CH 16 Alcohol

Wednesday, August 06, 2025 6:27 PM

Hydroxy Compounds

R — OH (Alcohol

suffix -ol

$C_nH_{2n+1}OH$

Acidity of Alcohol

$\boxed{\overset{+}{H}}$ (no $\bar{e}$) (no neutrons) only proton

Acid : (H^+) Proton donor

$\underset{100}{HCl} \longrightarrow \boxed{\underset{100}{\overset{+}{H}} + \underset{100}{\bar{Cl}}}$

strong acid

Alcohols low dissociation

$\boxed{ROH}$ more

$\boxed{R\bar{O}\ \overset{+}{H}}$

weak acid

$\underset{100\ \ (aq)}{\boxed{ROH}} \rightleftharpoons \underset{20}{R\bar{O}_{(aq)}} + \underset{20}{\overset{+}{H}_{(aq)}}$

left Alkoxide side

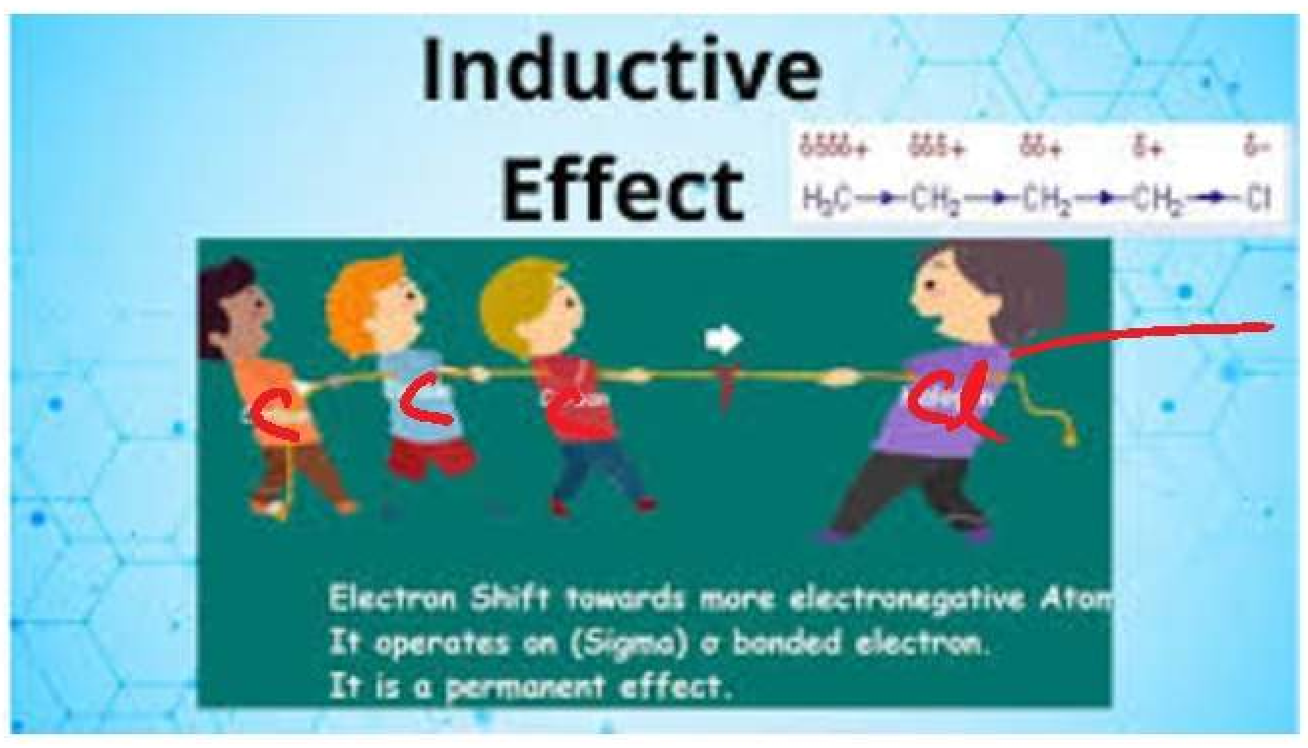
equilibrium is shifted more towards left

When H_2O dissociates

$H_2O_{(l)} \rightleftharpoons \bar{O}H_{(aq)} + \overset{+}{H}_{(aq)}$

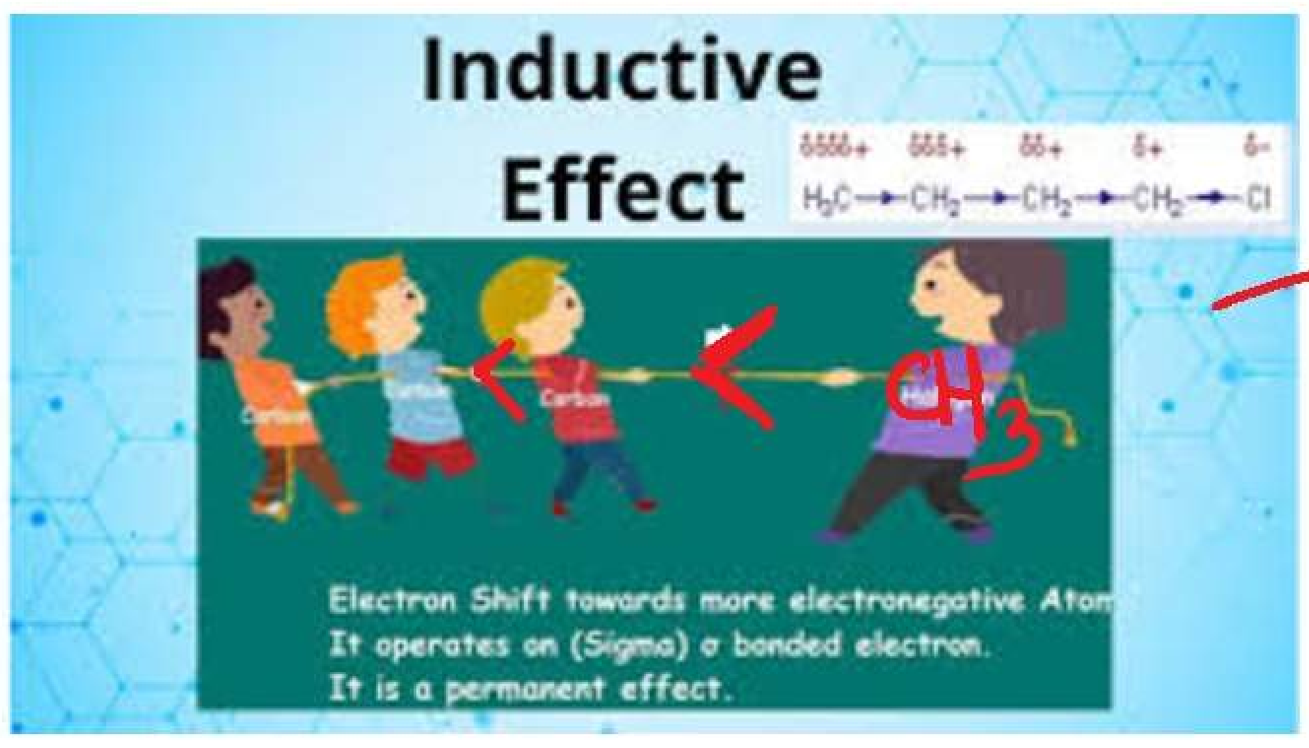
Alcohols are weaker acids as compare to H_2O

$\boxed{\text{Inductive effect}}$ <
- $\bar{e}$ donating (donating $\bar{e}$ density)
- $\bar{e}$ withdrawing (taking away



Electron Shift towards more electronegative Atom
It operates on (Sigma) σ bonded electron.
It is a permanent effect.

$\bar{e}$ withdrawing effect



Electron Shift towards more electronegative Atom
It operates on (Sigma) σ bonded electron.
It is a permanent effect.

$\bar{e}$ Donating

$CH_3-\underset{(aq)}{OH} \rightleftharpoons \boxed{\boxed{CH_3} \rightarrow \underset{(aq)}{\bar{O}}} + \overset{+}{H}_{(aq)}$

Methoxide

$\bar{e}$ donating group

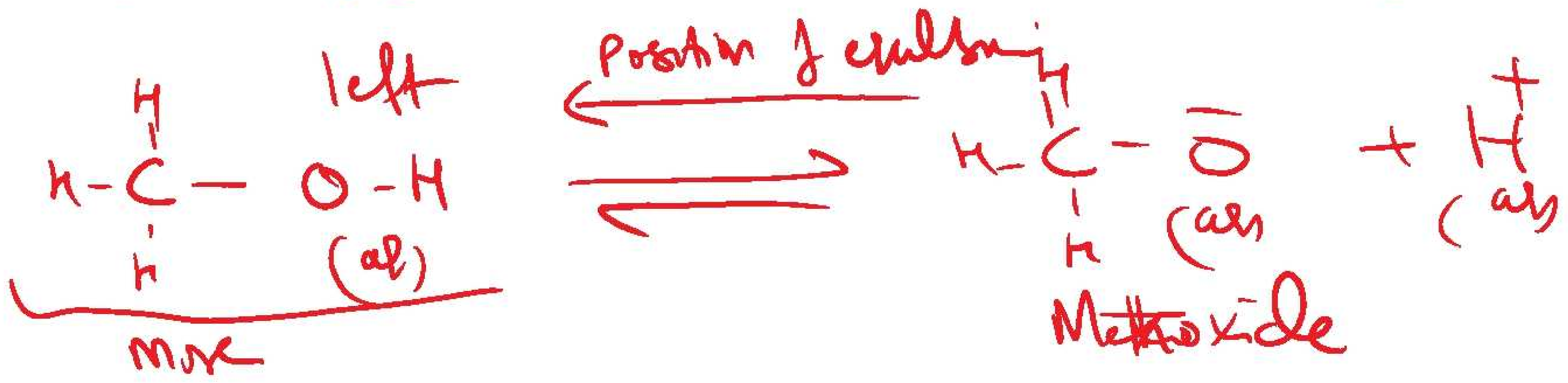
effect

Alkyl group show ē donating

Oxygen of alcohol is bonded to ē donating alkyl group $R \rightarrow OH$

This will creat more ē density on O atom.

Therefore alkoxide is more likely to accept the H^+ and form an alcohol again.



But in H_2O there is no electron donating group, $\bar{O}-H$ is not that much negative

$$\boxed{H-OH_{(l)}} \rightleftharpoons H^+_{(aq)} + \bar{O}-H_{(aq)}$$

unionized

more

← equilibrium will be shifted towards left but less than alcohol

ionized

less

Combustion of Alcohol

Complete $CH_3OH + 2O_2 \longrightarrow CO_2 + 2H_2O$

$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$

Incomplete $2CH_3CH_2OH + 3O_2 \longrightarrow 2C + 2CO + 6H_2O$

$2C_2H_5OH$

$2C + 2C$

Donating [O] atom

Oxidation of Alcohol

We use oxidizing agent for this purpose

(1) Acidified $KMnO_4$ (dil H_2SO_4 + $KMnO_4$)
Purple to colourless

(2) Acidified $K_2Cr_2O_7$
(orange to green)

In alkene we use acidified $KMnO_4$ because it is stronger O.A.

$KMnO_4 + \text{dil } H_2SO_4 \rightarrow [O]$ Atomic oxygen
Very reactive

2C

$\text{Primary alcohol} + [O] \xrightarrow[\text{heat under distillation}]{MnO_4^- / H^+} \text{Aldehyde}$

2H

$'' + [O] \xrightarrow[\text{under reflux}]{''} \text{Aldehyde} \xrightarrow[+[O] \text{ under reflux}]{\text{heat}} \text{Carboxylic Acid}$

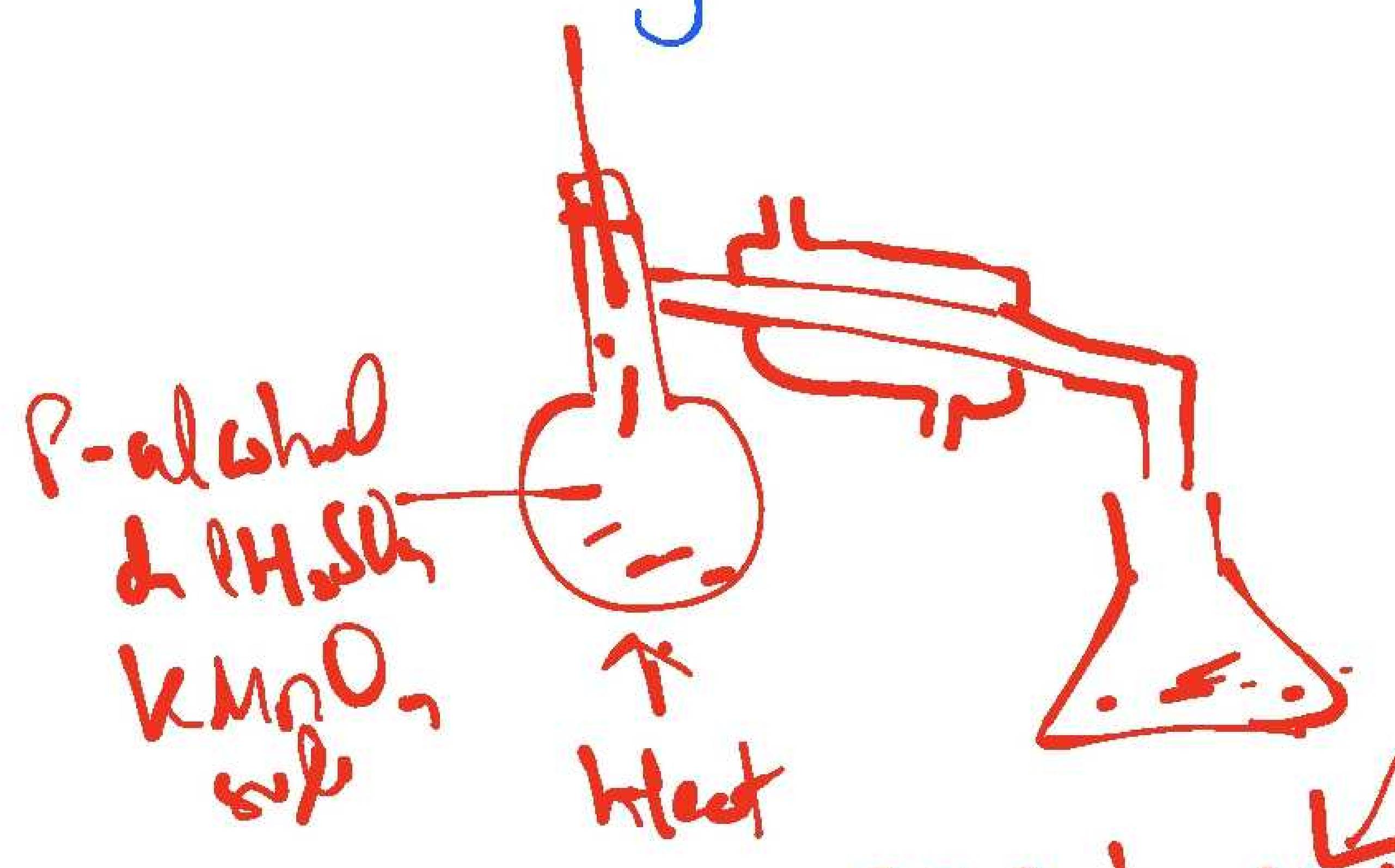
$\text{Secondary alcohol} + [O] \xrightarrow[\text{heat under reflux}]{''} \text{Ketone}$

$\text{Tertiary alcohol} + [O] \xrightarrow{''} \text{No reaction}$

Oxidation of Primary alcohol to Aldehyde

(Heat under distillation) [Incomplete oxidation]

Reactants
$\text{Primary alcohol}_{(l)} + \text{dil } H_2SO_{4(aq)} + KMnO_{4(s)}$



P-alcohol → Aldehyde

→ low B.P of Aldehyde as compared to alcohol

→ Vapours of Aldehyde will formed first

Due to H-bond

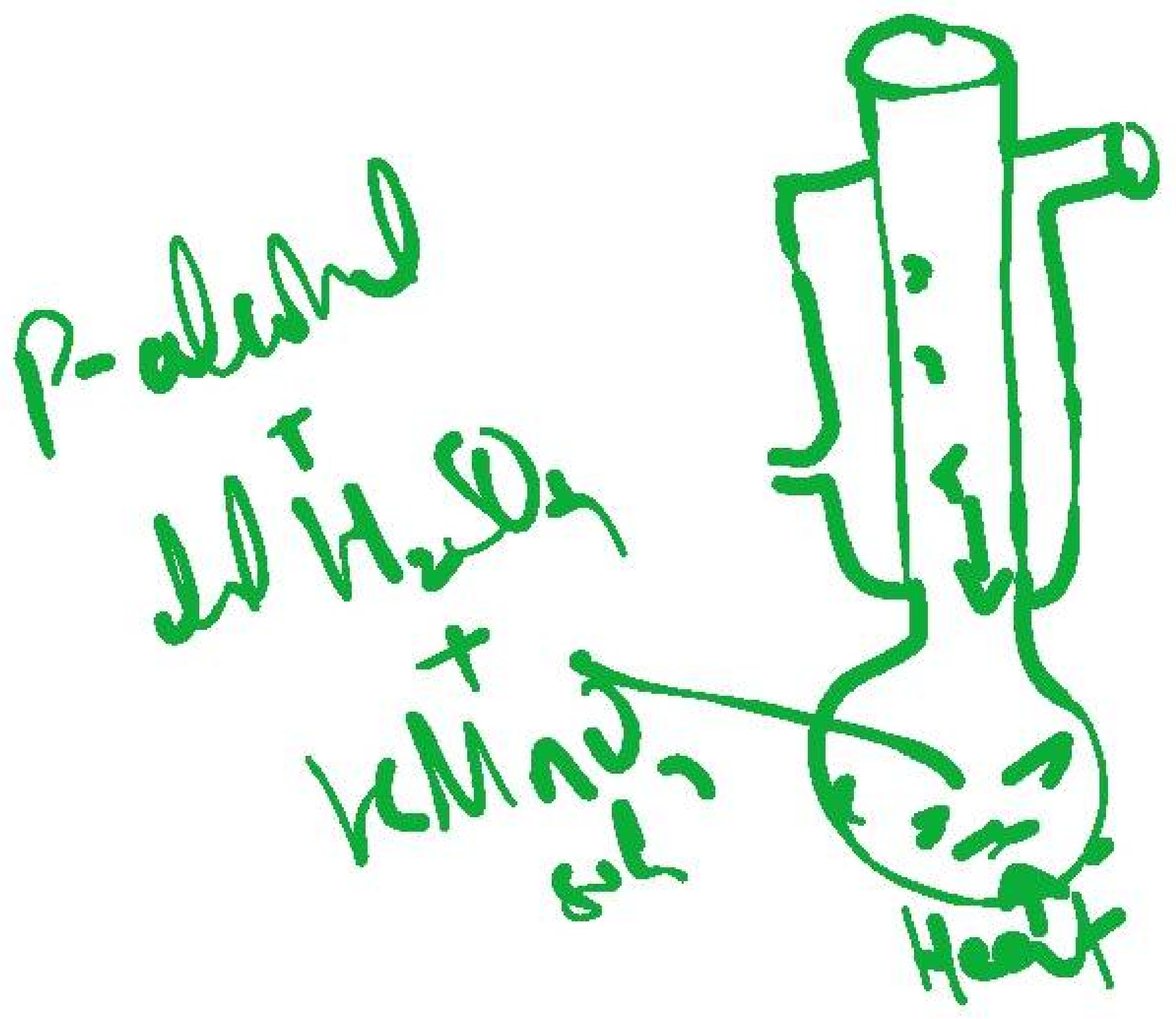
in Alcohol.

P- alcohol oxidation to Carboxylic acid

Heat under reflux — complete oxidation

↓

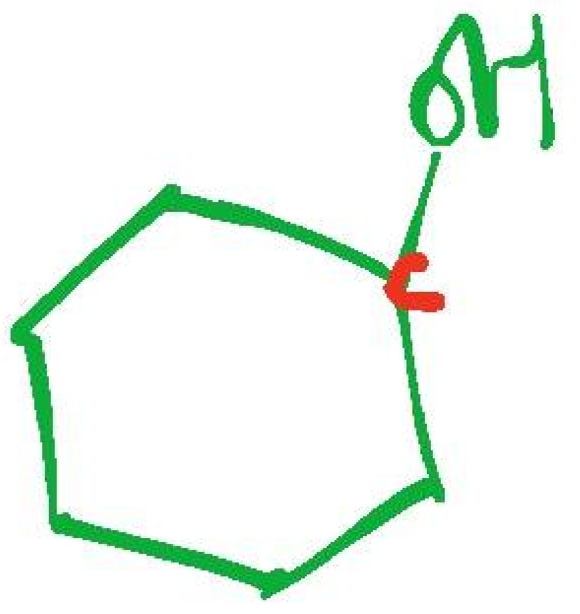
continuous heating without evaporating



$$\text{P-alcohol} + [O] \longrightarrow \text{Aldehyde} + [O] \longrightarrow \text{Carboxylic acid}$$

$$\text{P-alcohol} + 2[O] \xrightarrow[\text{under reflux}]{\text{heat}} \text{Carboxylic acid}$$

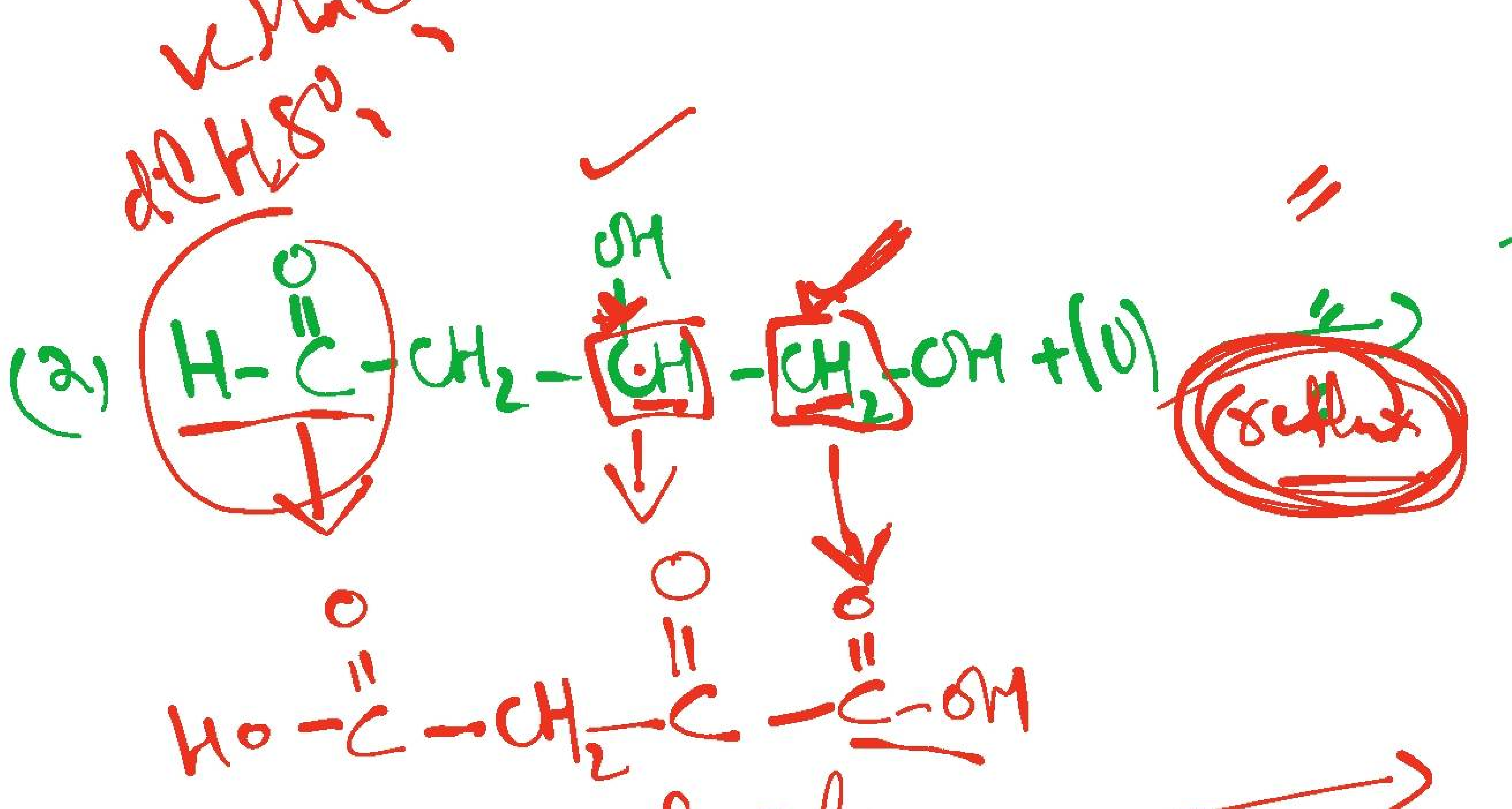
(1)



$$+ [O] \xrightarrow[\text{heat reflux}]{MnO_4^-/H^+} ?$$

✓ Ketone

(2)



$$H-\overset{O}{\overset{\|}{C}}-CH_2-\overset{OH}{CH}-CH_2-OH + [O] \xrightarrow{reflux} ?$$

$$HO-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH$$

Purple → colourless

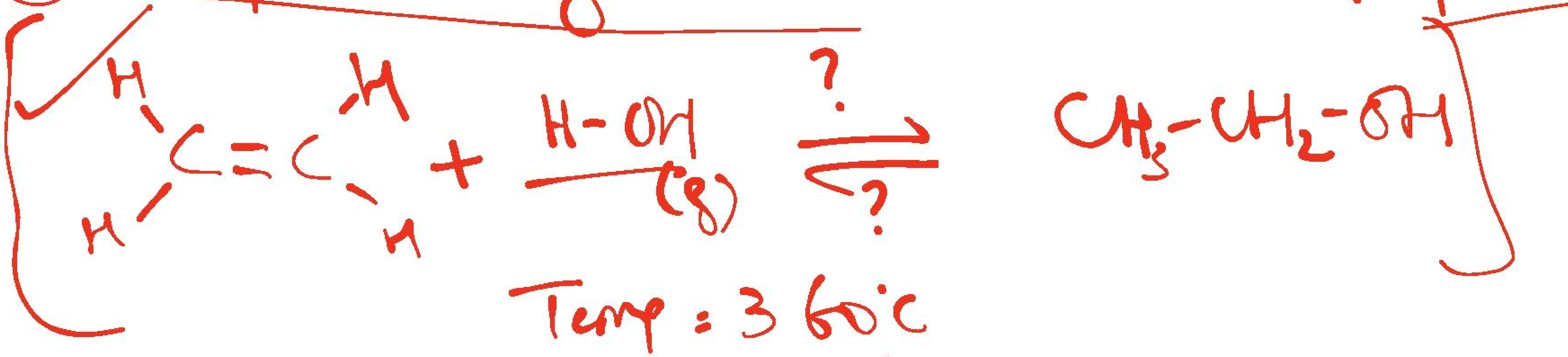
$KMnO_4$ + dil H_2SO_4 → [O] atomic Oxygen very reactive

$K_2Cr_2O_7$ + dil H_2SO_4 → [O]

orange → Green

② Preparation of Alcohol

Preparation



Temp: 360°C

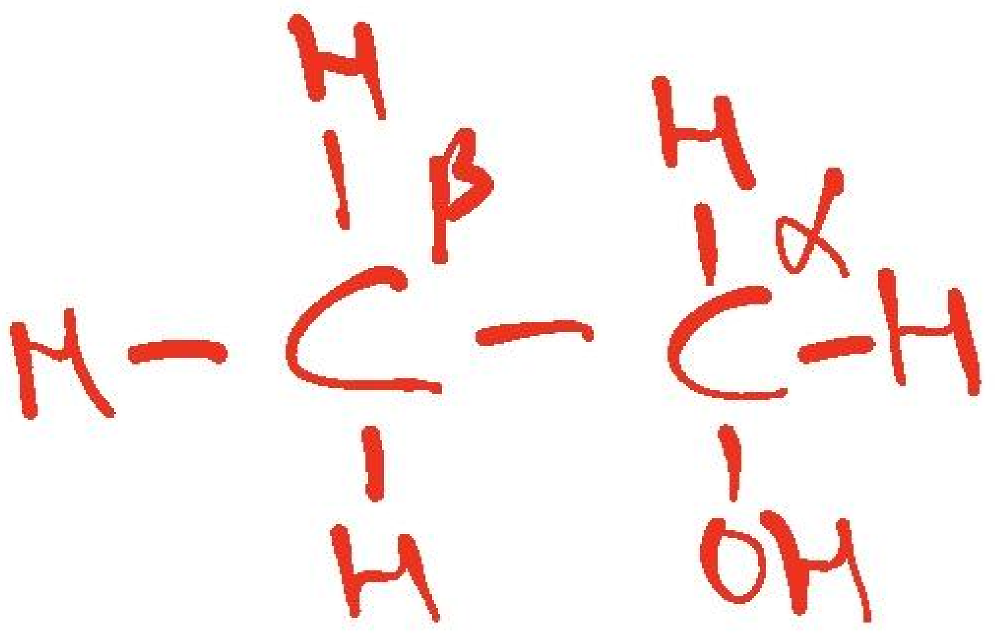
P = 60 atm

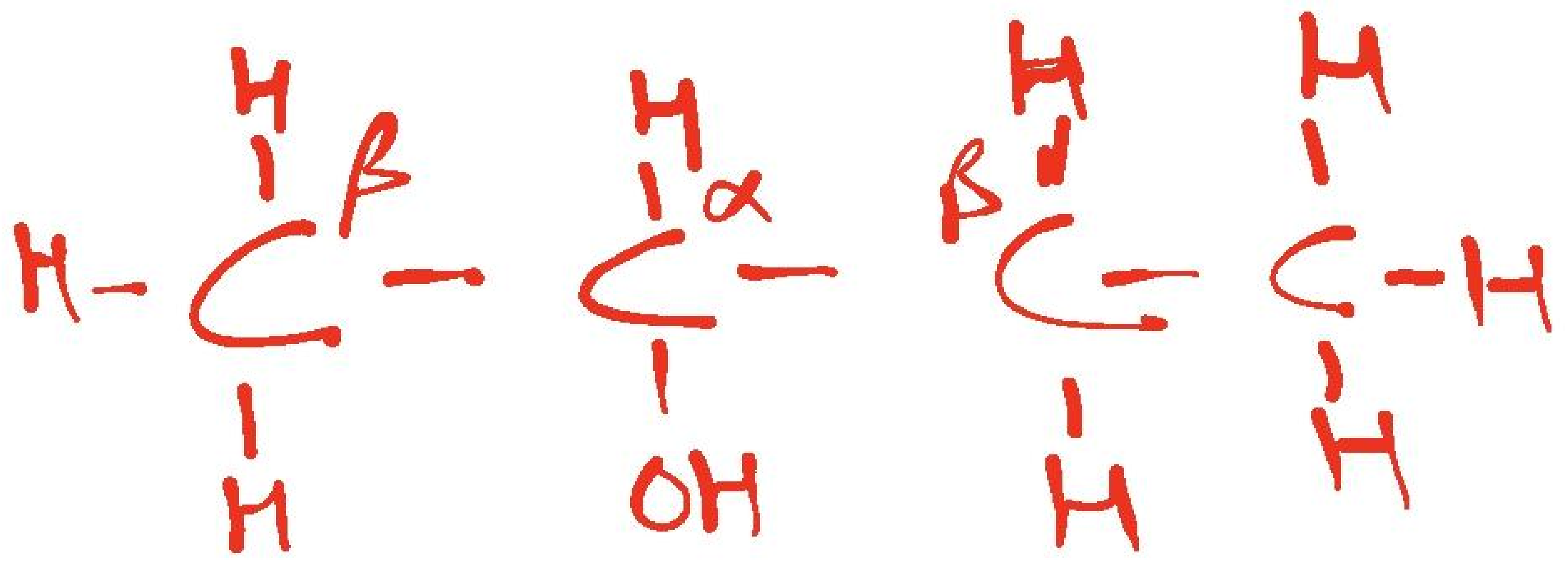
Catalyst: H_3PO_4

Dehydration of Alcohol

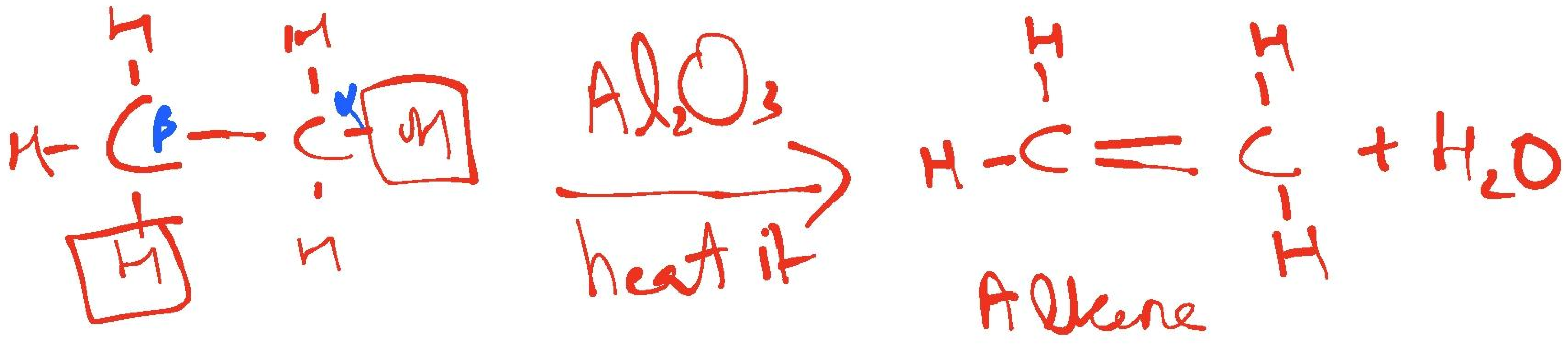
OH removed from α C

H " from β C





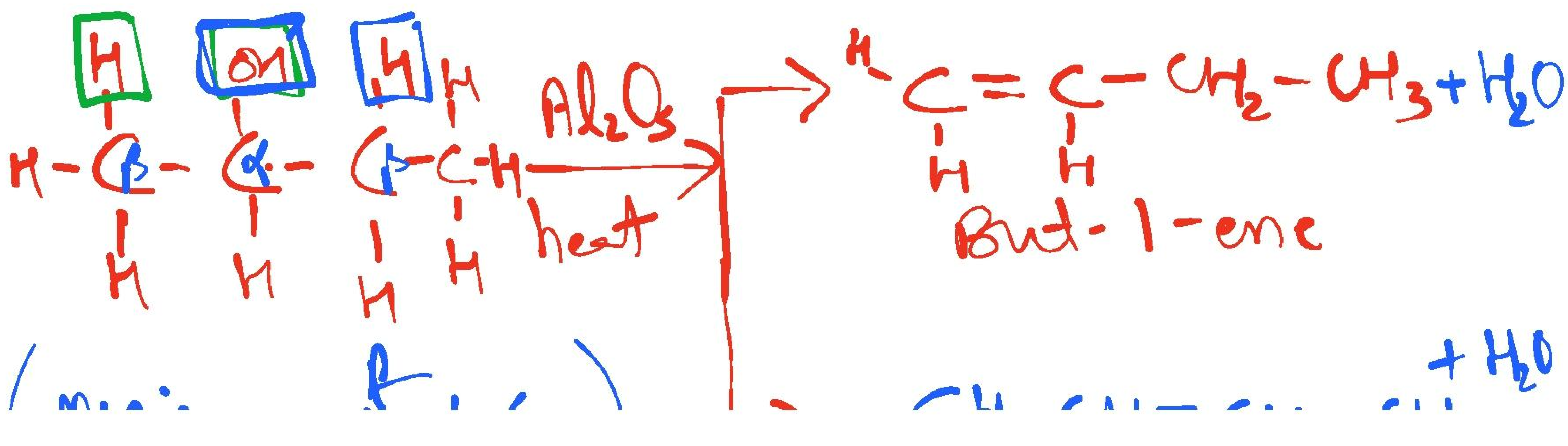
(2β will give you 2 products)



Condition (1) Al_2O_3 and heat

or

Conc H_2SO_4



(minimum of HC) ↳ $CH_3-CH=CH-CH_3$
But-2-ene

Reaction of Alcohol with Metal (Group 1) because they are very reactive

$CH_3-CH_2-OH + Na \rightarrow CH_3CH_2\overset{-}{O}\overset{+}{\underline{Na}} + \frac{1}{2}H_2$

sodium ethoxide

(Fizzing)

$CH_3-CH_2-CH_2-\overset{-\delta}{O}-\overset{+\delta}{H} + \underline{Na} \rightarrow CH_3CH_2-CH_2-\overset{-}{O}\overset{+}{Na}$

Alcohol

Sodium Propoxide

$R-\overset{-}{O}\overset{+}{Na}$ (sodium Alkoxide)

Reduction of Carboxylic Acid (Preparation of Alcohol)

Reducing agent — Gain of H Reduction

Donating the atomic hydrogen [H]

strong

$LiAlH_4$ (R.A) in dry ether

Lithium tetrahydrido aluminate

is reactive it can react with H_2O

(weak R.A)

$NaBH_4$ in aqueous alkaline sol ($NaOH_{aq}$) or (KOH_{aq})

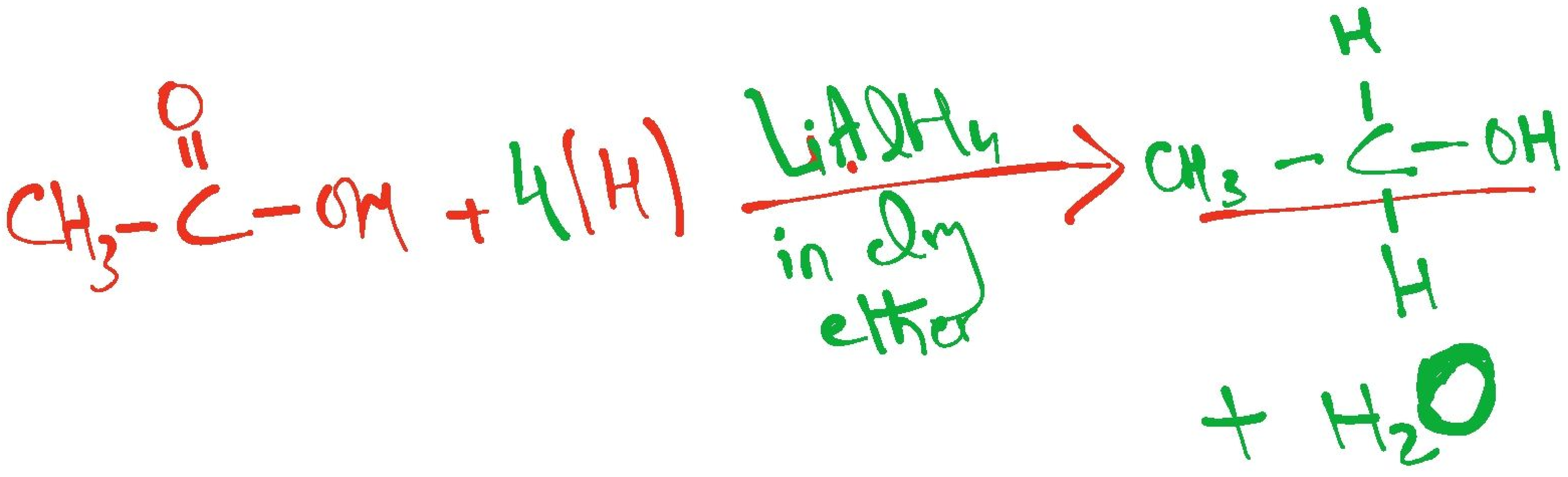
Sodium tetrahydrido borate

- For reduction of carboxylic acid we use $LiAlH_4$ in dry ether
- For the reduction of carbonyl compounds (Aldehyde & ketones) you can use both R.A
- Both reducing agents are unable to reduce the Alkenes

Reduction are opposite to oxidation

$$\text{Carboxylic acid} + [H] \xrightarrow[\text{in dry ether}]{LiAlH_4} \text{Aldehyde} + [H] \xrightarrow[\text{"}]{\text{"}} \text{P. alcohol}$$

$$\text{Keton} + [H] \xrightarrow[NaOH\,(aq)]{NaBH_4} \text{secondary Alcohol}$$



$$CH_3-\overset{\overset{O}{\|}}{C}-OH + 4[H] \xrightarrow[\text{in dry ether}]{LiAlH_4} CH_3-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-OH + H_2O$$