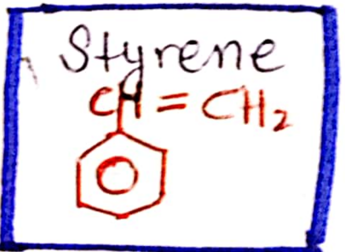
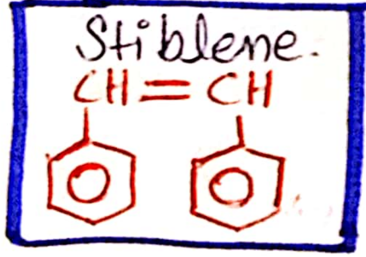
# * Unsaturated Hydrocarbon *

- **Allenes**
  - Cummulated double bonds. $>C=C=C<$
  - Highly reactive.
  - Difficult to prepare.
- **Conjugated double bonds** $>C=C-C=C<$ Butadiene
- **Isolated double bonds** $>C=C-C-C=C<$ 1,4-pentadiene.

$>C=C<$ Ethene.


Styrene

$CH=CH_2$


Stiblene.

$CH=CH$

## Preparation of ALKENE

**Natural Source:-** Petroleum → cracking → High mol. wt. alkenes.

### ① From alkyl halides : Dehydrohalogenation

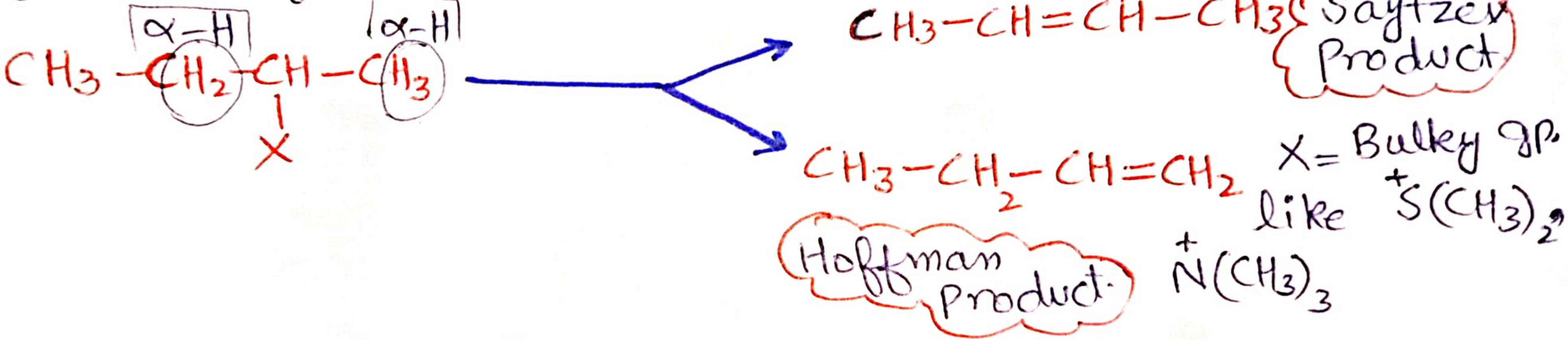
$$R-CH_2-CH_2-X \xrightarrow[\text{Room T}]{\text{Alcoholic } C_2H_5ONa} R-CH=CH_2 + HX$$

- or heat R–X at 300-400°C.
- Potassium ter-butoxide in t-Butyl alcohol → Best Reagent.
- 2° and 3° R–X → give satisfactory results.

R–X must have β–H

- **Base used:-**
  - $C_2H_5ONa$ in ethanol → can cause both < Substituition / Elimination.
  - KOH in refluxing ethanol may be used.
- $((CH_3)_3CO)K^+$ in $(CH_3)_3COH$ → Best

→ If α-H of more than 1 type. (X = Br, ...)



$CH_3-CH_2-\underset{|\atop X}{CH}-CH_3$

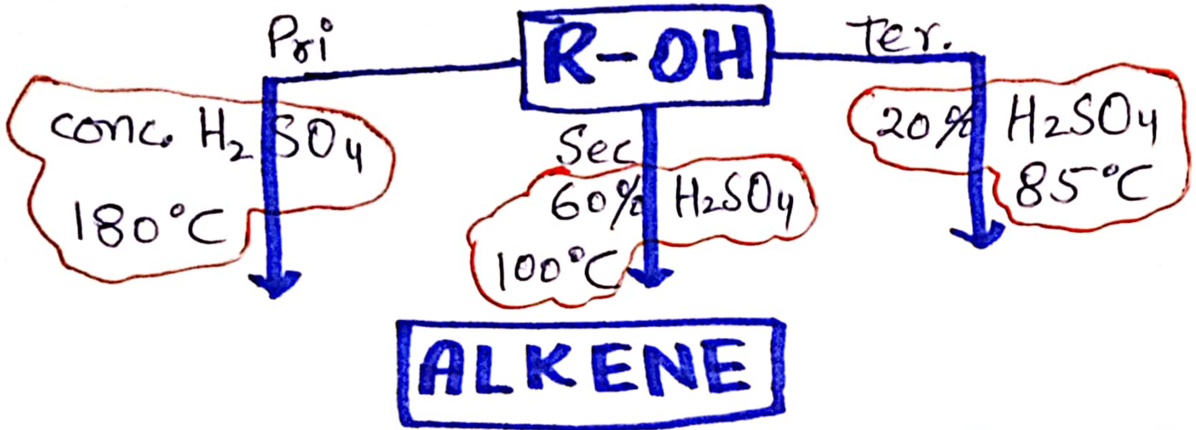
$CH_3-CH=CH-CH_3$ Saytzev Product

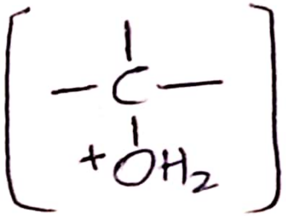
$CH_3-CH_2-CH=CH_2$ Hoffman Product

X = Bulky gp. like $\overset{+}{S}(CH_3)_2$, $\overset{+}{N}(CH_3)_3$

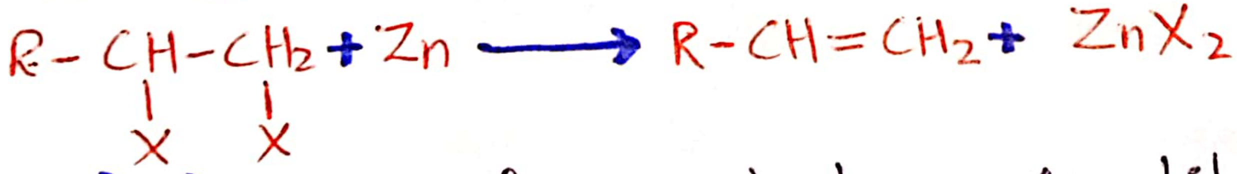
## ② From Alcohol (Dehydration)

- Catalyzed by acid:
  - $H_3PO_4$ or $H_2SO_4$ —— in laboratory.
  - Lewis acid like $Al_2O_3$, $SiO_2$ or other oxides at 400°C in industries.



- Rate of dehydration $3° > 2° > 1°$
- Intermediate formed = Alkyloxonium ion  $\left[-\overset{|}{\underset{\underset{+OH_2}{|}}{C}}-\right]$ that eliminates $H_2O$ to form $C^+$
- To avoid Rearrangment, heated $Al_2O_3$ in presence of $NH_3$ or Pyridine used.

## ③ From Vicinal dihalide: (Dehalogination)


$R-\underset{X}{\underset{|}{CH}}-\underset{X}{\underset{|}{CH_2}} + Zn \longrightarrow R-CH=CH_2 + ZnX_2$

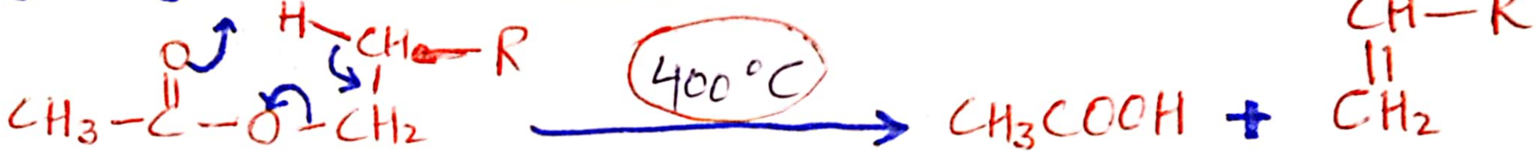
**Limitation:-** Little impantant, vic. dihalides itself prepared from alkene.

**Importance:-** Bromination + Debromination — used for protection and Purification of alkene.

## ④ Pyrolytic Elimination:-

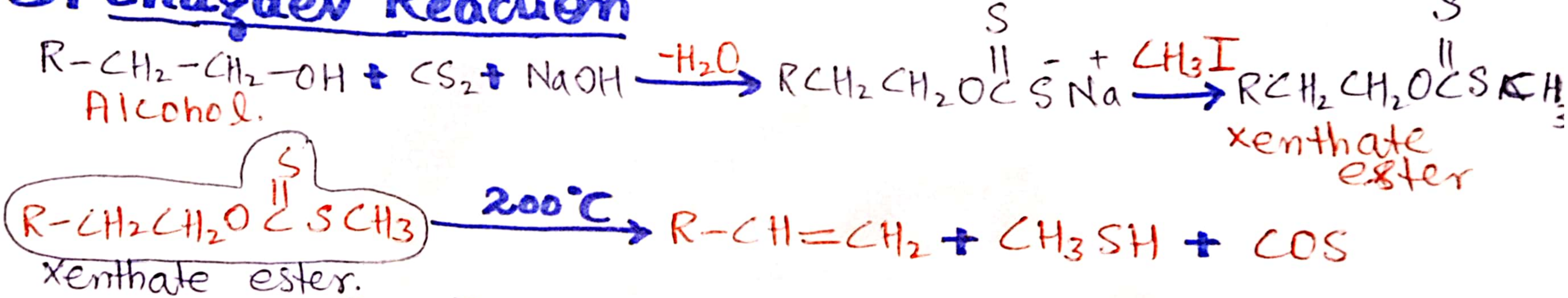
- Non-polar mechanism → gives cis alkene while polar mechanism → gives trans alkene.
- No Rearrangment.

### A. Pyrolysis of ester:-



$$\overset{H-CH-R}{CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2} \xrightarrow{400^\circ C} CH_3COOH + \underset{CH_2}{\underset{\|}{CH-R}}$$

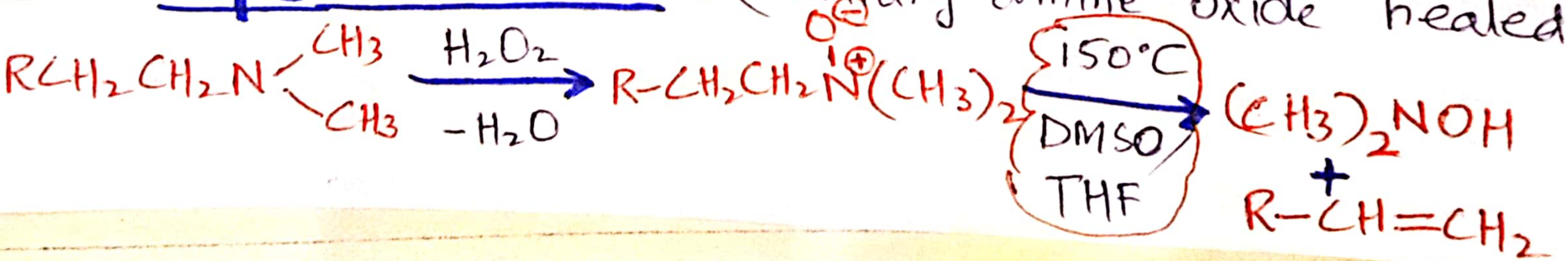
### B. Chugaev Reaction



$$\underset{\text{Alcohol.}}{R-CH_2-CH_2-OH} + CS_2 + NaOH \xrightarrow{-H_2O} RCH_2CH_2O\overset{S}{\overset{\|}{C}}\overset{-}{S}\overset{+}{Na} \xrightarrow{CH_3I} \underset{\text{xenthate ester}}{RCH_2CH_2O\overset{S}{\overset{\|}{C}}SCH_3}$$

$$\underset{\text{xenthate ester.}}{R-CH_2CH_2O\overset{S}{\overset{\|}{C}}SCH_3} \xrightarrow{200^\circ C} R-CH=CH_2 + CH_3SH + COS$$

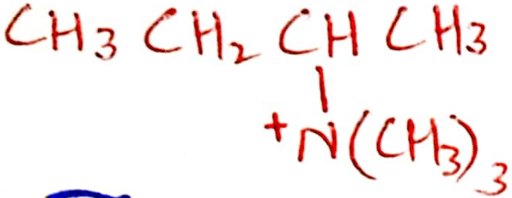
### C. Cope Reaction:- (Tertiary amine oxide heated)



$$RCH_2CH_2N\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix} \xrightarrow[-H_2O]{H_2O_2} R-CH_2CH_2\overset{O^{\ominus}}{\overset{|}{\overset{\oplus}{N}}}(CH_3)_2 \xrightarrow[\text{DMSO, THF}]{150^\circ C} (CH_3)_2NOH + R-CH=CH_2$$

## ⑤ The Hoffman Reaction :- (Quaternary ammonium hydroxide)

- E2 (Elimination)

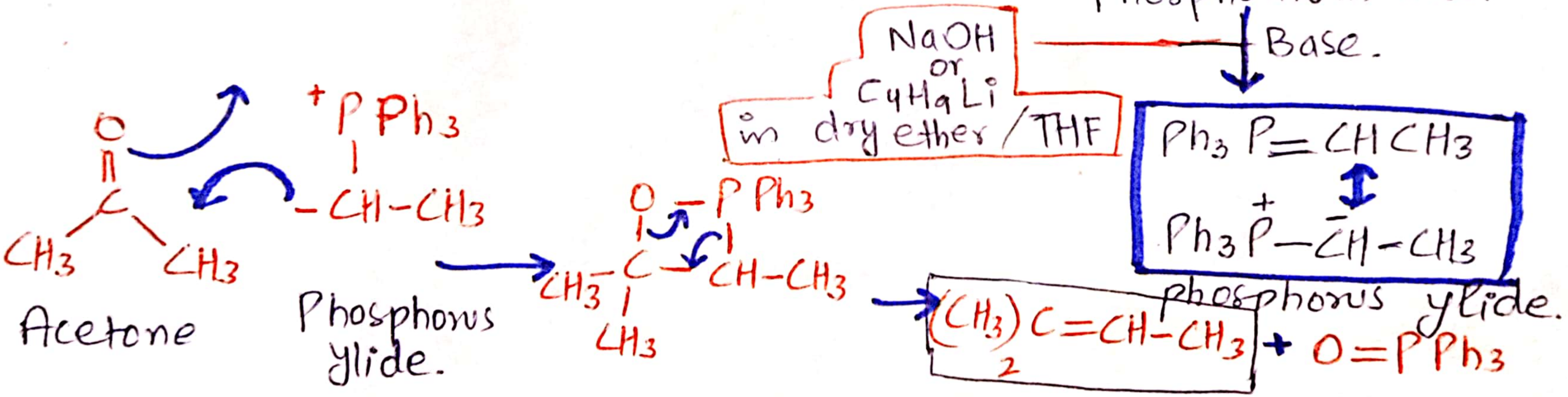


$$\underset{\overset{|}{{}^{+}N(CH_3)_3}}{CH_3CH_2CHCH_3} \xrightarrow{\Delta} \underset{\text{Minor}}{CH_3CH=CHCH_3} + \underset{\text{Major}}{CH_3CH_2CH=CH_2}$$

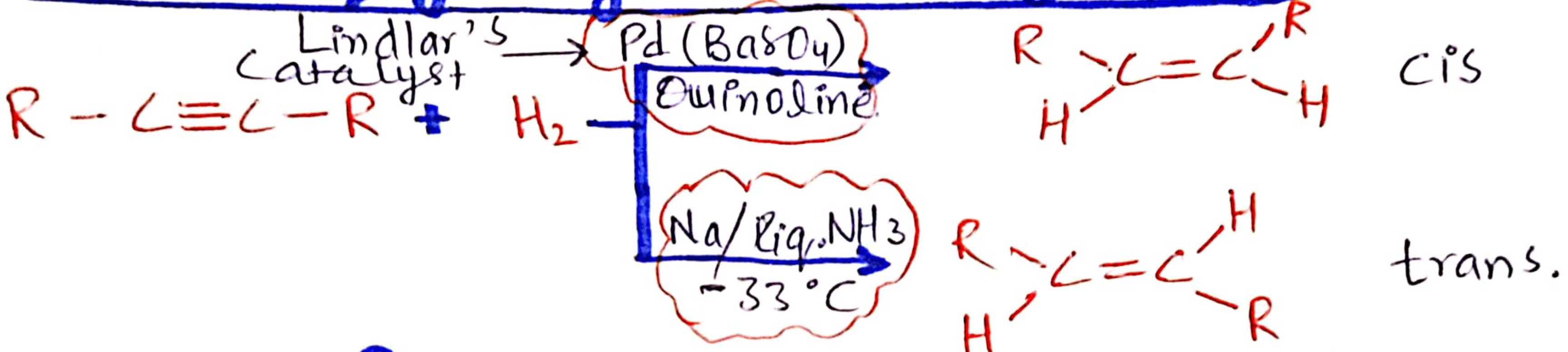
## ⑥ The Wittig Reaction :- Aldehyde/ketone + phosphorous ylide.

very useful reaction.

**Wittig Reagent :-** $Ph_3P + CH_3CH_2Br \longrightarrow \boxed{Ph_3\overset{+}{P}CH_2CH_3Br}$ Phosphonium salt



# ⑦ Partial Hydrogenation of Alkyne :-



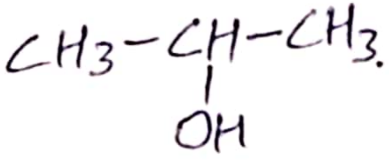
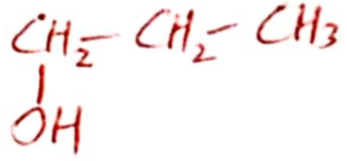
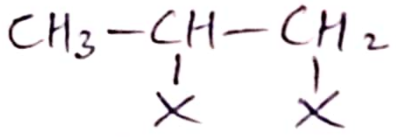
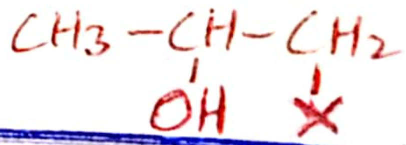
## PHYSICAL PROPERTIES :-

- upto $C_4$ (Gases), $C_5 - C_{17}$ (Volatile liquids), $> C_{18}$ (solids)
- Relative stability $\propto \frac{1}{\Delta H_c} \propto \frac{1}{\text{Reactivity}}$
- $R_2C=CR_2 > R_2C=CRH > R_2C=CH_2 > \overset{\text{trans > cis}}{HCR=CRH} > HRC=CH_2 > CH_2=CH_2$

## REACTIONS :-

- Electrophilic addition reactions.

| **Reaction** | **Alkene** | **Reagent** | **Conditions** | **Product** |
|---|---|---|---|---|
| **1.** Hydrogenation<br>*Exothermic | $CH_2=CH_2$ | $H_2$ | Raney Ni<br>($Ni-Al+NaOH$) | Alkane<br>$CH_3-CH_3$ |
| **2.** Addition of Hydrogen halide(HX) | $CH_2=CH-R$ | HX<br>$HI > HBr > HCl > HF$ | Markonikov's Rule followed. | Alkyl halid<br>$CH_3-\underset{X}{CH}-R$ |
|  | $CH_2=CH-R$ | HX | $H_2O_2$<br>Anti-markonikov product (Peroxide effect) | $\underset{X}{CH_2}-CH_2-R$ |
| **3.** Hydration (a)<br>Alkene $\underset{\text{conc. acid, high T}}{\overset{\text{dil acid, low T}}{\rightleftharpoons}}$ Alcohol. | $CH_3-CH=CH_2$ | ① $H-OSO_3H$ cold. conc.<br>② $H_2O$ | Δ<br>*used to separate alkene from alkane. | $CH_3-\underset{OH}{CH}-CH_3$ |
| (b) | $CH_3-CH=CH_2$ | $H_2O$ | $H_2SO_4$ or $H_3PO_4$ | $CH_3-\underset{OH}{CH}-CH_3$ |

| **Reaction** | **Alkene** | **Reagent** | **Condition** | **Product** |
|---|---|---|---|---|
| oxymercuration ⓒ demercuration.<br>● avoid Rearrangement. | $CH_3-CH=CH_2$ | ① $Hg(OAc)_2 + H_2O$ /THF<br>② $NaBH_4$/aq. NaOH | Markonikov Addition. |  $CH_3-\underset{OH}{\underset{\vert}{CH}}-CH_3$. |
| Hydroboration ⓓ oxidation. | $CH_3-CH=CH_2$ | ① $BH_3$/THF<br>② $H_2O_2$, NaOH | Anti-Markonikov Addition |  $\underset{OH}{\underset{\vert}{CH_2}}-CH_2-CH_3$ |
| 4. Addition of Halogen. | $CH_3-CH=CH_2$<br>● Test for double bond → if $Br_2/CCl_4$ used, red color vanishes. | $X_2$ | $CCl_4$ solvent. |  $CH_3-\underset{X}{\underset{\vert}{CH}}-\underset{X}{\underset{\vert}{CH_2}}$<br>vic. dihalide |
| 5. Addition of Hypohalous acid | $CH_3-CH=CH_2$ | $H\overset{-}{O}\overset{+}{X}$<br>$(X_2 + H_2O)$ | | Halohydrin<br> $CH_3-\underset{OH}{\underset{\vert}{CH}}-\underset{X}{\underset{\vert}{CH_2}}$ |
| 6. Polymerization | $CH_2=CH_2$<br>or<br>$CH_3-CH=CH_2$. | traces of $O_2$<br>(0.1%) | 400 °C<br>100 atm | Polyethylene<br>or<br>Polypropylene. |

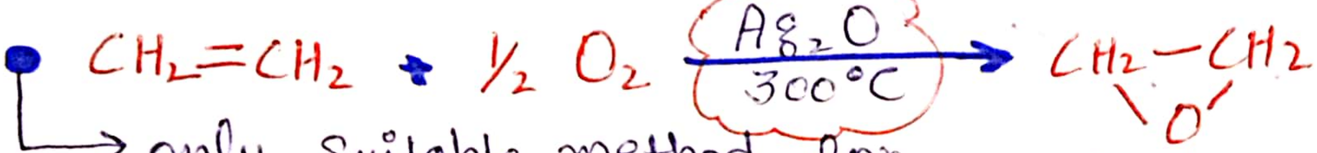
# 7. Oxidation:-

## A. Epoxidation:-

$$>C=C< + CH_3-\overset{O}{\overset{\|}{C}}-O-OH \longrightarrow >C\overset{O}{-}C< + CH_3COOH$$

Peracetic acid
($H_2O_2$ in acetic acid with trace of $H_2SO_4$)

Epoxide



$$CH_2=CH_2 + \tfrac{1}{2}\,O_2 \xrightarrow[300°C]{Ag_2O} \underset{\ \ O\ \ }{CH_2-CH_2}$$

→ only suitable method for ethylene oxide.

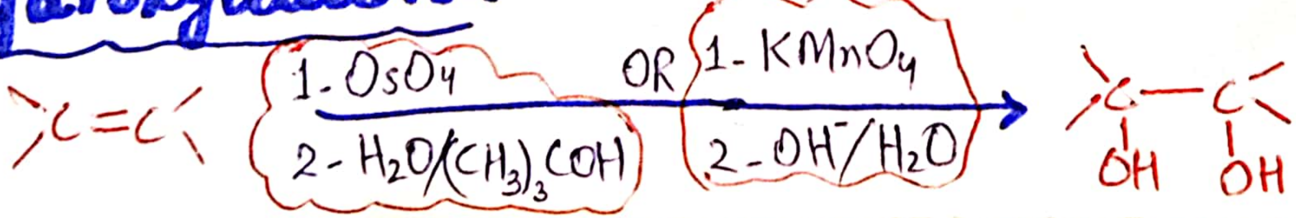
Ethylene oxide (Important Industrial chemical)

$$\underset{\ \ O\ \ }{CH_2-CH_2} \xrightarrow{H^+} \underset{OH\quad OH}{CH_2-CH_2}$$

Glycol.
anti-1,2-diol

Glycol can be obtained direct from alkene by using 30% aq. $H_2O_2$ soln. in acetic acid

## B. Hydroxylation:-



$$>C=C< \xrightarrow[2-H_2O/(CH_3)_3COH\ \text{OR}\ 2-OH^-/H_2O]{1-OsO_4\ \text{OR}\ 1-KMnO_4} >\underset{OH}{C}-\underset{OH}{C}<$$

Syn 1,2-diol.

<u>Reagents</u>

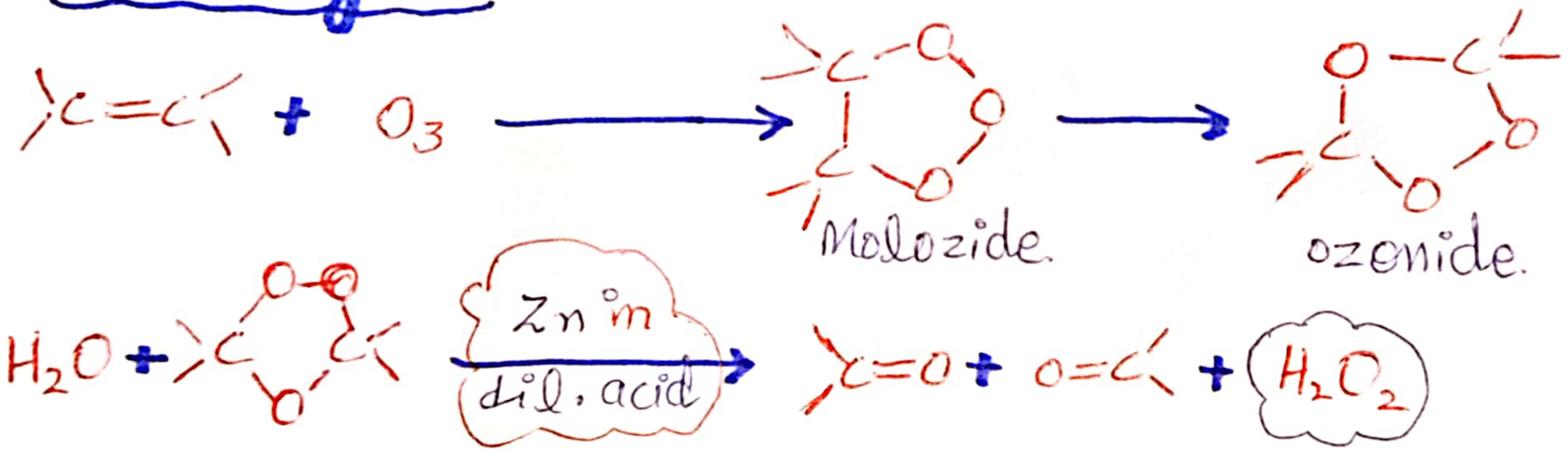
**1.** $OsO_4$ then $H_2O_2$

- → better reagent
- → $OsO_4$ is expensive and higly toxic.

**2.** $KMnO_4$ then base hydrolysis.

- → $KMnO_4$ is strong oxidizing agent. so, difficult to restrict at diol.
- → furthur oxidized to carbonyl or carboxylic acid.

## C. Ozonolysis :-

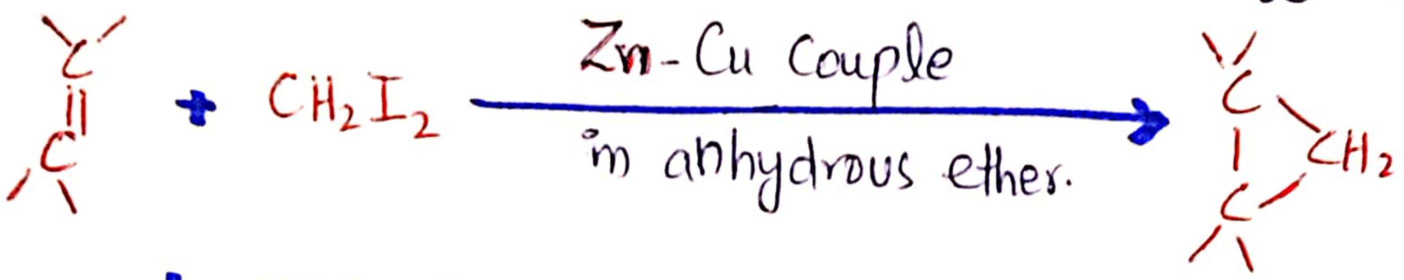


- $H_2O_2$ formed, furthur oxidizes aldehyde to carboxylic acid.

**Imp:** to locate double bond

**8. Isomerization :-** Alkene heated at high T (500-700°C) or lower T (200-300°C) in presence of $AlCl_3$ isomerizes. (double bond tends to move towards inner-side)

## 9. Simmons - Smith Reaction:- Addition of methylene to alkene.



$$>C=C< + CH_2I_2 \xrightarrow[\text{in anhydrous ether.}]{\text{Zn-Cu Couple}} >C(CH_2)C<$$

## Uses of Ethylene :-

Anesthetic

Artificial ripening of fruits

Preparation of different important chemicals like (Glycol, ethyl alcohol, ethyl halide etc)

Preparation of polyethene

Preparation of Mustard gas. (Powerful vesicant i.e causes blisters)

$$2\,CH_2=CH_2 + S_2Cl_2 \longrightarrow S + S(CH_2-CH_2-Cl)_2$$

β,β'- Dichloroethyl sulphide.