# HALOALKANES AND HALOARENES
# POLYHALOGEN COMPOUNDS

## POLYHALOGEN DERIVATIVES

Trichloromethane (Chloroform), $CHCl_3$

**1. Preparation**

$$CH_4 + Cl_2 \xrightarrow{hv} CH_3Cl + HCl$$
Chloromethane

$$CH_3Cl + Cl_2 \xrightarrow{hv} CH_2Cl_2 + HCl$$
Dichloromethane

$$CH_2Cl_2 + Cl_2 \xrightarrow{hv} CHCl_3 + HCl$$
Trichloromethane

$$CHCl_3 + Cl_2 \xrightarrow{hv} CCl_4 + HCl$$
Tetrachloromethane

The mixture of $CH_3Cl$,$CH_2Cl_2$,$CHCl_3$ and $CCl_4$ can be separated by fractional distillation.

**2. From chloral hydrate, Pure chloroform can prepare.**

$$NaOH + CCl_3CHO \rightarrow HCOONa + CHCl_3$$
chloral

$$NaOH + CCl_3CH(OH)_2 \rightarrow HCOONa + CHCl_3 + H_2O$$
Chloral hydrate — sodium format — Chloroform

**3. Laboratory Method:** By reacting with a mixture of bleaching powder and water, one can obtain it from either ethanol or acetone.

In case of ethanol, the reaction occurs as follows

$$CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$$

$$CH_3CH_2OH + Cl_2 \xrightarrow{\text{Oxidation}} CH_3CHO + 2HCl$$

$$CH_3CHO + 3Cl_2 \xrightarrow{\text{Chlorination}} CCl_3CHO + 3HCl$$
Chloral

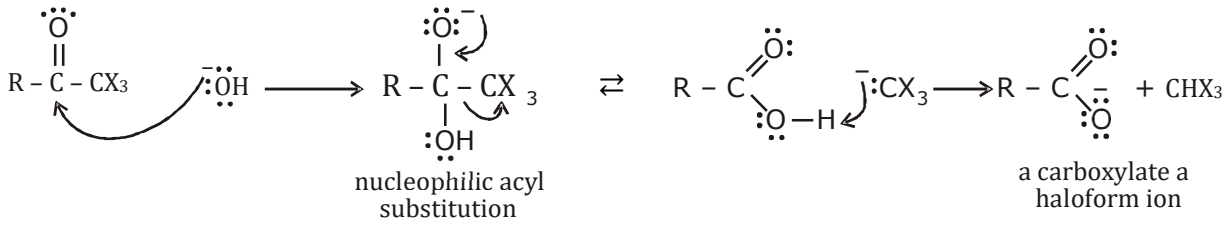
$$Ca(OH)_2 + 2CCl_3CHO \xrightarrow{\text{Hydrolysis}} 2CHCl_3 + (HCOO)_2Ca$$
Chloroform — Calcium formate

**4. From carbon tetrachloride**

$$CCl_4 + 2[H] \xrightarrow[\text{Heat}]{Fe/H_2O} CHCl_3 + HCl \text{ (partial reduction)}$$

**5. Haloform reaction**

$$\underset{\text{methyl ketone}}{R-\overset{O}{\overset{\|}{C}}-CH_3} + 3X_2 + 3OH^- \longrightarrow \underset{\text{Tri halomethyl ketone}}{R-\overset{O}{\overset{\|}{C}}-CX_3} + 3X^- + 3H_2O$$
(methyl ketone)



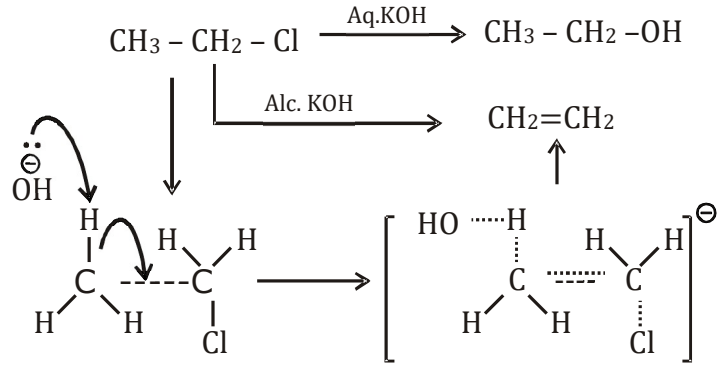

(Haloform)

Step 1: Attack of the nucleophile

Step 2: Elimination of the leaving group

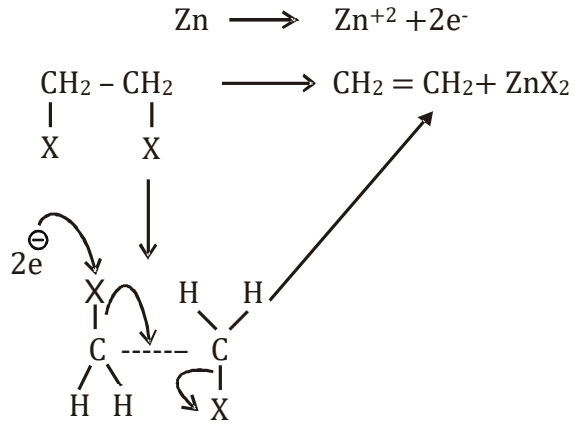
Step 3: Proton transfer

**Dehyodro halegenation (–HX) E2**




Anti-elimination

**Dehalogenation: – ($-X_2$) E2**



Anti-elimination

**$E_c$ or $E_i$ (Intramolecular or cyclic elimination mechanism)**

(1) Lg and Base present in same molecule

(2) It proceeds by cyclic transition state.

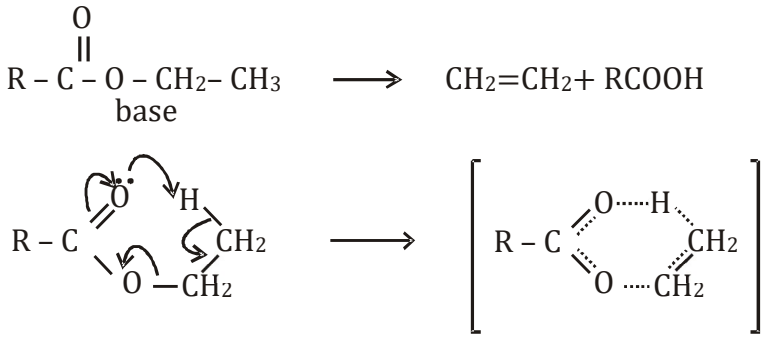
(3) Overall, it is syn ellimination.

(4) Hoffmann is major product as it is obtain by least hinberd site/cyclic transition state.

(5) No rearrangement.

**Example of $E_C/E_i$**

**Pyrolysis of Ester**



1. $CH_3{-}CH_2{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}O{-}CD_2CH_3 \xrightarrow[E/E]{\Delta} CH_2{=}CD_2{+}CH_3CH_2COOD$

2. $CH_3{-}CH_2{-}CH_2{-}\overset{\overset{O^{18}}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}CH_3 \xrightarrow[E_C/E_i]{\Delta} CH_3{-}CH{=}CH_2{+}CH_3CH_2{-}\overset{\overset{O^{18}}{\|}}{C}{-}OH$

## PHYSICAL PROPERTIES OF CHLOROFORM

Chloroform is a colorless, dense liquid with a sweet and somewhat unpleasant odor and taste. It has a boiling point of 334º K and exhibits slight solubility in water. Being denser than water, chloroform can induce unconsciousness when its vapors are inhaled, making it suitable for use as an anesthetic agent in surgical procedures.

## CHEMICAL PROPERTIES OF CHLOROFORM

**1. Action of sun light and air**

$$2\,CHCl_3 + O_2 \xrightarrow{\text{SUN LIGHT}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

To maintain the high purity of chloroform for its anesthetic use, it is recommended to store it in opaque bottles (such as brown or blue) that block out active light radiation. Additionally, the bottles should be filled to the brim to exclude air. Furthermore, a small amount of ethanol (usually around 1%) is often added to chloroform bottles. This addition of ethanol helps to convert the toxic $COCl_2$ into non-poisonous diethyl carbonate.

$$COCl_2 + 2C_2H_5OH \rightarrow \underset{\text{diethyl carbonate}}{O = C(OC_2H_5)} + 2HCl$$

**2. Hydrolysis**

$$H - CCl_3 + (aq.)\ 3KOH \xrightarrow[-H_2O]{-3kcl} H - \underset{\underset{O}{\|}}{C} - O - H \xrightarrow[-H_2O]{+KOH} HCOOK$$

**3. Reduction**

$$Zn + 2HCl \rightarrow ZnCl_2 + 2[H]$$

$$CHCl_3 + 2[H] \rightarrow CH_2Cl_2 + HCl$$

Dichloromethane
(Methylene chloride)

$$CHCl_3 \xrightarrow{Zn + H_2O} CH_4 + 3HCl$$

**4. Reaction with acetone**

$$(CH_3)_2C = O + CHCl_3 \xrightarrow{KOH} CH_3-\underset{\underset{CCl_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

Chlroetone

**Use:** Chlroetone is used as hypnotic (a sleep inducing) drug.

**5. Reaction with nitric acid**

$$2CHCl_3 + HONO_2 \rightarrow CCl_3.NO_2 + H_2O$$

(chloropicrin)

**Use:** Chloropicrin is used as an insecticide and war gas.

**6. Reaction with silver powder**

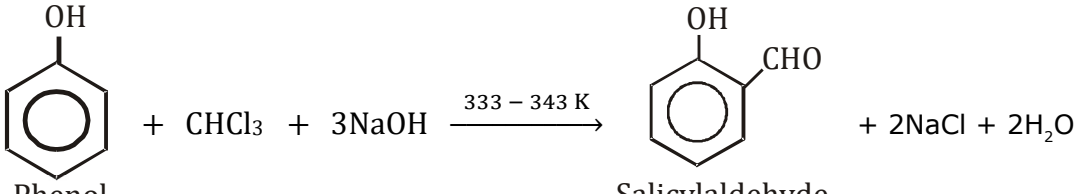
$$2CHCl_3 + 6\ Ag \xrightarrow{Heat} CH \equiv CH + 6\ AgCl$$

(Acetylene)

**7. Chlorination**

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} CCl_4 + HCl$$

**8. Reimer-Tiemann reaction**




Phenol

Salicylaldehyde
(2-Hydroxybenzeldehyde)

## USES OF CHLOROFORM

1. As solvent in oils and varnishes
2. As preservative for anatomical specimens
3. As laboratory reagent
4. As an anaesthetic