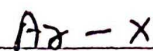


# HALOALKANES & HALOARENES



Haloalkane



Haloarene

⇒ Classification of Haloalkane & Haloarene.

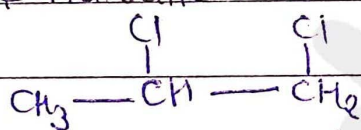
① On the basis of no. of Halogen atom

(a) Haloalkane

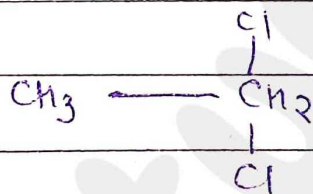
(i) Monohaloalkane.



(ii) Dihalooalkane

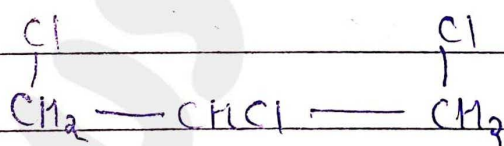


1,2-dichloropropane.



1,1-dichloroethane

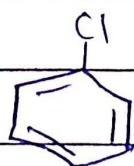
(iii) trihaloalkane



1,2,3-trichloropropane.

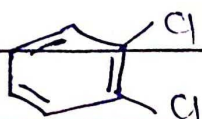
(b) Haloarene.

(i) Monohaloarene.



chlorobenzene

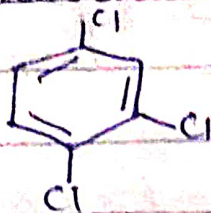
(ii) Dihalooarene



1,2-dichlorobenzene,

o-dichlorobenzene.

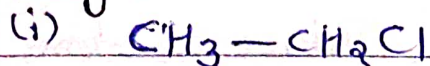
(iii) trihaloarene



1,2,4-trichlorobenzene

## ② Compound Containing $sp^3$ C-x bond

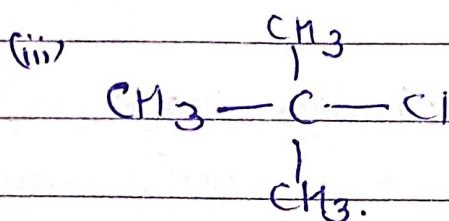
(a) Alkyl halide



chloroethane ( $1^\circ$ )

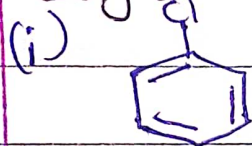


2-chloropropane ( $2^\circ$ )

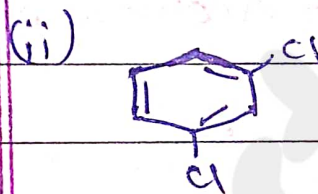


2-chloro-2-methylpropane ( $3^\circ$ )

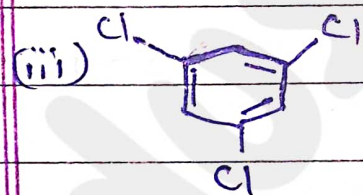
(b) Aryl Halide



chlorobenzene



1,3-dichlorobenzene



1,3,5-trichlorobenzene

(c) Allylic Halide

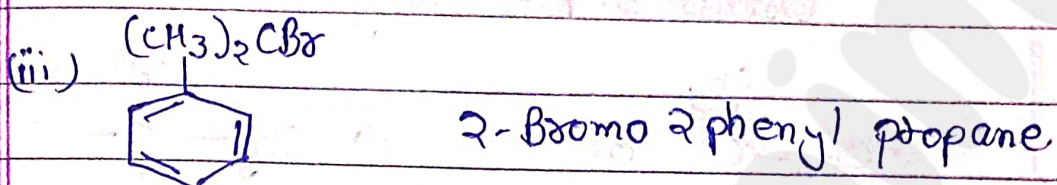
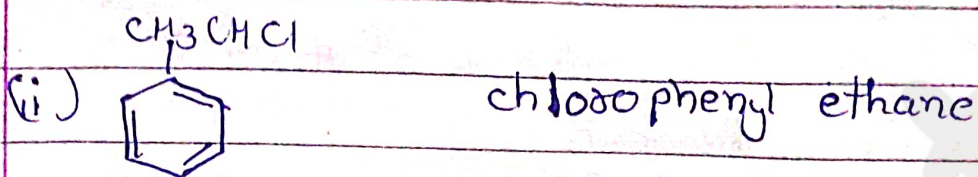
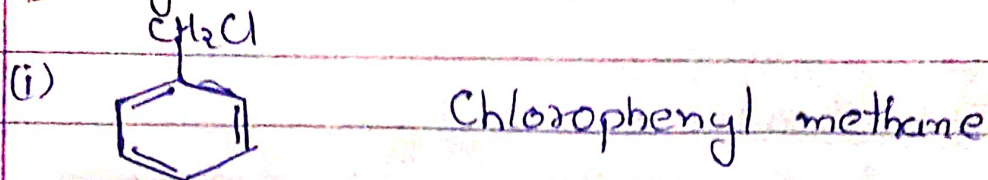


3-chloropropene



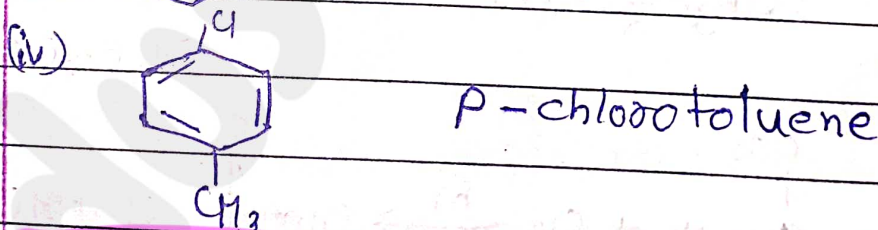
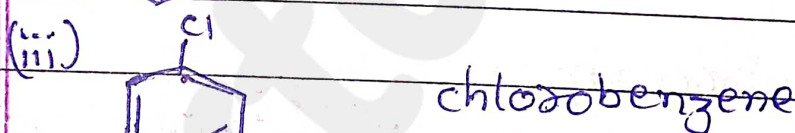
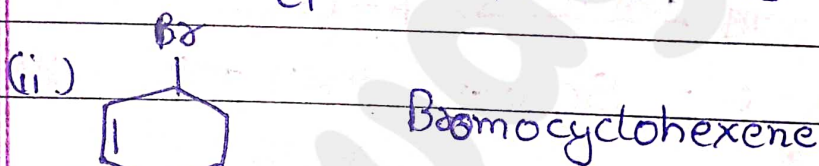
3-bromocyclohexene

(d) Benzylic halide:-

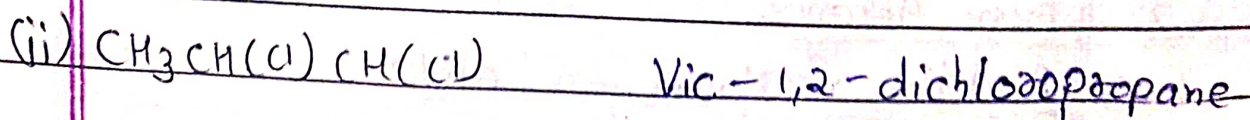
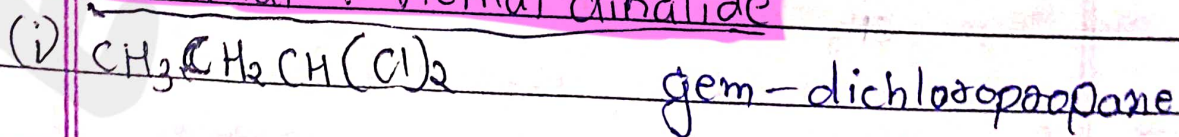


### ③ Compound Containing $sp^2$ C-X Bond

Vinyl Halide:-

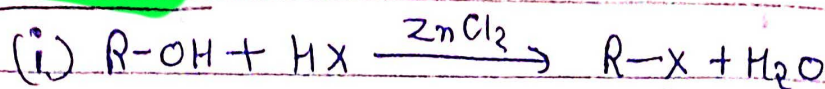


Geminal & Vicinal dibalide



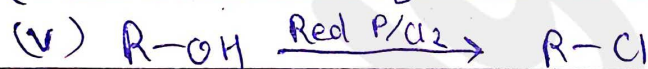
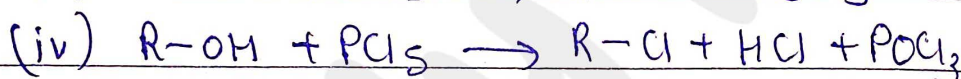
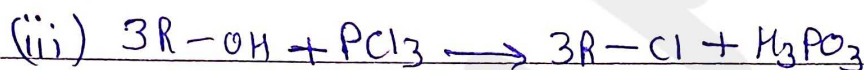
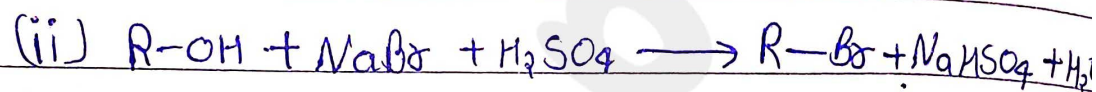
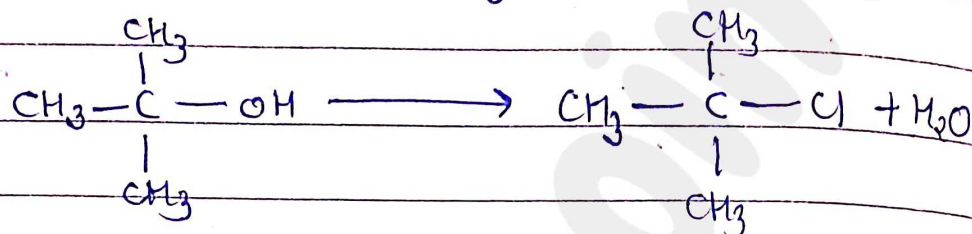
# # Preparation of Haloalkane

## ① from Alcohol :-

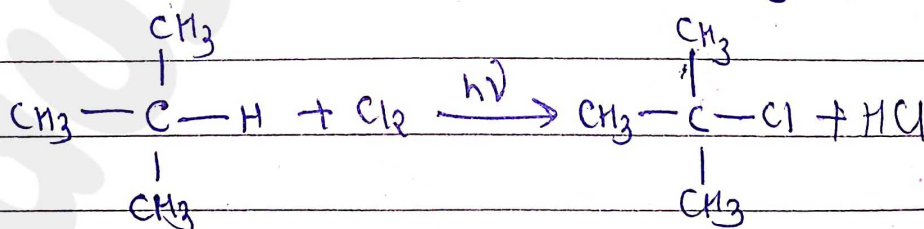
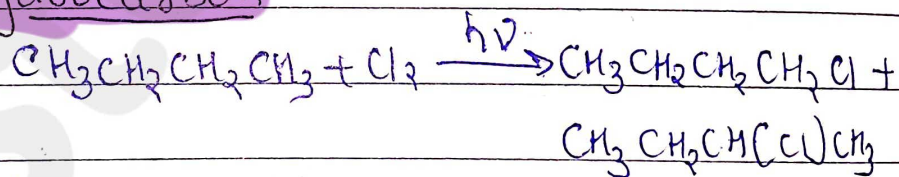


The equimolar mixture of HCl & ZnCl<sub>2</sub> is known as Gas Reagent.

Order of Reactivity - 3° > 2° > 1°

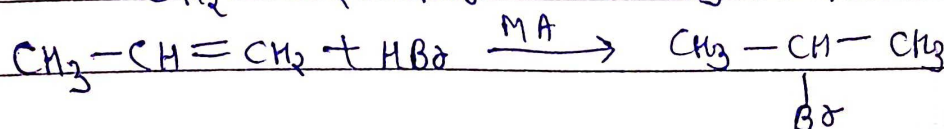
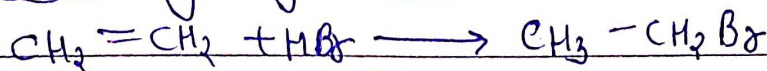


## ② from Hydrocarbon :-

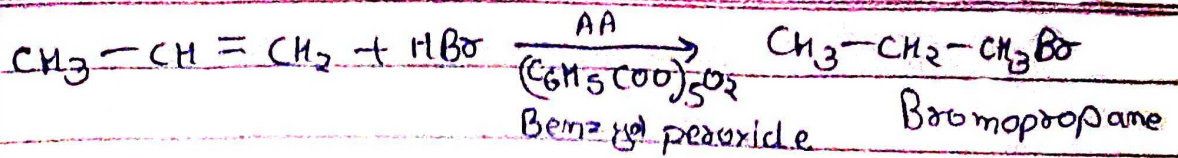


## ③ from Alkene :-

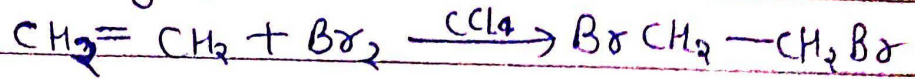
(a) Addition of Hydrogen halide



2-Bromo propane

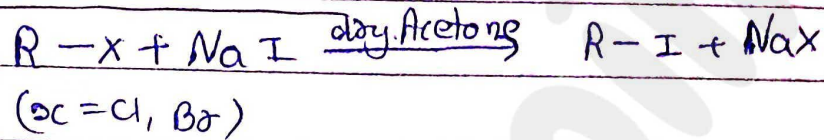


### (b) Addition of Halogen

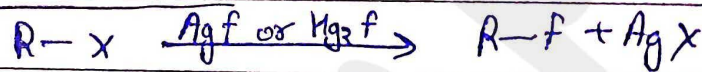


## ④ from Halogen exchange

### (a) Finkelstein Reaction

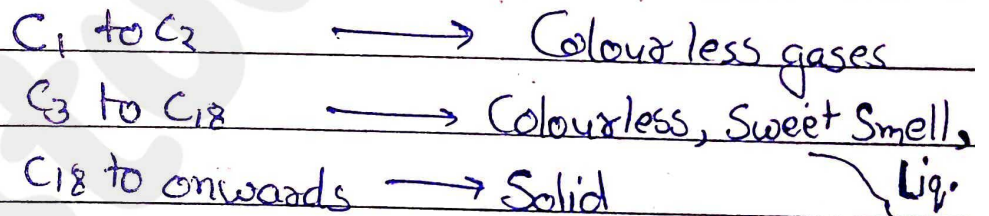


### (b) Swanst Reaction

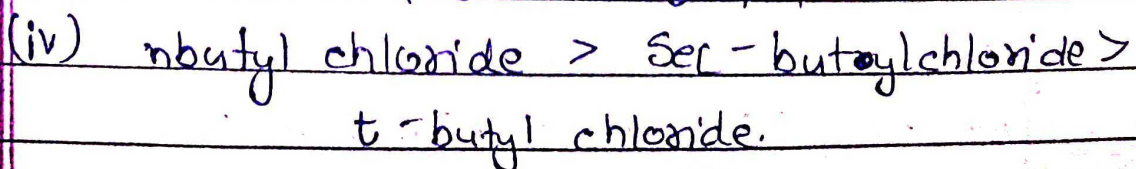
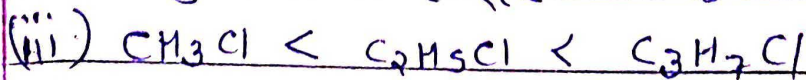
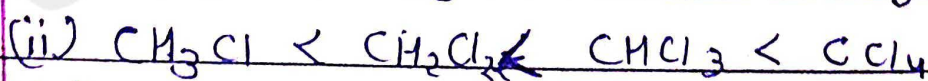
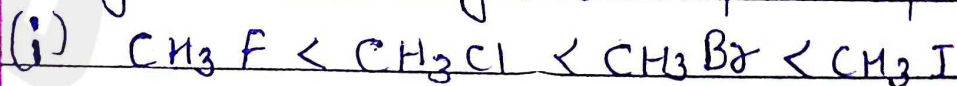


## # Physical Properties of Haloalkanes

### ① Physical State :-



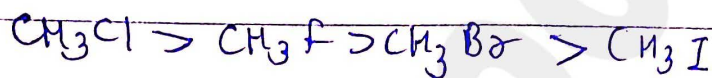
② Melting & Boiling Point :- Haloalkane has higher B.P. than alkane because of the polarity of CX bond & greater strength of Dipole - Dipole Interaction



③ Density:  $\text{CH}_3\text{F} < \text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_3\text{I}$   
 $\text{CH}_3\text{Cl} < \text{CH}_2\text{Cl}_2 < \text{CHCl}_3 < \text{CCl}_4$

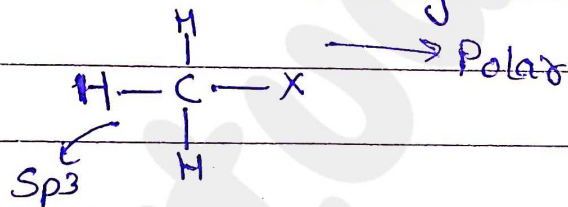
④ Solubility: Haloalkane are not Soluble in water because they are not able to form H-bond. It Soluble in organic Solution like Benzene, ether, Acetone,  $\text{CCl}_4$  etc.

⑤ Dipole Moment: (Polarity of Bond)



## # Chemical properties of Haloalkanes:

Nature of Reactivity (C-X bond)



$\text{I} > \text{Br} > \text{Cl}$  (Size of Halogen atom)

$3^\circ > 2^\circ > 1^\circ$  (No. of Halogen)

$\text{CH}_3\text{Cl} < \text{C}_2\text{H}_5\text{Cl} < \text{C}_6\text{H}_5\text{Cl}$  (Nature of Alkyl halide)

(i) Polarity of Bond -  $\text{CH}_3\text{Cl} > \text{CH}_3\text{F} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$

(ii) Bond length -  $\text{CH}_3\text{F} < \text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_3\text{I}$

(iii) Bond Enthalpy -  $\text{CH}_3\text{F} > \text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$

Types of Chemical Reactions:

① Nucleophilic Substitution Reaction.

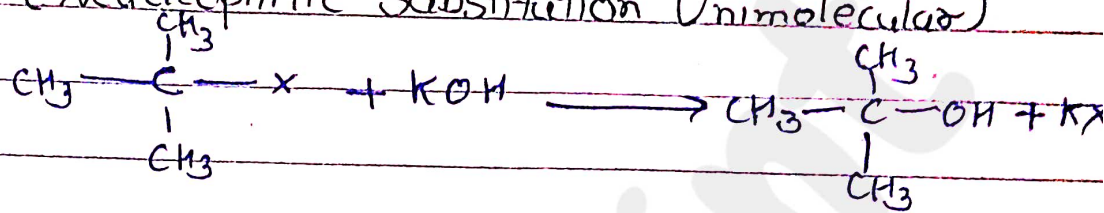
②  $\beta$ -elimination / Dehydrohalogenation

③ Reaction with Metal

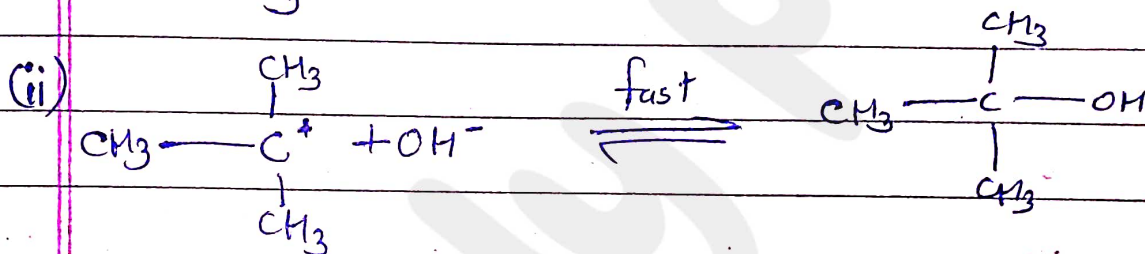
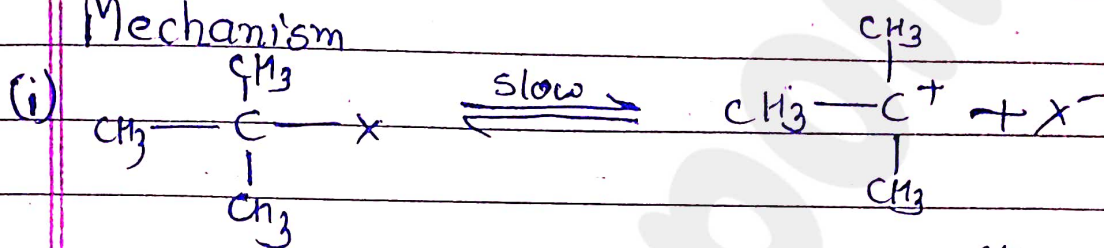
# ① Nucleophilic Substitution Reaction



(a)  $S_N1$  (Nucleophilic Substitution Unimolecular)

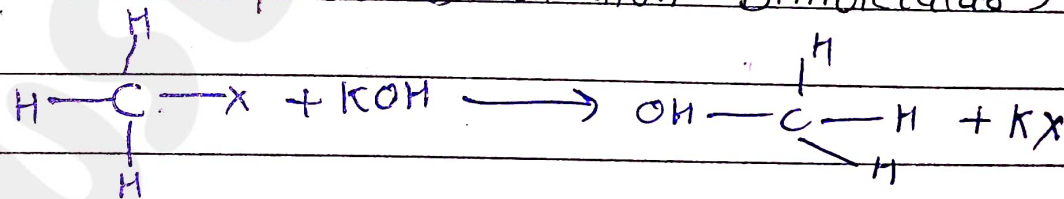


Mechanism

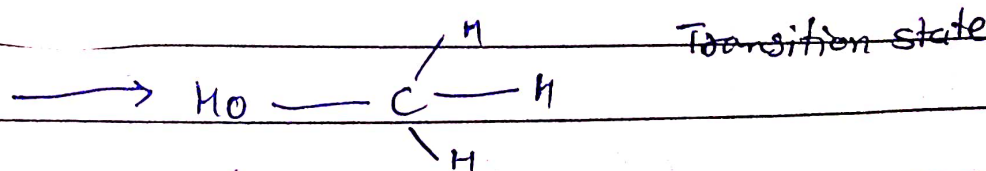
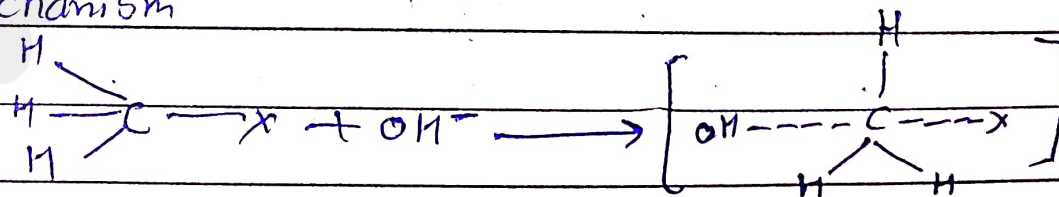


The order of reactivity of Alkyl halide in  $S_N1$  is  $3^\circ > 2^\circ > 1^\circ$

(b)  $S_N2$  (Nucleophilic Substitution Bimolecular)

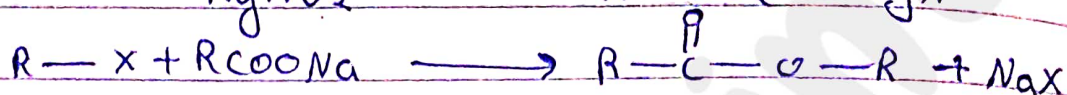
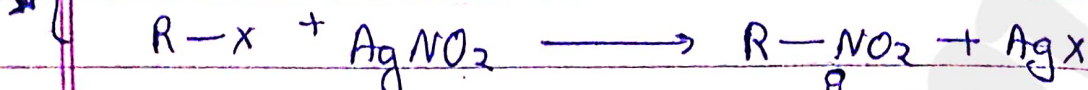


Mechanism

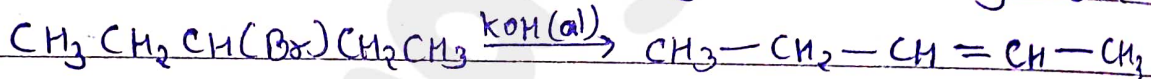
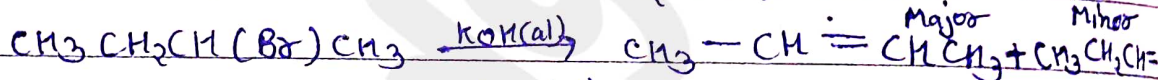


The order of Reactivity of Alkyl halide in  $S_N2$  is  $1^\circ > 2^\circ > 3^\circ$

## Nucleophilic Substitution Reaction

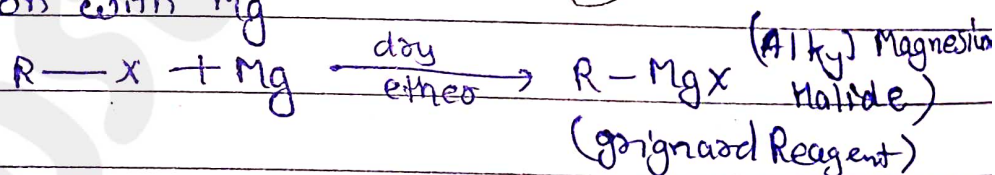


## ② $\beta$ -elimination Reaction (Dehydrohalogenation)

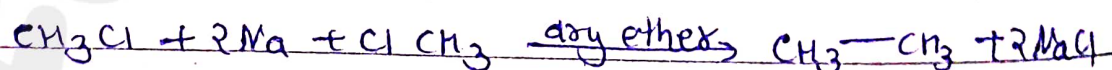
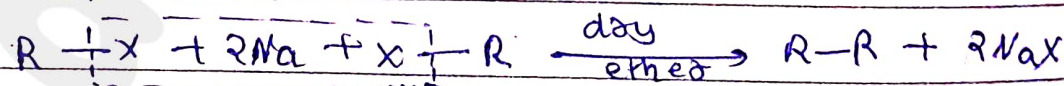


## ③ Reaction with Metal

(a) Reaction with Mg

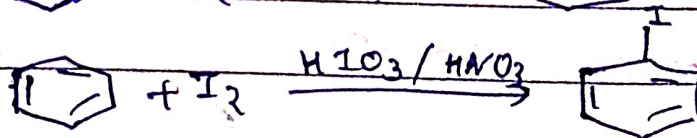
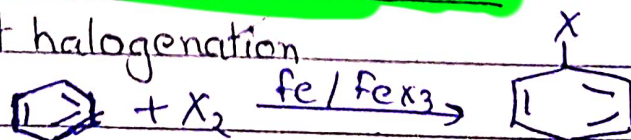


(b) Reaction with Na



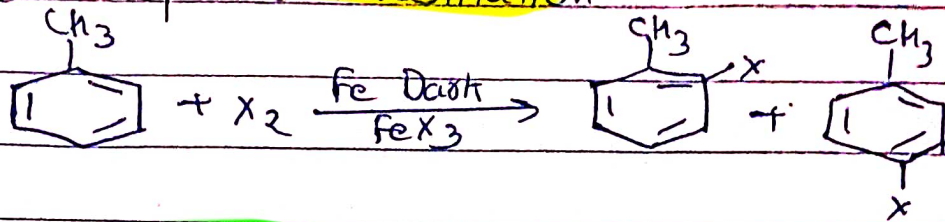
## # Preparation of Haloarenes

① By direct halogenation

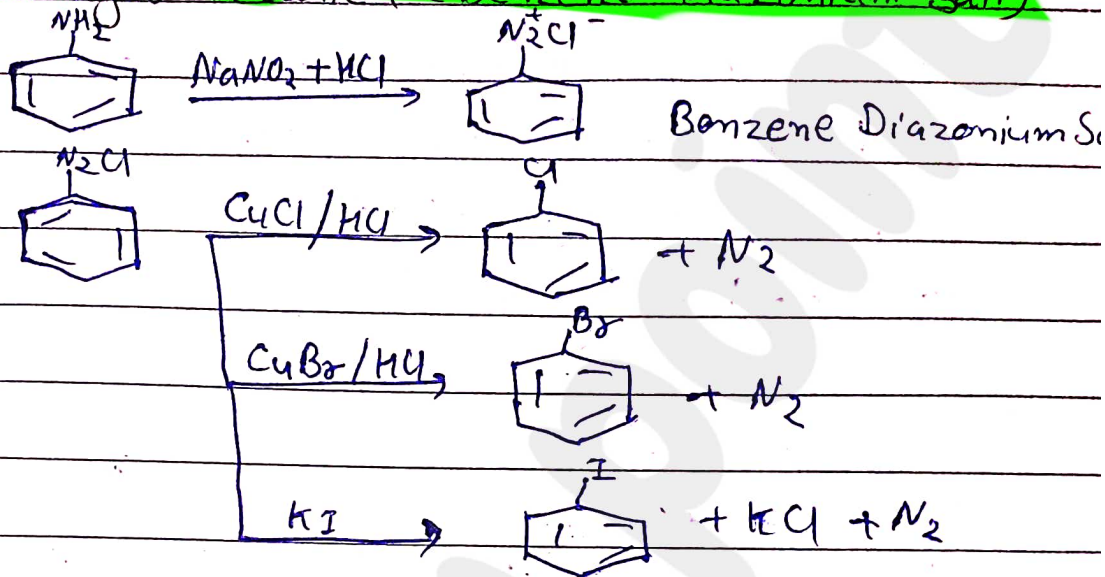




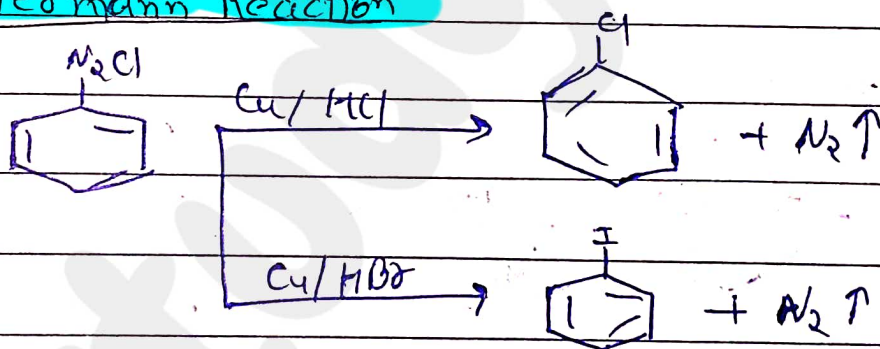
## ② By electrophilic Substitution



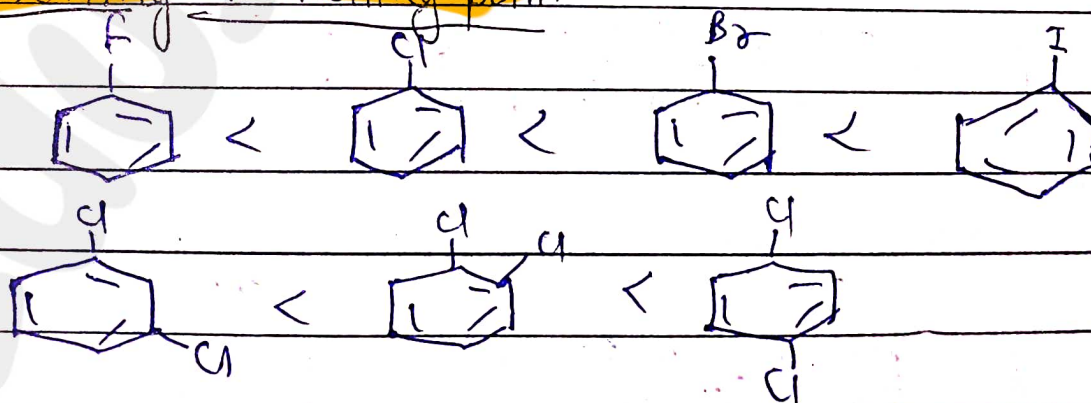
## ③ Sandmeyer Reaction (Benzene Diazonium salt)



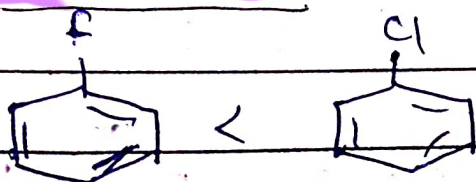
## ④ Gattermann Reaction



## Melting & Boiling point



## Dipole moment

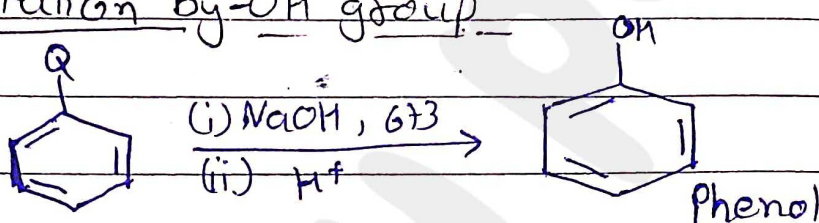


# # Chemical properties:

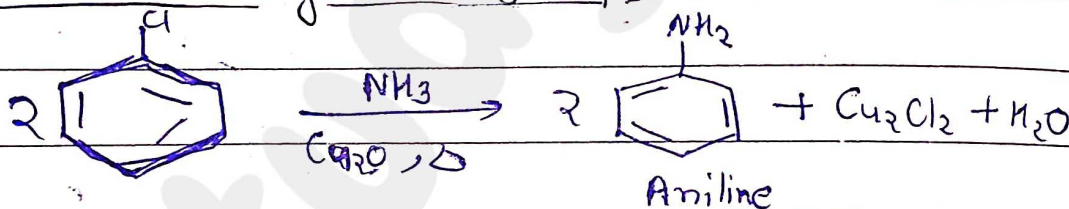
① Nucleophilic Substitution Reaction:- Aryl halide are less reactive towards Nucleophilic Substitution Rxn due to following reasons -

- (i) C-X bond Acquire partial double bond character because of the Resonance.
- (ii) Due to  $sp^2$  Hybridised Carbon
- (iii) In-Stability of Phenyl cation.

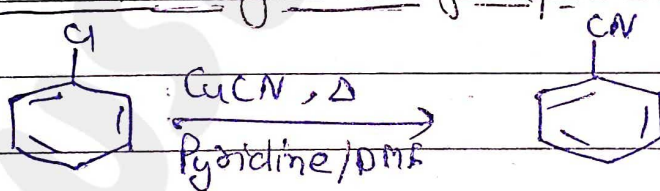
(a) Substitution by -OH group



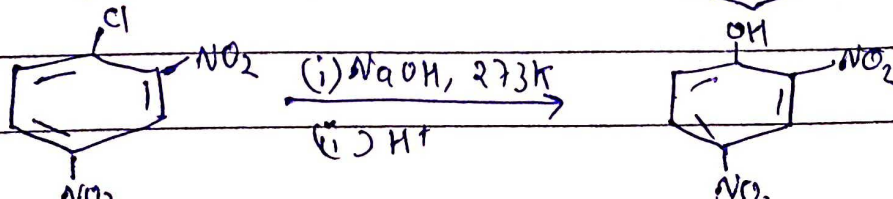
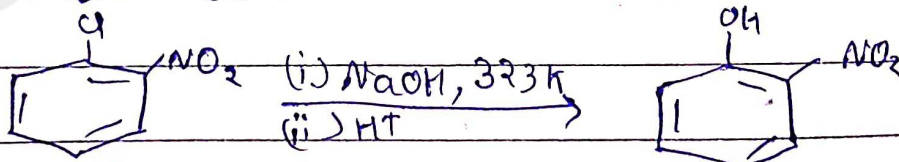
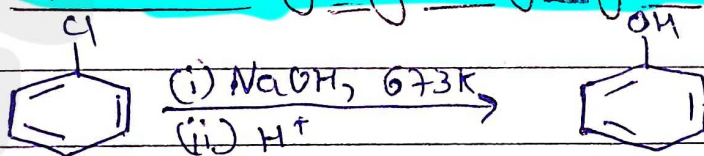
(b) Substitution by -NH<sub>2</sub> group

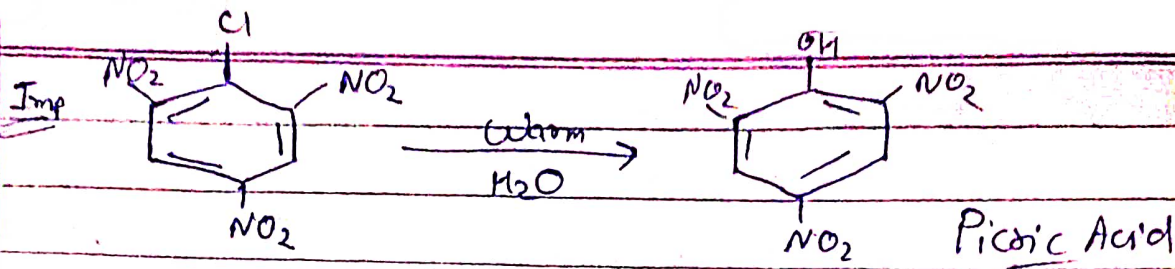


(c) Substitution by -CN group



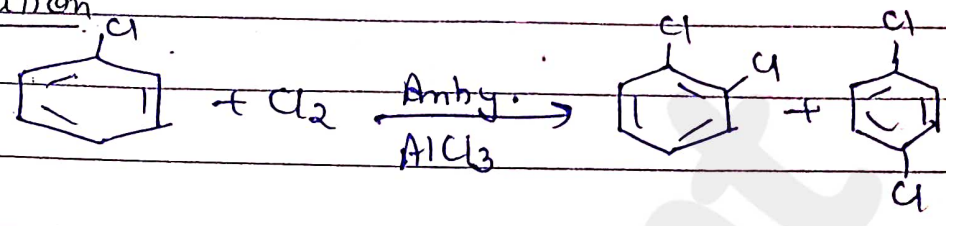
② Replacement by hydroxyl group



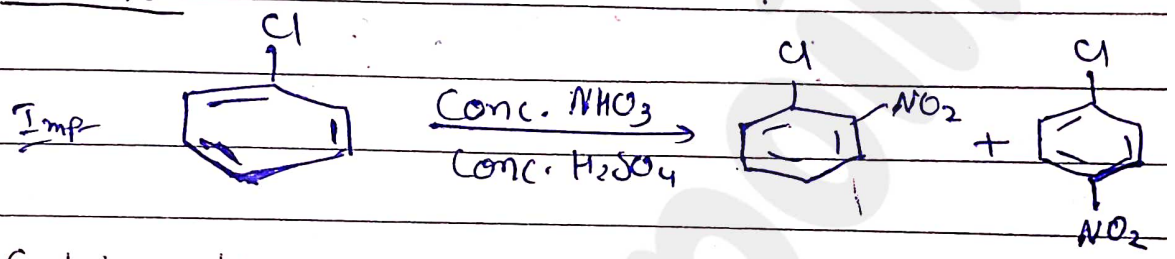


### ③ Electrophilic Substitution Reaction

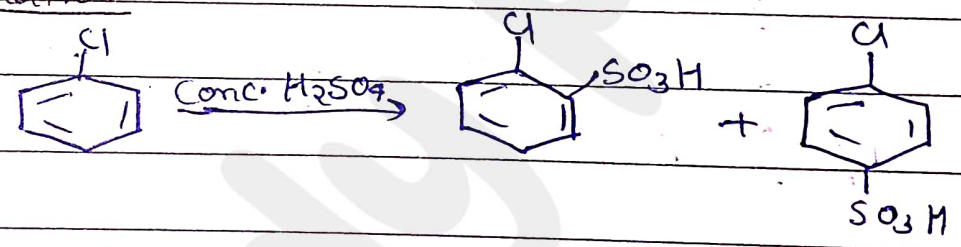
(a) Halogenation



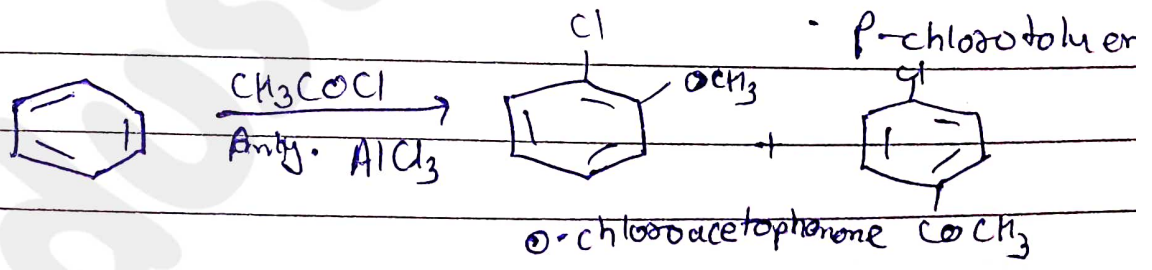
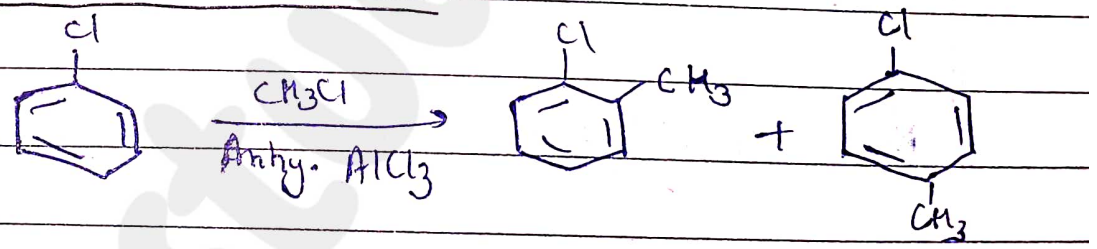
(b) Nitration



(c) Sulphonation

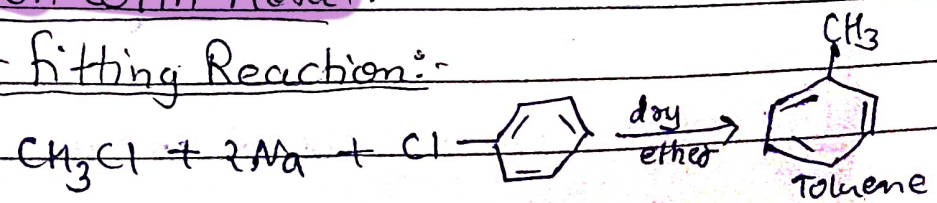


(d) Friedal Craft Reaction :-

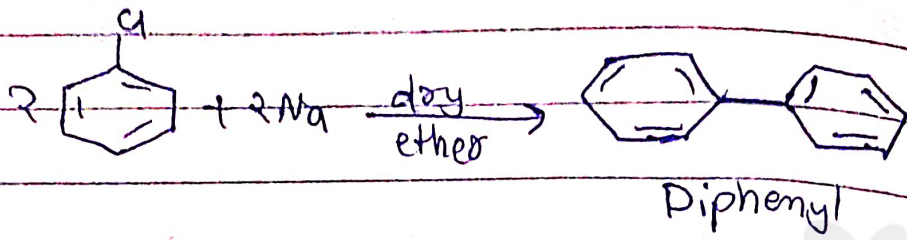


### ④ Reaction with Metal:-

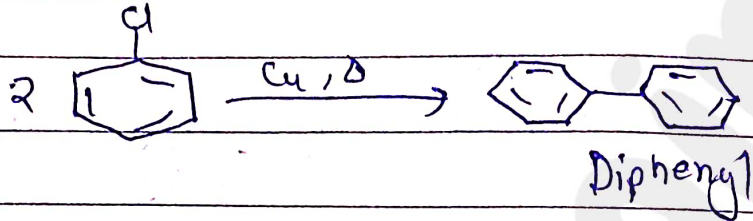
(a) Wurtz-fitting Reaction:-



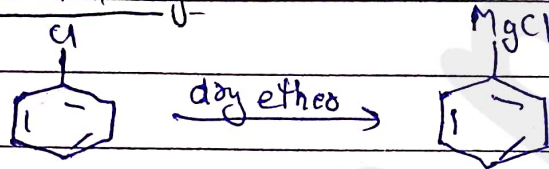
(b) Fittig Reaction



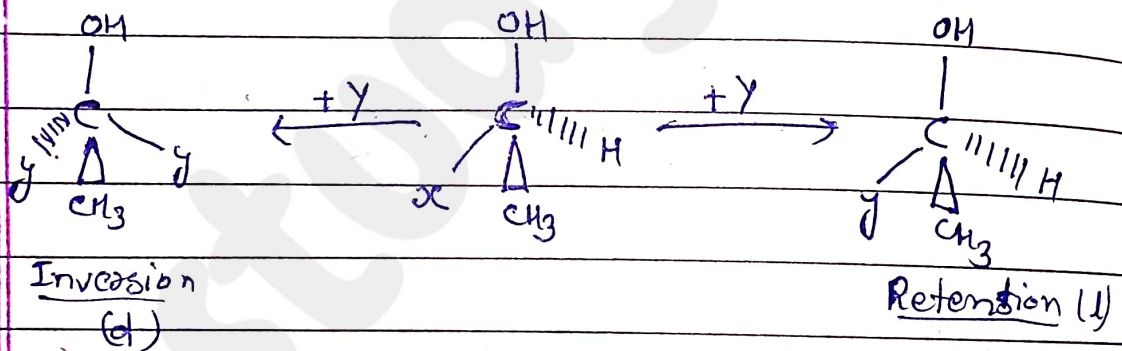
(c) Ullmann Reaction



(d) Reaction with Mg



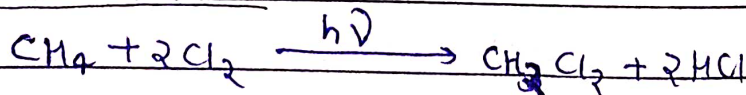
# Retention, Inversion & Racemic mixture:



Racemic Mixture :- Retention + Inversion  
50% 50%

# Polyhaloalkane

(1) Dichloromethane

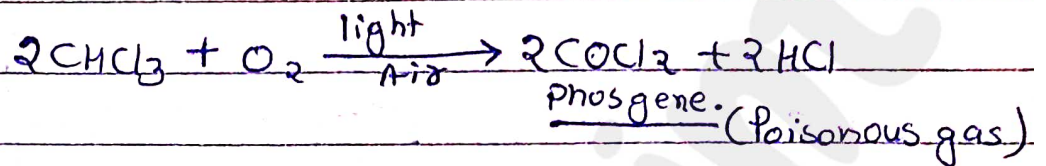


Use :- Used as a solvent in pharmaceutical & food industry

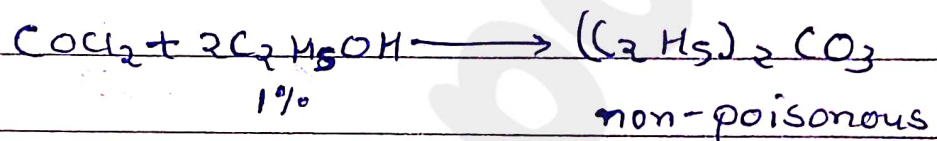
### ② CHCl<sub>3</sub> (chloroform)



It is stored in dark colour bottle because it get oxidised in the presence of light & Air to form a poisonous gas phosgene (COCl<sub>2</sub>)

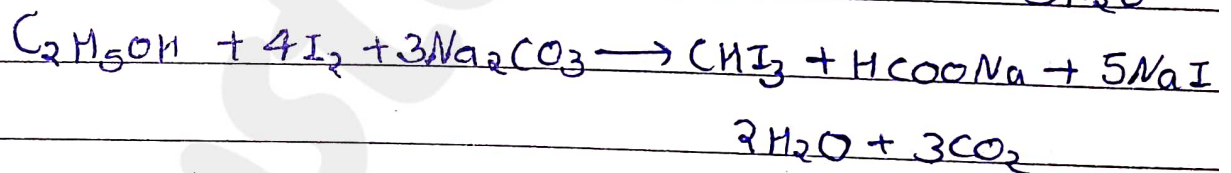
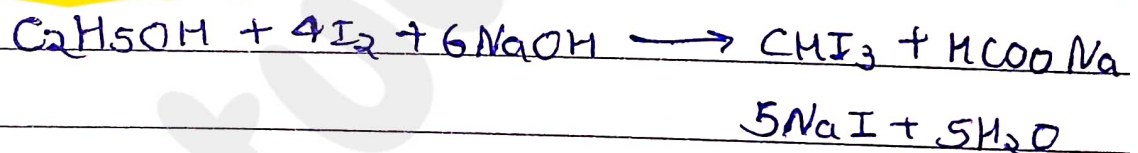


1% ethanol added to chloroform it produce diethyl carbonate which are non-poisonous:



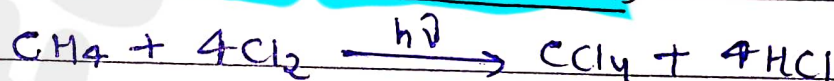
Use:- It is used as a solvent in industry for waxes, rubber, & resins.

### ③ Iodoform (CHI<sub>3</sub>)



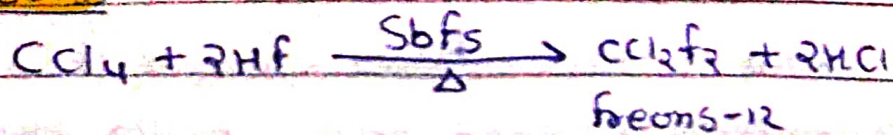
Use:- it is used as antiseptic.

### ④ Carbon tetrachloride (CCl<sub>4</sub>)



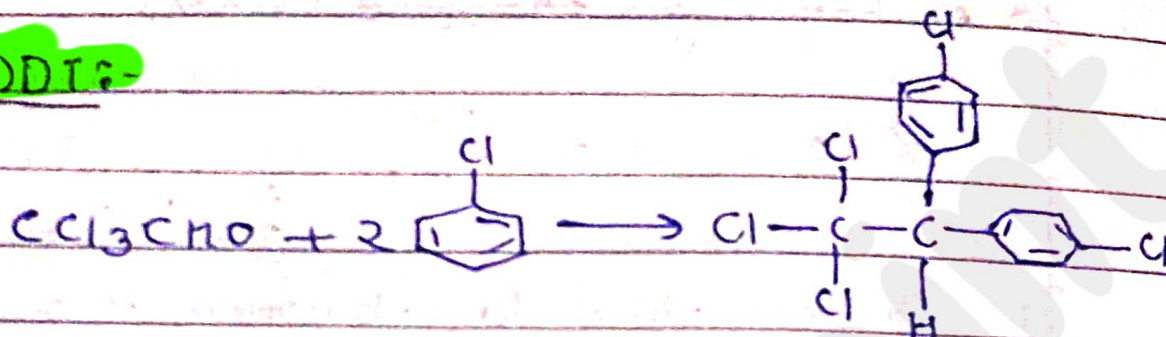
It is used as a solvent in laboratory. It is used in manufacture of Refrigerants & propellants for Aerosol cans.

⑤ freons :-



It is also used as a refrigerant for cooling

⑥ DDT :-



p,p'-dichlorodiphenyltri-  
chloroethane

(2,2-bis(4-chlorophenyl))

(1,1,1-trichloroethane)

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