Contents

Reaction with Mg metal

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

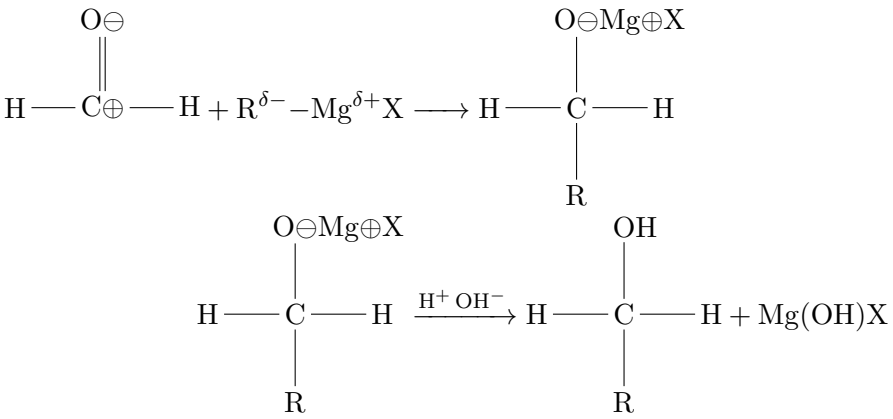
$$\mathrm{R{-}X + Mg \xrightarrow[\text{Dry Ether}]{\text{Inert Condition}} RMgX}$$

$$\mathrm{CH_3{-}CH_2{-}X + Mg \xrightarrow[\text{Dry Ether}]{\text{Inert Condition}} CH_3{-}CH_2{-}MgX}$$

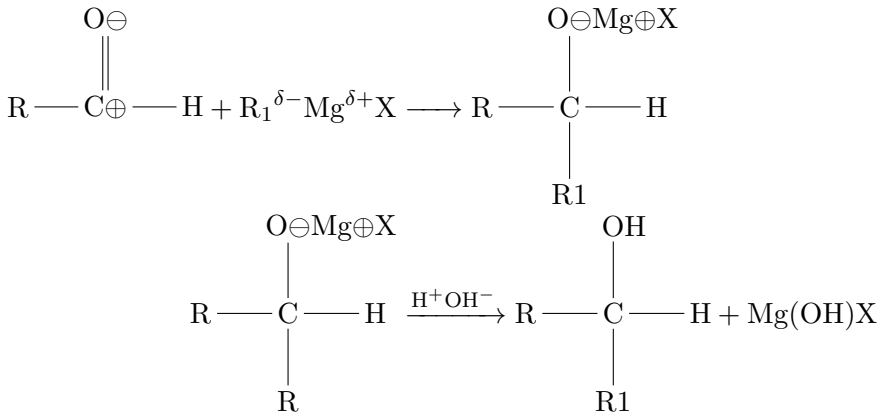
Applications of Grignard Reagent

Reaction with Carbonyl Compounds

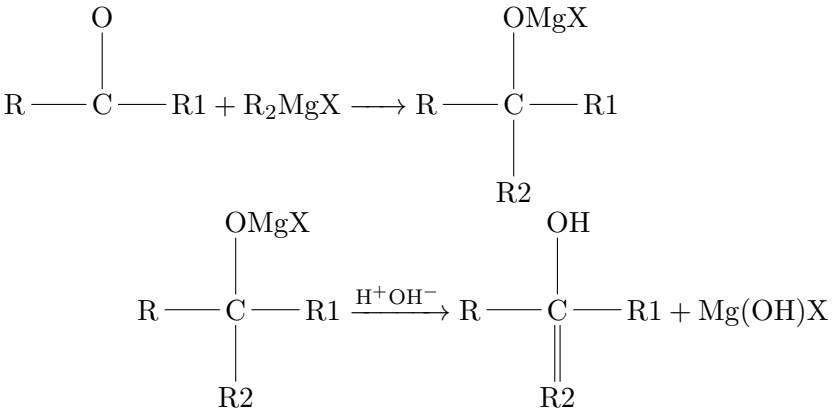
- Reaction with **formaldehyde**
  - **Formaldehyde** reaction with **Grignard reagent** always yields 1° alcohol on **hydrolysis** .



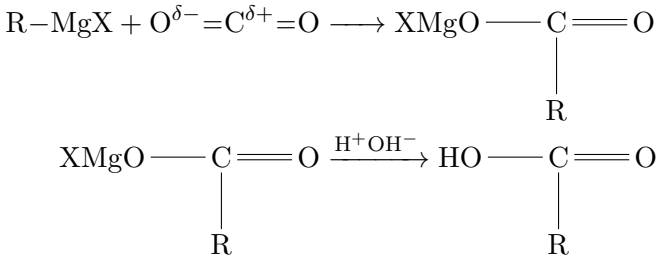
- Reaction with *aldehydes* other than **formaldehyde.**
  - **Aldehydes** other than *formaldehyde* always yield **secondary** alcohol on **hydrolysis**



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



- 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

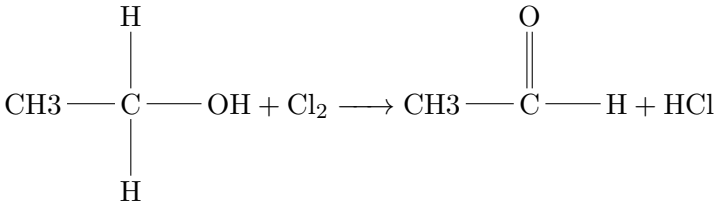
- **Bleaching Powder** treated with *water* is taken in *preparation* .

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

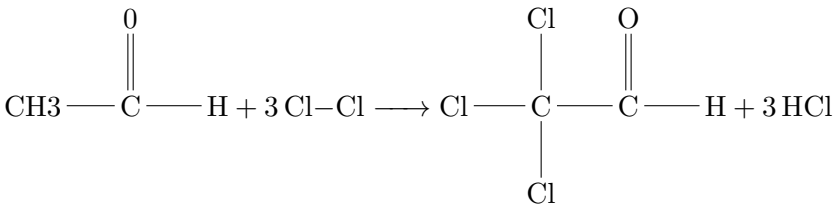
- acts as:
  1. **hydrolysing** agent.
- acts as:
  1. **chlorinating** agent.
  2. **oxidising** agent.

Reaction with Ethanol

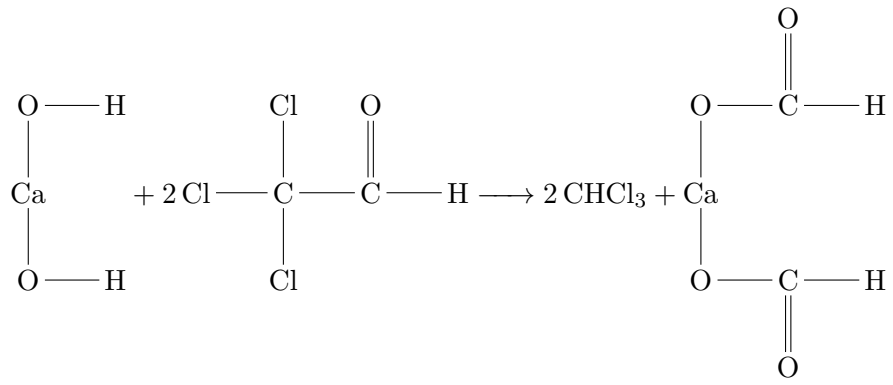
1. **Oxidisation** of Ethanol into **acetaldehyde** :



2. **Chlorination** of **acetaldehyde** to form **trichloroacetaldehyde**

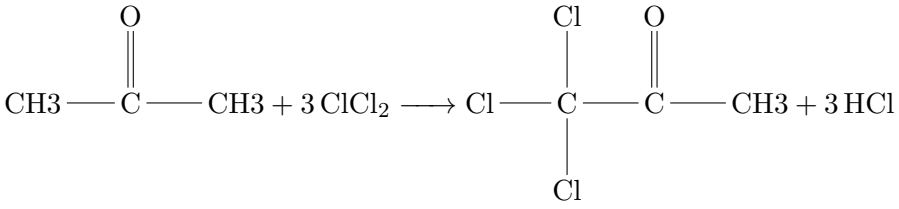


3. **Hydrolysis** of **trichloroacetaldehyde**

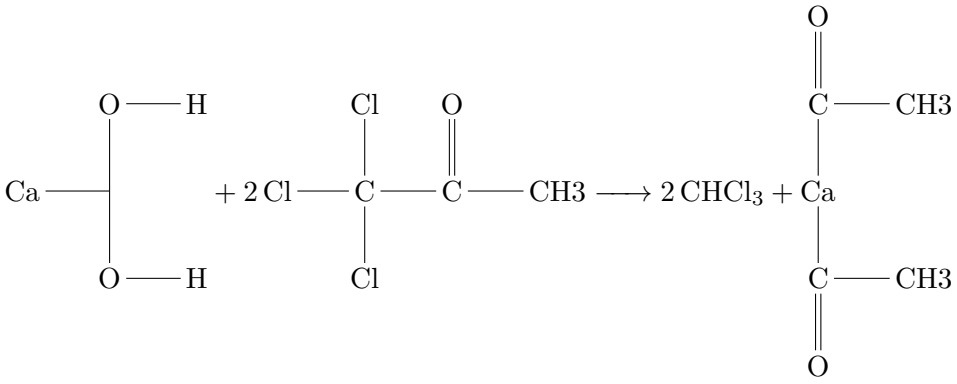


Reaction with propanone

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 $61°$.
9. **Chloroform** obtained is:
    - **pure**
    - **dry**

Physical Properties

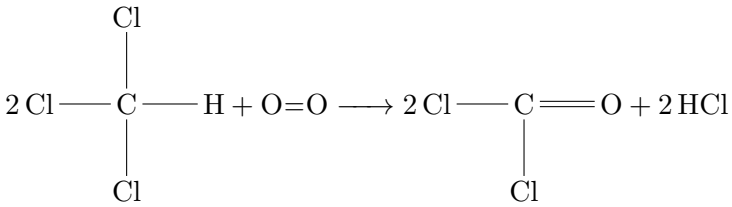
- **Chloroform** is **sweet** .
- **Boiling point:** $61°$.
- **Melting point:** $-63°$.
- **Chloroform** dissolves **organic substances.**

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

Chemical Properties

Phosgene

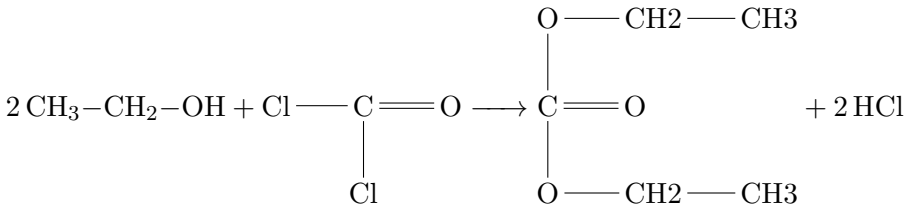
- **Reaction** of **chloroform** with **oxygen** yields **carbonyl chloride** .
- **Carbonyl chloride** is also called **phosgene** .
- This reaction occurs in the **presence** of *sunlight* .



- **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** .

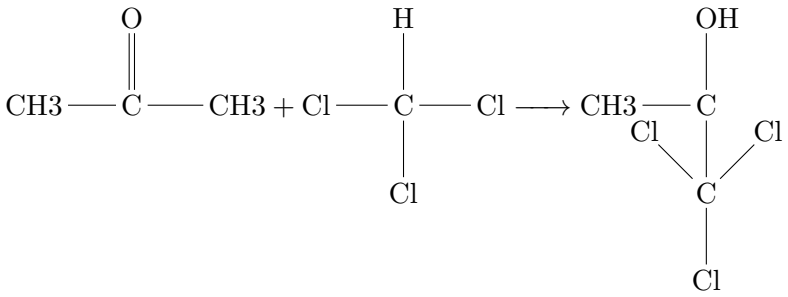


Test of purity of chloroform

- *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.

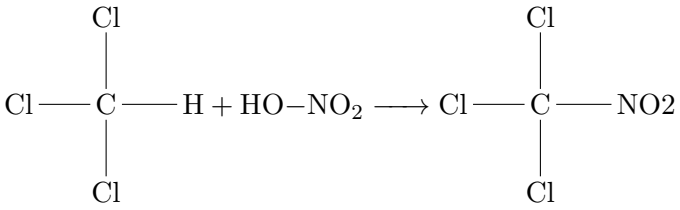


Reaction with Nitric Acid

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

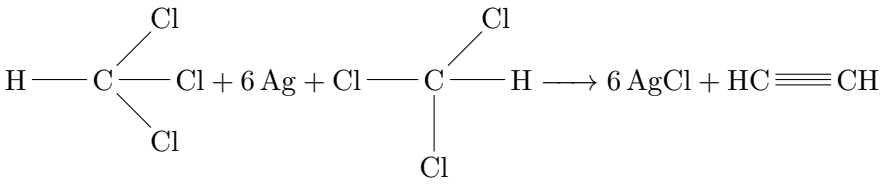
- The another name for **chloropicrin** is **war gas** .
- The another name for **chloropicrin** is **tear gas** .
- The another name for **chloropicrin** is **trichloromethane** .

- **Chloropicrin** is used as *insecticide* .



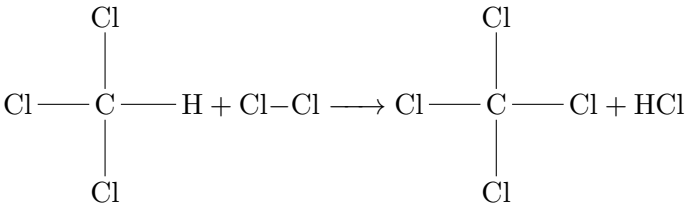
Reaction with silver powder

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



Reaction with chlorine

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



Reduction

Reduction with Zn, H_2O

- produces **nascent hydrogen** .

- **Nascent hydrogen** replaces all **chlorine** to form **methane** .

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

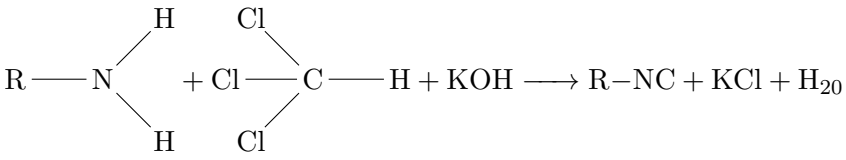
Reduction with Zn, HCl

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

$$\mathrm{CHCl_3 + 2\,[H] \longrightarrow CH_2Cl_2 + HCl}$$

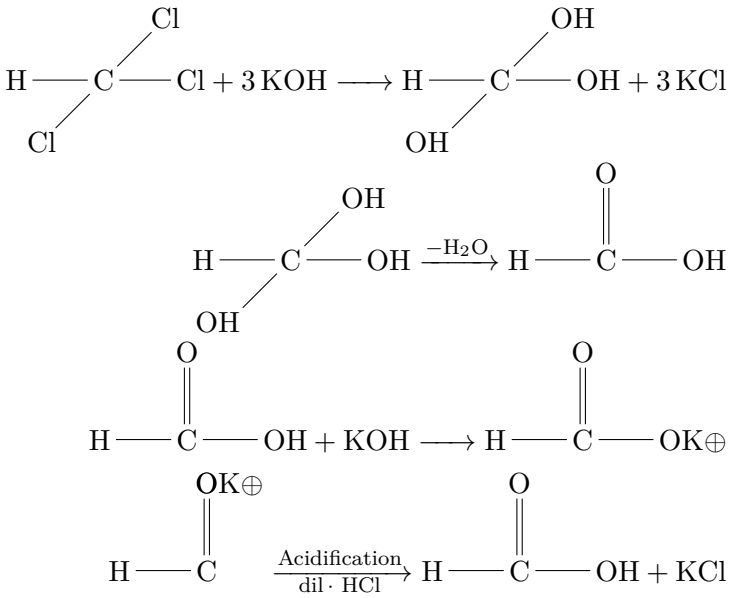
Reaction with primary amine

- **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** .



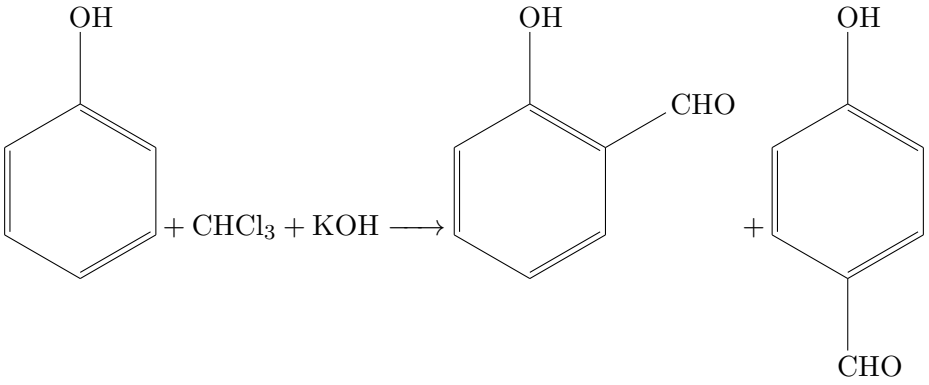
Reaction with aqueous KOH or $NaOH$

- **Reaction** of aqueous or $NaOH$ **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**



Uses of Chloroform

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

- in test of **primary amine**

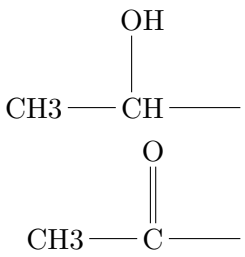
Iodoform

The molecular formula for iodoform is .

- Iodoform has almost similar chemical properties to chloroform.

Iodoform 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 iodoform.

Uses of iodoform

Iodoform is use in:

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

Alcohols

$$2\,\mathrm{NaOH} + \mathrm{I_2} \longrightarrow \mathrm{NaOI} + \mathrm{NaI} + \mathrm{H_2O)} \times 4$$

$$\mathrm{CH3-\overset{\overset{\mathrm{OH}}{|}}{CH}-R} + \mathrm{NaOI} \xrightarrow{\text{oxidation}} \mathrm{CH3-\overset{\overset{\mathrm{O}}{\|}}{C}-R} + \mathrm{NaI} + \mathrm{H_2O}$$

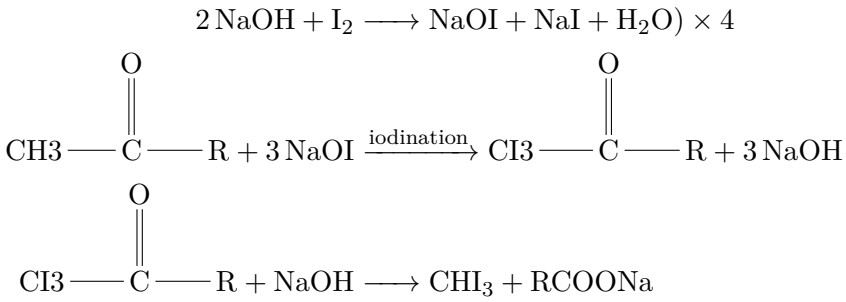
$$\mathrm{CH3-\overset{\overset{\mathrm{O}}{\|}}{C}-R} + 3\,\mathrm{NaOI} \xrightarrow{\text{iodination}} \mathrm{CI3-\overset{\overset{\mathrm{O}}{\|}}{C}-R} + 3\,\mathrm{NaOH}$$

$$\mathrm{CI3-\overset{\overset{\mathrm{O}}{\|}}{C}-R} + \mathrm{NaOH} \longrightarrow \mathrm{CHI_3} + \mathrm{RCOONa}$$

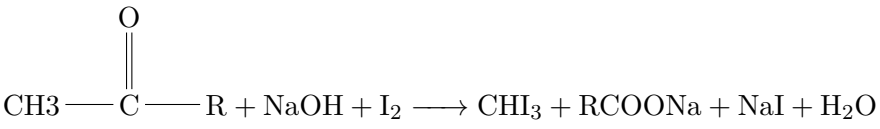
The final reaction can be expressed as:

$$\mathrm{CH3-\overset{\overset{\mathrm{OH}}{|}}{C}-R} + \mathrm{NaOH} + \mathrm{I_2} \longrightarrow \mathrm{CHI_3} + \mathrm{RCOONa} + \mathrm{NaI} + \mathrm{H_2O}$$

Aldehydes and Ketones



The final reaction can be expressed as:



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