocyanide is formed, therefore this reaction is used for the test of primary aliphatic and aromatic amine.

Ex.18 What will be the reduction product of following reaction –

$$CHCl_3 \xrightarrow[\text{Zn/HCl(alc.)}]{+2H} \xrightarrow[\text{Zn/HCl(aq.)}]{+4H} \xrightarrow[\text{Zn/}H_2O]{+6H}$$

(A) CH_2Cl_2, CH_3Cl, CH_4

(B) CH_4, CH_3Cl, CH_2Cl_2

(C) CH_3Cl, CH_2Cl_2, CH_4

(D) CH_3Cl, CH_4, CH_2Cl **Ans. (A)**

Sol. $CHCl_3 \xrightarrow[\text{Zn/HCl(alc.)}]{+2H} CH_2Cl_2 + HCl$

$$CHCl_3 \xrightarrow[\text{Zn/HCl(aq.)}]{+4H} CH_3Cl + 2HCl$$

$$\xrightarrow[\text{Zn/}H_2O]{+6H} CH_4 + 3HCl$$

8. TETRAHALIDE 'PYRENE'

8.1 General method of preparation : –

8.1.1 From CS_2 : –

$$CS_2 + 3Cl-Cl \xrightarrow[\text{Fe dust} + I_2]{\Delta\, 500°C} CCl_4 + S_2Cl_2$$

sulphur monochloride

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

The reaction is used for industrial production of CCl_4.

8.1.2 From CH_4 : –

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

$$\xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

8.1.3 From $CHCl_3$: –

$$CHCl_3 + Cl\text{ - }Cl \xrightarrow{\text{ultra violet light}} CCl_4 + HCl$$

8.2 Physical Properties : –

(a) It is colourless liquid with specific smell. It is insoluble in water and soluble in organic solvent.

(b) It is the only organic solvent which is non-combustible. So used as fire-extinguisher called as '**Pyrene**'.

8.3 Chemical Properties : –

(a) It reacts with hot H_2O or with water vapour and forms poisonous gas '**Phosgene**'.

$$CCl_4 + H_2O(g) \xrightarrow{\Delta} COCl_2 + 2HCl.$$

(b) It reacts with aqueous or alcoholic KOH and forms inorganic salt potassium carbonate.

$$CCl_4 + 4KOH\ (aq.) \xrightarrow[-4KCl]{} \underset{\text{(unstable)}}{C(OH)_4}$$

$$\xrightarrow[-2H_2O]{} CO_2 \xrightarrow{+2KOH} K_2CO_3 + H_2O$$

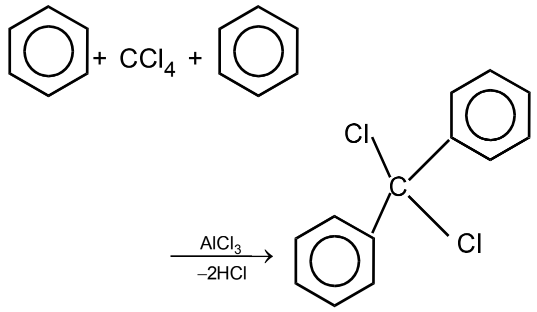
(c) It reacts with phenol and forms salicylic acid.

$$+ CCl_4 \xrightarrow{\text{alc.KOH}}$$

The reaction is called as '**Riemer-Tieman**

Carboxylation'.

(d) Reaction with benzene.



dichloro diphenyl methane

Examples based on

Tetra halide

Ex.19 Which one is used as a fire-extinguisher –

(A) CCl_4

(B) Pyrene

(C) Tetra chloro methane

(D) All the above **Ans. (D)**

Sol. Carbon tetra chloride (CCl_4) is also known as commercial name 'Pyrene' and used as a fire-extinguisher due to the incombustible vapour.

Ex.20 Water vapour react with CCl_4, to give a poisonous gas named as –

(A) Chloral (B) Chloroform

(C) Carbonyl chloride (D) tear gas

Ans. (C)

Sol. $CCl_4 + H_2O(g) \xrightarrow{\Delta} COCl_2 + 2HCl.$

9. FREONS

These are poly chlorofluoro derivative of alkane.

9.1 Preparation of freons : –

$$CCl_4 + HF \xrightarrow{SbCl_5} CCl_3F + HCl$$

$$C_2Cl_6 + 2HF \xrightarrow{SbCl_5} C_2F_2Cl_4 + 2HCl$$

hexachloro ethane freons–112

9.2 Nomenclature of Freons : –

The common name of freons is Freon - cba or freon C - 1, H + 1, F, where c = no. of carbon atom –1, b = no. hydrogen atom + 1, a = total no. of atoms of fluorine eg. $CFCl_3$ C – 1 = 0, H + 1 = 1, F = 1 Freon - 11

Formula	C-1	H + 1	F	Name
$CFCl_3$	1 – 1 = 0	0 + 1 = 1	1	Freon-11
CF_2Cl_2	1 - 1 = 0	0 + 1 = 1	2	Freon-12
$C_2F_2Cl_4$	2 - 1 = 1	0 + 1 = 1	2	Freon-112
$C_2F_3Cl_3$	2 - 1 = 1	0 + 1 = 1	3	Freon-113
$C_2F_4Cl_2$	2 - 1 = 1	0 + 1 = 1	4	Freon-114
C_2F_5Cl	2 - 1 = 1	0 + 1 = 1	5	Freon-115

9.3 Properties & uses of freons : –

(a) Freons are colourless, odourless, unreactive & non-combustible liquids.

(b) Having very low boiling points (e.g CF_2Cl_2 = – 29.8ºC).They easily converted from gaseous state to liquid state, therefore they are used as a coolant in A.C. & Refrigerator.

(c) Used as a aerosole propellant in aroplane & rockets.

(d) Also used as a solvent.

Note : Main cause of Ozone layer decay (CFC – chlorofluoro carbon)

Examples based on

Freons

Ex.21 Freon–112 is formed by –

(A) $C_2F_2Cl_4$ (B) CCl_4

(C) $CHCl_3$ (D) $CHCl_2F$

Ans. (A)

Sol. $CCl_4 + HF \xrightarrow{SbCl_5} CCl_3F + HCl$

$CHCl_3 + HF \xrightarrow{SbCl_5} CHCl_2F + HCl$

$C_2Cl_6 + 2HF \xrightarrow{sbcl_5} C_2F_2Cl_4 + 2HCl$

hexachloro ethane freon – 112

Ex.22 $C_2F_3Cl_3$ is named as –

(A) Freon–112 (B) Freon–111

(C) Freon–113 (D) Freon–114

Ans. (C)

Sol. Named as follows –

C – 1, H + 1, F

or C – 1 = 1, O + 1 = 1, 3

SOLVED EXAMPLE

Ex.1 Addition of bromine on propene in the presence of brine yields a mixture of -

(A) $CH_3CHClCH_2Br$ and $CH_3CHBrCH_2Cl$

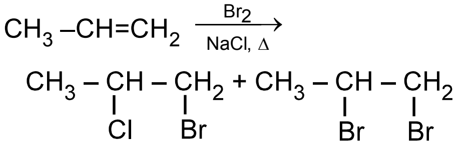
(B) $CH_3CHClCH_2Br$ and $CH_3CHBrCH_2Br$

(C) $CH_3CHClCH_2Cl$ and $CH_3CHBrCH_2Br$

(D) $CH_3CHClCH_2Cl$ and $CH_3CHBrCH_2Cl$

(Ans. B)

Sol. Addition of bromine on propene in the presence of brine solution yields a mixture of $CH_3CHClCH_2Br$ and $CH_3CHBrCH_2Br$.



$$CH_3-CH=CH_2 \xrightarrow[NaCl,\ \Delta]{Br_2} \underset{Cl}{CH_3-\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}} + CH_3-\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}}$$

1 - bromo, 2-chloro propane 1,2 dibromo propane

Ex.2 The reaction of $SOCl_2$ on alkanols to form alkyl chlorides gives good yields because -

(A) Alkyl chlorides are immiscible with $SOCl_2$

(B) The other products of the reaction are gaseous and escape out

(C) Alcohol and $SOCl_2$ are soluble in water

(D) The reaction occurs via intermediate formation of an alkyl chloro sulphite

(Ans.B)

Sol. The reaction of $SOCl_2$ on alkanols to form alkyl chlorides gives good yields because the other products of the reaction are gaseous and escape out.

$$\underset{\text{ethanol}}{C_2H_5OH} + Cl\text{-}SO\text{-}Cl \rightarrow \underset{\text{ethylchloride}}{C_2H_5Cl} + SO_2\uparrow + HCl$$

It is one of the most important methods for preparing alkyl halides.

Ex.3 A carbon compound A forms B with sodium metal and again A forms C with PCl_5 but B and C form diethylether. Therefore A, B & C are -

(A) C_2H_5OH, C_2H_5ONa, C_2H_5Cl

(B) C_2H_5Cl, C_2H_5ONa, C_2H_5OH

(C) C_2H_5OH, C_2H_6, C_2H_5Cl

(D) C_2H_5OH, C_2H_5Cl, C_2H_5ONa

(Ans.A)

Sol.

$$\underset{(A)}{2C_2H_5\text{-}OH} + 2Na \rightarrow \underset{(B)}{2C_2H_5ONa} + H_2$$

$$\underset{(A)}{C_2H_5\text{-}OH} + PCl_5 \rightarrow \underset{(C)}{C_2H_5\text{-}Cl} + POCl_3 + HCl$$

$$\underset{(B)}{C_2H_5\text{-}ONa} + \underset{(C)}{C_2H_5\text{-}Cl} \rightarrow \underset{\text{diethyl ether}}{C_2H_5\text{-}O\text{-}C_2H_5} + NaCl$$

Ex.4 The best reagent for converting ethanol to chloroethane is -

(A) PCl_3 (B) PCl_5

(C) $SOCl_2$ (D) $HCl + ZnCl_2$

(Ans.C)

Sol. $ROH + SOCl_2 \rightarrow RCl + SO_2 + HCl$. It is evident that products other than RCl, are both gases (SO_2, HCl)

Ex.5 In Hunsdiecker reaction -

(A) A sodium salt of an acid reacts with bromine

(B) A calcuim salt of an acid reacts with HBr

(C) A silver salt of an acid reacts with bromine

(D) A silver salt of an acid reacts with HBr

(Ans.C)

Sol. In Hunsdiecker reaction a silver salt of an acid reacts with bromine in the presence of CCl_4.

$$\underset{\text{silver ethanoate}}{CH_3COOAg} + Br_2 \xrightarrow{CCl_4} \underset{\text{bromomethane}}{CH_3Br} + CO_2 + AgBr$$

It is an important method of preparing an alkyl halide from a silver salt of an alkanoic acid.

Ex.6 The yield of alkyl bromide obtained as a result of heating the dry silver salt of carboxyic acid with bromine what will be the order of formation w.r.t. alkyl bromide –

(A) 1° > 3° > 2° bromides

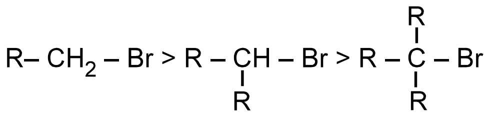
(B) 1° > 2° > 3° bromides

(C) 3° > 2° > 1° bromides

(D) 3° > 1° > 2° bromides **(Ans.B)**

Sol. $R - COOAg + Br_2 \xrightarrow{CCl_4} R - Br + CO_2 + AgBr\downarrow$

The yield of alkyl bromide has the following order



$$R-CH_2-Br > R-\underset{R}{\underset{|}{CH}}-Br > R-\overset{R}{\overset{|}{\underset{R}{\underset{|}{C}}}}-Br$$

Since the mechanism of this reaction involves formation of free radicals.

Ex.7 The compound with no dipole moment is -

(A) Methyl chloride

(B) Carbon tetrachloride

(C) Methylene chloride

(D) Chloroform **(Ans.D)**

Sol. Carbon tetrachloride (CCl_4) has tetrahedral structure and its 4 polar C-Cl bond cancels each others dipole moment which results in net dipole moment zero.

Ex.8 True about alkyl halides is/are -

(A) Tertiary alkyl halides undergo S_N^2 substitutions

(B) Alkyl iodides on exposure to sunlight gradually darken

(C) Alkyl chlorides do not give beilstein test

(D) A nucleophilic substitution is most difficult in alkyl iodides

(Ans.B)

Sol. When alkyl halides are exposed to sunlight they becomes darken.

Ex.9 The correct order of density is -

(A) $C_2H_5I > C_2H_5Br > C_2H_5Cl$

(B) $C_2H_5 > C_2H_5Br > C_2H_5I$

(C) $C_2H_5Cl > C_2H_5I > C_2H_5CBr$

(D) None **(Ans.A)**

Sol. Density of a given alkyl group increases with increase in atomic weight of halogen atom. but for a given halogen density decreases with increase in size of alkyl group.

Ex.10 Action of alcoholic $AgNO_3$ on chlorobenzene is similar to the action on -

(A) Allyl chloride (B) Vinyl chloride

(C) Isopropyl chloride (D) Benzyl chloride

(Ans.B)

Sol. Both vinyl chloride and chlorobenzene give no precipitate with alcoholic $AgNO_3$ because both have chlorine atoms which are not reactive.

Ex.11 The number of steps involved in S_N^1 and S_N^2 mechanisms are given by the set -

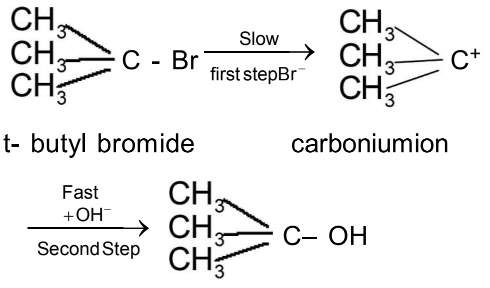
(A) 1,2 (B) 3,1

(C) 2,1 (D) 2,2

(Ans.C)

Sol. The number of step involved in S_N^1 and S_N^2 mechanisms are given by the set 2,1

The S_N^1 reaction takes place in 2 steps as follows



t- butyl bromide carboniumion

t-butanol

The S_N^{II} reaction takes place in 1 step as follows -

$$CH_3 - Br \xrightarrow[Slow]{+OH^-} [HO----CH_3----Br]$$

methyl bomide (one step transition state)

$$\xrightarrow{fast} CH_3OH + Br^-$$

methanol

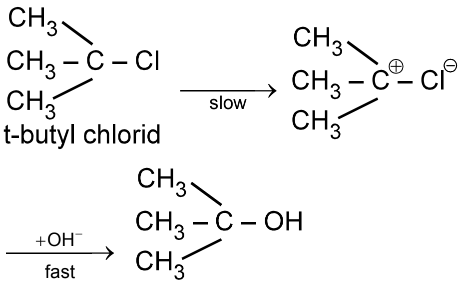
Ex.12 Tertiary butyl halide on boiling with water gives tertiary butyl alcohol. The reaction follows -

(A) SE mechanism (B) S_N^I mechanism

(C) S_N^2 mechanism (D) E^1 mechanism

(Ans.B)

Sol. Tertiary butyl halide on boiling with water gives tertiary butyl alcohol. The reaction following S_N^I mechanism.



t-butyl chlorid

t-butyl alcohol

The slow step is the formation of a carbonium ion, hence the reaction takes place via S_N^I mechanism.

Ex.13 Inversion of configuration of the product alcohol during the hydrolysis of an optically active halide is an experimental evidence for-

(A) S_N^2 mechanism (B) S_N^i mechanism

(C) S_N^1 mechanism (D) A carbanion

(Ans. A)

Sol. Inversion of configuration of the product alcohol during the hydrolysis of an optically active halide is an experimental evidence for S_N2 mechanism. The reaction takes place as follows :

$CH_3 - Cl + OH^- \rightarrow [HO \text{-------} CH_3 \text{-----} Cl]$
chloromethane transition state

$\rightarrow HO - CH_3 + Cl^-$
methanol

Here OH^- attacks from the back side on CH_3Cl molecule, hence the product formed has an inverted configuration.

Ex.14 Ethyl bromide and isopropyl chloride can be distinguished by -

(A) Alcoholic $AgNO_3$
(B) Comparing their colours
(C) Burning the compounds on spatula
(D) Aqueous KOH solution **(Ans.A)**

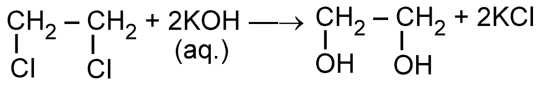
Sol. With alcoholic $AgNO_3$, ethyl bromide gives a light yellow and isopropyl chloride gives white ppt.

Ex.15 The compound $C_2H_4Cl_2$ has two isomers and they can be distinguished by the reaction with -

(A) Aq. KOH (B) Alc. KOH
(C) Bromine water (D) $NaNH_2$

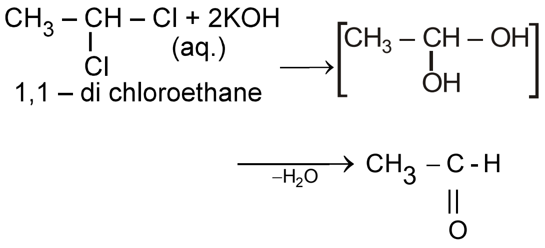
(Ans.A)

Sol.



$$\underset{Cl}{CH_2} - \underset{Cl}{CH_2} + \underset{(aq.)}{2KOH} \longrightarrow \underset{OH}{CH_2} - \underset{OH}{CH_2} + 2KCl$$

1,2 dichloroethane ethane – 1,2 – diol



$$CH_3 - \underset{Cl}{CH} - Cl + \underset{(aq.)}{2KOH} \longrightarrow \left[CH_3 - \underset{OH}{CH} - OH\right] \xrightarrow[-H_2O]{} CH_3 - \underset{\overset{||}{O}}{C} - H$$

1,1 – di chloroethane

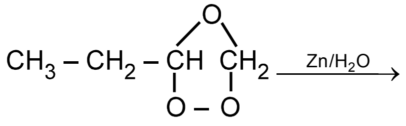
Ex.16 An unkown alkyl halide (A) reacts with alcoholic KOH to produce a hydrocarbon (C_4H_8). Ozonolysis of the hydrocarbon affords one mole of propionaldehyde and one mole of formaldehyde. Suggest which organic structure among the following is the correct structure of the above alkyl halide (A) -

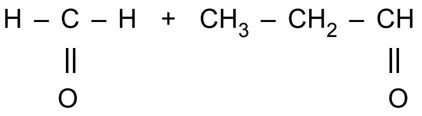
(A) $CH_3(CH_2)_3$ Br
(B) $CH_3CH(Br)$ $CH(Br)CH_3$
(C) $CH_3CH_2CH(Br)CH_3$
(D) $Br(CH_2)_4$ Br **(Ans.A)**

Sol. $CH_3–CH_2–CH_2–CH_2–Br$ + KOH (Alcoholic)

$\xrightarrow{\Delta} CH_3 - CH_2 - CH = CH_2$
1– butene

$CH_3 - CH_2 - CH = CH_2 + O_3 \longrightarrow$





$$H - \underset{\overset{||}{O}}{C} - H + CH_3 - CH_2 - \underset{\overset{||}{O}}{CH}$$

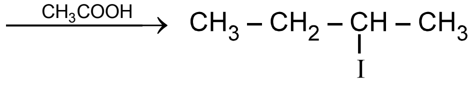
Ex.17 Which one of the following pairs of reaction types included in the reaction sequence below -

$CH_3CH = CHCH_3$ + HI (in CH_3COOH)
$\rightarrow CH_3CH_2CHICH_3$
$CH_3CH_2CHICH_3$ + NaOH(aq)
$\rightarrow CH_3CH_2CH(OH)CH_3$

(A) Electrophilic addition and electrophilic substitution
(B) Electrophilic addition and nucleophilic substitution
(C) Nucleophilic addition and electrophilic substitution
(D) Nucleophilic addition and free radical substitution

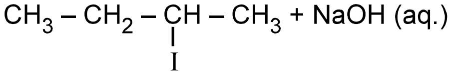
(Ans.B)

Sol. $CH_3 - CH = CH - CH_3 + HI$

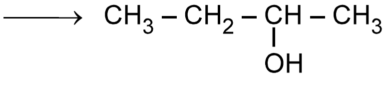


$$\xrightarrow{CH_3COOH} CH_3 - CH_2 - \underset{I}{CH} - CH_3$$

(electrophilic addition reaction)



$$CH_3 - CH_2 - \underset{I}{CH} - CH_3 + NaOH\ (aq.)$$



$$\longrightarrow CH_3 - CH_2 - \underset{OH}{CH} - CH_3$$

(nucleophilic substitution reaction)

Ex.18 An alkyl isocyanide is prepared by -

(A) Heating an amide with P_2O_5
(B) Reacting an alcohol with NH_3
(C) The action of AgCN on alkyl halide
(D) The action of KCN on alkyl halide

(Ans.3)

Sol. An alkyl isocyanide is prepared by the action of AgCN on alkyl halide

$$CH_3\ Cl + AgCN \longrightarrow \underset{\text{methanisonitrile}}{CH_3\ N \overset{\rightarrow}{=} C} + AgCl$$

Isonitrile on reduction produces secondary amine.

Ex.19 $CH_3Br \xrightarrow{AgCN} A \xrightarrow{H_3O^+} B$, [B] is -

(A) $CH_3\ NH_2$ (B) $(CH_3)\ NH$

(C) $C_2H_5\ NH_2$ (D) $CH_3\ COOH$

(Ans. A)

Sol. $CH_3 - Br + AgCN \longrightarrow CH_3 - N \overset{\rightarrow}{=} C\ (A)$

$\xrightarrow{H_3O^+} CH_3NH_2\ (B) + HCOOH$

Ex.20 Action of sodium ethoxide on an alkyliodide is -

(A) A nucleophillic addition

(B) An electrophillic addition

(C) A nucleophillic substitution

(D) An electrophillic subsititution

(Ans.C)

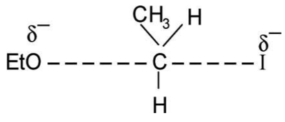
Sol. Action of sodium ethoxide on an alkyl iodide is a nucleophillic substitution.

$C_2H_5I + NaOC_2H_5 \rightarrow C_2H_5OC_2H_5 + NaI$

$C_2H_5I\ +\ EtO^- \rightarrow C_2H_5\ O\ C_2H_5 + I^-$

The reaction takes place by $S_N{}^2$ mechanism

$C_2H_5\ O^- + C_2\ H_5\ I \rightarrow$



$\rightarrow C_2\ H_5\ OC_2H_5\ +\ I^-$

transition state

Ex.21 Reaction of ethyl bromide and silver acetate gives -

(A) Ethyl ethanoate

(B) Methyl ethanoate

(C) Ethanoic anhydride

(D) 2-Butanone **(Ans.A)**

Sol. Reaction of ethyl bromide and silver acetate gives ethyl ethanoate It is an ester formation and has got a fruity smell.

$CH_3COO\ Ag + BrC_2H_5$

silver acetate

$\rightarrow CH_3COOC_2H_5 + AgBr \downarrow$

ethyl ethanoate

Ex.22 Ethyl bromide reacts with lead sodium alloy to form -

(A) Tetraethyl lead

(B) Tetraethyl bromide

(C) (A) and (B) both

(D) Lead bromide **(Ans.C)**

Sol. $C_2H_5 - Br + 4Pb/Na \xrightarrow[\Delta]{\text{High pressure}}$

$\underset{\text{tetraethyl lead}}{(C_2H_5)_4Pb} + 4\ NaBr + 3Pb$

T.E.L. is used as antiknocking agent.

Ex.23 The name of the reaction of an alkyl halide with an arene in the presence of anhydrous $AlCl_3$ is -

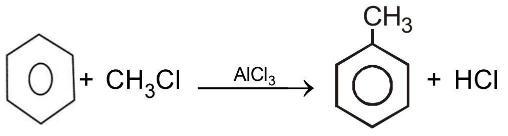
(A) Friedel Craft's reaction

(B) Grignard reaction

(C) Wurtz-fitting reaction

(D) Wurtz reaction **(Ans.A)**

Sol. The name of the reaction of an alkyl halide with an arene in the presence of anhydrous $AlCl_3$ is Friedel Craft's reaction



benzene toluene

It is an electrophillic substitution reaction.

Ex.24 Br - CH_2 - CH_2 - CH_2Br can be converted into HOOC - CH_2 - CH_2 - CH_2COOH by employing -

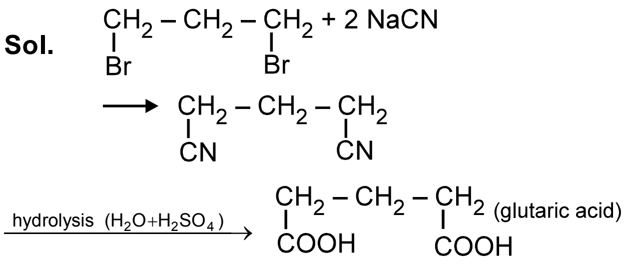
(A) NaCN, $H_2O + H_2SO_4$

(B) NaCl, $H_2O + H_2SO_4$

(C) $H_2O + H_2SO_4$, $KMnO_4$

(D) KCl, $H_2O + H_2SO_4$ **(Ans.A)**

Sol.



$$\underset{\mid \atop Br}{CH_2}-CH_2-\underset{\mid \atop Br}{CH_2}+2\,NaCN \longrightarrow \underset{\mid \atop CN}{CH_2}-CH_2-\underset{\mid \atop CN}{CH_2}$$

$$\xrightarrow{\text{hydrolysis }(H_2O+H_2SO_4)} \underset{\mid \atop COOH}{CH_2}-CH_2-\underset{\mid \atop COOH}{CH_2} \text{ (glutaric acid)}$$

Ex.25 Which of the following statements is correct-

(A) Formaldehyde on heating with I_2 and alkali gives a yellow ppt.

(B) Ethanol is the only primary alcohol which gives haloform reaction.

(C) All secondary alcohols give haloform reaction.

(D) All ketones give haloform reaction.

(Ans.2)

Sol. The correct statement is that ethanol is the only primary alcohol which gives haloform reaction.

$$CH_3\,CH_2\,OH \xrightarrow[+NaOH]{+I_2} I_3\,C.\,CHO$$

ethanol　　　　　iodal

$$\xrightarrow{+NaOH} CHI_3 \text{ (Iodoform)} + HCOONa$$

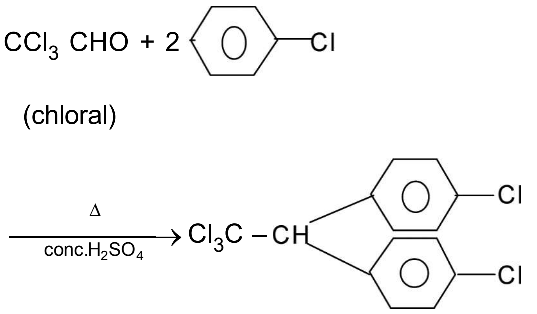
Ex.26 The main compound obtained when chlorobenzene is heated with chloral in presence of conc. H_2SO_4 -

(A) DDT　　(B) TNT

(C) BHC　　(D) Chloretone

(Ans.A)

Sol.



β, β ' - dichloro diphenyl trichloroethane (D.D.T)

Ex.27 Which of the following does not give white precipitate when boiled with alcoholic silver nitrate -

(A) Allyl chloride　　(B) t-butyl chloride

(C) Chlorobenzene　　(D) Benzyl chloride

(Ans. C)

Sol. In chlorobenzene the electron lone pair of chlorine atom is in conjugation with benzene ring and hence chlorine atoms takes part in resonance and chlorobenzene does not show removal of chloride ion readily therefore it does not give white precipitate with alcoholic silver nitrate.

Ex.28 A sample of chloroform being used as an anaesthetic is tested by -

(A) Fehling solution

(B) Ammoniacal CuCl solution

(C) $AgNO_3$ solution

(D) $AgNO_3$ solution after boiling with alc. KOH

(Ans.C)

Sol. Chloroform is tested by silver nitrate solution if chloroform is oxidised to phosgene then HCl will also be present which reacts with $AgNO_3$ to form white precipitate (AgCl). If this reaction occur then chloroform is not used for anaesthesia.

Ex.29 The hydrogen atom in chloroform is -

(A) Acidic　　(B) Basic

(C) Neutral　　(D) None

(Ans.A)

Sol. Due to - I effect, Cl atoms tend to attract the electrons of C - H bond towards themselves.

Ex.30 Iodoform gives a precipitate with $AgNO_3$ on heating but chloroform does not because -

(A) Iodoform is ionic

(B) Chloroform is covalent

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

(D) None

(Ans.C)

Sol. On heating C - I bond breaks, but C - Cl bond does not break. Thus, $AgNO_3$ gives AgI with iodoform.

Ex.31 Pyrene is the commerical name of -

(A) Degreasing agent $CHCl_3$

(B) Fire extinguisher CCl_4

(C) Insecticide CHI_3

(D) Aerosol, propellant, $C_2Cl_4\,F_2$

(Ans.B)

Sol. Pyrene is the commerical name of a fire extinguisher CCl_4. It is the only organic cmpound which is non inflammable and which is used to extinguish fire.