Alcohols, Phenols & Ethers – 05

Chemical properties of Alcohols – I

① ⟶ Reactions due to cleavage of R–O–H bond
(Acidic Nature of Alcohols)

② ⇒ Reactions due to cleavage of R–O–H bond

③ ⇒ Elimination Reaction : Dehydration of Alcohols

④ ⇒ Oxidation Reactions

⑤ ⇒ Haloform Reaction (oxidation + Test)

① Reactions due to cleavage of R–O–H bond
⇒ Acidic Nature of Alcohols

$$R\text{-}O\text{-}H \rightleftharpoons H^+ + RO^-$$

Acidic Strength

Alcohols are weaker Acids than water
(except CH_3OH)

$$H_2O \rightleftharpoons H^+ + OH^-$$
(more stable)

$$C_2H_5\text{-}OH \rightleftharpoons H^+ \; C_2H_5\text{-}O^-$$
less stable due to +I effect

$$H_2O > R\text{-}OH > CH\equiv CH$$
Acidic order

Note: Methyl Alcohol CH_3OH is Stronger Acid than water

CH_3-O-H $\quad$ CH_3

Acidic character

1° methyl CH_3O-H > 1° ethyl CH_3-CH_2O-H > 2° $CH_3-CH(CH_3)-O-H$ > 3° $(CH_3)_3C-O-H$

$-H^+$ $\quad$ $-H^+$ $\quad$ $-H^+$ $\quad$ $-H^+$

$CH_3\rightarrow O^-$ $\quad$ $CH_3\rightarrow CH_2\rightarrow O^-$ $\quad$ $CH_3-CH(CH_3)-O^-$ $\quad$ $(CH_3)_3C-O^-$

Most stable due to minimum +I effect $\quad$ least stable due to +I effect (max)

i) Reaction with active metals:

$$2ROH + 2Na \longrightarrow 2RO^-Na^+ + H_2$$

$$2C_2H_5OH + 2Na \longrightarrow 2C_2H_5O^-Na^+ + H_2$$

$$2CH_3OH + Mg \longrightarrow (CH_3O)_2Mg + H_2$$

ii) with Metal Amide ($NaNH_2$)

$$ROH \xrightarrow{NaNH_2} RO^-Na^+ + NH_3$$

$$C_2H_5OH \xrightarrow{NaNH_2} C_2H_5O^-Na^+ + NH_3$$

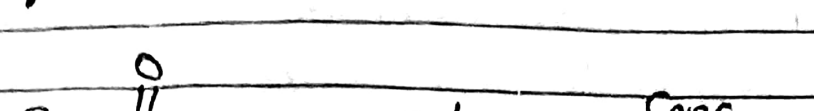
iii) with aq. NaOH OR aq. KOH

Alcohols are not acidic enough to react with aq NaOH or aq KOH like Carboxylic Acids do

exception: Methyl Alcohol (CH_3OH)

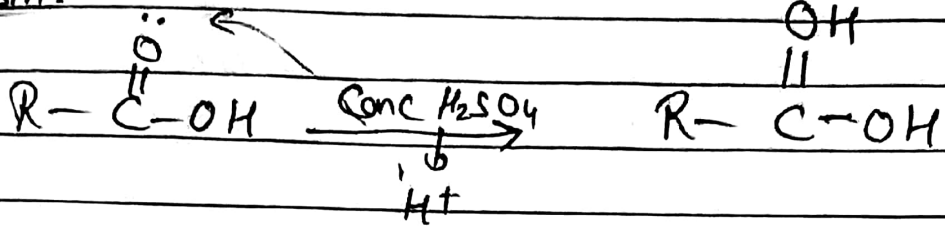
$$ROH + \underset{aq.}{NaOH} \not\rightleftharpoons R\bar{O}\overset{+}{Na} + H_2$$

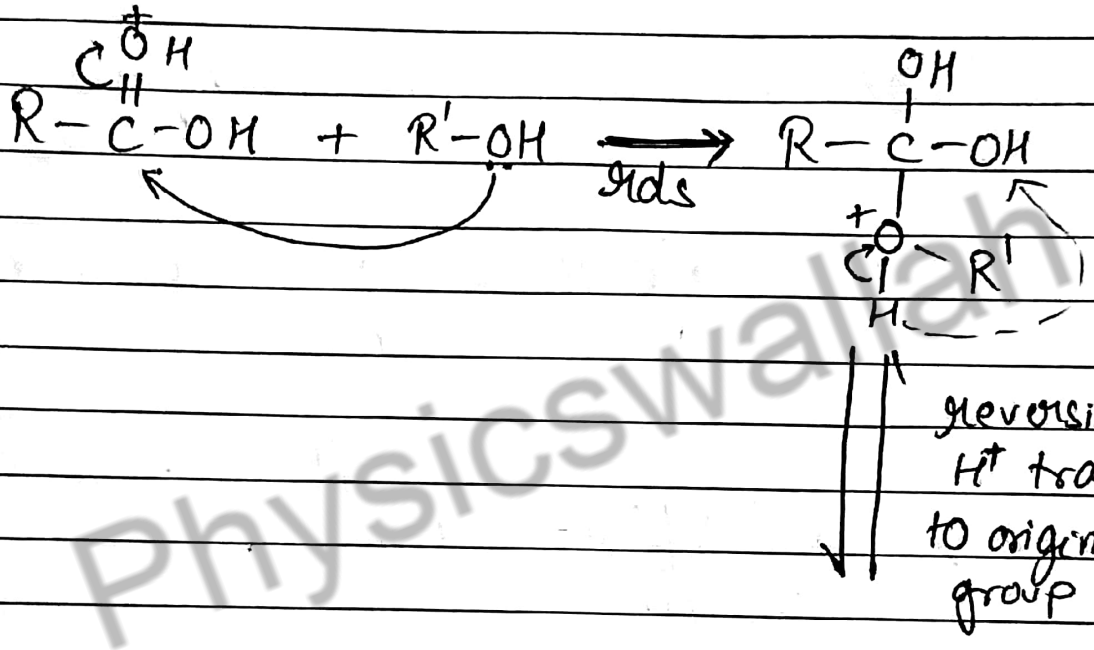
(iv) Esterification: Reaction with Carboxylic Acid

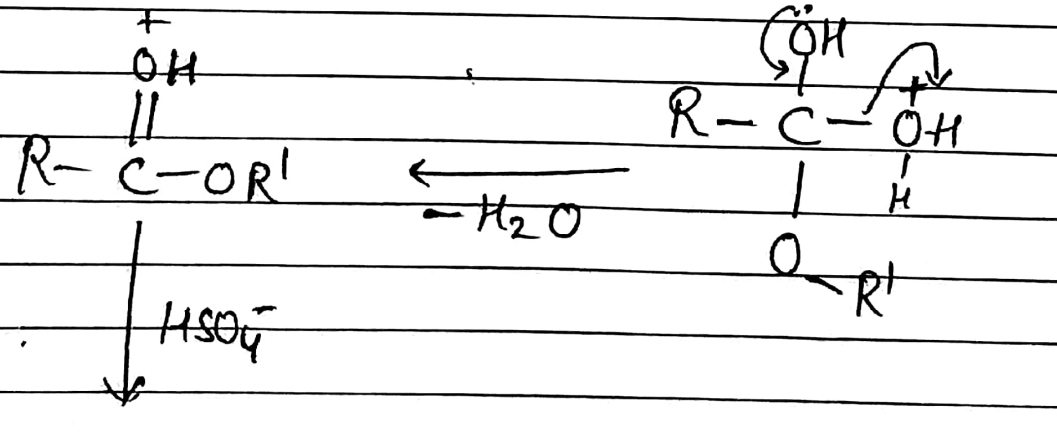


Surprisingly, it looks as alcohol loses H^+ & acid loses OH^-.

Mechanism:







$$R-\overset{O}{\overset{\|}{C}}-OR' + H_2SO_4$$

(This 'O' atom is of alcohol taken)
& it seems as if alcohol looses H^+ & Acid OH^-

Q) Find the Product

i) $C_2H_5-\overset{\overset{O}{||}}{C}-\overset{16}{O}H + CH_3\overset{18}{O}H \xrightarrow{H^+} C_2H_5-\overset{\overset{O}{||}}{C}-\overset{18}{O}CH_3$

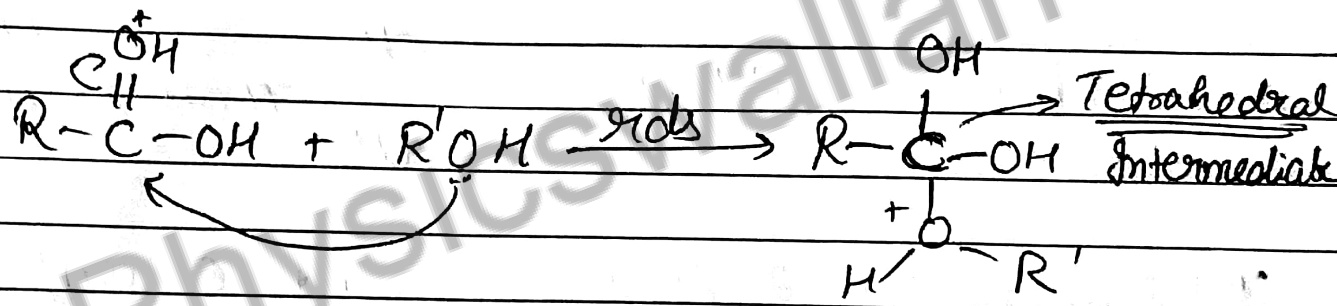
(O^{16} isotope) (O^{18} isotope)

(Isotopic labelling)

ii) $CH_3-\overset{\overset{O}{||}}{C}-\overset{18}{O}H + C_2H_5\overset{16}{O}H \xrightarrow{H^+} CH_3-\overset{\overset{O}{||}}{C}-\overset{16}{O}C_2H_5$

Rate of Esterification:

In rds step:



More steric hinderance (Bulky group) ⇒ less stable Intermediate

So, Rate of Esterification $\propto \frac{1}{\text{steric hinderance}}$

for alcohols $1° > 2° > 3°$
for Acid $1° > 2° > 3°$

For Acids:

$$HCOOH > CH_3COOH > CH_3-CH_2COOH > \begin{matrix} CH_3 \\ \diagdown \\ CH-COOH \\ \diagup \\ CH_3 \end{matrix} > \begin{matrix} CH_3 \\ \diagdown \\ CH_3-C-COOH \\ \diagup \\ CH_3 \end{matrix}$$

For Alcohols:

$$CH_3OH > CH_3-CH_2OH > \begin{matrix} CH_3 \\ \diagdown \\ CHOH \\ \diagup \\ CH_3 \end{matrix} > \begin{matrix} CH_3 \\ \diagdown \\ CH_3-COH \\ \diagup \\ CH_3 \end{matrix}$$

Note: In case of 3° Alcohol or 3° Acid, esterification do not takes place, ⇒ No ester formed as Intermediate is very very unstable

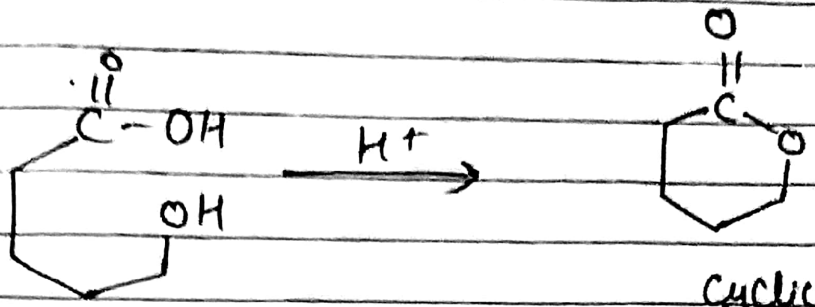
Find the product:

i) $CH_3\overset{16}{O}H + H\overset{\overset{O}{\|}}{C}OO\overset{18}{H} \xrightarrow{H^+} H-\overset{\overset{O}{\|}}{C}-O^{16}CH_3$

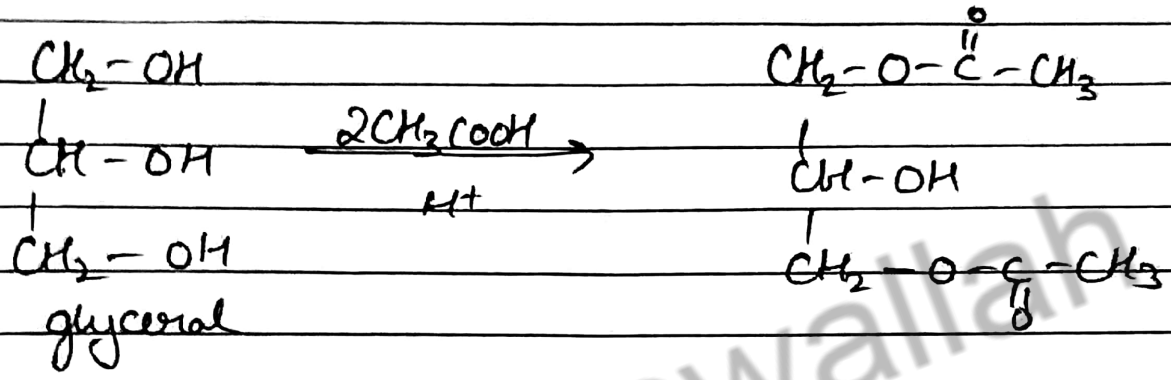
ii) $\begin{matrix} CH_2-OH \\ | \\ CH_2-OH \\ \text{glycol} \end{matrix} + \begin{matrix} CH_3-\overset{\overset{O}{\|}}{C}-OH \\ \\ CH_3-\overset{\overset{O}{\|}}{C}-OH \end{matrix} \xrightarrow{H^+} \begin{matrix} CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3 \\ | \\ CH_2-O-\underset{\underset{O}{\|}}{C}-CH_3 \end{matrix}$

Intramolecular

iii)

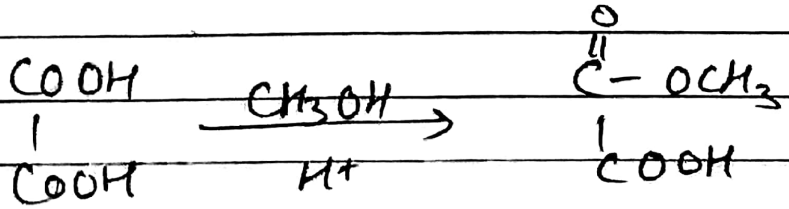


iv)



Attack on corners not on middle alcohol due to steric factor

v)



vi)