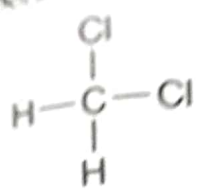
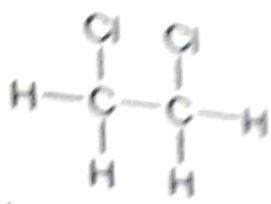


## DIHALOGEN DERIVATIVES

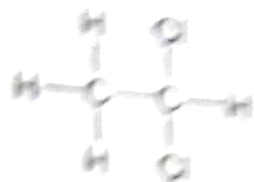
Dihalogen derivatives are compounds obtained by replacing two hydrogen atoms of a hydrocarbon by two halogen atoms. The presence of the identical halogen atoms is indicated by the prefix di- and position numbers. For example,



Dichloromethane  
(Methylene dichloride)



1,2-Dichloroethane  
(Ethylene dichloride)

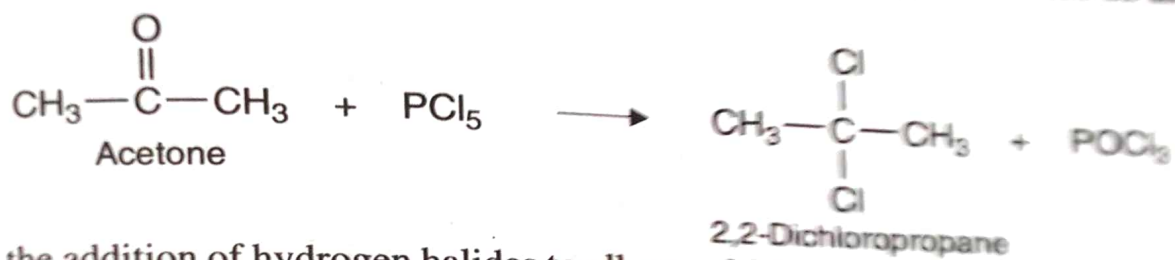


1,1-Dichloroethane  
(Ethylene dichloride)

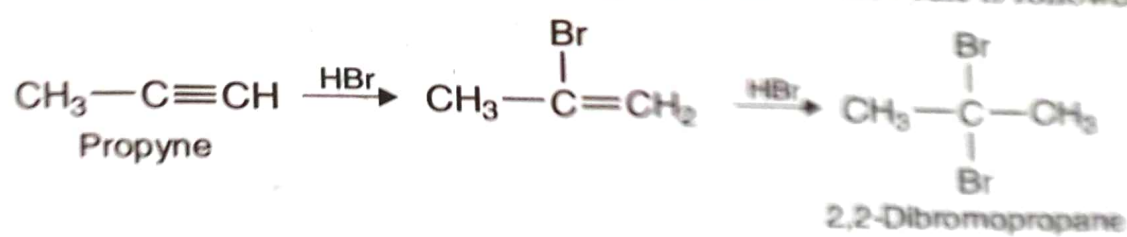
If two halogen atoms are attached to adjacent carbons, the compound is referred to as a vicinal (*vic-*) dihalide. If two halogen atoms are attached to the same carbon, then it is known as a geminal (*gem-*) dihalide. Notice that in the above examples, 1,2-dichloroethane is a *vic*-dihalide and 1,1-dichloroethane is a *gem*-dihalide.

## METHODS OF PREPARATION

*gem*-Dihalides are prepared : (1) By the action of phosphorus pentahalides on aldehydes and ketones.



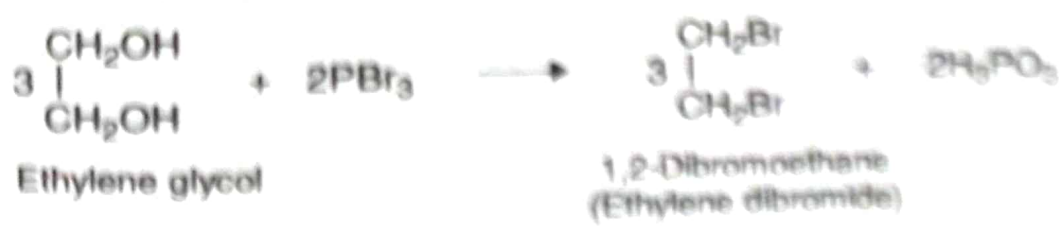
(2) By the addition of hydrogen halides to alkynes. Markovnikov rule is followed.



*vic*-Dihalides are prepared : (1) By the addition of halogens to alkenes.



(2) By the action of phosphorus halides (or hydrogen halides) on glycols



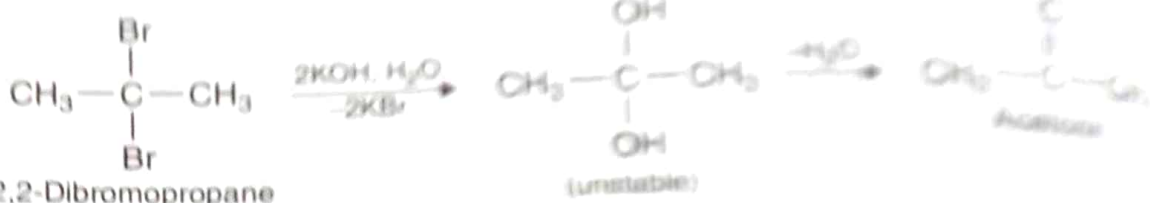
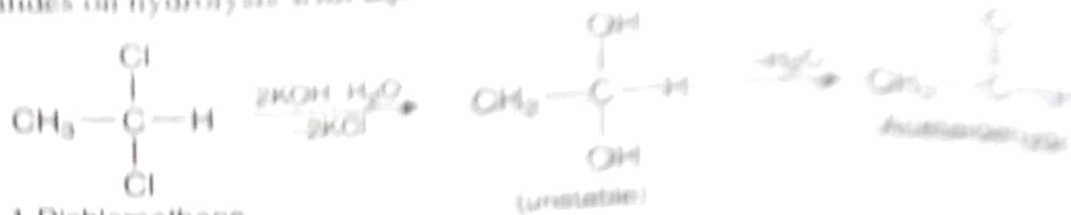
## PHYSICAL PROPERTIES

- (1) Dihalides are sweet-smelling, colorless liquids. They have relatively high boiling points.
- (2) They are insoluble in water and soluble in organic solvents.
- (3) They are heavier than water. Diiodomethane ( $\text{CH}_2\text{I}_2$ ) is the densest organic liquid. Its density is 4.93 g/cm<sup>3</sup>.

(1) **Hydrolysis with Aqueous NaOH or KOH** - vic-Dihalides on treatment with aqueous hydroxide give glycols

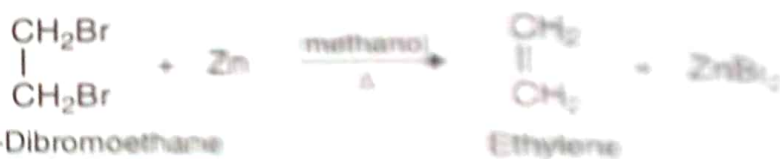


*gem*-Dihalides on hydrolysis with aqueous KOH give an aldehyde or a ketone



This reaction is used to distinguish *vic*-dihalides from *gem*-dihalides. Notice that *vic*-dihalide hydrolysis give glycols while *gem*-dihalides give aldehydes or ketones.

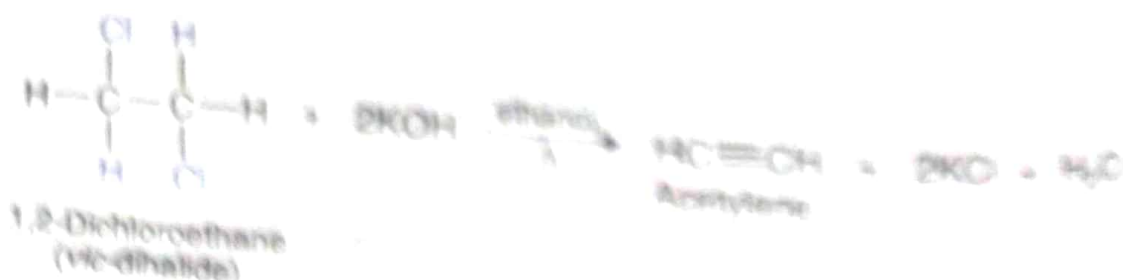
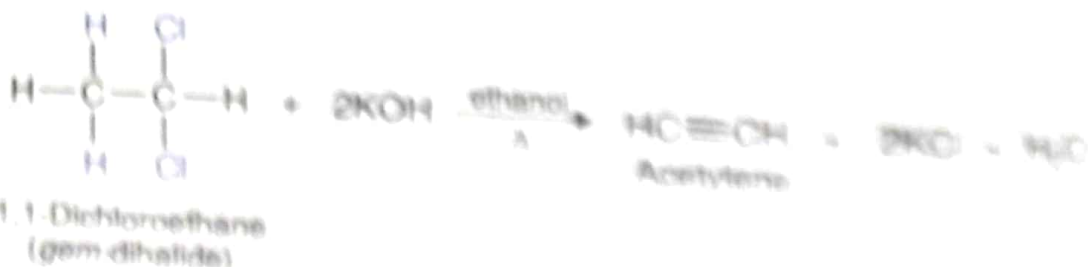
(2) **Reaction with Zinc ; Dehalogenation.** *vic*-Dihalides and *gem*-dihalides on treatment with zinc dust in methanol give alkenes.



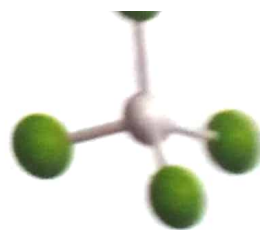
1,3- to 1,6-Dihalides give cycloalkanes.



(3) **Reaction with Alcoholic KOH ; Dehydrohalogenation.** *vic*-Dihalides and *gem*-dihalides on treatment with alcoholic potassium hydroxide give alkynes.



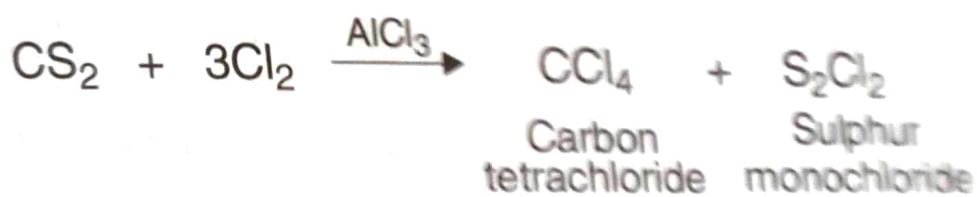
## CARBON TETRACHLORIDE, Tetrachloromethane, $\text{CCl}_4$



Carbon tetrachloride is the most important tetrahalogen derivative of methane.

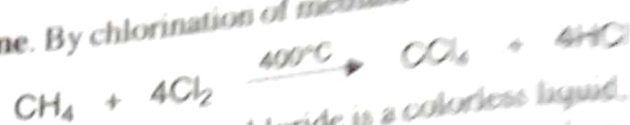
**Preparation.** Carbon tetrachloride is manufactured :

(1) **From Carbon Disulfide.** By the action of chlorine on carbon disulfide. Aluminium chloride is used as a catalyst.



Carbon tetrachloride is removed from the mixture by fractional distillation.

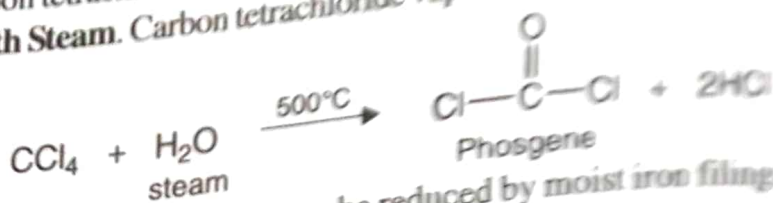
(2) **From Methane.** By chlorination of methane with excess of chlorine at  $400^{\circ}\text{C}$ .



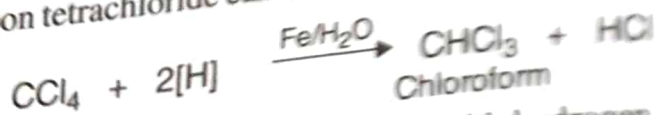
**Properties (Physical).** Carbon tetrachloride is a colorless liquid, bp  $77^{\circ}\text{C}$ . It is insoluble in water but soluble in ethanol and ether. It is an excellent solvent for oils, waxes, fats, and greases. Carbon tetrachloride is used as a fire-extinguisher under the name *Pyrene* because it is non-flammable. When a spray of carbon tetrachloride is directed at fire, its dense vapors prevent fire from reaching the burning articles. However, carbon tetrachloride also forms phosgene using *Pyrene* to extinguish a fire, the room should be well ventilated.

**(Chemical).** Carbon tetrachloride is inert to most organic reagents. It gives the following reactions:

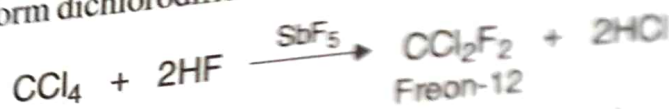
(1) **Reaction with Steam.** Carbon tetrachloride vapors react with steam at  $500^{\circ}\text{C}$  as follows:



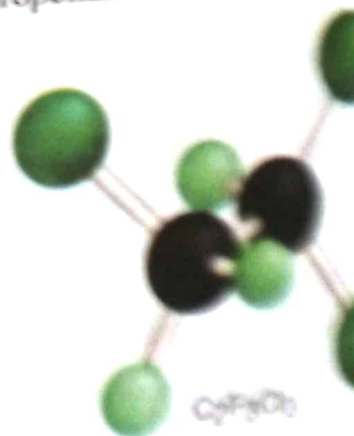
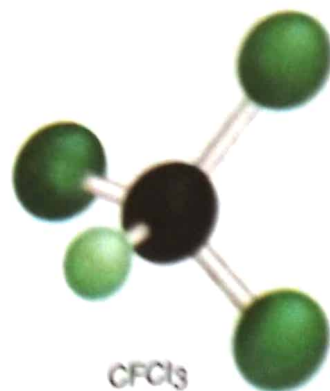
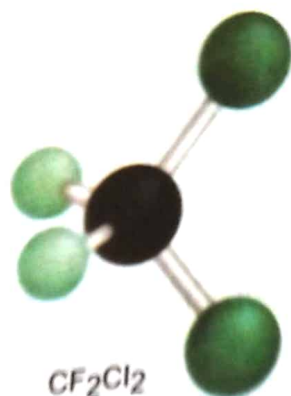
(2) **Reduction.** Carbon tetrachloride can be reduced by moist iron filings to give:



(3) **Reaction with HF.** Carbon tetrachloride reacts with hydrogen fluoride in the presence of antimony pentafluoride to form dichlorodifluoromethane (*Freon-12*).



*Freon-12* (bp  $-29^{\circ}\text{C}$ ) is widely used as a refrigerant and propellant in aerosol sprays.



$\text{CF}_2\text{Cl}_2$  is Freon-12. Other CFCs include  $\text{CFCl}_3$  (Freon-11) and  $\text{C}_2\text{F}_5\text{Cl}$  (Freon-114).

## UNSATURATED HALIDES