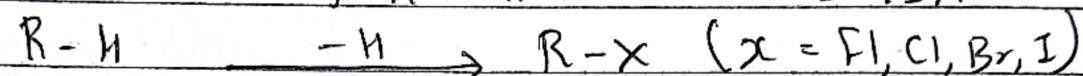


#

Haloalkane

Organic Compounds derived from the replacing of one or more hydrogen from Saturated hydrocarbon by halogen ( $X - F, Cl, Br, I$ ) group is called alkyl halide or simply haloalkane.

General formula of haloalkane  $\rightarrow C_nH_{2n+1}X$



Hydrocarbon + X      R may be :  $CH_3^-$ ,  $C_2H_5^-$ ,  $C_3H_5^-$  etc.

↳ Example of alkyl halide:  $CH_3-Cl$ ,  $CH_3-CH_2-Br$   
                                   (Chloromethane)    (Bromoethane)

↳ In haloalkane carbon attached to halogen is  $sp^3$  hybridization.

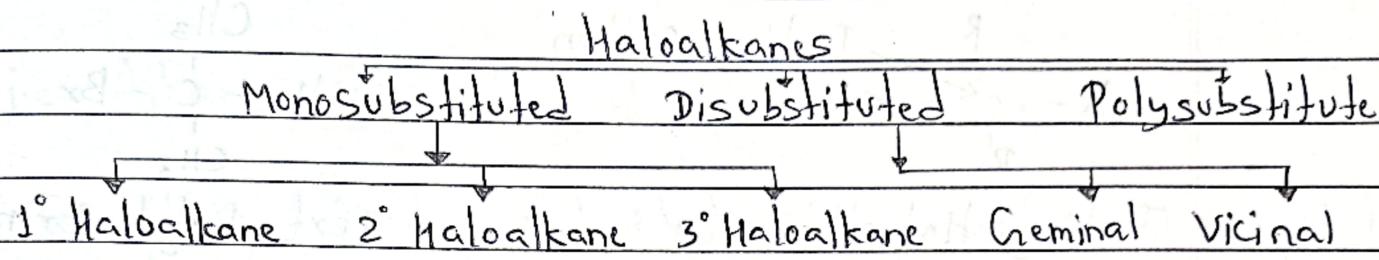
# Uses of Haloalkane

- Starting material for the preparation of several organic compounds like alcohols, acids, amines, aldehydes, hydrocarbons, ether etc.
- Used to prepare Grignard reagent.
- Used as an alkylating agent.
- Used as Solvent ( $CCl_4$ ) and Coolent ( $CF_3CS$  gas).
- Commercially used as fire retardants, fire extinguisher, refrigerents, propellents and pharmaceuticals.

(But many shown to be serious pollutants and toxins)

## # Classification

Haloalkanes are classified based on the number of halogen atoms and the nature of carbon atoms bonded with halogen atoms.

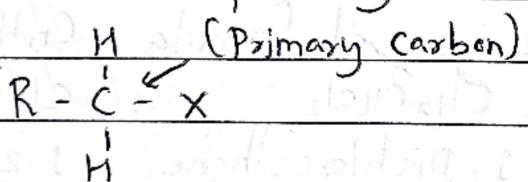


a. Based on nature of carbon atom

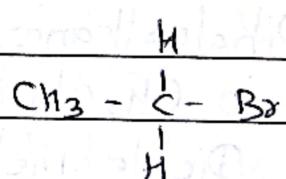
Depending upon the nature of carbon atoms bonded with halogens, monohaloalkanes are classified into primary ( $1^\circ$ ), secondary ( $2^\circ$ ) and tertiary ( $3^\circ$ ) haloalkanes.

### i. Primary Haloalkane

The haloalkane in which carbon atom ( $1^\circ$  carbon) carrying halogen is further linked to only one carbon atoms are known as primary haloalkanes. General formula:  $RCH_2-X$



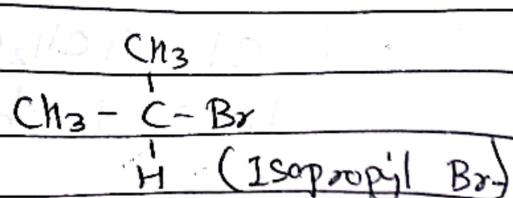
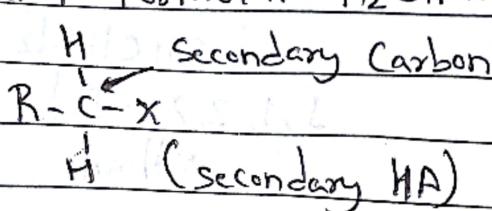
Primary Haloalkane



Ethyl Bromide

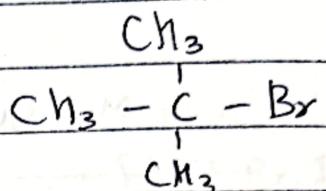
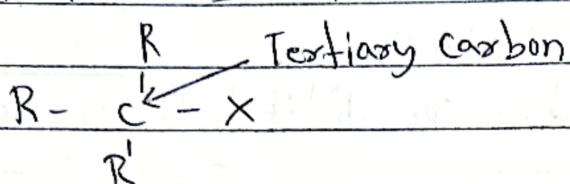
### ii. Secondary Haloalkane

The haloalkanes in which carbon atom ( $2^\circ$  carbon) carrying halogen atom is further linked to two other, carbon atoms are known as secondary haloalkane. General formula:  $R_2CH-X$



### iii. Tertiary Haloalkane

The haloalkanes in which carbon atom ( $3^\circ$  carbon) carrying halogen is further linked with three other atoms are known as tertiary haloalkanes. General formula :  $R_3C - X$



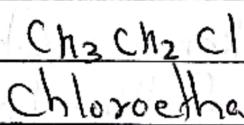
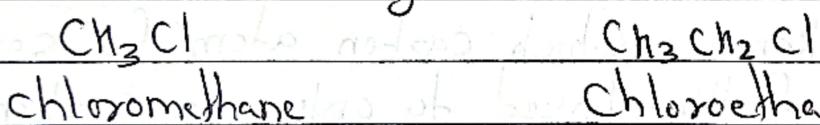
Tertiary Haloalkane

Ter-Butyl Bromide

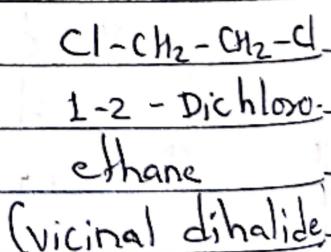
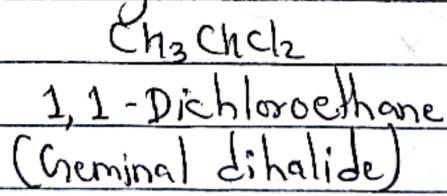
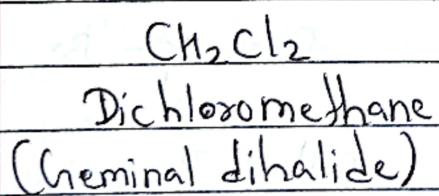
### b. Based on the number of halogen atoms

A haloalkane may be mono, di, tri, tetra haloalkane for one, two, three and four halogen atoms presented in a molecule respectively.

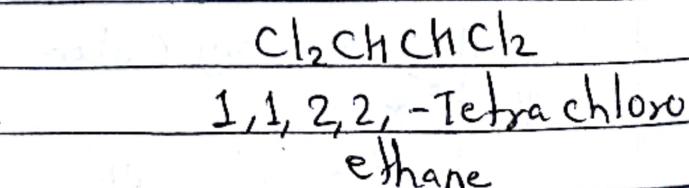
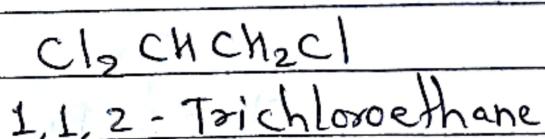
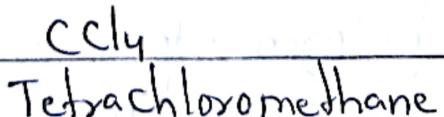
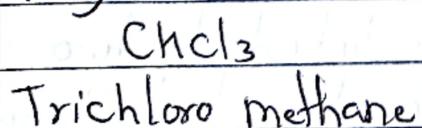
#### i. Monohaloalkane : Eg.



#### ii. Dihaloalkane : They have general formula : $C_nH_{2n}X_2$



#### iii. Polyhaloalkane : Eg.



#

## Nomenclature : (a) Common / Trivial System

Common names of alkyl halides (monohalogen) are derived by writing the names of the alkyl group followed by the names of halogen. The name of alkyl halide is written in two separate words.

i.e. Alkane  $\xrightarrow[-\text{ane}]{+\text{yl}}$  Alkyl  $\xrightarrow{+\text{halide}}$  Alkyl halide

Eg:  $\text{CH}_3\text{Cl}$  (Methyl chloride),  $\text{CH}_3\text{CH}_2\text{Br}$  (Ethyl bromide) etc. The prefix like n-, ISO-, Sec-, Tet- Text- and Neo- are used for higher members of haloalkane in trivial system. Compound containing branch chain of carbon, prefix like ISO-, sec-, Text- and Neo- are used and for straight chain haloalkane, n- is used.

## b. IUPAC System

In this system, alkyl halides are named as halogen derivatives of alkanes. The name of halogen is prefixed to the name of alkane and the name of alkyl halide is written as one word. In higher homologs, the position of halogen is indicated along with its locants.

i.e. Halo + alkane  $\longrightarrow$  Haloalkane  
Prefix Word root

Where,

halo = chloro, bromo, iodo etc.

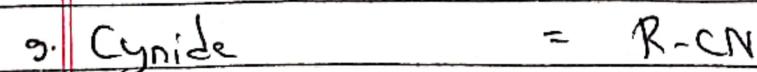
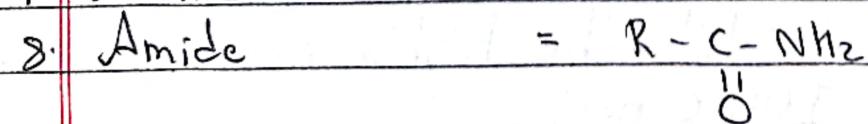
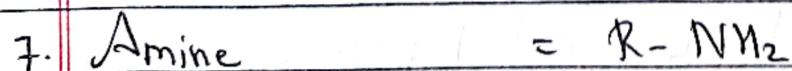
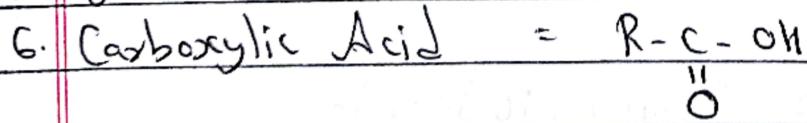
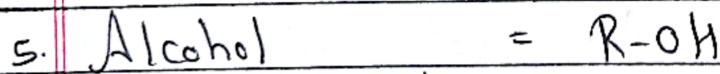
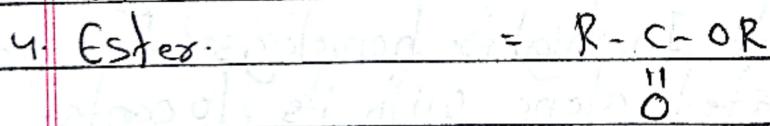
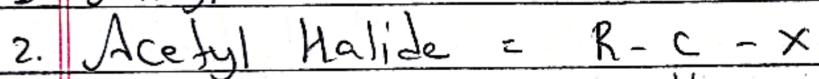
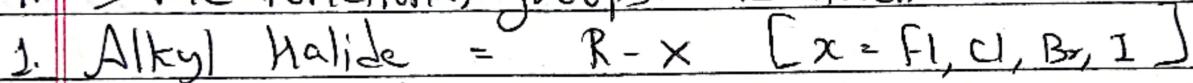
E.g.  $\text{CH}_3\text{Cl}$  (chloromethane),  $\text{CH}_3\text{CH}_2\text{Br}$  (bromoethane)

Usually, simple and lower alkyl halides are named with common name while the higher homologs are named with the IUPAC name.

## # Significance of functional group

- i. They form the basis of the classification of organic compounds. All compounds having the same functional group belongs to the same class or families
- ii. The naming (nomenclature) of the organic compound is done based on the functional group.
- iii. Functional group possess the characteristics property of the compound and is one of the reactive site of the molecules. All the compounds having the same functional group have similar chemical properties.

## # Some functional groups and their classes



11. Nitro Compound =  $R-NO_2$

12. Aldehyde =  $R-C(=O)H$

13. Ketone =  $R-C(\overset{||}{O})R$

## # Isomerism

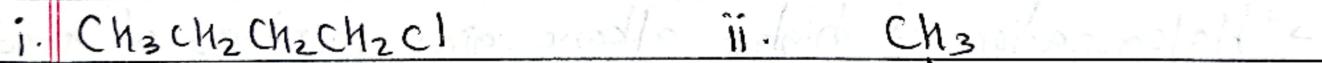
Compounds having same molecular formula but different in their physical or chemical properties are called isomers and the phenomenon is called isomerism.

### # Isomerism in Haloalkanes

#### 1. Chain Isomerism

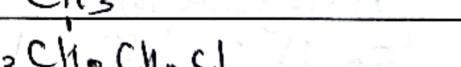
Compounds having same molecular formula and same functional group but differ in the length of the carbon chain are called chain isomers or skeletal isomers.

Eg:  $C_4H_9Cl$  has three chain isomers



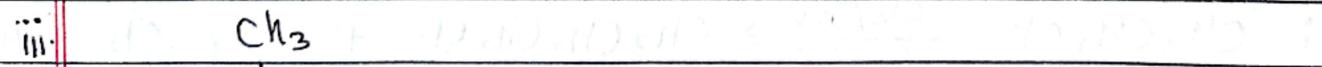
1-chlorobutane

(n-butyl chloride)



1-chloro-2-methylpropane

(isobutyl chloride)



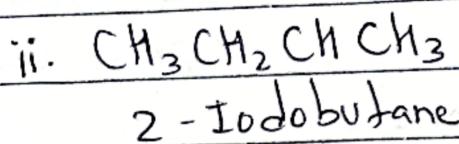
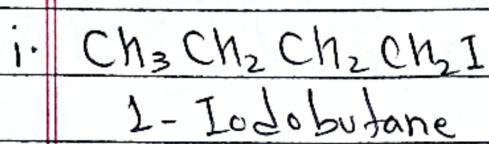
2-chloro-2-methyl propane

#### 2. Position Isomerism

Position isomerism are the compounds having same molecular formula and same carbon chain but differ

Date: / /

in the position of the substituent group (halogen atom)  
Eg:  $\text{C}_6\text{H}_5\text{Cl}$  has two position isomerisms as follows:



## # General Method of preparation of Haloalkanes

→ Major source of haloalkanes are:

Hydrocarbons (alkane, alkenes) and alcohols

## A: From Hydrocarbons

## i. Halogenation of Alkanes

→ Alkyl halide is prepared by halogenation of alkanes in the presence of sunlight.

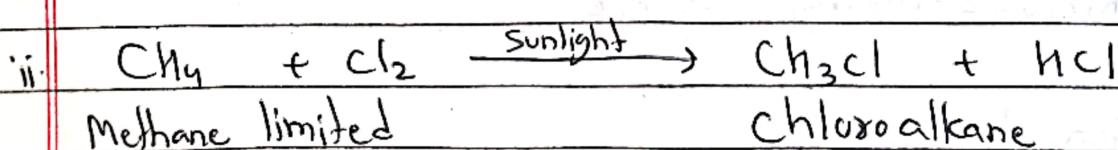
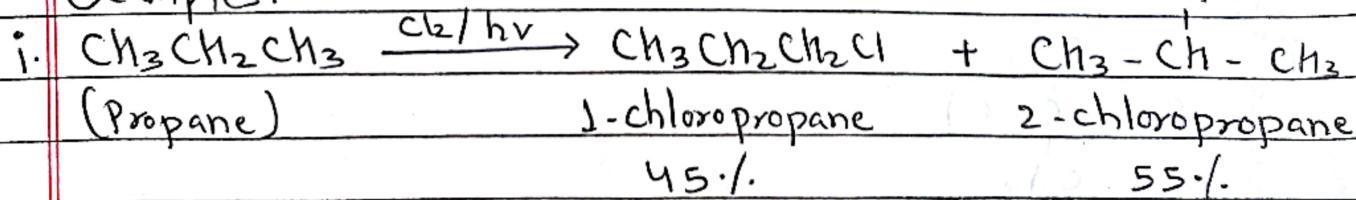
→ Reaction occurs by free radical ( $3^\circ > 2^\circ > 1^\circ$ )

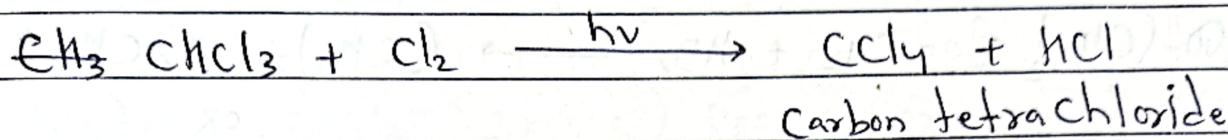
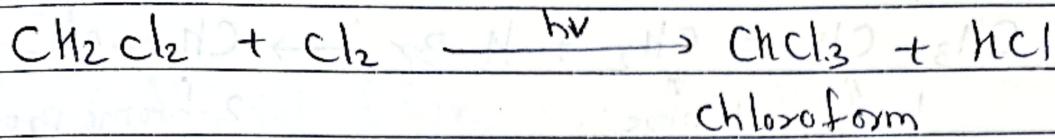
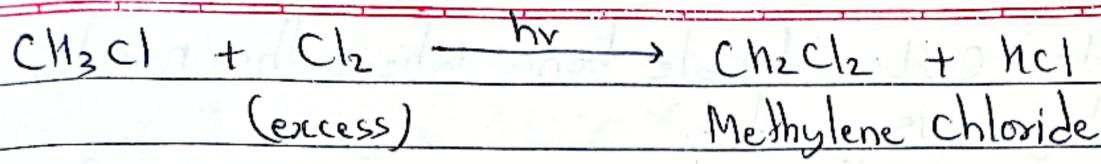
→ Reactivity of Halogen ( $F_2 > Cl_2 > Br_2 > I_2$ ). It is due to low bond dissociation energy.

$\rightarrow$   $F_2$  react (violetly),  $Cl_2$  (Radially),  $Br_2$  (difficult),  
 $I_2$  (reaction is reversible)

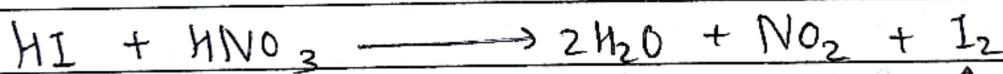
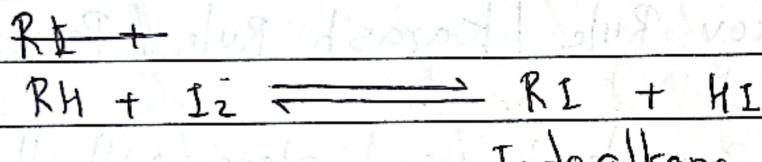
→ Halogenation of higher alkane gives mixtures of product. So it is difficult to separate. Hence, it is not suitable method of preparation.

## Examples:





But, to prepare iodoalkane, oxidizing agent ( $\text{HNO}_3$ ,  $\text{HIO}_3$ ) should be used. It is because  $\text{HI}$  (reducing) agent is produced during the reaction which again converts  $\text{RI}$  to  $\text{RH}$ .



This produced I<sub>2</sub> further increase the rate of iodo-alkane preparation.

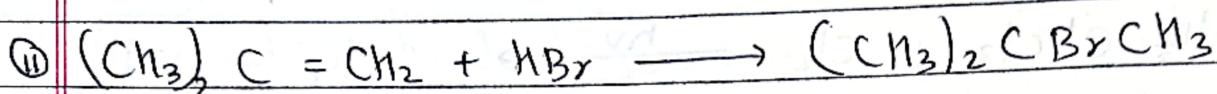
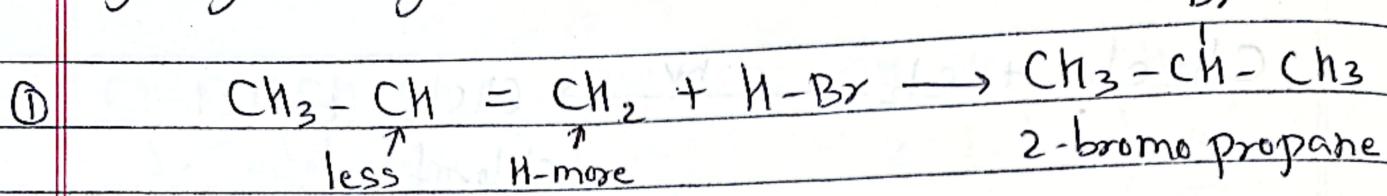
ii) Addition of hydrogen halide on Alkan Alkenes

Addition of  $Hx$  ( $x = Cl, Br, I, F$ ) on alkene occurs by two rules.

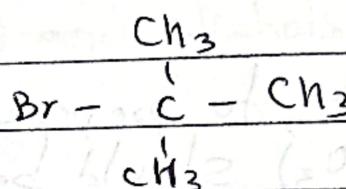
a. Markonikov's Rule : When only  $HX$  is present as reagent.

Markonikov's rule state that "When unsymmetrical reagent reacts with unsymmetrical alkene, Hydrogen of reactant goes (added) to that side of reagent  $\text{C=C}$ "

Carbon-Carbon double bond where the number of hydrogen is greater."



OR



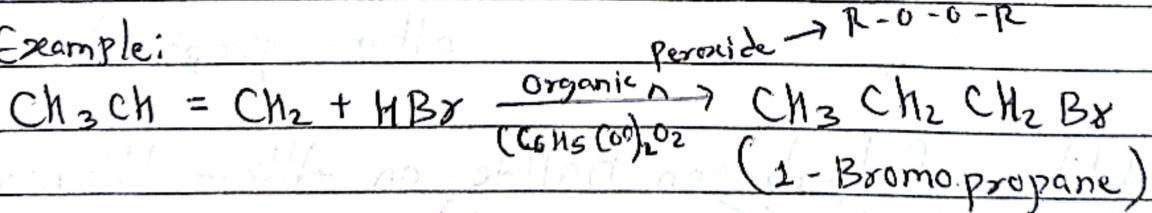
2-Bromo-2-methylpropane.

b. Anti-Markonikov Rule / Krasch Rule / Peroxide effect or Mayer effect

When organic Peroxide is used along with the Hydrogen halide.

→ Addition of H is just opposite of Markonikov rule.  $\text{C}_6\text{H}_5 \text{C} - \overset{\text{O}}{\underset{\text{O}}{\text{O}}} - \text{C} - \text{C}_6\text{H}_5$

Example:



Note: Antimarkonikov's rule is applied only in case of HBr as it has reasonable bond dissociation energy (homolytically) to produce free radical by peroxide.

But, H-Cl is quite stable, at high temperature it gets dissociated heterolytically.

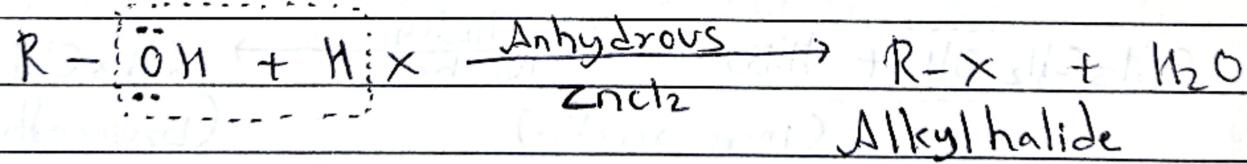
H-I weak bond again I obtained reunite with another I to give  $I_2$  rather than attacking double bond.

### B. From Alcohol (Groove's Process)

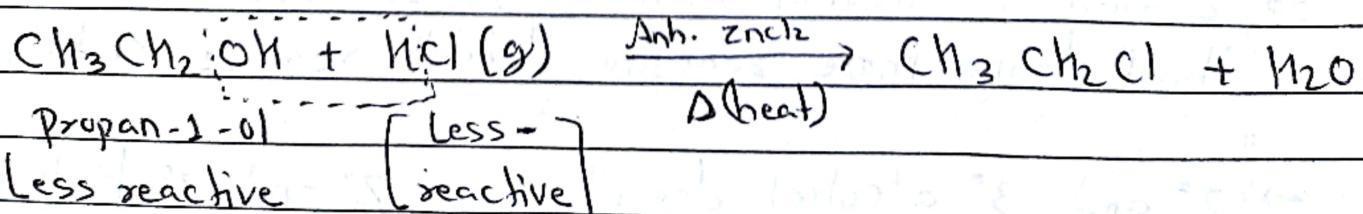
- i. Haloalkane can be obtained from alcohol by reacting it with (HCl, HBr, HI) in the presence of catalyst anhydrous  $ZnCl_2$  (groove) process or Conc.  $H_2SO_4$ .

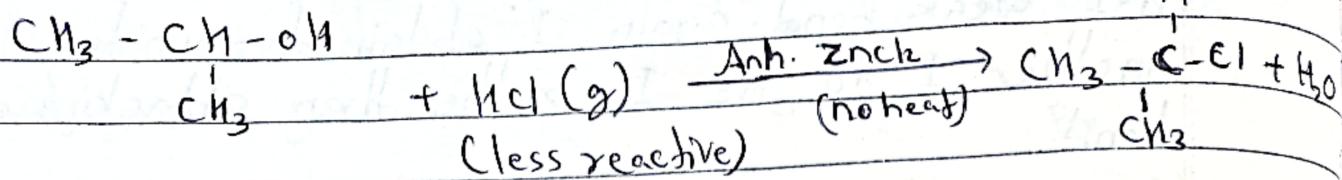
Lucas Reagent : (Mixture of conc. HCl + anhy.  $ZnCl_2$ )

- 1<sup>st</sup> removal of OH and formation of cation.
- 3° cation > 2° cation > 1° cation
- Greater the No. of electron donating group in alcohol weaker the C-OH bond. (Polarity increases)
- Catalyst helps in cleavage of C-OH bond to form cation.



- 1° alcohol gives 1° cation
  - 2° alcohol gives 2° cation
  - 3° alcohol gives 3° cation
- Reactivity order →
- $3^\circ \text{ alcohol} > 2^\circ \text{ alcohol} > 1^\circ \text{ alcohol}$

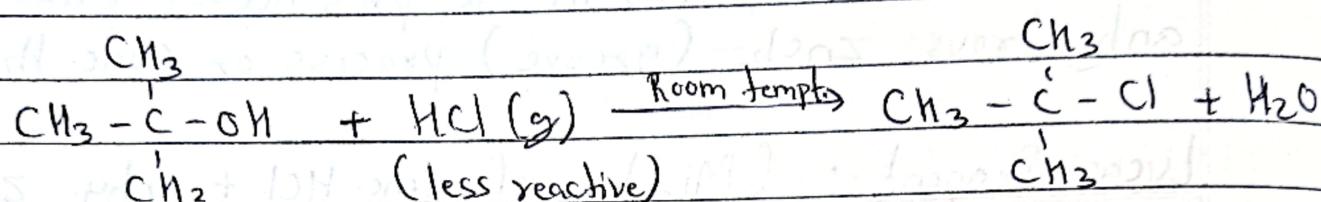




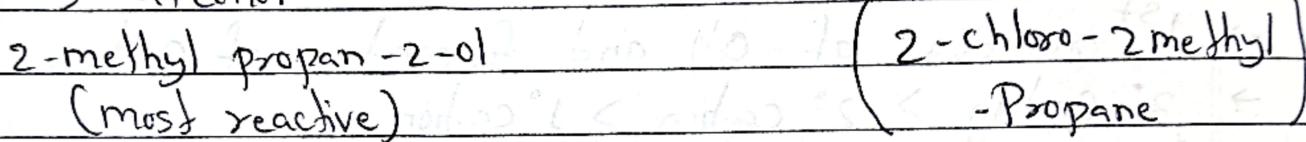
$2^\circ$  Alcohol

Propan-2-ol

(more reactive)



$3^\circ$  alcohol

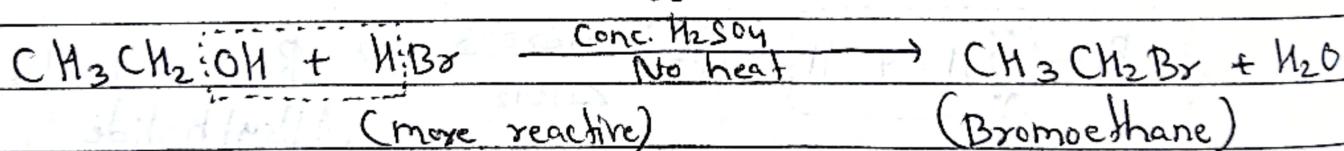


## # Effect

↳ In case of HCl, HBr, HI in reaction

Anhy. ZnCl<sub>2</sub>

or



(more reactive)

(Bromoethane)

$1^\circ$  alcohol

Ethanol

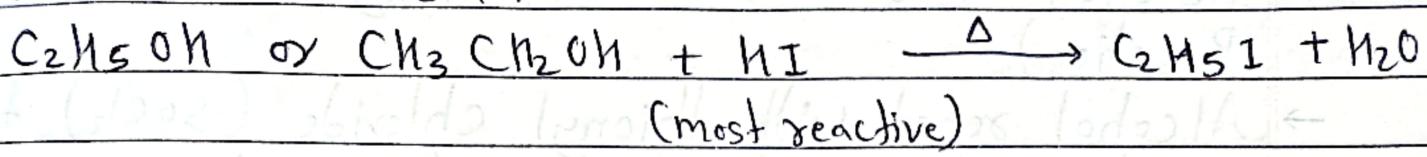
(least reactive)

→  $2^\circ$  and  $3^\circ$  alcohol being more reactive and also HBr itself being more reactive doesn't require catalyst.

→  $2^\circ$  and  $3^\circ$  alcohol doesn't form  $2^\circ$  and  $3^\circ$  haloalkane in the presence of Conc. H<sub>2</sub>SO<sub>4</sub> because Conc. H<sub>2</sub>SO<sub>4</sub> converts alcohol to alkene.

→ HI being most reactive, doesn't require catalyst

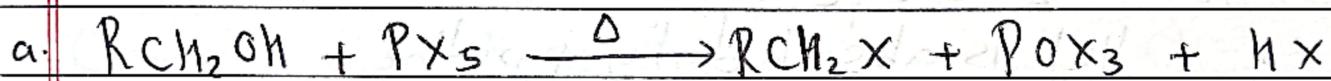
to even 1° alcohol.



→ For good yield of primary alkyl halide, vapour of alcohol and halogen acid are passed over the heated alumina ( $\text{Al}_2\text{O}_3$ ) at 350°C.

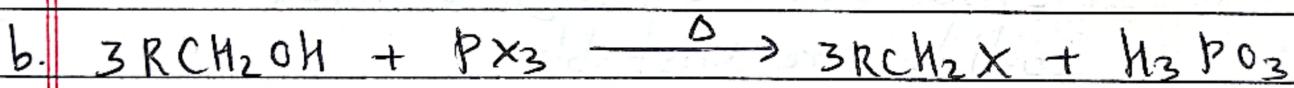
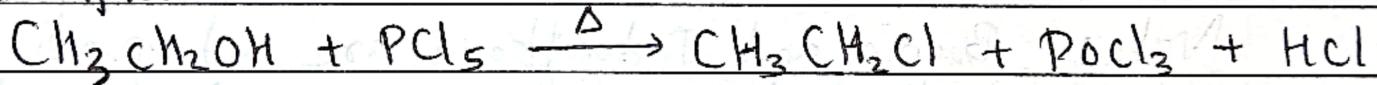
# ii. Reaction of Alcohol with Phosphorous halide

→ Alcohol heated with Phosphorous-halide ( $\text{PX}_3$  or  $\text{PX}_5$ ) gives haloalkane.



(phosphorous oxyhalide)

Example:



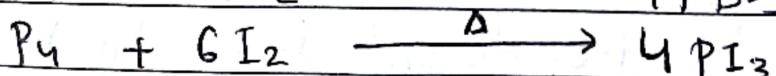
(Phosphorous acid)

Example:



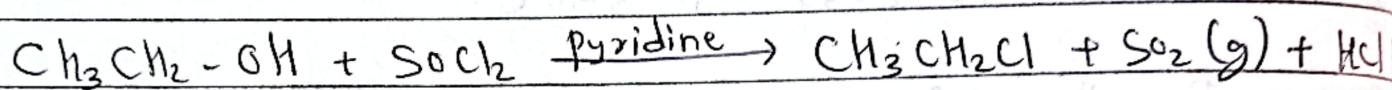
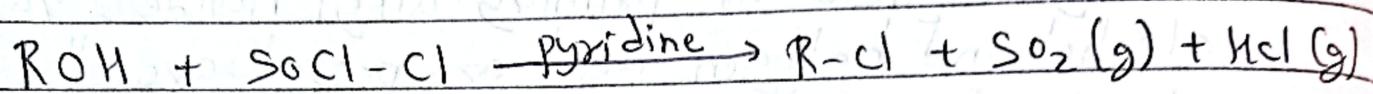
Note:

$\text{PB}_3$  and  $\text{PI}_3$  are unstable. So are prepared in situ by reacting Phosphorous on  $\text{B}_2\text{O}_3$  or  $\text{I}_2$ .



### iii. Reaction of Alcohol with Thionyl chloride (Dazén's Reaction)

→ Alcohol react with Thionyl chloride ( $\text{SOCl}_2$ ) to give pure haloalkane in presence of pyridine as a catalyst.



→ This is the best method of preparation of alkyl halide because both biproduct are obtained in gaseous State:  $\text{SO}_2$  escape out

$\text{HCl}$  is absorbed by pyridine

∴ Chloroalkane is obtained in pure state.

Note: Bromo and Iodoalkane are not produced by this method because thionyl Bromide and thionyl Iodide are unstable.

### # Physical Properties of Haloalkane.

State: Iodomethane

→ Lower member Eg: chloromethane → colourless gases  
Bromomethane

Some higher member → Colourless Sweet smelling liquid  
other higher member → Colourless solid

### Solubility:

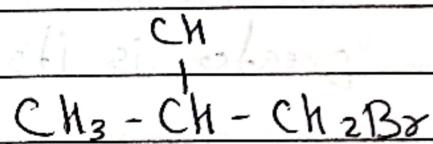
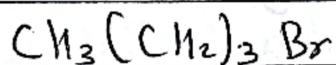
Insoluble in water i.e. doesn't forms hydrogen bonding with water but soluble in non-Polar organic Solvent.

Eg: Ether,  $\text{CCl}_4$ , Benzene etc.

M.P and B.P :

- Have higher m.p and B.P than corresponding alkane due to polarity in bond.  
Also, increase in size of halogen and increase in number of carbon in alkyl group. The increase in M.P and B.P is due to increase in VanderWaal force of attraction.
- In case of isomeric alkyl halide branching has less B.P than long chain due to small surface area.

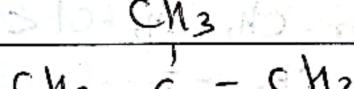
Compound



Boiling Point

95.6°C

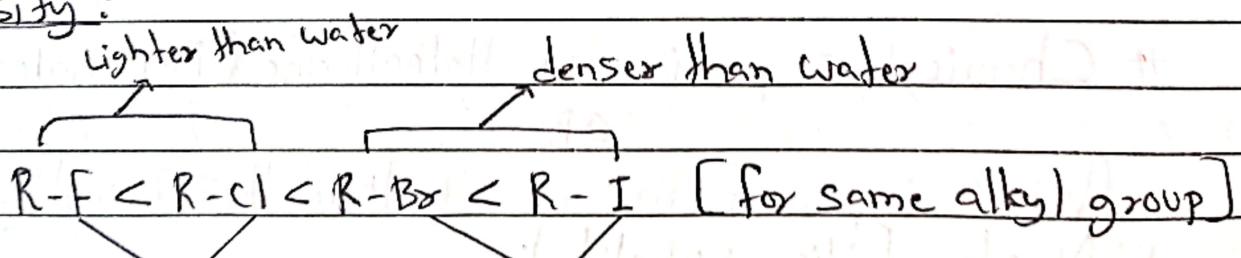
89°C



72°C

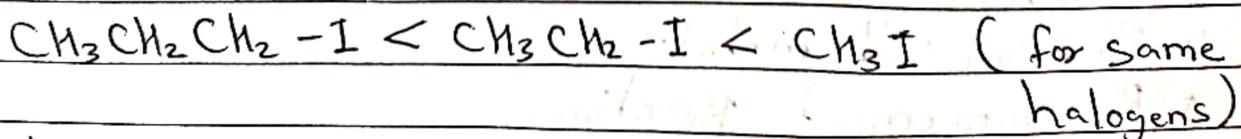
↓ less Surface Area ↓ Vanderwaal force ↓ B.P

Density :



Less atomic Mass

Has more atomic mass



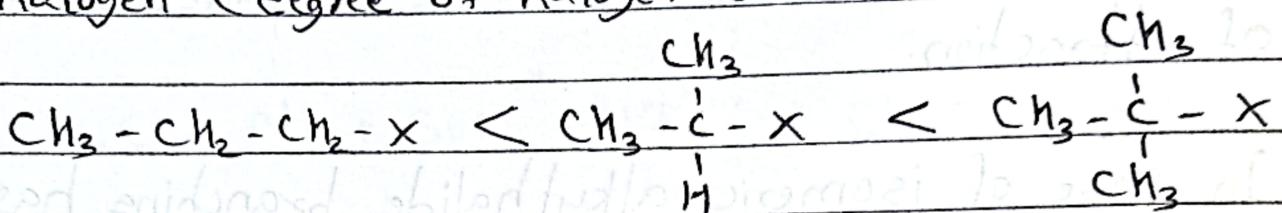
Note:

More the weight contribution of halogens i.e. here I,

- the more density the alkyl halide has.
- Alkyl halide burns with green edged flames.

## # Chemical Properties of Haloalkanes

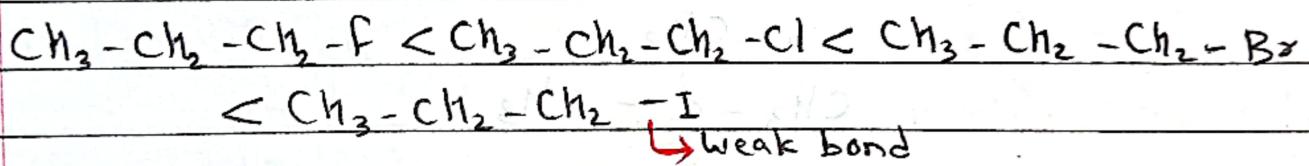
- i. Number of alkyl group in carbon directly attached to halogen (degree of halogen haloalkane)



Note:

Greater the No. of alkyl group attached to haloalkane greater is its reactivity.

- ii. Types of halogen in alkyl halide



Note:

Greater the size of halogen in alkyl halide, reactivity increases.

## # Chemical properties of Haloalkane (Monohaloalkane)

OR

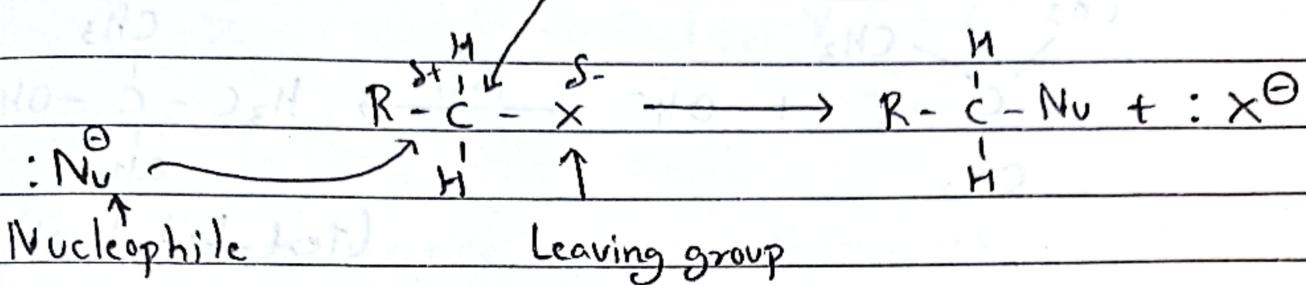
(What types of Rxn doesn't Haloalkane Undergoes)

1. Nucleophilic substitution
2. Elimination Reaction
3. Reduction Reaction
4. Reaction with metals
5. Rearrangement Reaction

# 1. Nucleophilic Substitution Rxn: $SN^1$ and $SN^2$

→ The chemical Rxn in which strong Nucleophile displace weak nucleophile is Nucleophilic Substitution Rxn.

electron deficient c atom



$:Nu^-$  may be =  $OH^-$ ,  $CN^-$ ,  $\ddot{NH}_3$ ,  $H_2\ddot{O}$  etc.

L.G = Halogen

## ↳ Types of Nucleophilic Substitution Rxn

- i.  $SN^1$  → For  $2^\circ$  and  $3^\circ$  alkyl halide
- ii.  $SN^2$  → for  $1^\circ$  alkyl halide

### i. $SN^1$ Rxn (by $2^\circ$ and $3^\circ$ ) alkyl halide

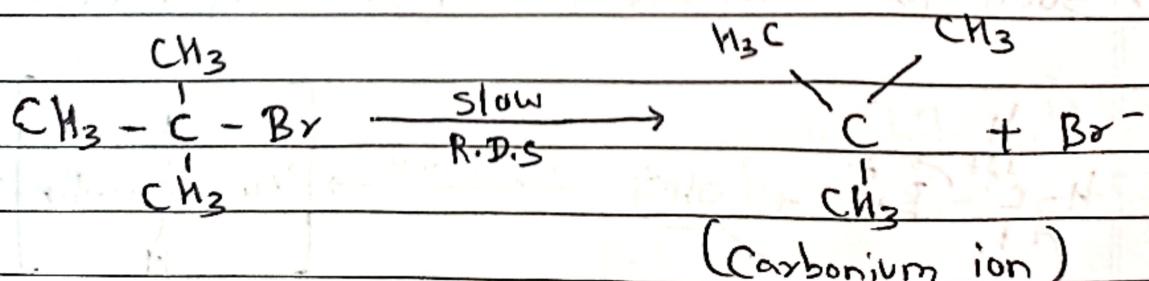
→ It stands for Nucleophilic Substitution 1<sup>st</sup> order Rxn.

→ 1<sup>st</sup> order in a sense that rate of such Rxn depend only on the conc. of one reactant (substrate).

$$\text{Rate of Reaction (ROR)} = k (\text{Substrate})$$

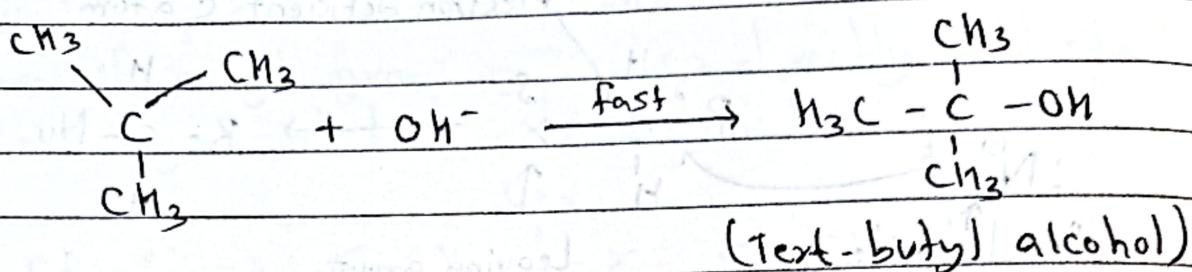
# Such Rxn complete in 2 steps:

- i. Formation of carbocation (L.G departs) forming planar structure ( $sp^2$  hybridized carbocation)  
i.e.

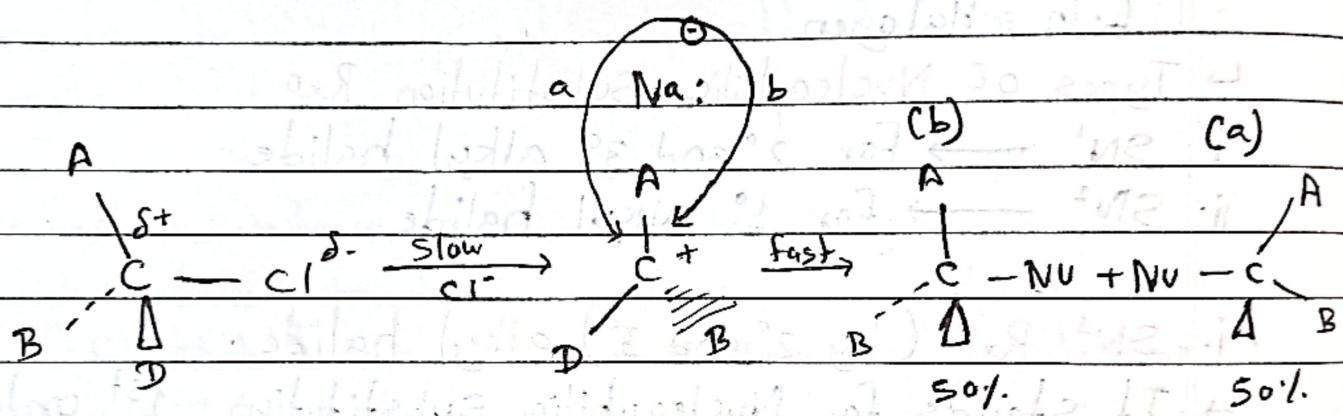


It is slow step hence Rate determining steps (RDS).

ii. Nucleophile attacks the carbocation giving 50% inversion and 50% retention configuration.  
 $\therefore$  Gives racemic product



Overall Steps:



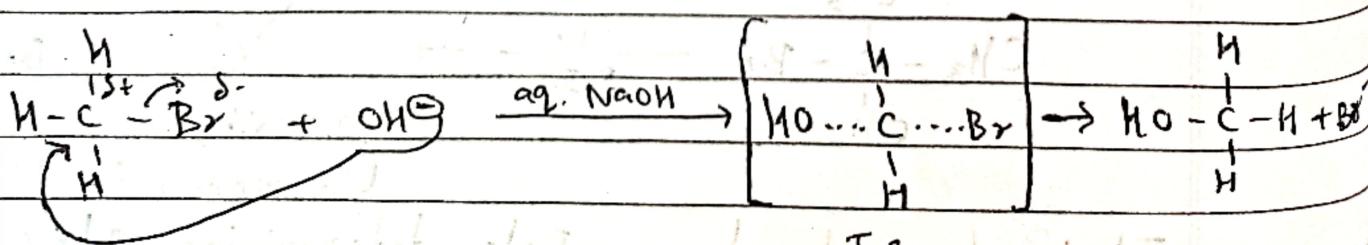
Substrate  $\rightarrow$  Planar Intermediate (Carbocation)  $\rightarrow$  Racemic Product

## 2. $\text{S}_{\text{N}}^2$ Rxn (by 1° alkyl halide)

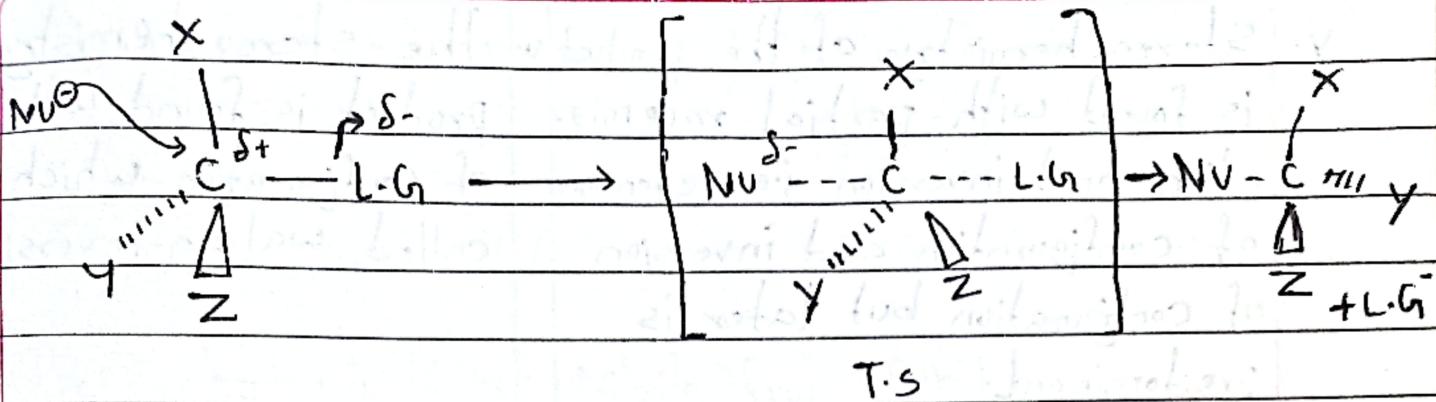
$\rightarrow$  It stands for Nucleophilic substitution bimolecular rxn.  
 $\rightarrow$  2<sup>nd</sup> order (bimolecular) in the sense that the rate of such reaction depends on the both the substrate and Nucleophile.

$$\text{ROR}' = k [\text{Substrate}][\text{Nucleophile}]$$

$\rightarrow$  Such Rxn complete in single Step. (R.D.S)



$\rightarrow$  Here bond formation and bond breaking occurs simultaneously



# Write the difference between  $\text{S}_{\text{N}}^1$  reaction and  $\text{S}_{\text{N}}^2$  Rxn

#### $\text{S}_{\text{N}}^1$ reaction

- i.  $\text{S}_{\text{N}}^1$  reaction is a unimolecular Substitution rxn and follows the first-order kinetics. i.e the rate of rxn depends on the concentration of substrate only.

$$\text{Rate} = k[\text{substrate}]$$

#### $\text{S}_{\text{N}}^2$ reaction

- i.  $\text{S}_{\text{N}}^2$  reaction is a bimolecular substitution rxn and follows the second-order kinetics. i.e. the rate of rxn depends on the concentration of substrate and nucleophile.

$$\text{Rate} = k[\text{substrate}][\text{Nucleophile}]$$

- ii. It proceeds in two steps to complete the reaction

- ii. It proceeds in a single step to complete the reaction.

- iii. It proceeds via carbocation formation and it is determined by electronic factor only.

- iii. It proceeds via transition state (partial bonding of nucleophile and leaving group) formation and determined by steric factors only.

- iv. The nucleophile attacks from both sides of the carbocation (carbonium ion).

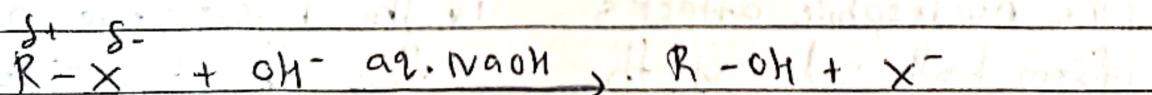
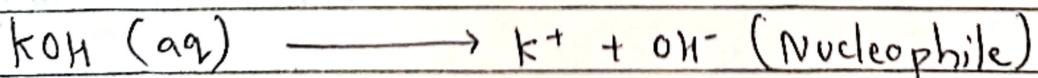
- iv. The nucleophile attacks from the backside of the substrate.

v.	Stereochemistry of the product is found with partial racemization and inversion i.e. retention of configuration and inversion of configuration but later is predominant.	The stereochemistry of the product is found with inversion of configuration which is also called walden inversion.
vi.	Tertiary alkyl halide undergoes $SN^1$ rxn easily and follows the reactivity order as: Tertiary > Secondary > Primary > methyl halide.	Primary alkyl halide undergoes $SN^2$ rxn easily and follow the reactivity order as: methyl halide > Primary > Secondary > Tertiary.
vii.	Methyl group may rearrange to form a stable carbocation.	No such rearrangement is possible during the Rxn.
viii.	Weak nucleophile and high polar solvent favour the reaction.	Strong nucleophile and less polar solvent favour the reaction.

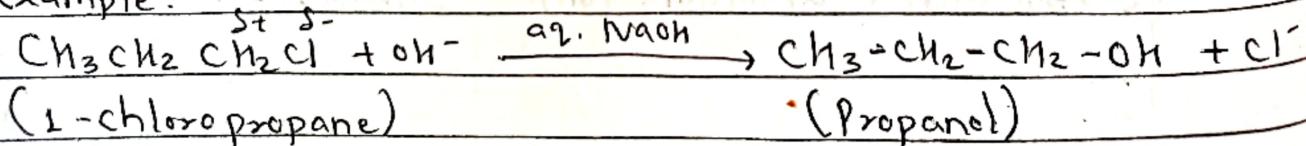
## # Substitution Reaction of Haloalkanes

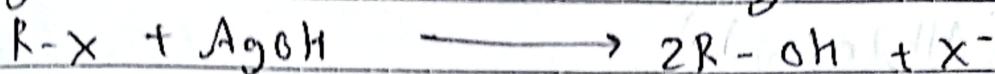
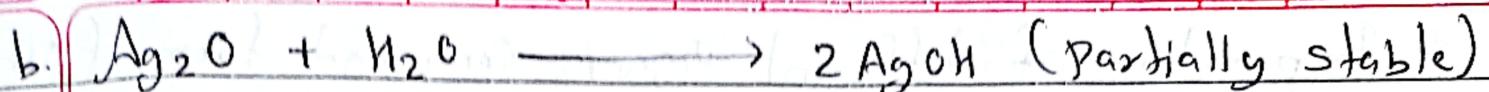
### 1. Preparation of Alcohol from Alkyl halide

→ When alkyl halide is boiled with aqueous KOH, NaOH or moist silver oxide ( $\text{Ag}_2\text{O} + \text{H}_2\text{O}$ ).

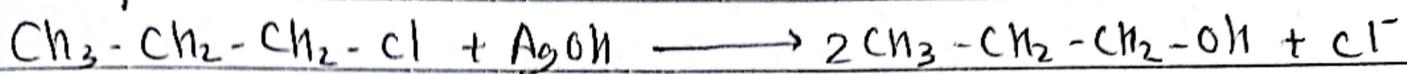


Example:



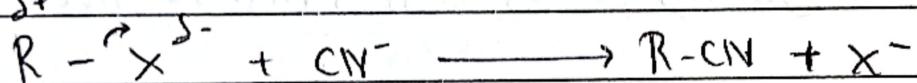
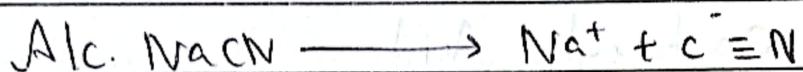


Example:

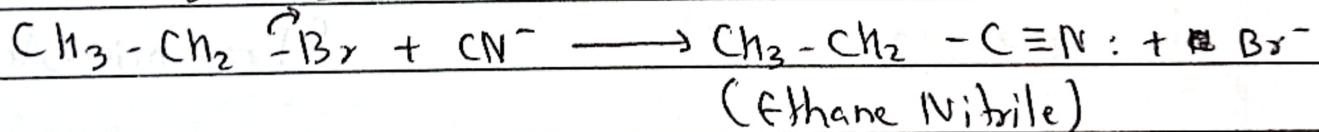


## 2. Preparation of Alkyl Nitrile from Alkyl halide

→ When alkyl halide is treated with alcoholic NaCN or KCN, alkyl nitrile is formed:



Example:



→ This prepared alkyl nitrile is very important starting material for the preparation of other organic compounds like aldehyde, carboxylic acid, Amine.

→ This reaction is used to increase the length of carbo-chain in organic compound.

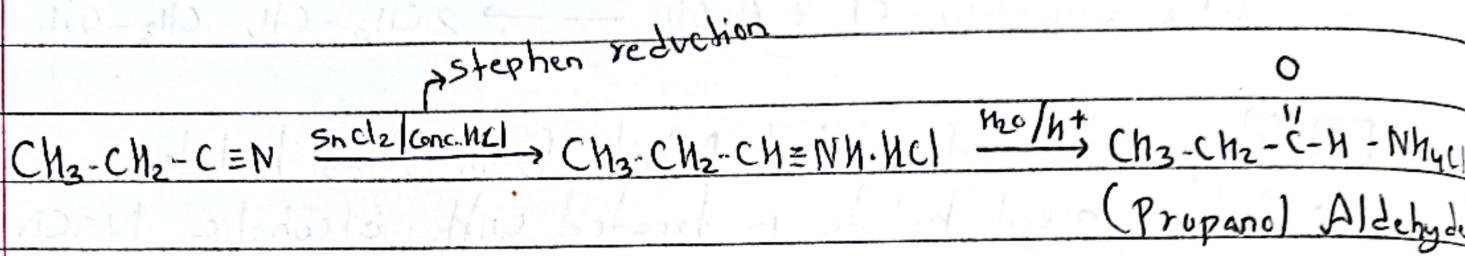
Note:

$\text{R-C}\equiv\text{N}$  is alkyl Nitrile

$\text{R-N}\equiv\text{C}$  is isocyanide.

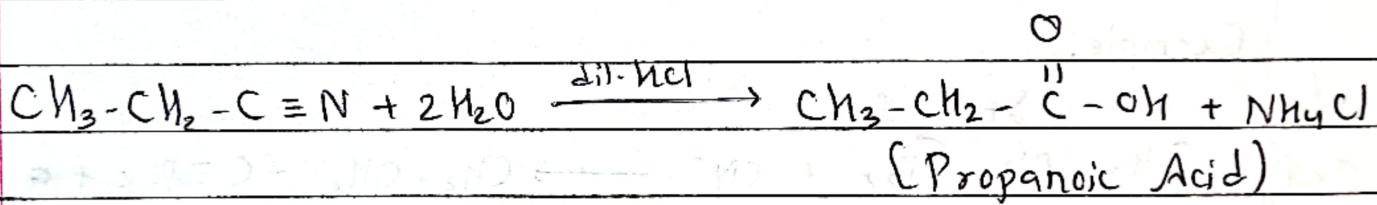
# Preparation of different organic compound from (Alkyl/Nitrile) (Alky) cyanide)

a. Preparation of Aldehyde

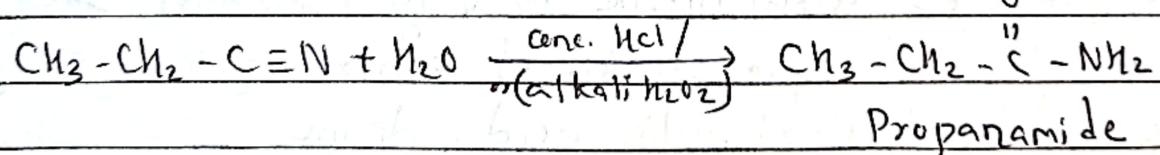


b. Preparation of Carboxylic Acid

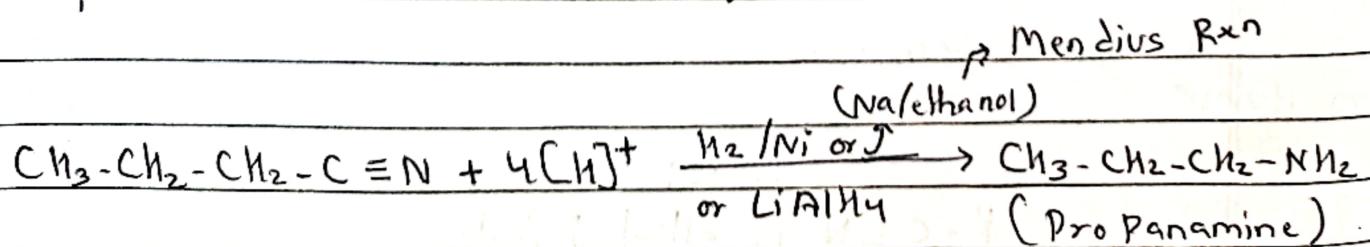
Complete acidic hydrolysis of Alkyl nitrile gives Carboxylic acid.



c. Preparation of Amide from Alkyl Nitrile : Partial Hydrolysis



~~v.v.t~~ d. Preparation of amine from Alkyl Nitrile



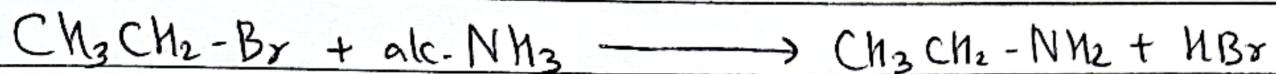
or

(1-amino Propane)

### 3. Formation of Amines from Alkyl halide

#### Case 1:

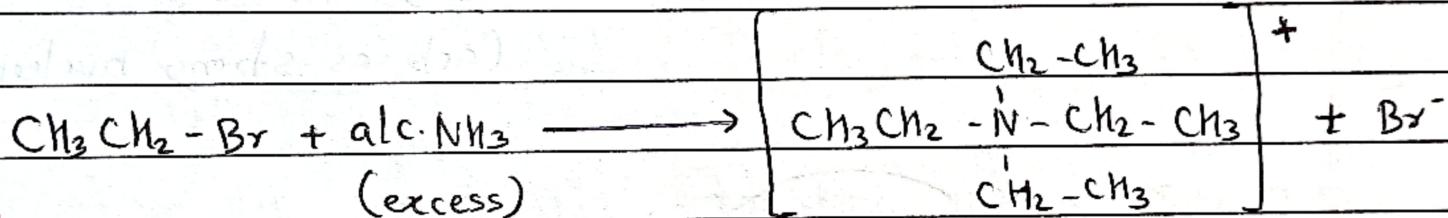
When equimolar alkylhalide is treated with alcoholic ammonia primary amine ( $1^\circ$  amine) is obtained.



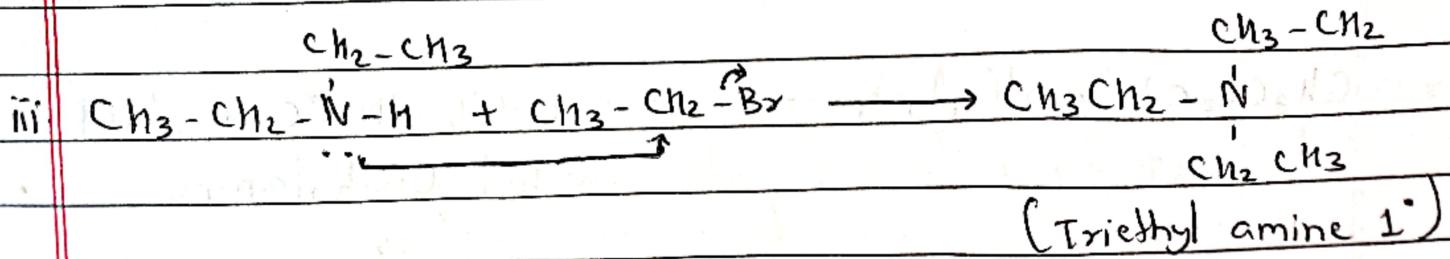
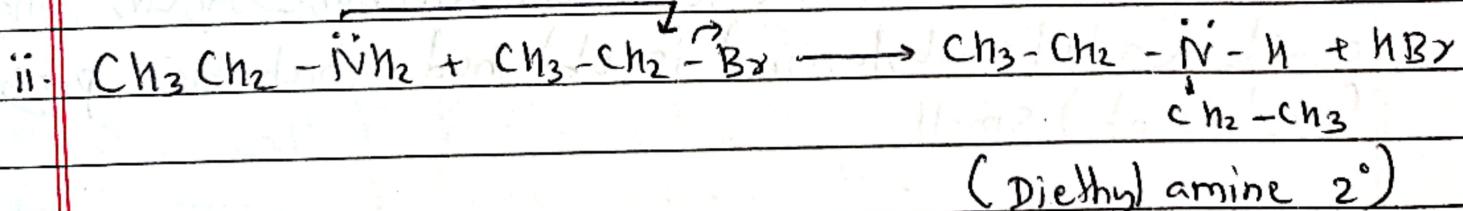
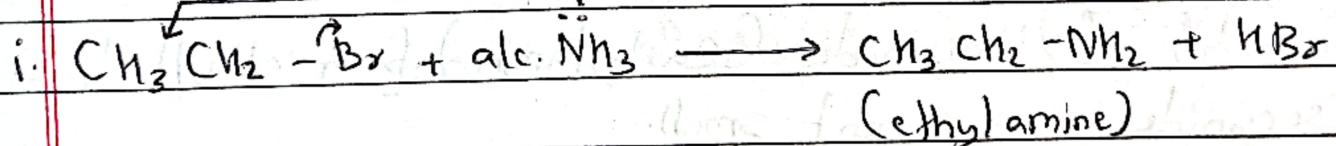
Ethylamine ( $1^\circ$  amine)

#### Case 2:

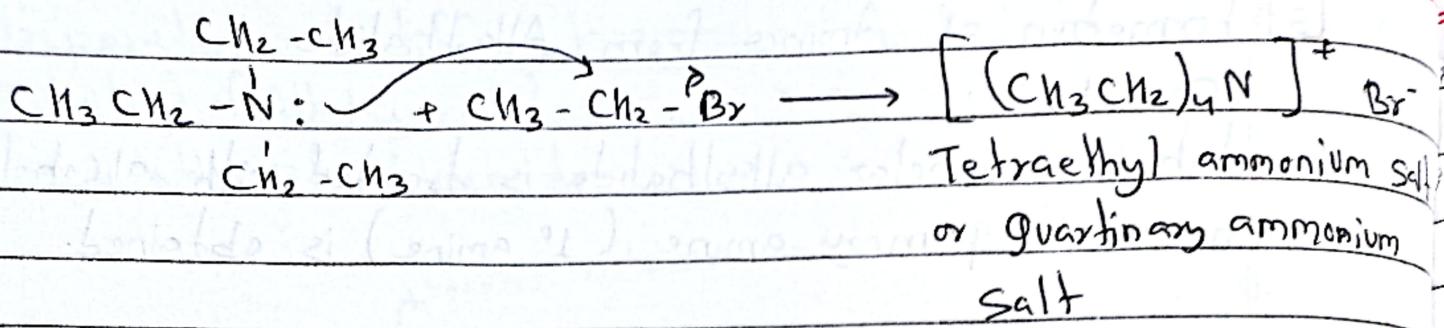
But if excess alcoholic ammonia or alkylhalide is kept, quaternary ammonium salt is obtained rather than  $1^\circ$  amine



↳ Steps:

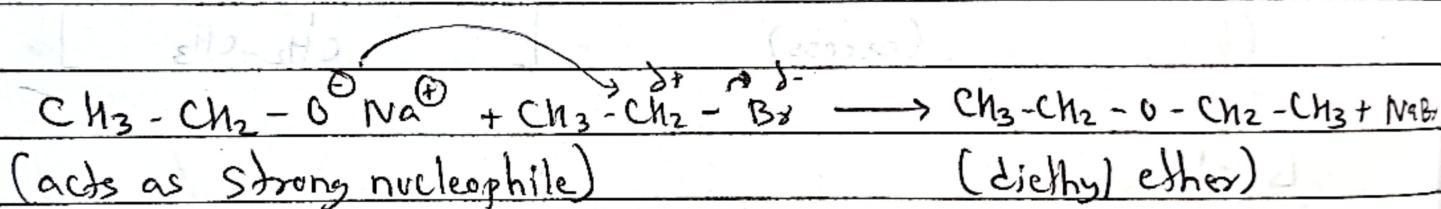
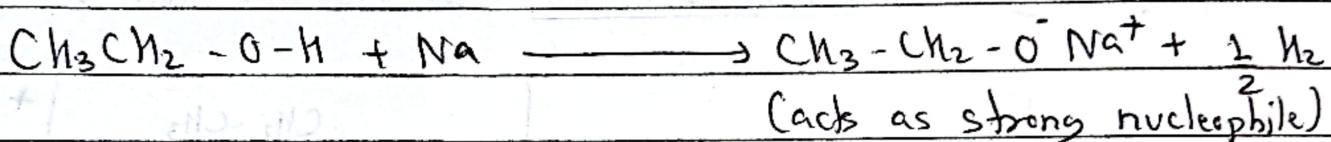


iv.



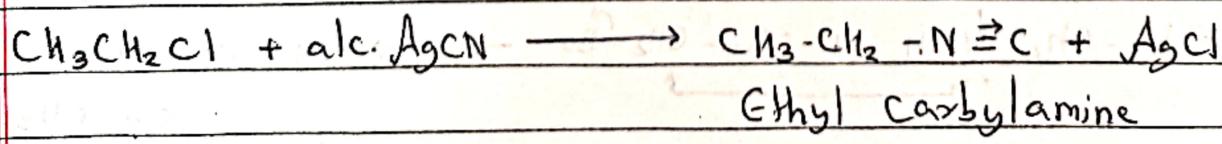
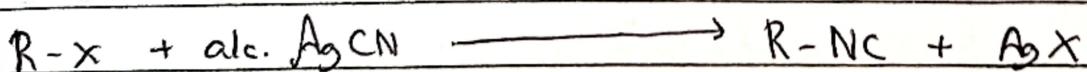
#### 4. Formation of ether from Alkyl halide

- It is also called Williamson's ether synthesis reaction.
- When metal alkoxide (obtained by treating alcohol with metal (Na)) is treated with alkylhalide, ether is obtained.



#### 5. Formation of isocynide (Carbylamine) from alkylhalide

- Isocynide gives pungent smell.
- When alkyl halide is treated with alcoholic  $\text{AgCN}$ , Alkyl isocynide (alkyl carbylamine) is obtained which has pungent (unpleasant) smell.



or

Ethyl Isocynide

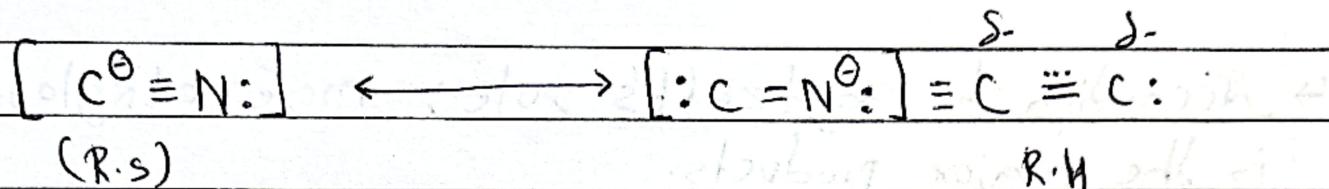
Note:

Isocynide on reduction gives  $2^\circ$  amine.

## # Ambident Nucleophile

→ Those Nucleophile that has more than one attacking site to the electrodeficient centre is called ambident Nucleophile.

Example:  $\text{C}^-\text{N}:$



Resonating Structure

Resonance Hybrid

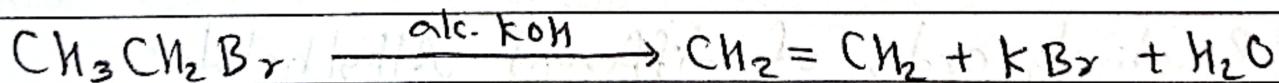
In the above case, cyanide can attack from both Carbon and Nitrogen side.

→  $\text{C}^{\ominus}\text{N}$  behaves as ambident Nucleophile, if  $\text{KCN}$  (strong electrolyte) is used.

But in case of  $\text{AgCN}$ , attacking side is only from nitrogen side.

## # Elimination Reaction

### 1. Dehydrohalogenation of Alkyl halide ( $\beta$ -elimination)

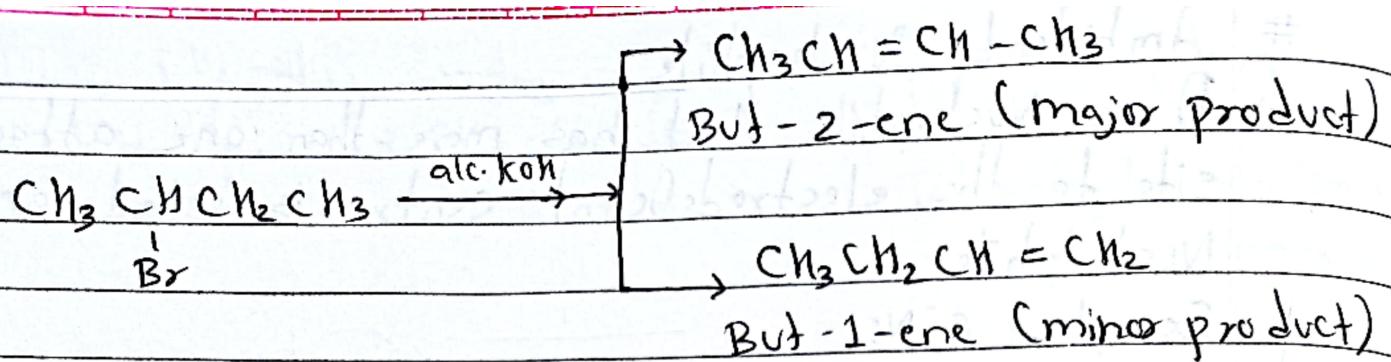


↳ Also called  $\beta$  elimination

↳ H- removed from  $\rightarrow \beta$ -Position

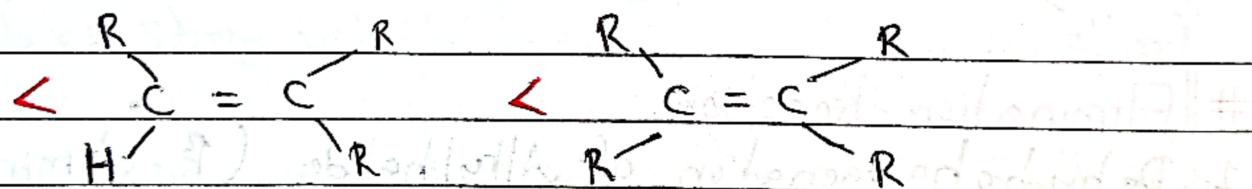
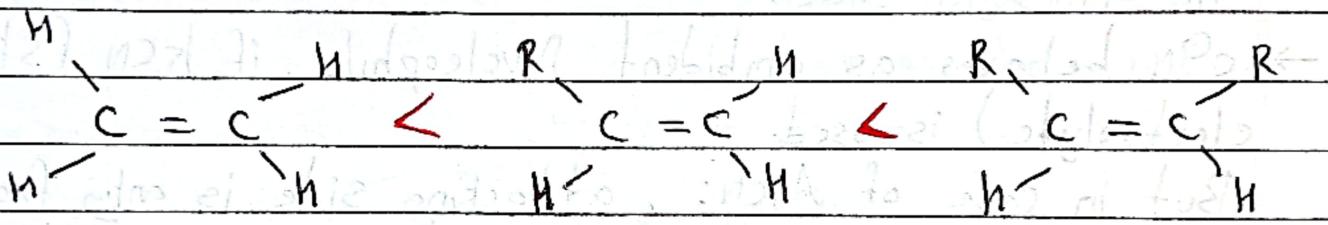
↳ Br removed from  $\rightarrow \alpha$  position.

↳ If dehydrohalogenation of alkyl halides can occur in two possible ways, the formation of product is given by, on the basis of Saytzeff's rule.



- According to Saytzeff's rule: more alkylated product is the major products.
- More substituted alkenes are more stable.

### Stability order

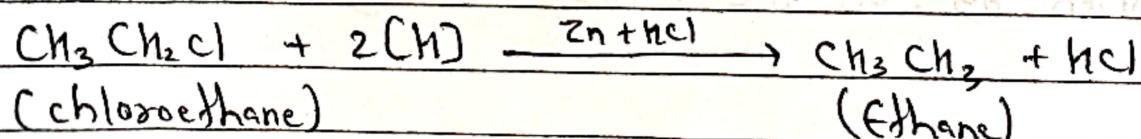
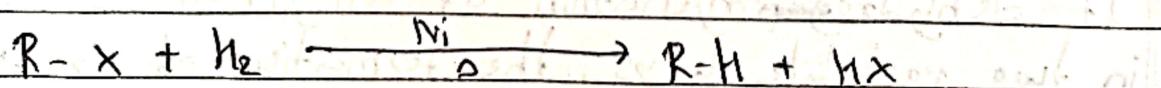


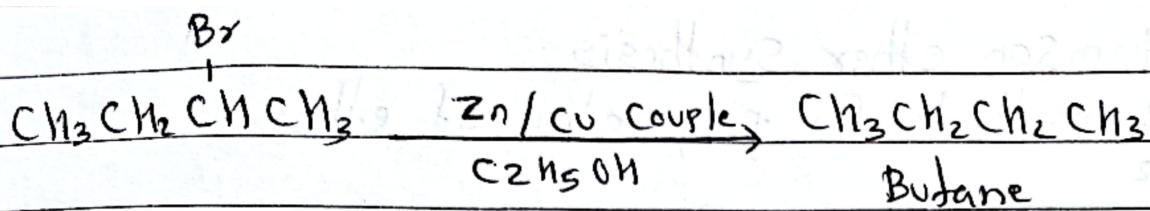
Reactivity order of different Alkyl halide:

$$3^\circ > 2^\circ > 1^\circ \text{ and } \text{RI} > \text{RBr} > \text{RCl}$$

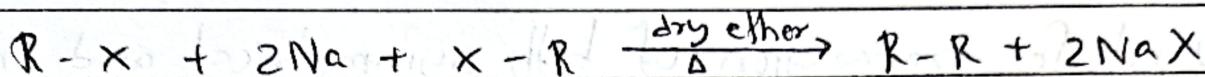
## 2. Reduction of Haloalkanes

Haloalkanes are reduced into alkanes in the presence of  $\text{H}_2/\text{Ni}$  or  $(\text{Zn} + \text{HCl})$  or  $\text{HI}/\text{Red PO}_4$  or  $\text{LiAlH}_4$





### 3. Wurtz Reaction or Wurtz Synthesis



→ 2 molecule of alkyl halide

→ with active metal → highly reactive.

→ Dry ether

    → very good non-polar aprotic solvent.

Product → symmetrical

    → Not suitable for the preparation of unsymmetrical alkanes.

→ Good method - for preparation of higher alkanes.

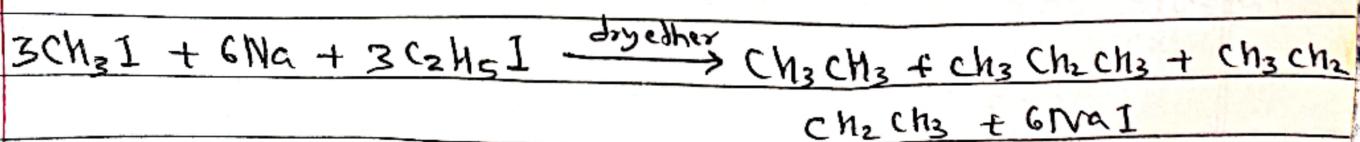
→ Methane can't be prepared by this method.

→ Shows free radical mechanism.

\* 3rd alkylhalides cannot be converted to alkane by this method because they are converted to alkenes due to elimination.

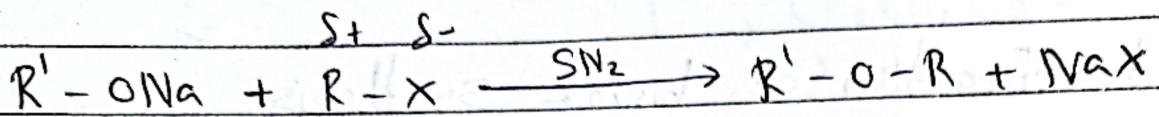
Reactivity order:  $\text{R}_1 > \text{RBr} > \text{RCl} > \text{RF}$

→ If different alkylhalide are used, a mixture of product alkanes are produced which cannot be easily separated.

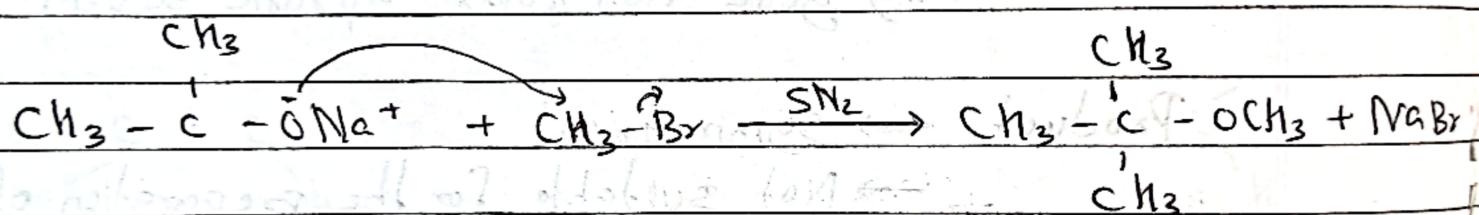
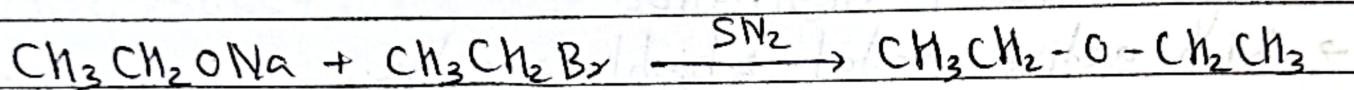


## # Williamson ether synthesis

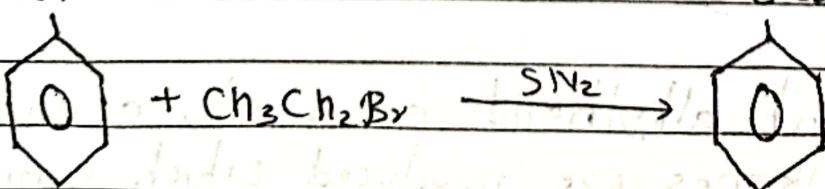
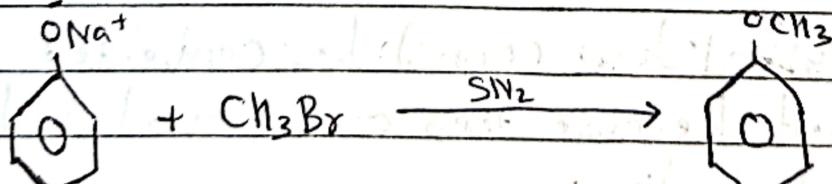
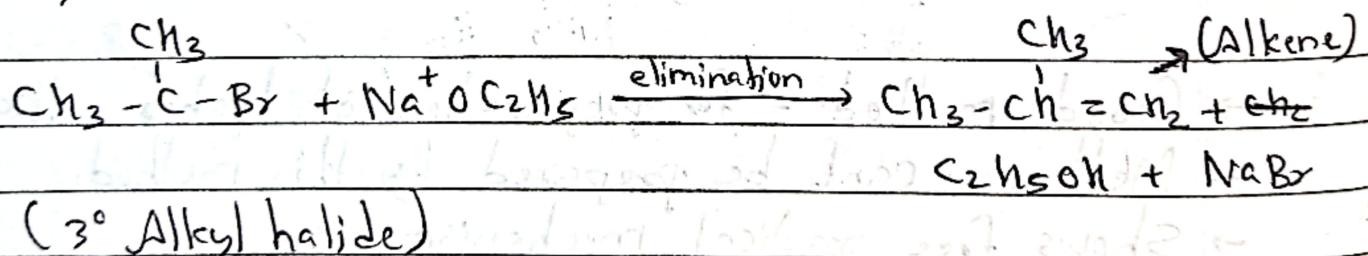
- Best methods for preparation of ether
- $SN_2$



- Used for preparation of both symmetrical and unsymmetrical ether

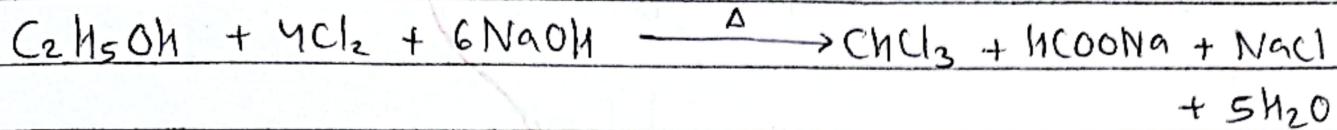


But,



## # Chloroform

→ Generally, it is prepared by treating ethyl alcohol with chlorine in the presence of alkali.



Note:  $\text{CHX}_3$  is haloform

If  $X = \text{Cl}$ , then  $\text{CHCl}_3$  is chloroform

If  $X = \text{Br}$ , then  $\text{CHBr}_3$  is bromoform

If  $X = \text{I}$ , then  $\text{CHI}_3$  is Iodo

## # Laboratory Preparation of chloroform

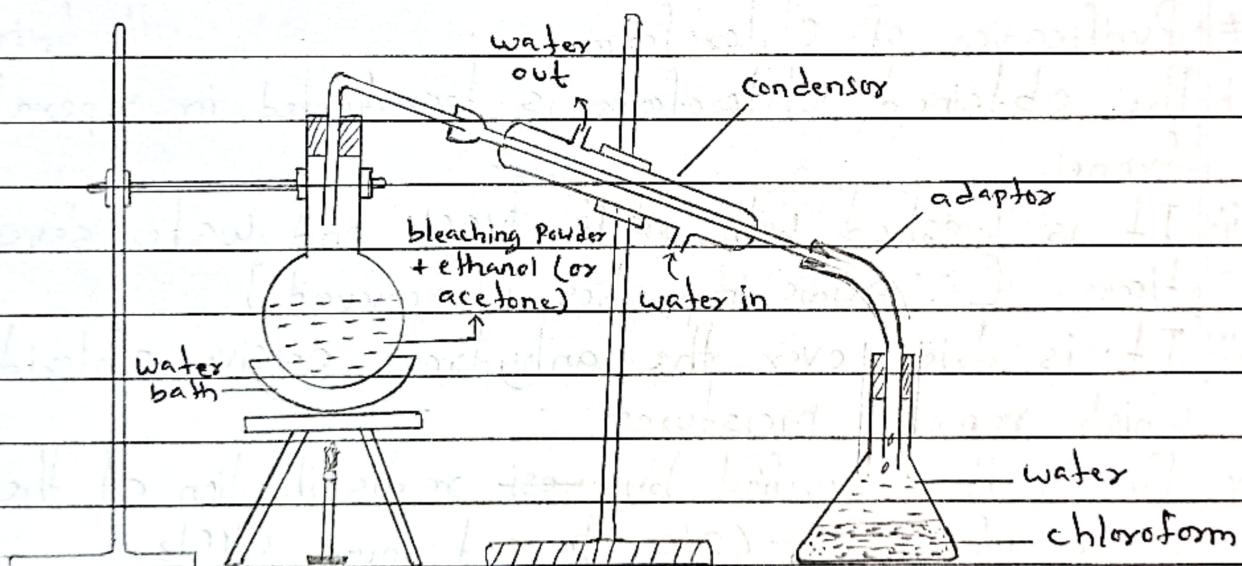


Fig: Lab preparation of chloroform

### → Steps:

- i. 1<sup>st</sup> solution of bleaching powder ( $\text{CaOCl}_2$ ) is prepared by mixing 100 gm of bleaching powder in 200 ml water.
- ii. Prepared paste of  $\text{CaOCl}_2$  is taken into roundbottom flask and mixed with either 25 ml ethanol or acetone slowly.
- iii. Experimental setup is made as shown in figure.

- iv. Vapour of water and chloroform is obtained in receivers.
- v. Chloroform being heavy settles below the water layer.
- vi. Finally, chloroform is collected in separate apparatus by the help of separating funnel.

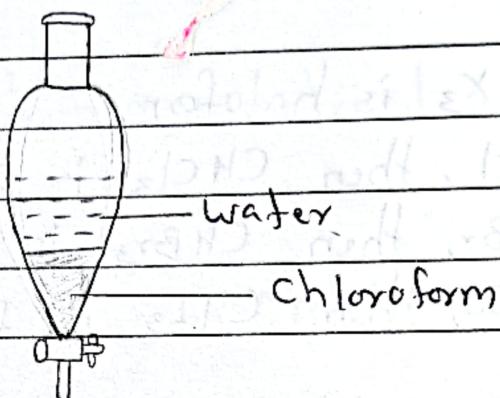


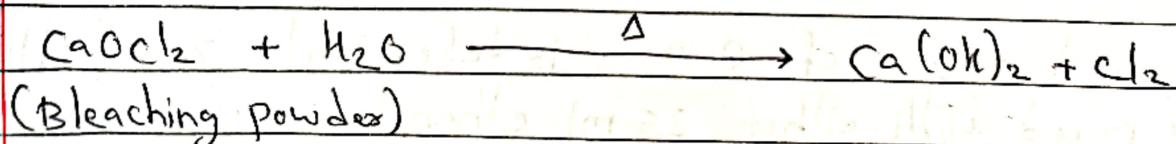
Fig: Separating funnel

### # Purification of chloroform

- i. The obtained chloroform is transferred in separating funnel.
- ii. It is washed with dilute NaOH and water several times. [∴ acidic impurities is removed]
- iii. It is dried over the anhydrous calcium chloride ( $\text{CaCl}_2$ ) which removes moistures.
- iv. Finally it is purified by redistillation at the temperature of  $60^\circ\text{C} - 62^\circ\text{C}$  to get pure  $\text{CHCl}_3$ .  
[∴ Boiling point of  $\text{CHCl}_3 = 61^\circ\text{C}$ ]

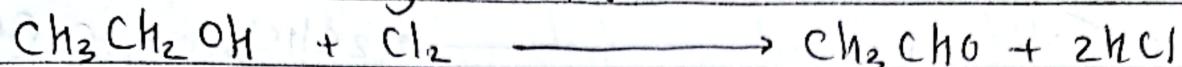
### # Reaction involved during chloroform formation

Note: Bleaching powder acts as chlorinating, hydrolyzing and oxidizing agent.



## 1. When ethanol is used:

### a. Oxidation of Ethyl Alcohol

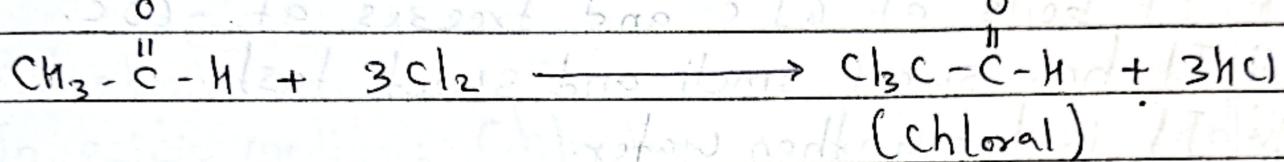


## Ethanol

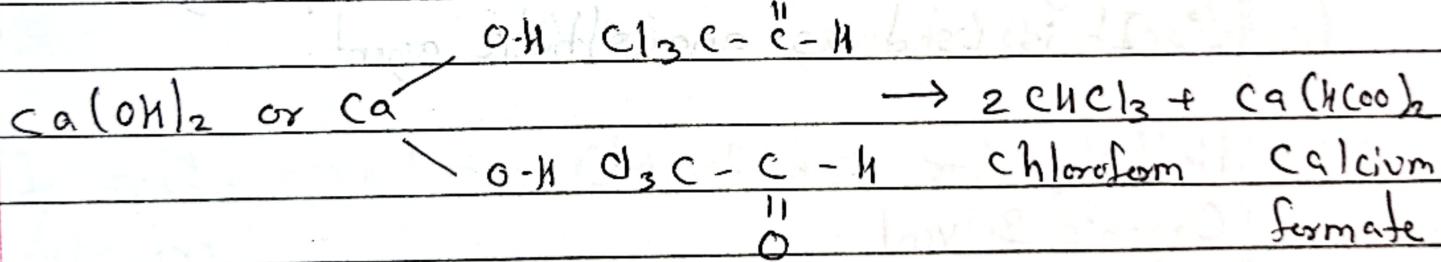
Ethanol

## (Acetaldehyde)

### b. Chlorination of Acetaldehyde

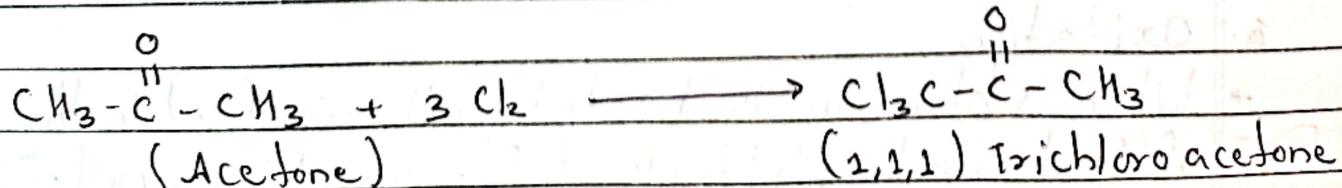


### c. Hydrolysis of chloral

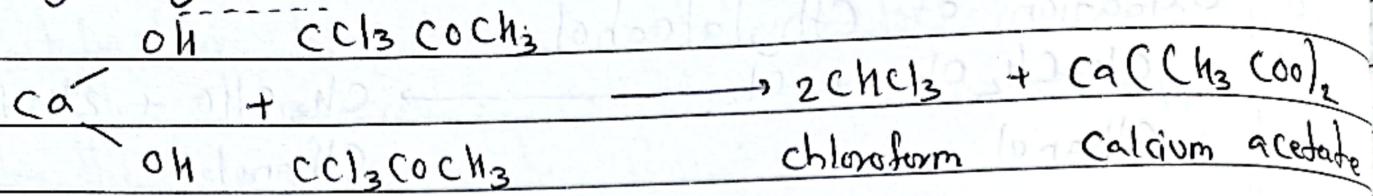


## 2. From Acetone

## a. Chlorination of Acetone



## b. Hydrolysis



## # Properties of Chloroform

- i. Chloroform is heavy colourless oily liquid.
- ii. It boils at  $61^\circ\text{C}$  and freezes at  $-60^\circ\text{C}$ .
- iii. It has sweet smell and sweet taste.
- iv. It is heavy than water.
- v. Sparingly soluble in water but readily soluble in organic Solvent like ether, alcohol etc.  
∴ It is good Solvent for oil and fats.
- vi. Inhaling its small amount causes temporary unconsciousness.  
∴ It is used as anaesthetic agent.

Note: ]

Organic Solvent

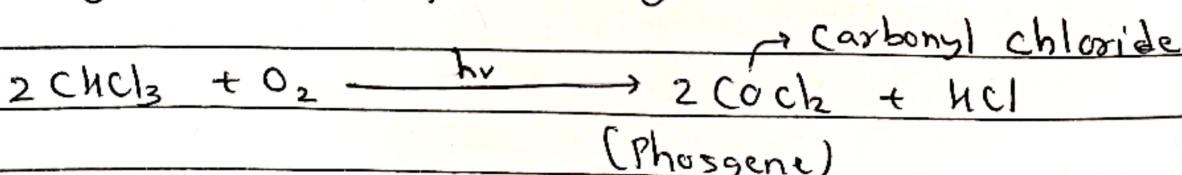
- a. Ether ( $\text{R}-\text{O}-\text{R}$ )
- b. Benzene ( $\text{C}_6\text{H}_6$ )
- c. Alcohol ( $\text{R}-\text{OH}$ )
- d.  $\text{CCl}_4$  (Carbon Tetrachloride)

## # Chemical Properties of chloroform

### 1. Oxidation

→ When chloroform is treated with air ( $\text{O}_2$ ) in the presence of light carbonyl chloride (Phosgene) is formed.

→ Phosgene is very poisonous gas.

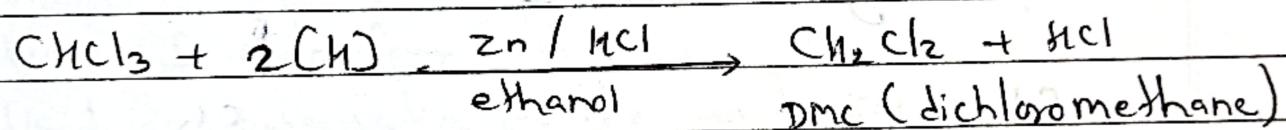


∴ To avoid the formation of phosgene from chloroform, following precaution should be adopted.

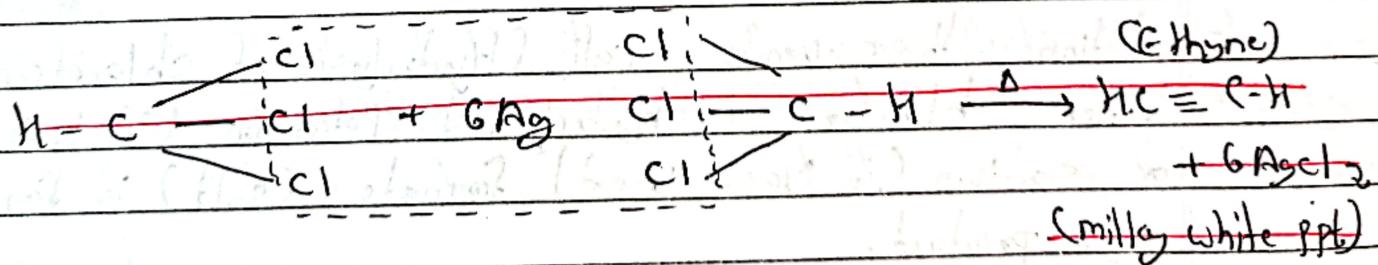
1. Chloroform is kept in dark or brown bottle to prevent from sunlight.
2. Chloroform should be filled up to the brim. So, no space for air is left. (Cap should be tightened)
3. 0-1% of ethyl alcohol is mixed along with chloroform to prevent from phosgene formation.

## 2. Reduction

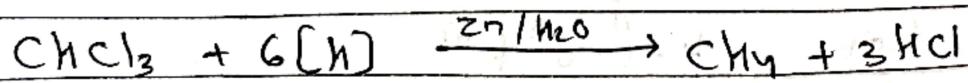
a. In acidic medium: Chloroform is reduced by  $\text{Zn/HCl}$  in the presence of ethanol to give dichloromethane (methylene chloride), a common organic solvent.



b. In neutral medium: Chloroform is reduced by  $\text{Zn/H}_2\text{O}$  (neutral medium) at low temperature, acetylene (calogone) is formed.

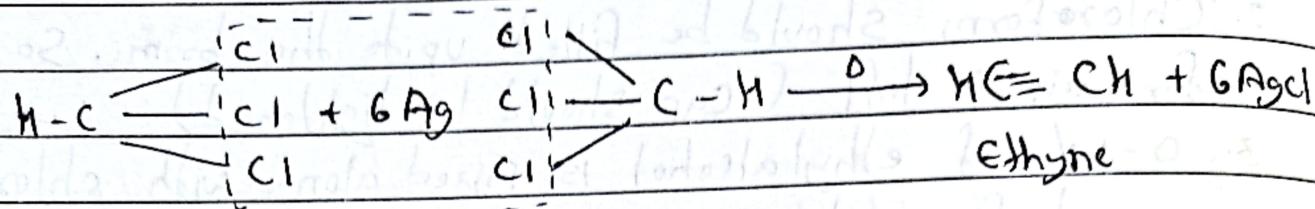


b. In neutral medium: chloroform is reduced by  $\text{Zn/H}_2\text{O}$  (neutral medium) to give methane.



### 3. Reaction with silver chloride

When chloroform is heated with silver powder, it gives ethyne (acetylene) gas.

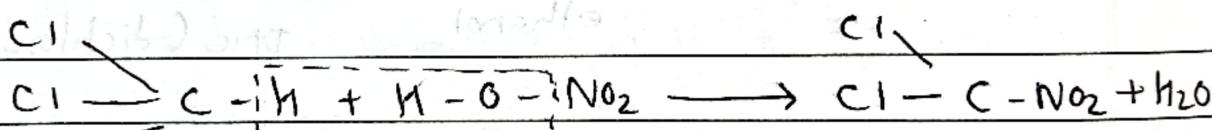


Note:

Iodoform gives similar reaction

### 4. Reaction with Nitric Acid ( $\text{HNO}_3$ )

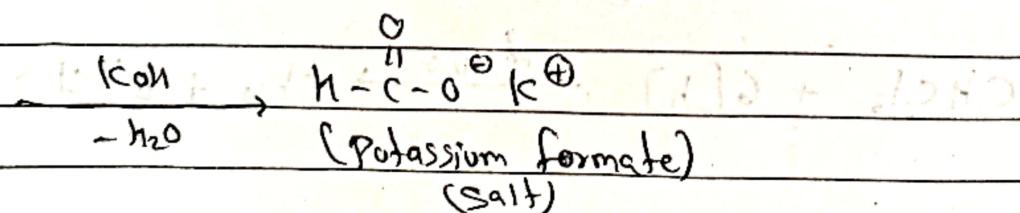
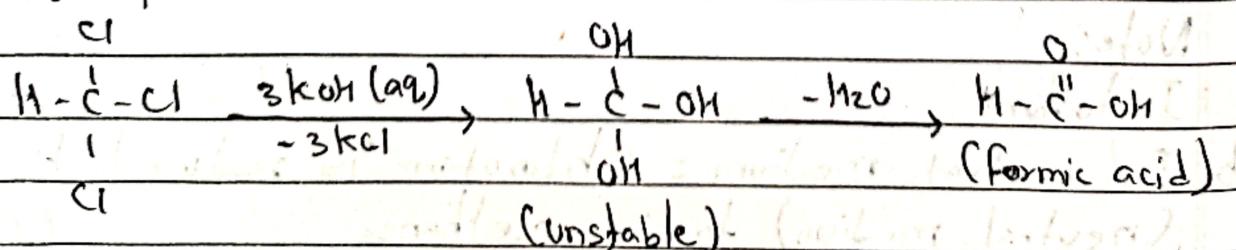
When chloroform reacts with nitric acid, poisonous chloropicrin gas is obtained.



(Chloropicrin)  
(Trichloro Nitro methane)

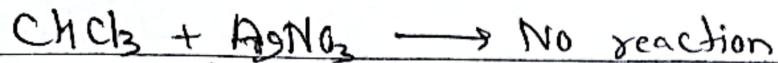
### 5. Action with aqueous alkali (Hydrolysis of chloroform)

When chloroform is hydrolysed Potassium (if KOH used) or sodium (if NaOH used) formate (salt) is formed as major product.



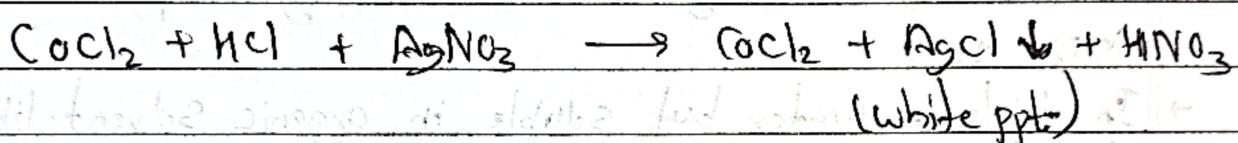
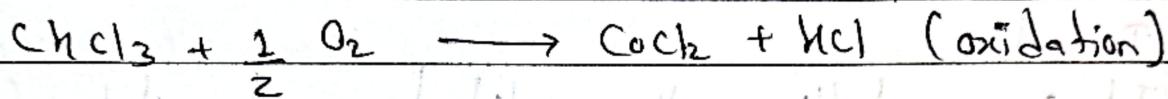
## 6. Action with silver Nitrate ( $\text{AgNO}_3$ )

- Pure chloroform doesn't react with  $\text{AgNO}_3$ .  
Hence there is no reaction and no formation of  $\text{AgCl}$ .



It is due to strong covalent bond between C-Cl in chloroform.

- But formation of white ppt. of  $\text{AgCl}$  occurs if impure  $\text{CHCl}_3$  is used. It is due to the oxidation of  $\text{CHCl}_3$ .



## # Uses of chloroform

- Used as preservative for the anatomical specimen.
- Used as solvent for waxes, rubber, fats, resins etc.
- Used for preparation of chloroform and chloropicrin etc.
- Used as anaesthetic.

## Note:

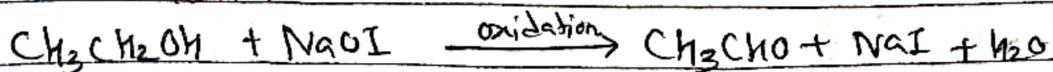
$\text{CHCl}_3$  is replaced by other safe anaesthetic it is because nowadays, it is because of probability of forming phosgene ( $\text{COCl}_2$ ) gas which cause heart and respiratory disorder.

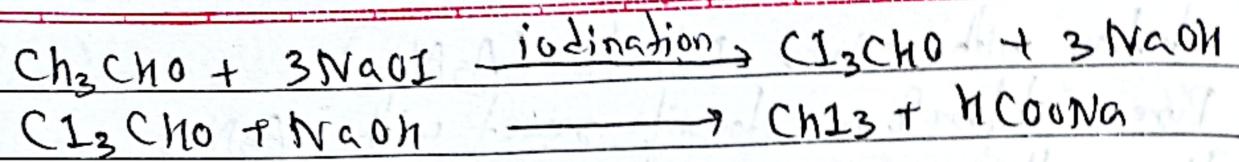
## # Iodoform ( $\text{CHI}_3$ )

- Also called Triiodomethane

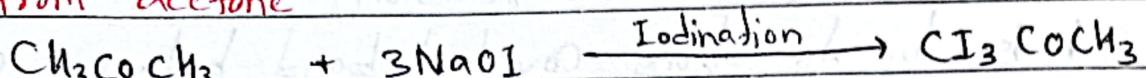
## # Preparation

- From Alcohol

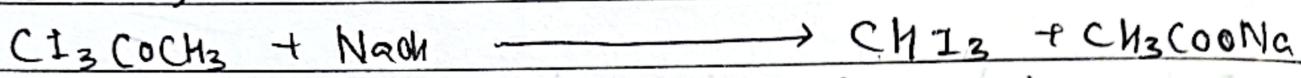




2. from acetone



(acetone)



(Iodoform)

### # Properties

- It is crystalline yellow solid having hospital smell with M.P. 119°C
- Insoluble in water but soluble in organic solvent like Benzene, ether, alcohol etc.
- Used as antiseptic as it release I<sub>2</sub> after slow decomposition
- Like chloroform, acetylene (CH≡CH) is produced when Iodoform is treated with silver powder.

### # Uses

- Used as antiseptic for heating of wounds as it liberates iodine.
- Used in pharmaceutical.
- Used for test of alcohol and carbonyl compound (-C=O) i.e. aldehyde and ketone.

### # Iodoform Test

- Iodoform test is shown by aldehyde and ketone having CH<sub>3</sub>-C=O group in it and also by alcohol that gives CH<sub>3</sub>-C=O group when (CH<sub>3</sub>-CH<sub>2</sub>-OH) is oxidized.

→