Short + long

DATE

CHLOROFORM

NEB

Lab preparation →

In lab, chloroform is prepared by heating ethyl alcohol or acetone with bleaching powder paste.

Bleaching powder paste behaves like an oxidizing agent, chlorinating agent and hydrolysing agent.

$$CaOCl_2 + H_2O \xrightarrow{\Delta} Ca(OH)_2 + Cl_2$$

(bleaching powder)

A. **From alcohol →**

1) Oxidation of ethyl alcohol → chlorine oxidises.

→ chlorine oxidises ethyl alcohol or ethanol

$$CH_3 - CH_2OH + Cl_2 \xrightarrow{\Delta} CH_3 - \underset{H}{\overset{O}{C}} + HCl$$

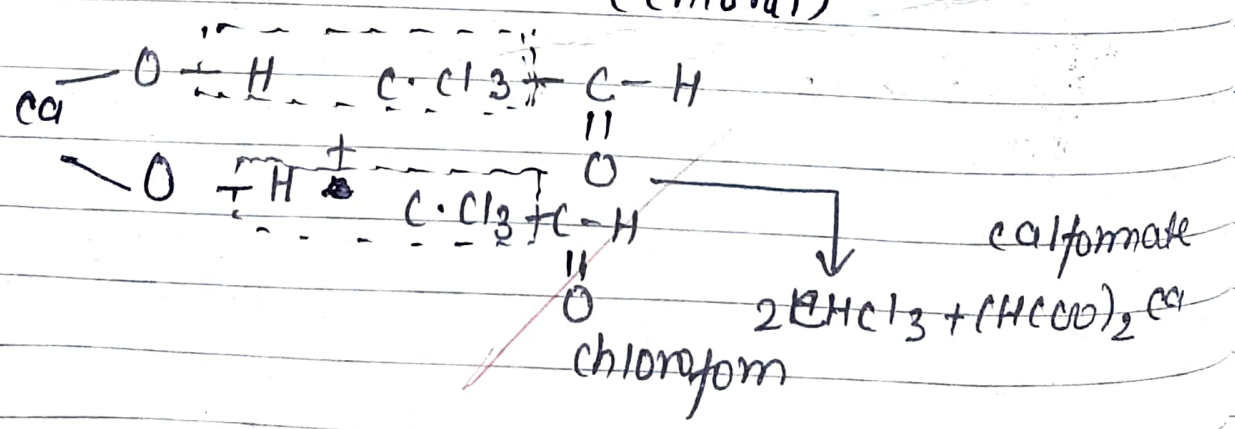
acetaldehyde

Here, bleaching powder acts as an oxidising agent.

2) **Chlorination of acetaldehyde →**

$$CH_3 - \overset{O}{\overset{\|}{C}} - H + 3Cl_2 \xrightarrow{\Delta} CCl_3 - \overset{O}{\overset{\|}{C}} - H + 3HCl$$

(chloral)



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From Acetone:→

a) chlorination of acetone →

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + 3Cl_2 \xrightarrow{\Delta} C \cdot Cl_3-\overset{O}{\overset{\|}{C}}-CH_3$$

1,1,1-trichloropropanone (Trichloro acetone ce)

b) Hydrolysis of trichloroacetone

$$Ca(OH)_2 + 2\,C\cdot Cl_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\Delta} 2CHCl_3 + (CH_3COO)_2Ca$$

calcium acetate.

Procedure:→

At first 30 gm bleaching powder is mixed with 100 ml of water in a 250ml R.B flask.

About 25 ml of alcohol or acetone is slowly added which is heated on water bath. chloroform along with water is collected in receiver by distillation.

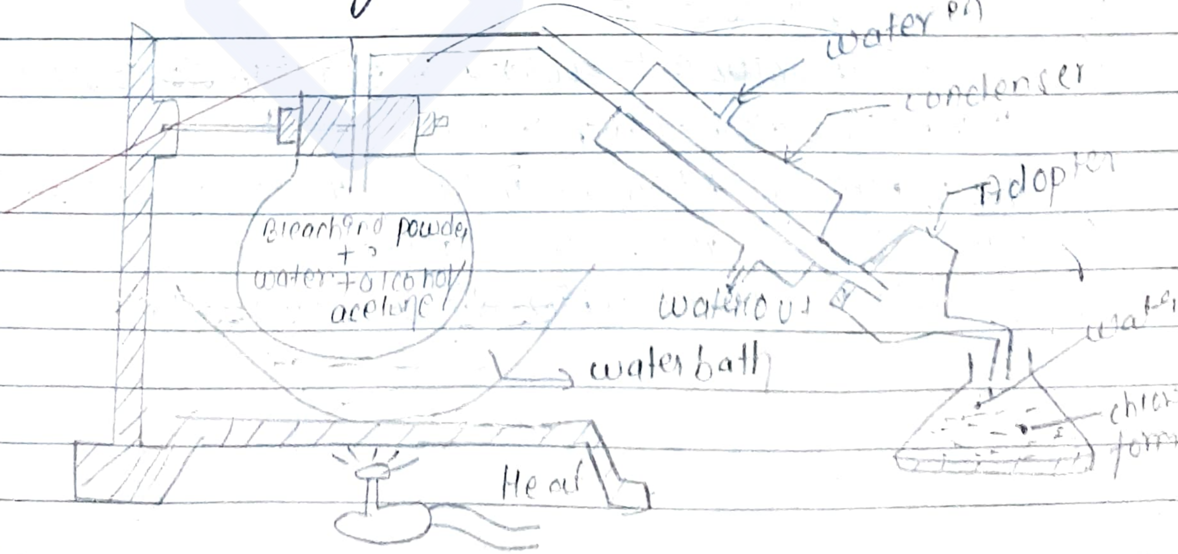


fig:- Laboratory preparation of chloroform

classmate

Purification:→

Chloroform thus obtained may contain acidic impurities. Impure chloroform is transferred in a separating funnel and first washed with dil NaOH solution to dissolve acidic impurities. then washed with water 2 or 3 times to remove water soluble impurities.

Finally it is dried over anhydrous $CaCl_2$ and further redistilled to get pure and dry $CHCl_3$.

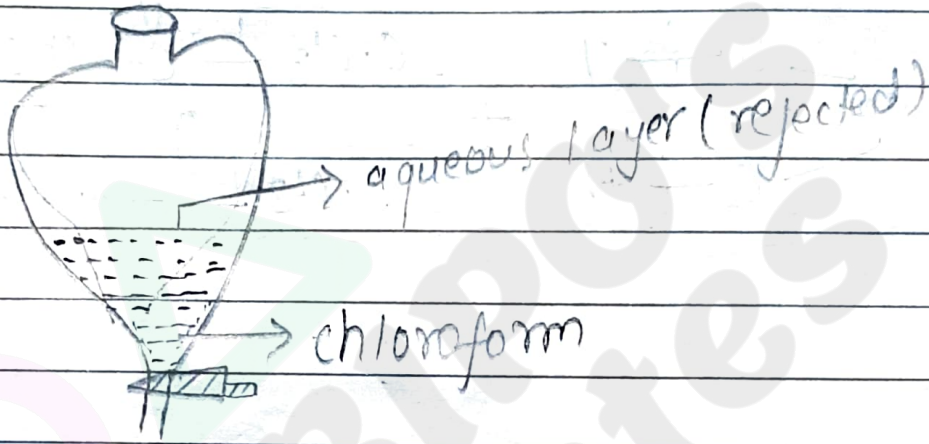


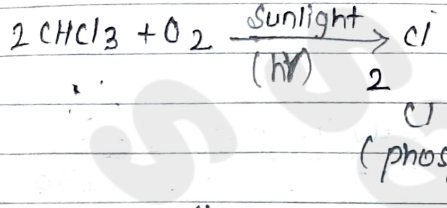
fig:- Separating funnel.

B. Physical properties:-

1) colourless sweet smiling liquid.
2) Bpt. 61°C & Mpt:- 63°C
3) Heavier than water.
4) Sparingly soluble in water but readily soluble in solvent like alcohol, ether etc.
5) The vapour of chloroform includes unconsciousness. therefore it is used as an aesthetic agent.
6) It act's as solvent which dissolve oils fats etc

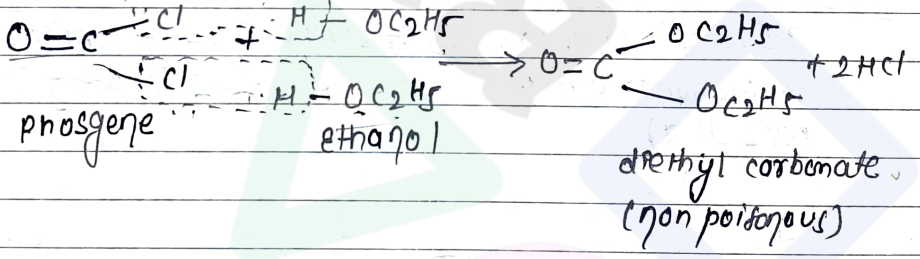
[C] chemical properties :-

(1) Reaction with air - (oxidation) → when chloroform reacts with air in presence of sunlight, chloroform is oxidised to phosgene gas (a highly poisonous.)



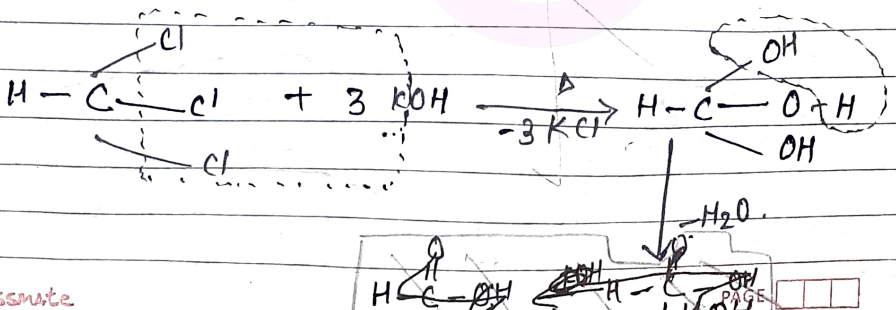
Therefore chloroform is stored in dark bottle to protect from sunlight and filled up to stopper to avoid the formation of phosgene.

Also a small amount of ethanol (2%) is added to bottle to chloroform. this convert phosgene gas formed into non poisonous diethyl carbonate.



(VII) NEB

(2) Reaction with KOH (aq) (Hydrolysis) → when chloroform is treated with aqueous KOH solution then potassium formate is formed which on acidification gives formic acid.



yeha bata suru

$$H-\overset{\overset{O}{\|}}{C}-O^{-}K^{+} \longleftarrow H-\overset{\overset{O}{\|}}{C}-OH$$

$$\downarrow H^{+}$$

$$K^{+} + H-\overset{\overset{O}{\|}}{C}-OH$$ (formic acid)

NEB VVImp

② **Reaction with conc. HNO_3** → when chloroform is heated with conc. HNO_3 gives chloropicrin which is used as an insecticides and tear gas (war gas)

$$Cl-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-H + HO-NO_2 \text{ (conc.)} \xrightarrow{\Delta} Cl-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-NO_2 + H_2O$$

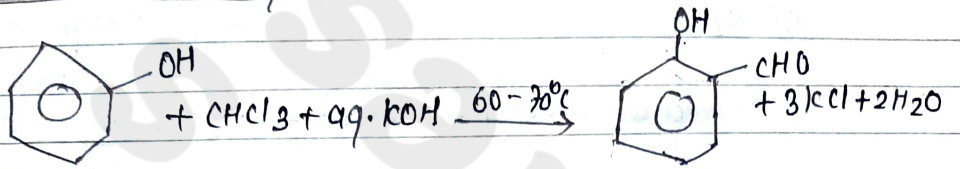
chloropicrin
war gas (tear gas)

VVImp ④ **Reaction with acetone** (or propanone) → when chloroform is treated with acetone in the presence of strong base it condenses to give chloretone, which is used as a sleep inducing drug (hypnotic drug)

$$(CH_3)(H_3C)C=O + H-C\cdot Cl_3 \xrightarrow{alc.\,KOH} H_3C-\underset{\underset{C\cdot Cl_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

chloretone (sleep inducing drug)

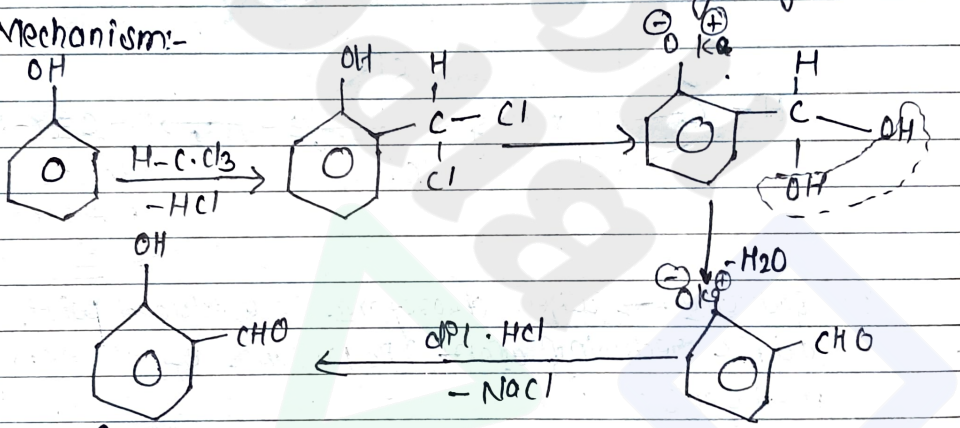
(5) Reimer–Tiemann reaction → When chloroform is heated with phenol in presence of alkali (alc. KOH or aq. KOH or NaOH) at 60–70°C followed by acidic hydrolysis, salicylaldehyde is formed as major product. This reaction is called Reimer–Tiemann reaction.



Phenol

O-hydroxybenzaldehyde (Salicylaldehyde)

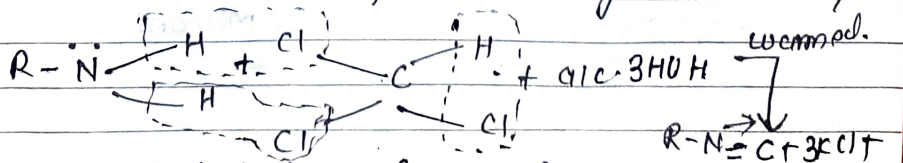
(x) Mechanism:-



Salicylaldehyde.

(6) Reaction with primary amines (carbylamines reaction)

when chloroform is warmed with primary amines in presence of alcoholic KOH, offensive smelling compounds called isocyanide or carbylamine is formed. Hence, this reaction is also refered as carbylamine reaction.



(alkyl isocyanide)

carbylamine (offensive smelling)

Eg:-

$$CH_3-NH_2 + CHCl_3 + 3alc.KOH \xrightarrow{\Delta} CH_3-N\overset{\rightarrow}{=}C + 3KCl + 3H_2O$$

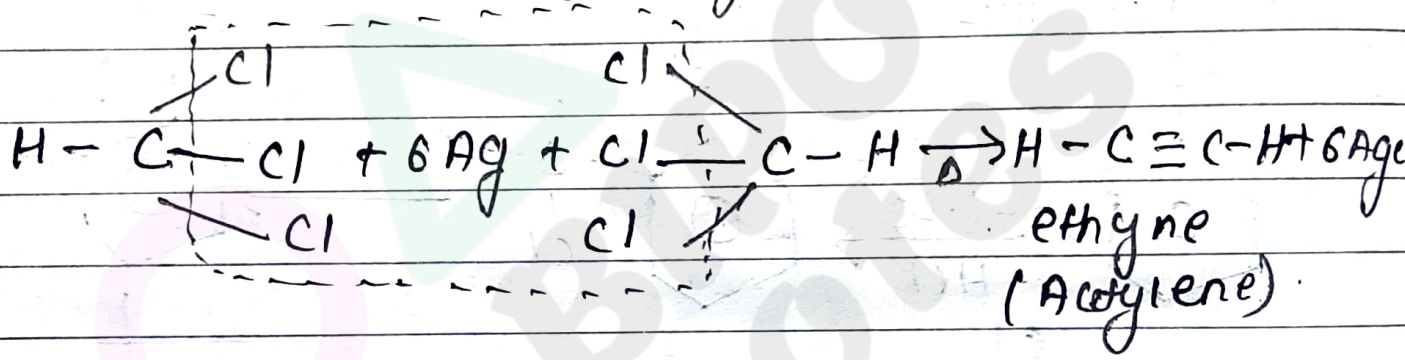
Methyl carbylamine or Isocyanide

$$C_6H_5-NH_2 + CHCl_3 + 3KOH\,(alc) \xrightarrow{\Delta} C_6H_5-N\overset{\rightarrow}{=}C + 3KCl + 3H_2O$$

Aniline — phenyl carbylamine

→ This reaction is used as a test for 'primary amines'

(7) Reaction with silver powder :- when chloroform is heated with silver powder acetylene gas is formed.



8. Reduction → when chloroform is reduced with Zn/HCl (acidic reducing agent) in presence of ethanol, gives methylene chloride

$$CHCl_3 + 2[H] \xrightarrow[C_2H_5OH]{Zn/HCl} CH_2Cl_2 + HCl$$

NEB

It is reduced to methane with Zn dust and water (Neutral medium)

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

Methane

(g) Reaction with $AgNO_3$ solutions → Test of purity of $CHCl_3$]

Chloroform doesn't give white ppt with aqueous $AgNO_3$ solution. It is because the carbon-chlorine bond in chloroform is covalent and doesn't ionize to produce $Cl^{\ominus}$ ions in aqueous solution.

But impure chloroform gives white ppt of AgCl due to presence of HCl. Therefore it is a test of purity of chloroform in lab

∴ (pure chloroform, $CHCl_3$) + $AgNO_3$ ⟶ No white ppt.

$$CHCl_3 + \frac{1}{2}O_2 \longrightarrow COCl_2 + HCl$$

$$HCl + AgNO_3 \longrightarrow AgCl + HNO_3$$

(white ppt)

USES OF CHLOROFORM

→ As organic solvents for fats, resin, rubber, waxes etc.
→ As anesthetic reagent in surgery.
→ As preservative of biological specimen.
→ As lab reagents for tests of primary amines
→ Used for preparation of phosgene, chloretone, chloropicrin etc.

IODOFORM →

preparation:-

It is obtained by warming ethanol or acetone with iodine in presence of alkali (NaOH or Na_2CO_3)

$$2NaOH + I_2 \longrightarrow NaOI + NaI + H_2O$$

Sod. Hypiodite

From ethanol:

I. oxidation:-

$$CH_3-CH_2-OH + NaOI \longrightarrow CH_3CHO + NaI + H_2O$$

~~Sod. hypoiodite~~

II. Iodination:-

$$CH_3CHO + 3NaOI \longrightarrow CI_3CHO + 3NaOH$$

TP- Podoacetaldehyde.

III. Hydrolysis:-

$$NaOH + CI_3CHO \longrightarrow CHI_3 + HCOONa$$

Iodoform Sod. ~~acetone~~ formate.

From acetone:-

I. Iodination

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + 3NOI \longrightarrow CI_3-\overset{O}{\overset{\|}{C}}-CH_3 + 3NaOH$$

TP- Podo acetone.

II. Hydrolysis

$$NaOH + CI_3-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow CHI_3 + CH_3COONO$$

; iodoform

DATE

* Physical properties:-

1. It is pale yellow crystalline solid having unpleasant smell.
2. Its melting point is 119 °C.
3. Insoluble in water but soluble in organic solvent.

\# Chemical properties

Chemical properties of iodoform are similar to that of chloroform but it is less stable than chloroform

$CHI_3 \longrightarrow$

- $HI / Red\ P_4$, $2[H]$ $\longrightarrow$ $CH_2I_2 + HI$
- $Ag \cdot KOH$ (Boil) $\longrightarrow$ $H-\overset{O}{\overset{\|}{C}}-OK$
- $Ag \cdot Powder$ $\longrightarrow$ $HC \equiv CH + AgI$
- $CH_3NH_2 + 3KOH \longrightarrow CH_3-N\overset{\rightarrow}{\equiv}C + 3KI + 3H_2O$
- Air moisture, Δ $\longrightarrow$ $CO_2 + H_2O + I_2$
- $AgNO_3$, Δ $\longrightarrow$ AgI (yellow ppt)

Uses:

1. As antiseptic in wounds.
2. In manufacture of pharmaceuticals.

DATE

IODOFORM TEST

This test is used to identify presence of $-CH_3-\overset{O}{\overset{\|}{C}}-$ or $CH_3-\overset{OH}{\underset{|}{CH}}-$ group in the given organic compound.

Example:-

$CH_3-\overset{O}{\overset{\|}{C}}-H$, $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$, CH_3CH_2-OH,

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

→ Ethanol is only primary alcohol.

Process:-

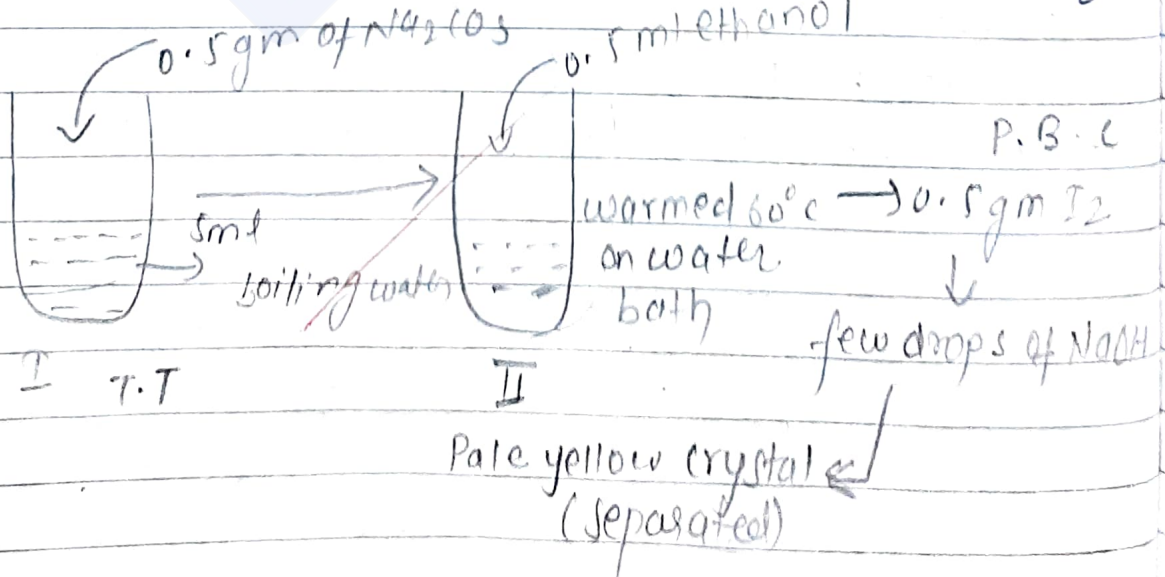
I. 0.5 gm of Na_2CO_3 is added to 5ml of boiling water in test tube.

II. 0.5 ml of ethanol given compound is added and warmed to 60°C on a water bath.

III. 0.5 gm of iodine is added till the permanent brown colour is obtained.

IV. At last few drops of NaOH solution are added to discharge the brown colour.

V. Pale yellow crystals of iodoform separate out i.e Iodoform



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Reactions.

I. $2NaOH + I_2 \longrightarrow NaOI + NaI + H_2O$

II. $2CH_3-\underset{OH}{CH}-R + NaOI \longrightarrow 2CH_3-\overset{O}{\overset{\|}{C}}-R + NaI + H_2O$.

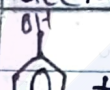
III. $CH_3-\overset{O}{\overset{\|}{C}}-R + 3NaOI \longrightarrow CI_3-\overset{O}{\overset{\|}{C}}-R + 3NaOH$.

IV. $NaOH + CI_3-\overset{O}{\overset{\|}{C}}-R \longrightarrow CHI_3 \longrightarrow RCOONa$.

R = H- atom or any alkyl group.

SUMMARY OF THE RXN:-

$CHCl_3$ →

- O_2/sunlight, Oxidation → $COCl_2 + HCl$
- aq. KOH, hydrolysis → $H-\overset{O}{\overset{\|}{C}}-O^{\ominus}K^{\oplus}$
- HNO_3/Δ, Nitration → $CCl_3-NO_2 + H_2O$
- acetone / AlC. KOH → $CH_3C(OH)(CCl_3)CH_3$
-  + KOH (aq), 60–70°C →  (RT rxn)
- RNH_2 + alc. KOH, Δ → $R-N\rightleftarrows C$ carbylamine rxn
- Ag / Δ → $HC\equiv C-H$
- Zn / HCl, reduction → CH_2Cl_2
- Zn / H_2O, Reduction → CH_4

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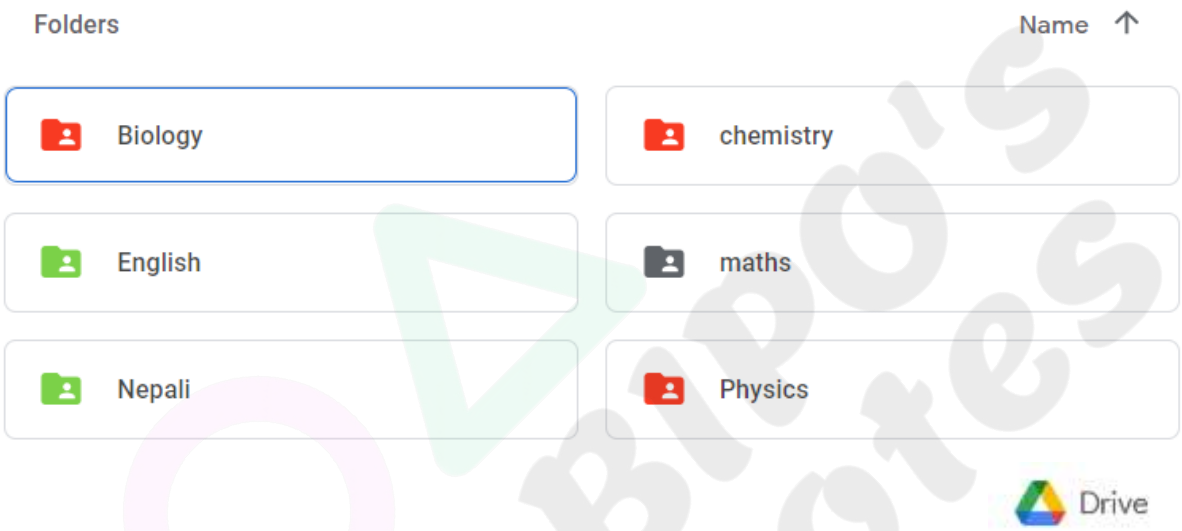
PAGE

Bipin Khatri

(Bipo)

Class 12 complete notes and paper collection.



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