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## Reaction with Mg metal

• **Grignard reagent** can be prepared by reacting *magnesium metal* with **haloalkane**.

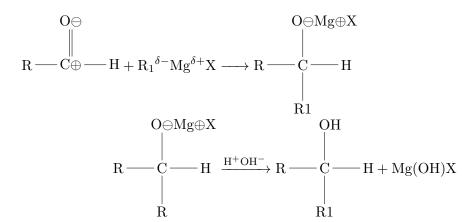
$$\begin{array}{c} R-X+Mg \xrightarrow{Inert\ Condition} RMgX \\ CH_3-CH_2-X+Mg \xrightarrow{Inert\ Condition} CH_3-CH_2-MgX \end{array}$$

## **Applications of Grignard Reagent**

### **Reaction with Carbonyl Compounds**

- Reaction with formaldehyde
  - Formaldehyde reaction with Grignard reagent always yields  $1^\circ$  alcohol on hydrolysis .

- Reaction with *aldehydes* other than **formaldehyde**.
  - Aldehydes other than formaldehyde always yield secondary alcohol on hydrolysis



- · Reaction with Ketones
  - Reaction with **ketones** always yields **tertiary alcohol** on hydrolysis.

$$\begin{array}{c|c} O & OMgX \\ \hline \\ R - C - R1 + R_2MgX \longrightarrow R - C - R1 \\ \hline & R2 \\ \hline & OMgX & OH \\ \hline \\ R - C - R1 \xrightarrow{H^+OH^-} R - C - R1 + Mg(OH)X \\ \hline \\ & R2 & R2 \end{array}$$

- · Reaction with Carbon Dioxide
  - Reaction of *Grignard reagent* with **Carbon dioxide** yields carboxylic acid on **hydrolysis**.

# Preparation of chloroform

## Reagents

- · Chloroform can be prepared by:
  - Acetone or Ethanol
  - Bleaching Powder

## Role of bleaching powder in preparation

• Bleaching Powder treated with water is taken in preparation.

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

- acts as:
  - 1. **hydrolysing** agent.
- acts as:
  - 1. **chlorinating** agent.
  - 2. oxidising agent.

#### **Reaction with Ethanol**

1. Oxidisation of Ethanol into acetaldehyde:

$$\begin{array}{c|c} H & O \\ \hline \\ CH3 & \hline \\ C & OH + Cl_2 & \longrightarrow CH3 & \hline \\ \\ H & \\ \end{array} \\ \begin{array}{c} CH3 & \hline \\ \\ C & \hline \\ \end{array} \\ H + HCl$$

2. Chlorination of acetaldehyde to form trichloroacetaldehyde

### 3. Hydrolysis of trichloroacetaldehyde

## Reaction with propanone

#### 1. Chlorination of acetone to trichloroacetone

#### 2. Hydrolysis of tricholoroacetone to chloroform

## **Labratory Praparation**

- 1. **Paste** of **bleaching powder** is dissolved in *water* .
  - Amount of bleaching powder: 100gm.
  - Amount of water: 200ml .

- 2. The *mixture* of **bleaching powder** is taken in
  - round bottom flask.
- 3. 25ml of **acetone** or **propanone** are added.
- 4. The **R.B.** flask is fitted with **condenser**.
- 5. The **condenser** is fitted with **reciever**.
- 6. **Chloroform** is formed.
- 7. Chloroform is distilled.

### **Purification of Chloroform**

- 1. The chloroform contains **acidic** *impurities* .
- 2. Chloroform is treated with dil. NaOH.
- 3. Aqueous layer is rejected by separating funnel.
- 4. **Chloroform** is washed with water.
- 5. Water removes salt by dissolution.
- 6. Chloroform is treated with anh. .
- 7. **Chloroform** is distilled.
- 8. The boiling point of **chloroform** is  $61^{\circ}$  .
- 9. Chloroform obtained is:
  - · pure
  - · dry

## **Physical Properties**

- · Chloroform is sweet.
- Boiling point: 61°.
- Melting point:  $-63^{\circ}$  .
- · Chloroform dissolves organic substances.

- Chloroform is heavier than water.
- · Vapour of chloroform induces unconsiousness.
- · Chloroform is used as anaesthetic.

## **Chemical Properties**

### **Phosgene**

- · Reaction of chloroform with oxygen yields carbonyl chloride.
- · Carbonyl chloride is also called phosgene .
- This reaction occurs in the **presence** of *sunlight* .

$$\begin{array}{c|c} Cl & & \\ \hline & \\ 2\,Cl & \hline & C & \hline \\ Cl & & Cl & \hline \\ & & \\ &$$

- Phosgene is highly poisonous.
- · Intake of phosgene attacks the C.N.S.
- This can result in immediate death.

#### **Precautions of storage of phosgene**

- · Phosgene is **stored** in:
  - dark brown bottle.
  - dark brown bottle reflects sunlight.
- Phosgene is **filled** till **stopper**.
  - This leaves **no air** inside the bottle.
- · Small amount of ethanol is added in the bottle.
  - Ethanol converts phosgene to diethyl carbonate.
  - Diethyl carbonate is non poisonous. Diethyl carbonate is volatile.

$$\begin{array}{c} O \longrightarrow CH2 \longrightarrow CH3 \\ \\ 2\,CH_3 - CH_2 - OH + Cl \longrightarrow C \longrightarrow C \longrightarrow O \\ \\ \\ Cl \end{array} + 2\,HCl \\ \\ Cl \longrightarrow CH2 \longrightarrow CH3 \end{array}$$

## Test of purity of chloroform

- Impure chloroform contains phosgene.
- Pure chloroform doesnot
  - give white ppt. on reaction with
- Impure chloroform containing phosgene
  - gives white ppt. on reaction with

### Reaction with acetone

- Reaction of acetone with chloroform yields:
  - Chlorotene
  - Chlorotene is a sleep inducing drug.
  - Chlorotene is a hypnotic drug.

### **Reaction with Nitric Acid**

• Reaction of *chloroform* with Nitric Acid yields chloropicrin.

- The another name for **chloropicrin** is **war gas**.
- The another name for **chloropicrin** is **tear gas**.
- The another name for **chloropicrin** is **trichloromethane**.
- Chloropicrin is used as insecticide .

$$\begin{array}{c|c} Cl & Cl \\ \hline \\ Cl & Cl \\ \hline \\ Cl & Cl \\ \hline \end{array}$$

## Reaction with silver powder

• Reaction of *chloroform* with *silver powder* yields **silver chloride** .

$$\begin{array}{c} Cl \\ H \longrightarrow C \longrightarrow Cl + 6 \, Ag + Cl \longrightarrow C \longrightarrow H \longrightarrow 6 \, AgCl + HC \Longrightarrow CH \\ Cl \end{array}$$

### Reaction with chlorine

• Reaction of *chloroform* with **chlorine** yields **carbon tetrachloride**.

$$\begin{array}{c|c} Cl & Cl \\ \hline \\ Cl & Cl \\ \hline \\ Cl & Cl \\ \hline \end{array}$$

#### Reduction

### Reduction with $Zn, H_2O$

· produces nascent hydrogen.

· Nascent hydrogen replaces all chlorine to form methane.

$$CHCl_3 + 6 [H] \xrightarrow{Zn, H_{20}} CH_4 + 3 HCl$$

### Reduction with Zn, HCl

- produces nascent hydrogen.
- · Nascent hydrogen partially replaces chlorine to form

$$\mathrm{CHCl}_3 + 2\,[\mathrm{H}] \longrightarrow \mathrm{CH}_2\mathrm{Cl}_2 + \mathrm{HCl}$$

## Reaction with primary amine

- · Chloroform on reacting only with
  - primary amine
  - gives alkyl isocyanide
    - \* Alkyl isocyanide is also called carbylamine.
    - \* Carbylamine has a pungent smell.
    - \* The smell is *analogus* to **rotten onion** .

## Reaction with aqueous KOH or NaOH

- Reaction of aqueous or  ${\it NaOH}$  yields methanoic acid .

## Reaction of Chloroform with Phenol

- Chloroform on reacting with phenol gives salicyaldehyde as major product .
- The other name for this reaction is **Reimer -Tiemann reaction**

OH OH CHO 
$$+ \mathrm{CHCl_3} + \mathrm{KOH} \longrightarrow + CHO$$

## **Uses of Chloroform**

- · Chloroform is used:
  - as **solvent**.
  - to prepare chloretene and chloropicrin

### - in test of **primary amine**

## lodoform

The molecular formula for iodoform is .

• lodoform has almost similar chemical properties to chloroform.

#### **lodoform test**

For iodoform test the molecules must have one among the two structures.

The term [?] in the box can be either or .

#### **Nature of iodoform**

When the molecules satisfying the above structural units are:

- treated with
  - aqueous alkali
  - excess

The product is an

- · yellow coloured
- crystalline
- solid

The nature of smell of such product is called hospital smell. The product obtained is iod-oform.

#### Uses of iodoform

lodoform is use in:

- antiseptic
  - This use of idoform comes form it's property to release iodine.

### **Alcohols**

$$\begin{array}{c|c} 2\operatorname{NaOH} + \operatorname{I}_2 & \longrightarrow \operatorname{NaOI} + \operatorname{NaI} + \operatorname{H}_2\operatorname{O}) \times 4 \\ & & OH & & O \\ & & & & \\ & & & & \\ & & & & \\ & & &$$

The final reaction can be expressed as:

## **Aldehydes and Ketones**

$$\begin{array}{c} 2\operatorname{NaOH} + \operatorname{I}_2 \longrightarrow \operatorname{NaOI} + \operatorname{NaI} + \operatorname{H}_2\operatorname{O}) \times 4 \\ \\ O & \\ O & \\ \\ \operatorname{CH3} \longrightarrow \operatorname{C} \longrightarrow \operatorname{R} + 3\operatorname{NaOI} \xrightarrow{\operatorname{iodination}} \operatorname{CI3} \longrightarrow \operatorname{C} \longrightarrow \operatorname{R} + 3\operatorname{NaOH} \\ \\ O & \\ \\ \operatorname{CI3} \longrightarrow \operatorname{C} \longrightarrow \operatorname{R} + \operatorname{NaOH} \longrightarrow \operatorname{CHI}_3 + \operatorname{RCOONa} \end{array}$$

The final reaction can be expressed as:

$$CH3 \longrightarrow C \longrightarrow R + NaOH + I_2 \longrightarrow CHI_3 + RCOONa + NaI + H_2O$$

### **Special Cases for alcohol**

- Only one primary alcohol can give iodoform test.
  - Methanol
- Tertiary alcohol donot give iodoform test.
- · Secondary alcohol only give iodoform test if:
  - the alcohol has an structure of 2-ol

### Special cases for carbonyl compounds

- The only aldehyde that gives iodoform test is:
  - ethanal
- Ketone only give positive iodoform test if there structure is 2-one