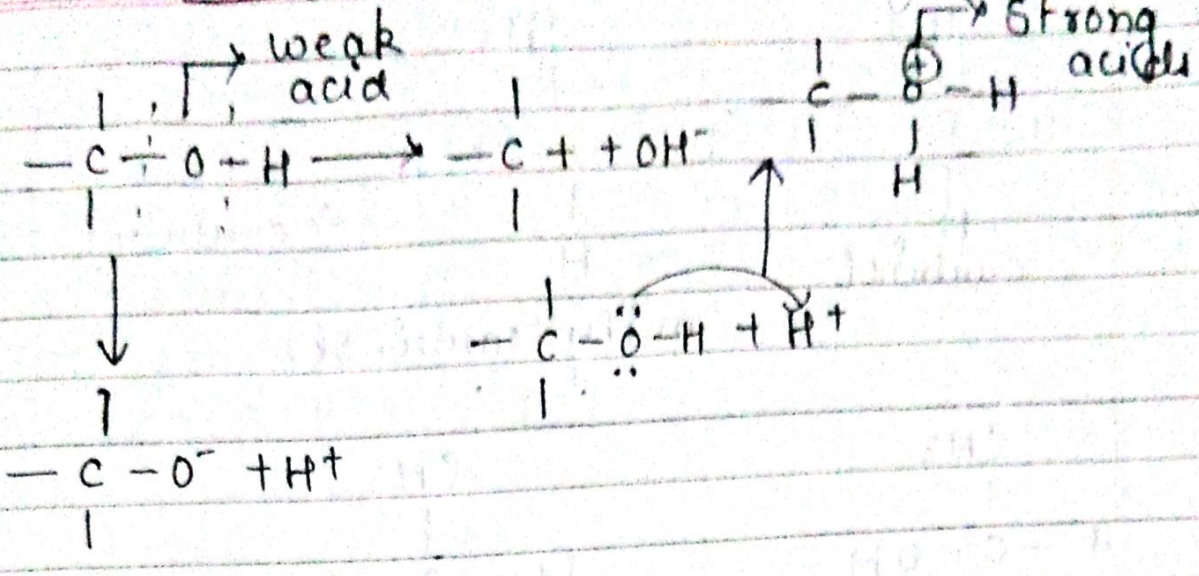
Alcohals



1) $pKa = -\log Ka$
2) Neutral
3) Amphoteric
4) Ka α acidity
5) Ka α $\frac{1}{pKa}$.

6) $-C(=O)-O-H \rightleftharpoons -C(=O)-O^-$ (carboxlate ion)

-COOH is more acidic then alcohals
why?
And :- Resonace resonance stabilized

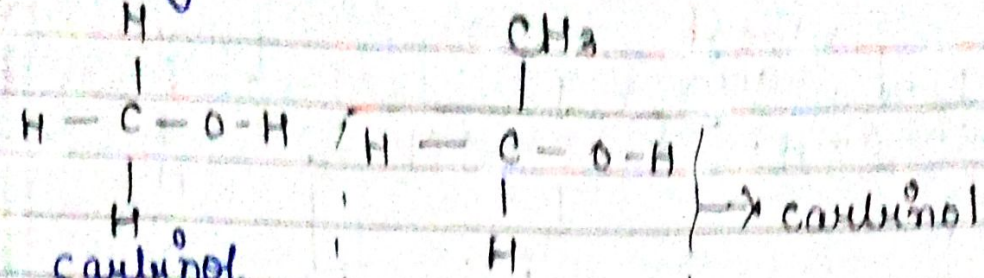
$-C(=O)-O^- \leftrightarrow -C(-O^-)=O$

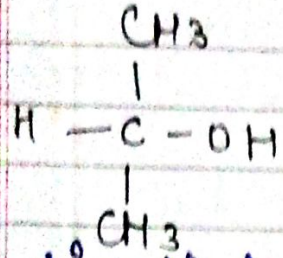
7) $R-O-H \rightleftharpoons R-O^- + H^+$ (alkoxide ion)
Not resonance stabilized

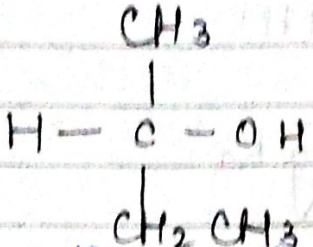
7) -I group α acidic strength

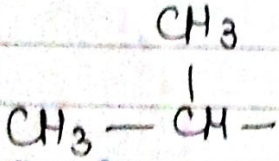
$W-CH_2-O-H$ >
$W-CH_3-CH_2-O-H$

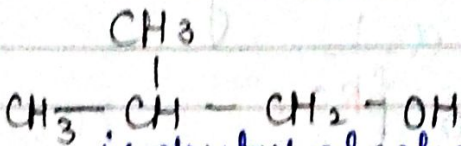
★ → for alcohols only amyl can be written in the place of pentyl.

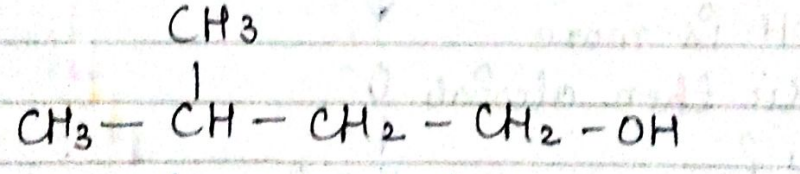



dimethyl carbinol


ethyl methyl carbinol.




is obutyl alcohol.


n-pentyl alcohol or amyl alcohol.

→ $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$ > n-propane.
n-hexane

M.W α b.p
H.W α van der wall interaction
on branching b.p decrease since surface area for van der wall interaction decrease.

$R-\overset{+\delta}{X}\cdots\cdots\overset{+\delta}{R}-\overset{-\delta}{X}$

↓

dipole - dipole interaction.

→ polarisibility of alkyl halide $\propto$ b.p.

eg → R-I > R-F

$R-\overset{\delta+}{O}-\overset{\delta+}{H}\cdots\cdots\overset{\delta-}{O}-R$

↓ |

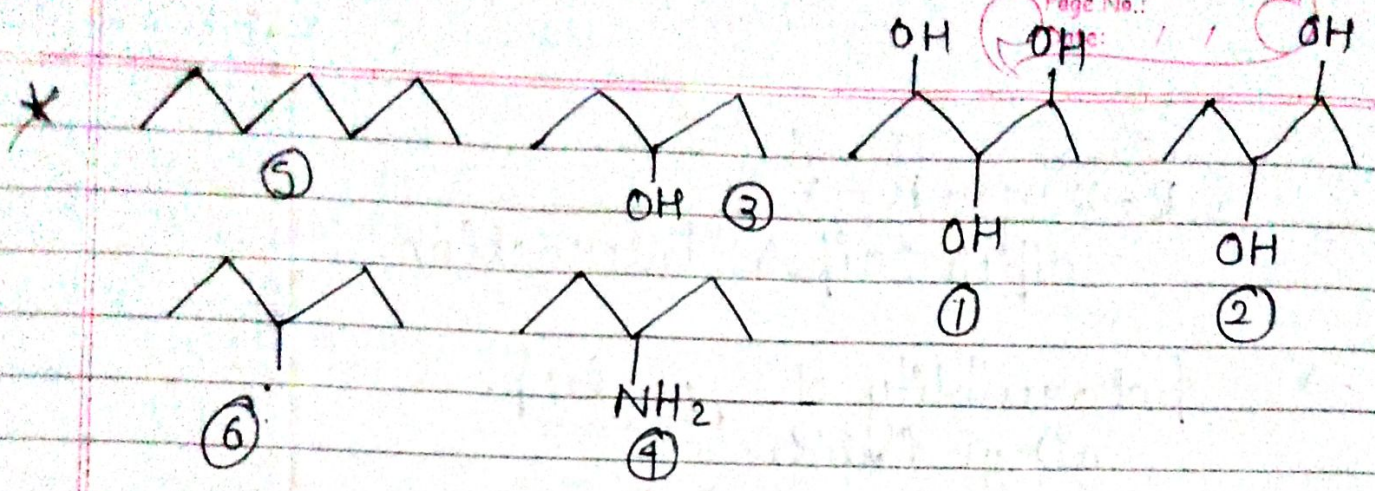
H-bonding $H^{\delta+}$

Strong dipole - dipole interaction

→ CH_3-CH_2-OH → Van der wall Interaction
dipole - dipole interaction
extensive H-bonding
Bp = 78°C.

CH_3-O-CH_3 → van der wall Interaction
dimethylether dipole - dipole interaction
No - H - bonding
BP = -24°C

★ R-O-H > $R-\underset{H}{N}-H$ → (for B.P)
alcohal amines



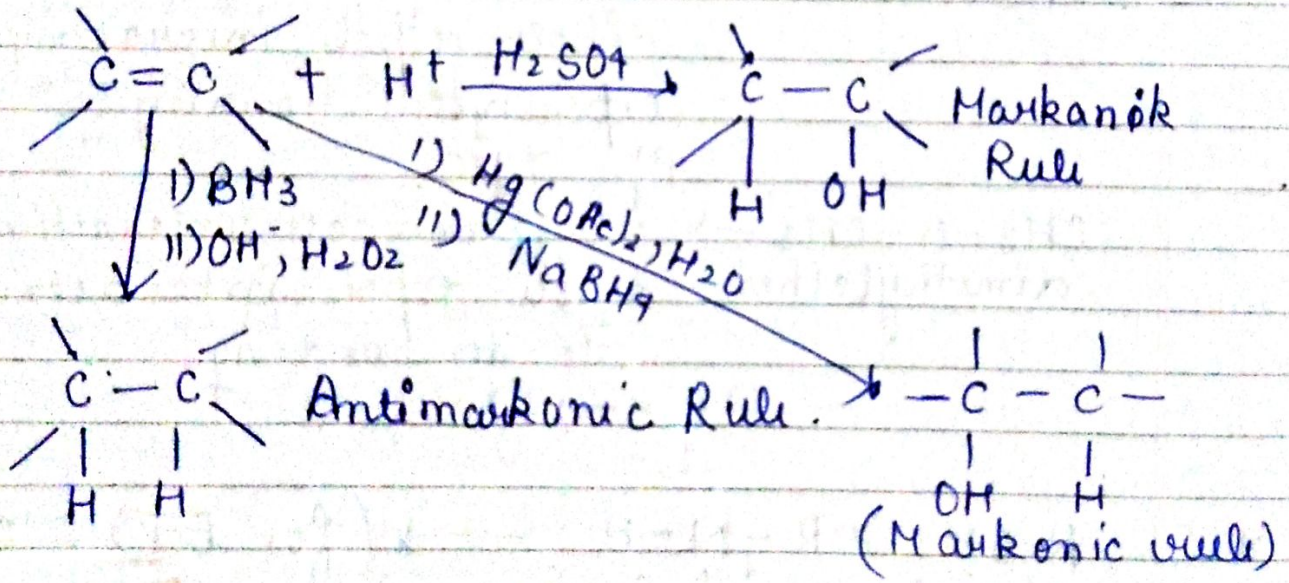
1 > 2 > 3 > 4 > 5 > 6 (B.P)

Synthesis of Alcohal

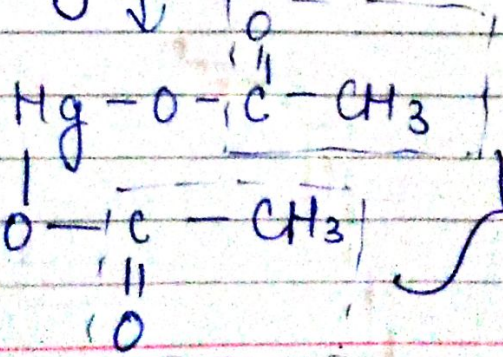
1) From alkane

$$CH_3-CH_2-Br + NaOH \xrightarrow[H_2O]{\Delta} CH_3CH_2-OH + NaBr$$

2) From alkene.

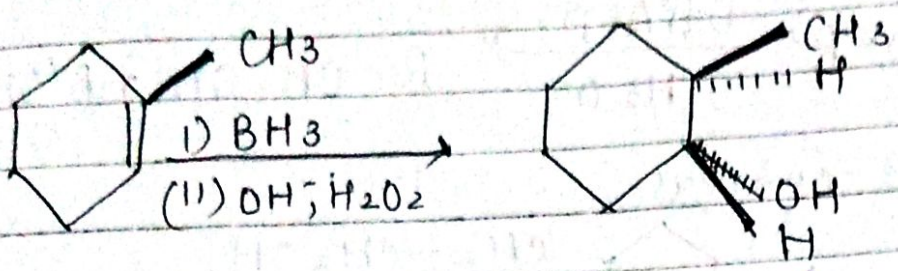


∴ $Hg(OAc)_2$



Ac in $Hg(OAg)_2$.
Acytyl.

→ $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2 \xrightarrow[II)\,NaBH_4]{I)\,Hg(OAc)_2} CH_3-\underset{\underset{CH_3}{|}}{C}-\underset{\underset{OH}{|}}{CH}-CH_3$

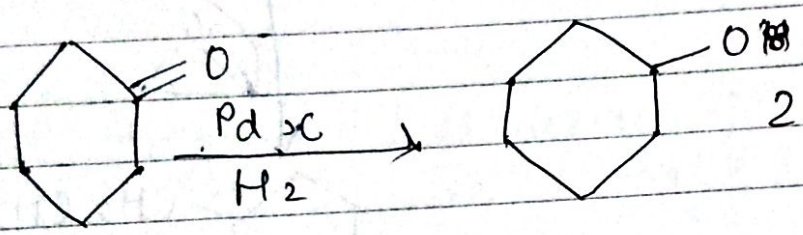
→ 

(Antimarkonic rule)

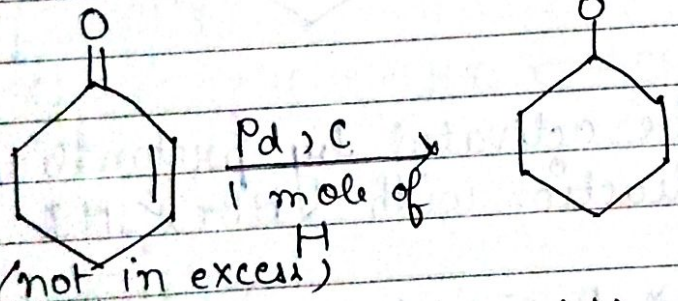
* from Carbonyl Compound

1) Reduction.

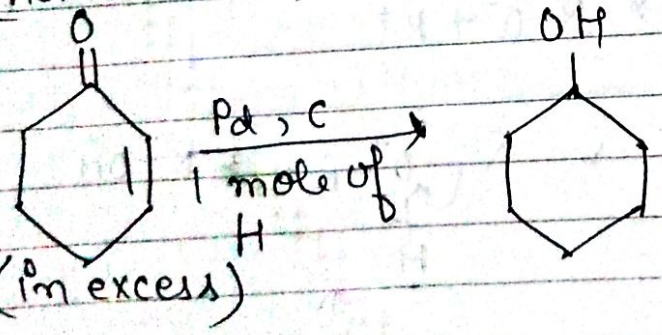
$CH_3-CH_2-CH_2-\underset{\underset{O}{||}}{C}-H \xrightarrow[H_2]{Pd;C} CH_3-\underset{1^\circ}{CH_2}-CH_2-\underset{\text{alcohol.}}{CH_2}-OH$

2) 

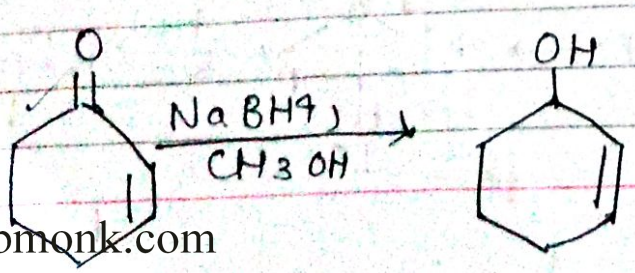
2° alcohol.

3) 

(not in excess)



(in excess)



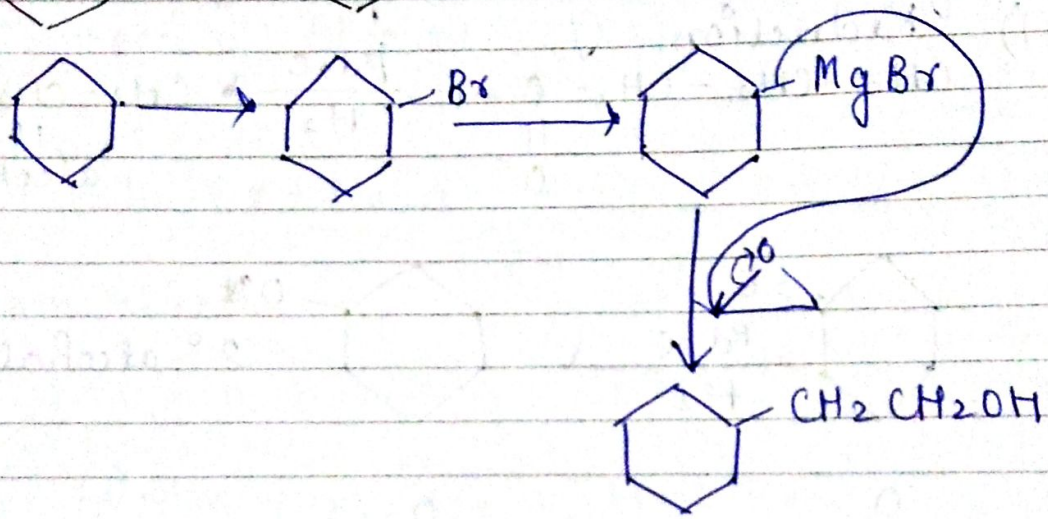
4) $CH_3-CH_2-CH_2-CHO \xrightarrow[\text{ii) } H_2O]{\text{i) } LiAlH_4} CH_3CH_2CH_2CH_2OH$

(Lithium Aluminium hydride)

5) $R-\overset{O}{\overset{\|}{C}}-O-R' \xrightarrow[\text{ii) } H_2O]{\text{i) } LiAlH_4} R-CH_2OH + R'OH$

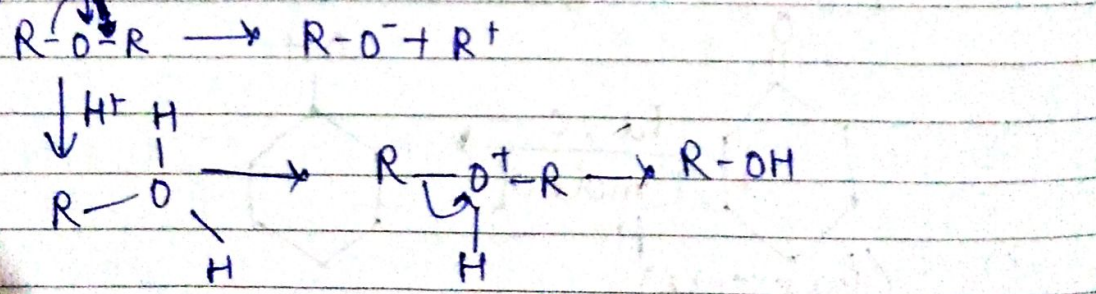
Q How to convert

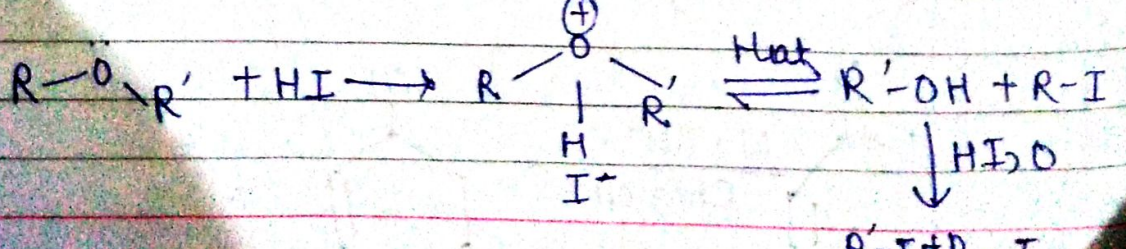
Ans



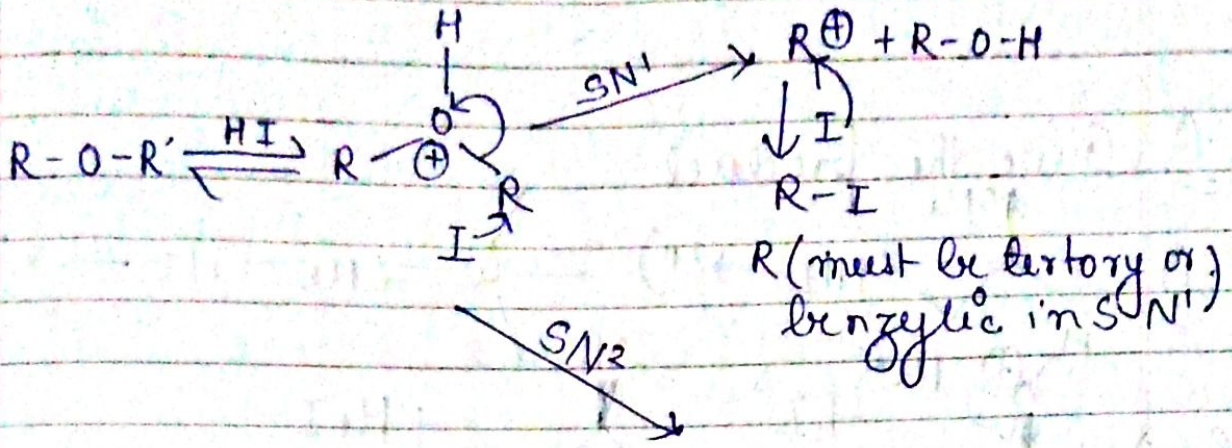
→ From Ether :-

Like ethers can be activated by protonation & undergo SN' Reaction with HBr & HI:

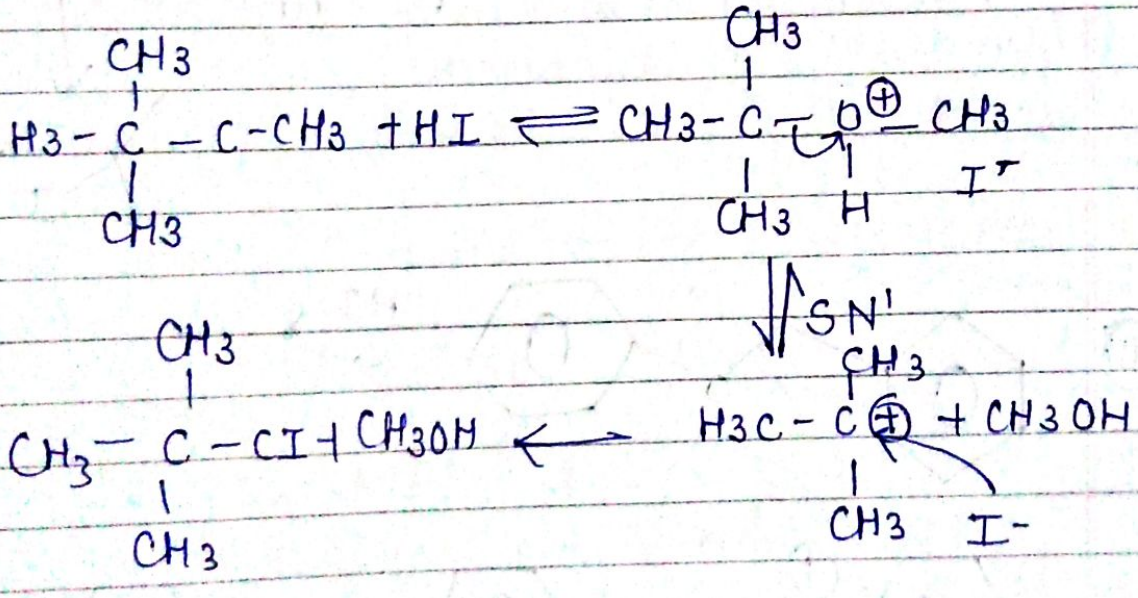




with 1 equivalent of HI alcohols & alkyl halides are formed but on heating on excess HI at only Alkyl halide is formed as major product.



depending on the structure of alkyl group the reactn will be SN' or SN2.



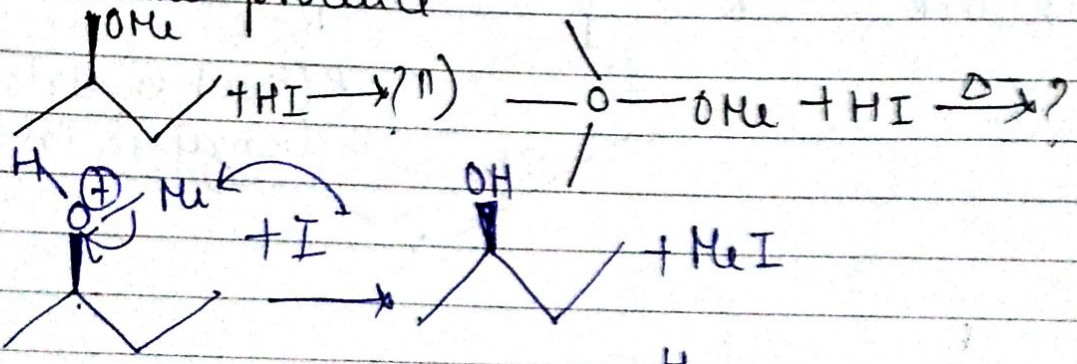
* SN reactn never happend at Sp^2 carbon

* $CH_3-CH_2-CH_2-O-CH_3 + HI \rightleftharpoons CH_3-CH_2-CH_2-O-CH_3$ (less hydrogen)

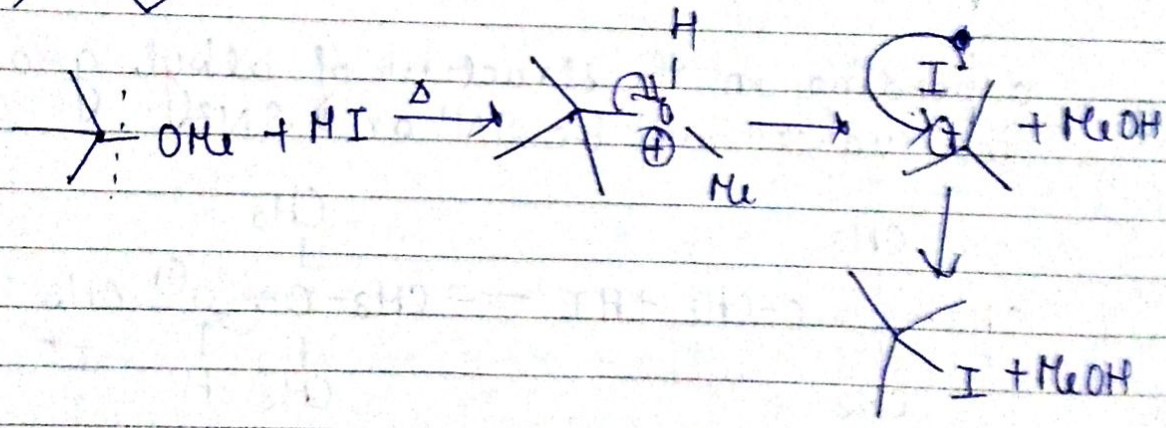
$CH_3-CH_2-CH_2-O-CH_3 \xrightarrow{H} CH_3-CH_2-CH_2-O-CH_3 \xrightarrow{I^-} S_N2$

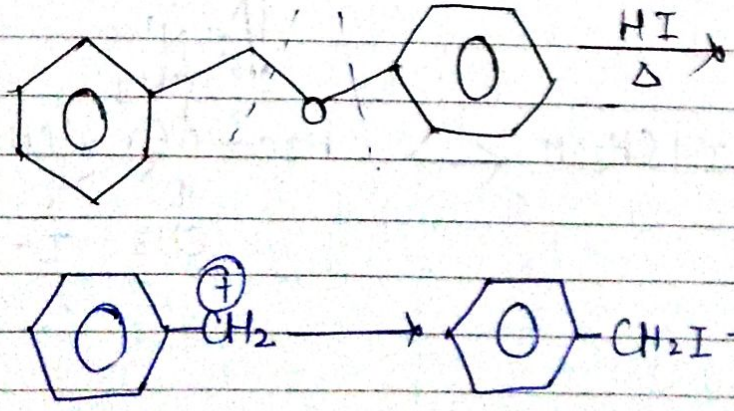
$CH_3-CH_2-CH_2-OH + CH_3I$

Q Give the product

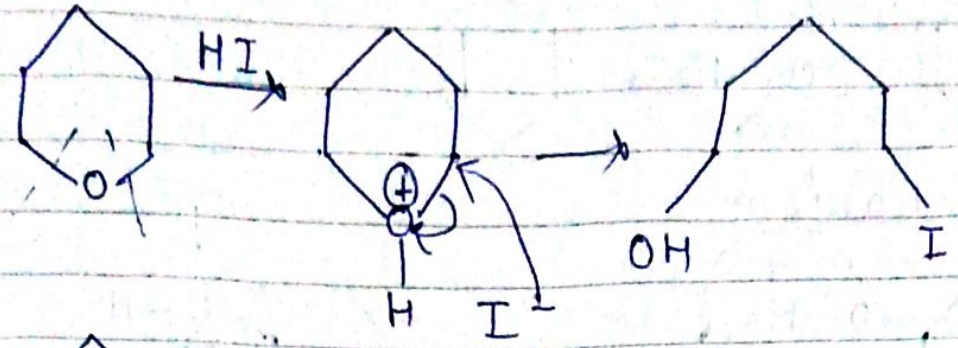
1) 

Ans 1)

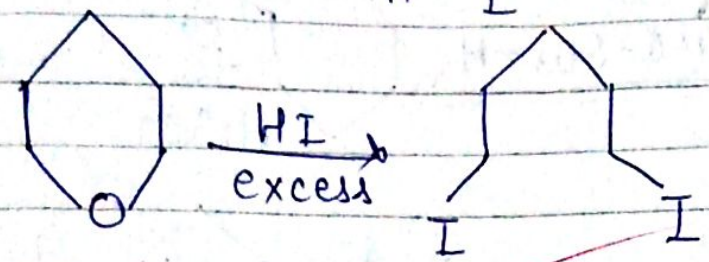
(ii) 

(ii) 

(iv)



(v)



★ MeOH (wood alcohol) (Methanol)

$$CO + H_2 \xrightarrow[200°-300\ atm]{300°-400°C} CH_3OH$$

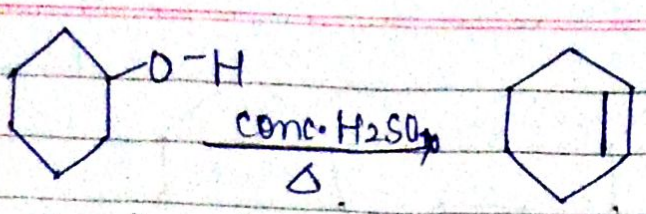
ZnO - Cr_2O_3

★ C_2H_5OH (grain alcohol) (Ethanol)
It is made by fermentation of sugar which is usually carried out by adding yeast.

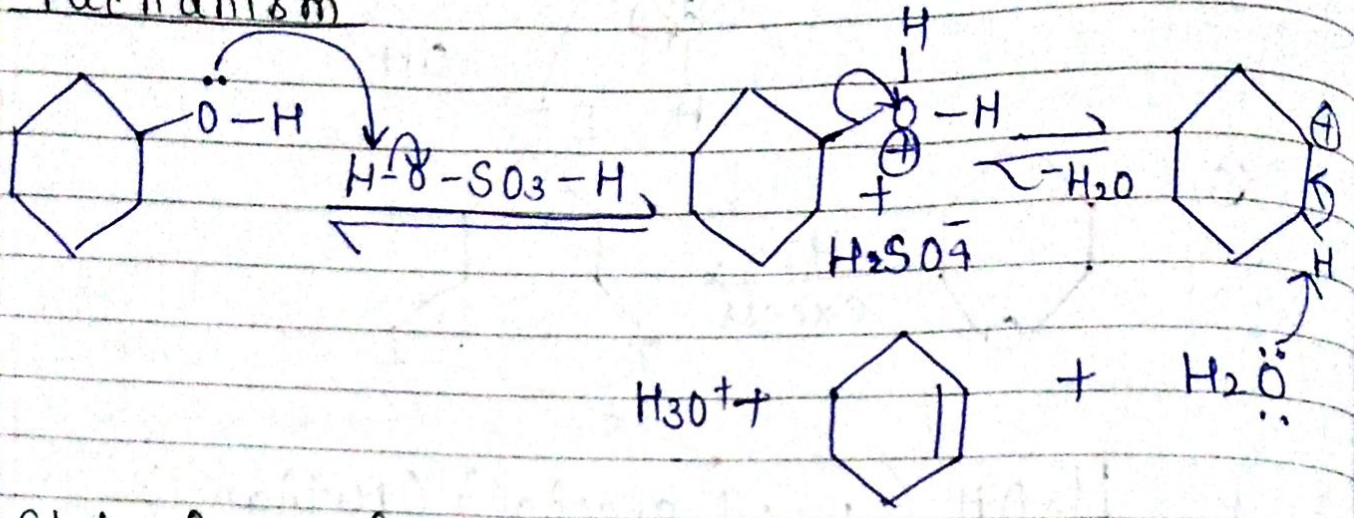
$$C_6H_{12}O_6 \xrightarrow{yeast} 2C_2H_5OH + CO_2$$

React^n of Alcohal :-

1) Dehydration of Alcohal :- (Imp. Topic)
alcohals undergo elimination react^n by loosing OH from one carbon & H from adjacent carbon to give alkene as major product.
The dehydration requires conc. H_2SO_4 + heating.



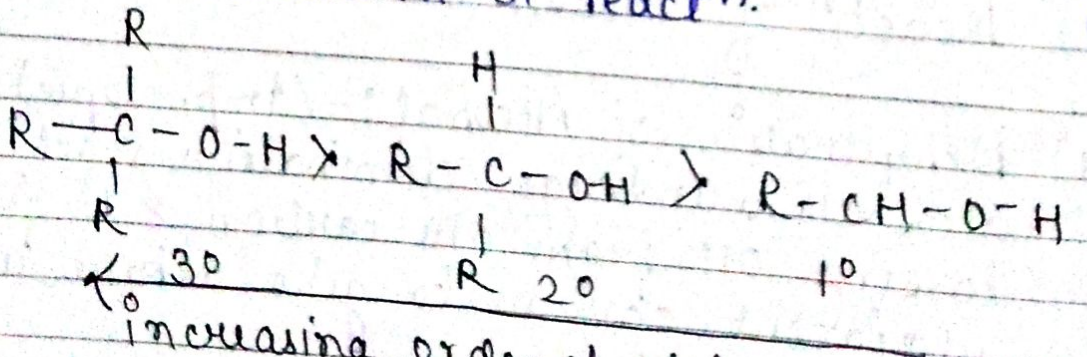
Mechanism



Steps in Mechanism:-

1) Protonation by H_2SO_4
2) dehydration from protonated alcohol to give carbocation intermediate
3) This carbocation intermediate on deprotation by water gives alkene.

The reactn is governed by this reactn so the rate of reactn will depend on stability of carbocation. Greater will be the stability of carbocation greater will be the rate of Reactn Since 3° carbocation is most stable thus they are most reactive in E1 reactn.



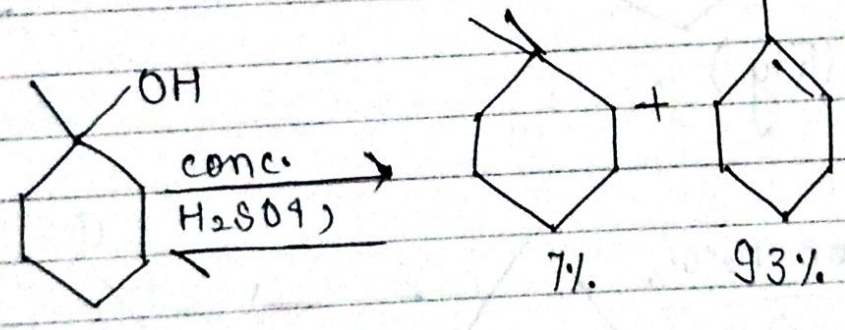
If during dehydration more than 1 product can formed then the major product will be more stable alkene. Since the transition state leading to the formation more stable alkene is more stable. This is in accordance with Stizzef Rule.

1) $CH_3-\underset{\underset{OH_2}{|}}{\overset{\overset{CH_3}{|}}{CH}}-CH_2-CH_3 \xrightarrow[\text{conc. } H_2SO_4]{\text{conc.}}$

$CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_3$ more stable because more substituted 84%.

+

$CH_2=\overset{\overset{CH_3}{|}}{C}-CH_2-OH$ less stable because less substituted 10%.

2) 

3) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{CH} \xrightleftharpoons[\Delta]{\text{conc. } H_2SO_4}$ $H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH=CH_2$ 3%

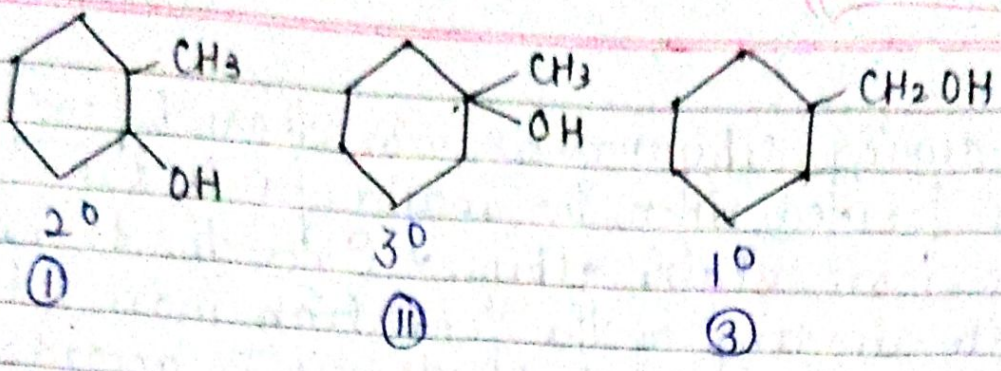
$\xrightarrow[\Delta]{\text{conc. } H_2SO_4}$ $H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{\oplus}{|}}{C}}-\overset{\overset{H}{|}}{C}-CH_3$ (from 1,2 methanoid shi

$\xleftarrow{H_2O}$

2^0 cabocation wi change into 3^0

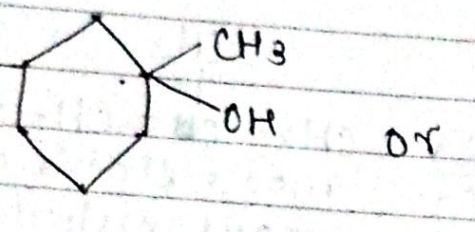
$CH_3-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH_3$ + $CH_2=\overset{\overset{CH_3}{|}}{\underset{3SA}{C}}-O-CH_3$

Q1

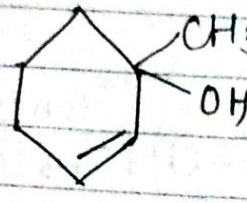


(II) > (I) > (3) → order of dehydration

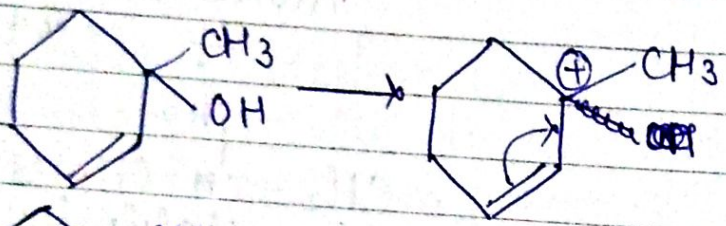
Q

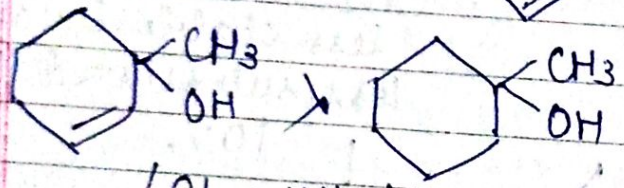


or

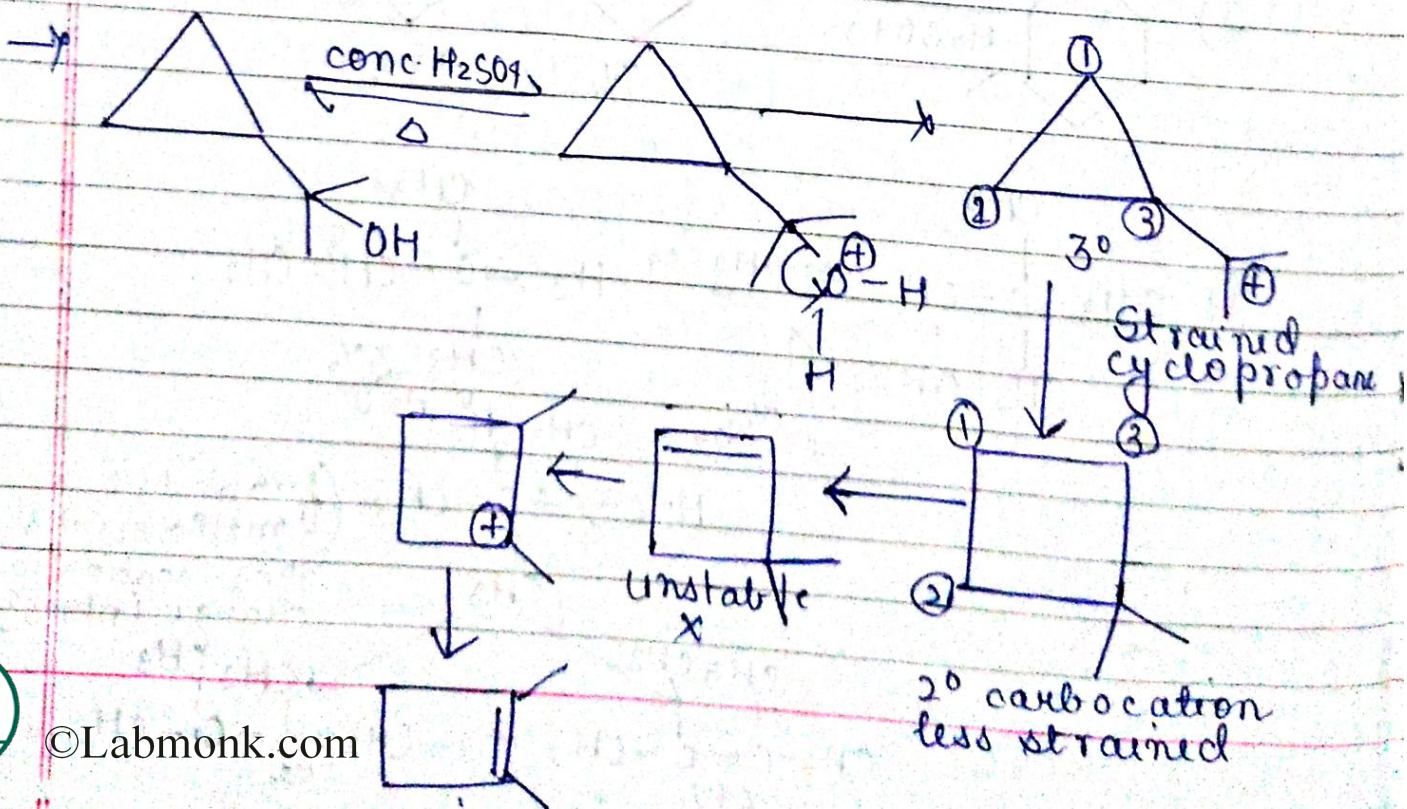


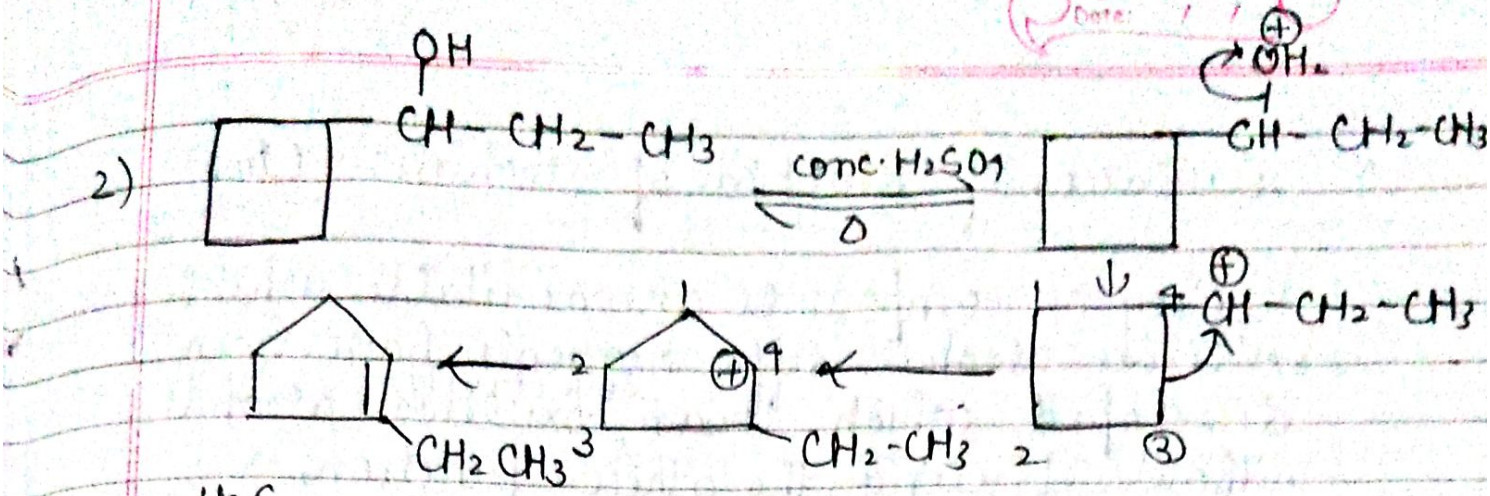
← which is more stable?

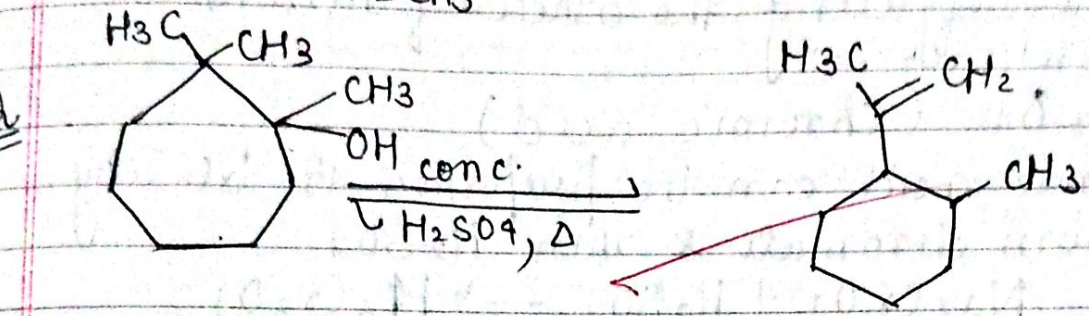




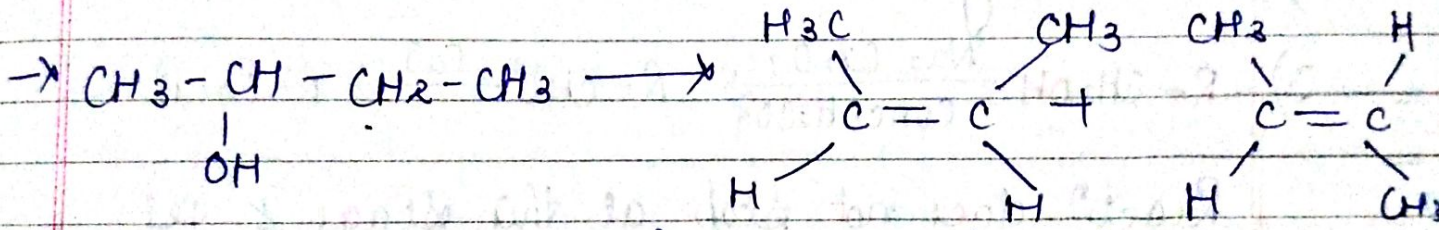
(Stability)



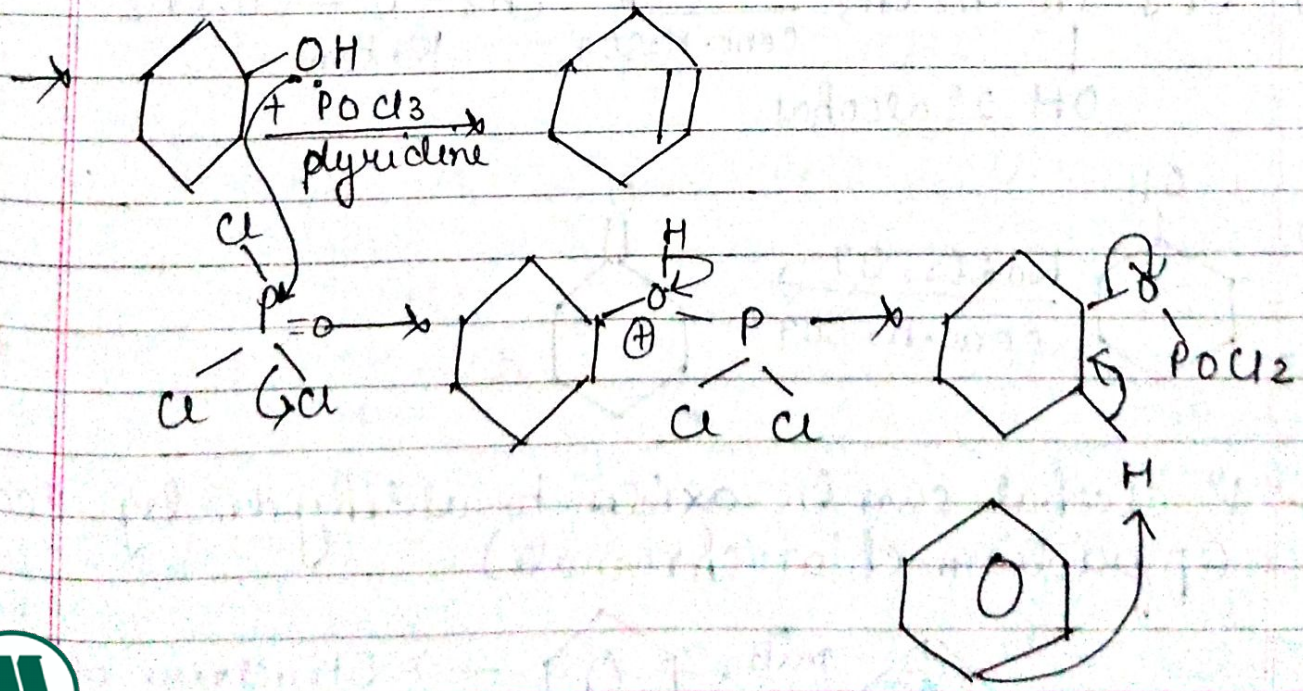




explain the mechanism (Homework, H.W)



* → Stable when bulky group is far.



★ Oxidation of Reaction of alcohals:- (Imp)

Variety of compounds are available which can oxidised alcohal. diff. reagents have been developed which can selectively oxidised alcohal without effecting the other function.

Reagent are -

1) $H_2Cr_2O_4$ (Chromic acid)

Chromic acid can be prepared in lab by Sodium chromate & then H_2SO_4

$$Na_2Cr_2O_7 + H_2SO_4 \longrightarrow H_2Cr_2O_4$$

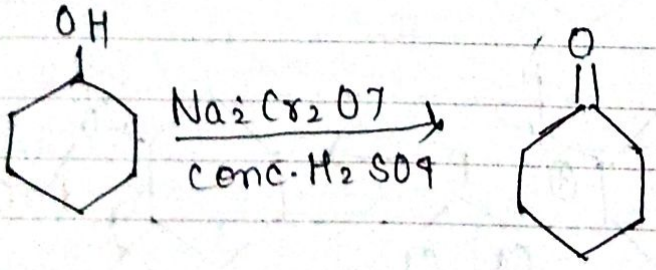
2) Jones Reagent

3) $$R-CH_2OH \xrightarrow[Conc.\ H_2SO_4]{Na_2Cr_2O_7} R-CHO \xrightarrow{[O]} R-COOH$$

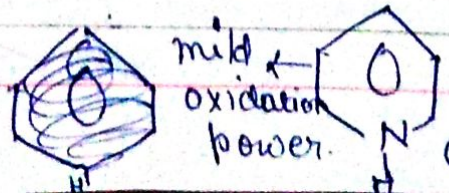
Reactⁿ does not stop at this stage & get carboxylic acid from 1° alcohal.

4) $$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2CH_3 \xrightarrow[Conc.\ H_2SO_4]{Na_2Cr_2O_7} CH_3-\overset{\overset{O}{||}}{C}-CH_2CH_2$$

2° alcohal — Ketone

5) 

Imp → 1° alcohal can be oxicles to aldehyde by PCC (pyridium chlorochromate)



→ Structure of PCC

Test for alcohols differentials.

Lucas Test
Dichromate Test

It must be remembered that during oxidation oxidation the H atom is removed from the carbon to which OH is attached. Hence 3° alcohols do not undergo oxidation reaction Since chromium based reagents are toxic hence another method is developed for the oxidation of alcohol. using HOCl.

HOCl → unstable, must be generated insite
(Hypochlorous)

$$CH_3OH + NaOCl \longrightarrow HOCl$$

$$R\text{-}CH_2OH + \xrightarrow[0^\circ C]{HOCl} R\text{-}CHO$$

$$R\text{-}\underset{\underset{OH}{|}}{CH}\text{-}R \xrightarrow{HOCl} R\text{-}\underset{\underset{O}{||}}{C}\text{-}R$$

when vapours of alcohol are passed over copper Gauze wool above 300°C diff. products are formed.

$$CH_3CH_2OH \xrightarrow[300^\circ C]{Cu} CH_3CHO$$

$$CH_3\text{-}\underset{\underset{OH}{|}}{CH}\text{-}CH_3 \xrightarrow{\quad} CH_3\text{-}\underset{\underset{O}{||}}{C}\text{-}CH_3$$

$$CH_3\text{-}\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{CH}}\text{-}CH_3 \xrightarrow{\quad} CH_3\text{-}\underset{\underset{CH_3}{|}}{C}=CH_2$$

Dichromate Test

This is based on the fact that diff. types of alcohal give diff. product from oxidation. the reactn is done at room temp. using Sodium dichromate & H_2SO_4

1) 1° alcohals gives carboxylic acid containing same no. of C-atom & soln becomes orange to green
2) 2° alcohals gives ketone & soln becomes orange to green with same no. of C-atom.
3) 3° alcohals do not react & soln remains orange.

$R-CH_2-OH$ $\xrightarrow[[O]]{Na_2Cr_2O_7/H_2SO_4}$ $R-CHO$ $\xrightarrow{[O]}$ $R-COOH$

soln becomes orange to green

$R-\underset{\displaystyle R}{\underset{|}{C}}H-OH$ $\xrightarrow{Na_2Cr_2O_7/H_2SO_4,\ [O]}$ $R-\underset{\displaystyle R}{\underset{|}{C}}=O$

soln becoms orange to green.

$R-\underset{\displaystyle R}{\underset{|}{C}}(R)-OH$ $\xrightarrow{Na_2Cr_2O_7/H_2SO_4,\ [O]}$ ✗

because not α-H, do not oxidised

Or CH_3CH_2OH $\xrightarrow[180°C]{conc.\ H_2SO_4}$ $CH_2=CH_2$ elimination product

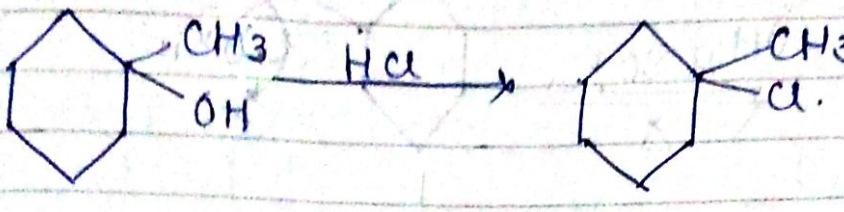
CH_3CH_2OH $\xrightarrow[140°C]{conc.\ H_2SO_4}$ $CH_3-CH_2-O-CH_2-CH_3$ SN^2 product.

1° → SN²
3° → SN¹

✱ Substitution Reaction

Reaction of alcohal with H-X is a general method for the preparation of, 1°, 2° & 3° alkyl halide.

$$CH_3-CH_2CH_2-OH \xrightarrow{HBr} CH_3CH_2CH_2-Br$$



→ Since chloride is a poor nucleophile the 1° alcohals does not undergo reactⁿ easily & the rate of Reactⁿ is increased by the addition $ZnCl_2$ & HCl, popularly known as Lucas Reagent
1° alcohals react with Lucas Reagent through SN^2 reactⁿ & the rate of Reactⁿ is slow.

✱ Lucas Test :-

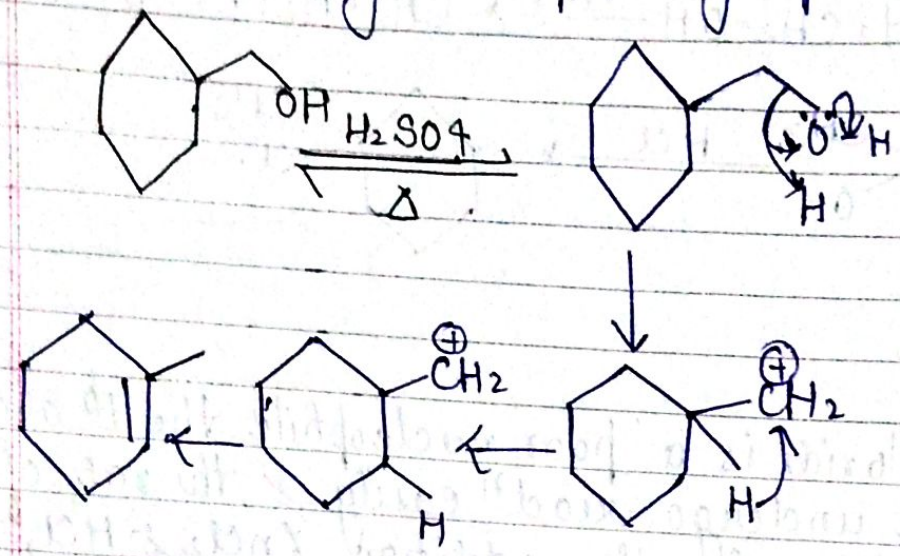
Low molecular weight alcohals are soluble in Lucas Reagent but the alkyl halide which is formed is not. This form the basis of Lucas Test.
In this method alcohals are treated with $ZnCl_2$ (anhydrous) & HCl.

$$R-OH + HCl \xrightarrow{ZnCl_2} R-Cl$$

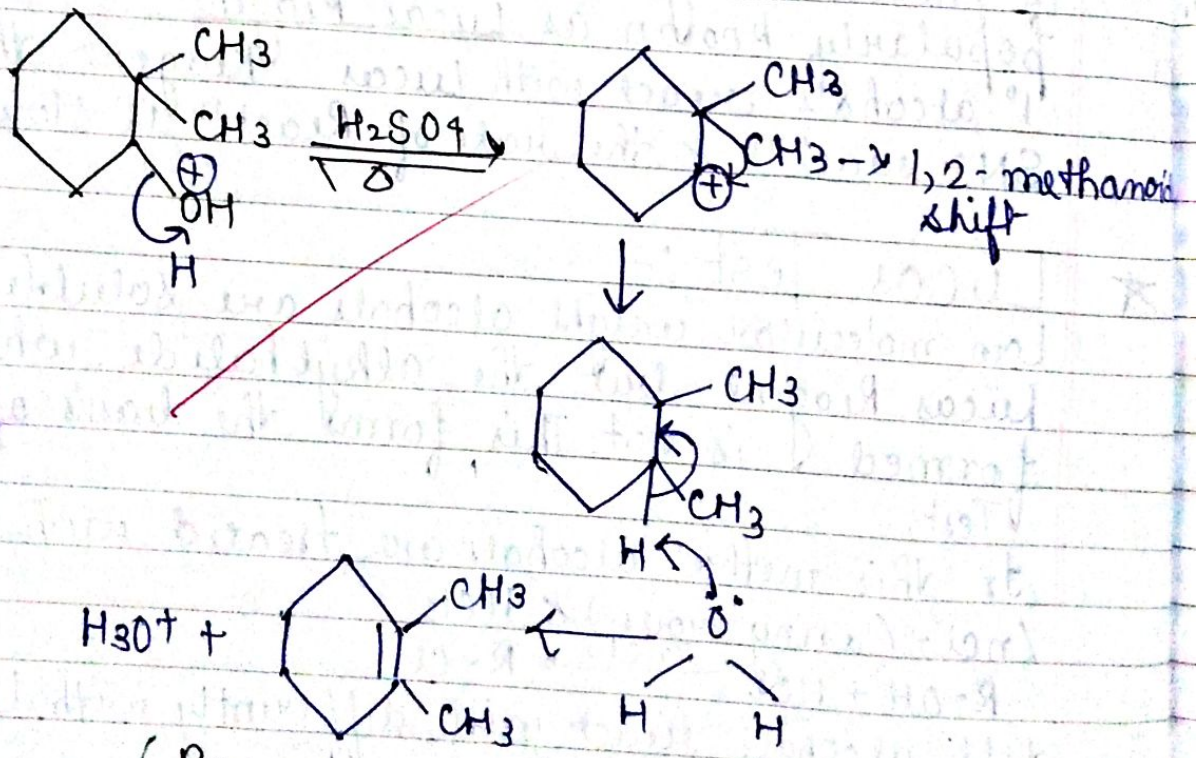
diff: alcohals react with differently with Lucas reagent.
→ 3° alcohals react very rapidly since the alkyl halide which is formed is insoluble in medium & turbudity develops immediately. when alcohal is 3° rate of reactⁿ is very high.

* when it is 2° the turbidity develops approximately in 1 to 5 min.
* when alcohol is 1° the soln remains clear & turbidity develops only upon heating.

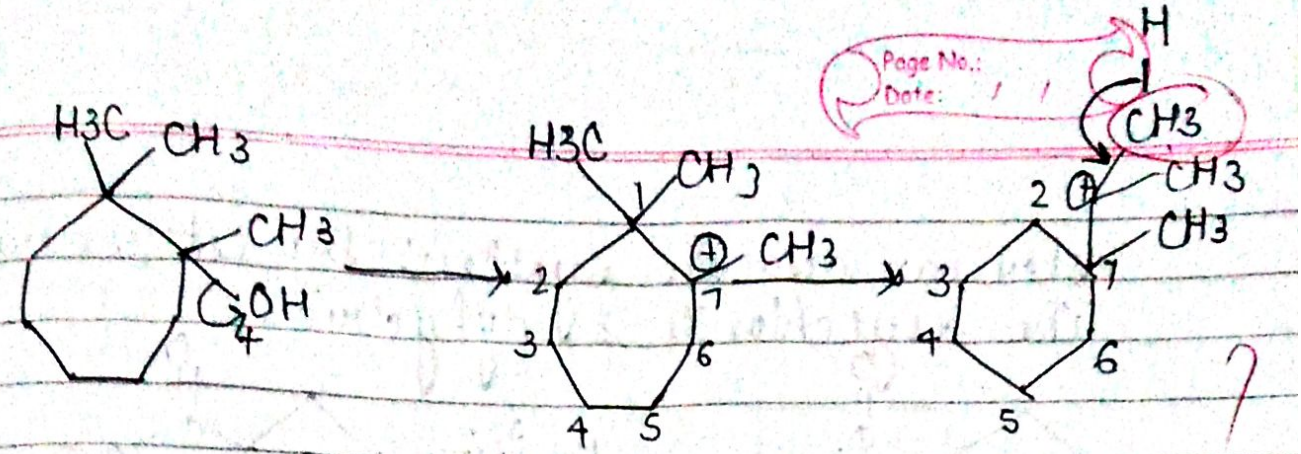
(1)



(2)



(Rearrangement Reaction.



Esterification Reactⁿ

It is acid catalysed condensation Reactⁿ of carboxylic acid & alcohals.

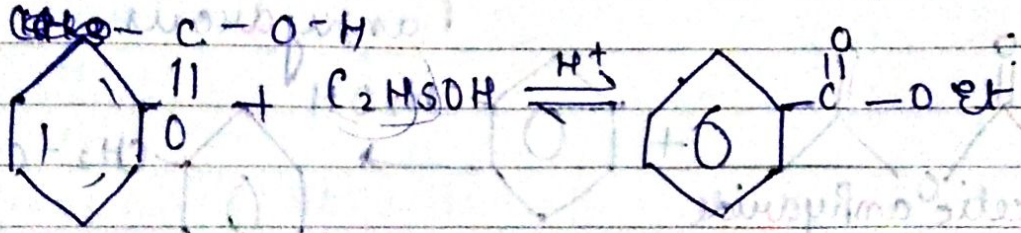
$$R-\overset{O}{\overset{\|}{C}}-O-H + R'-OH \underset{}{\overset{H^+}{\rightleftharpoons}} R-\overset{O}{\overset{\|}{C}}-O-R' + H_2O$$

ester

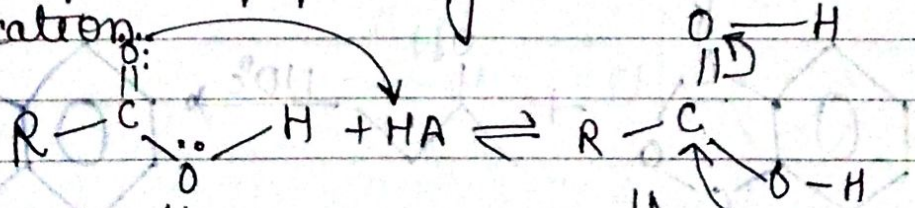
H atom of water comes from alcohal

$$CH_3-\overset{O}{\overset{\|}{C}}-O-H + Me-OH \overset{H^+}{\rightleftharpoons} CH_3-\overset{O}{\overset{\|}{C}}-O-Me + H_2O$$

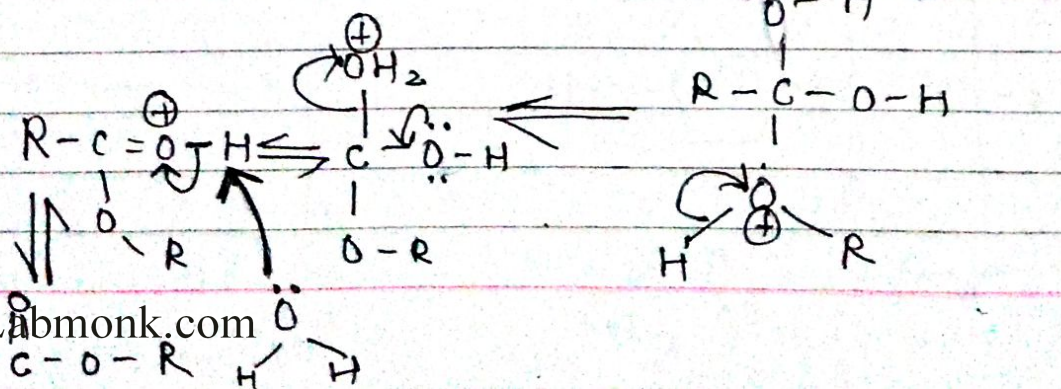
Acetic acid — Methyl am.



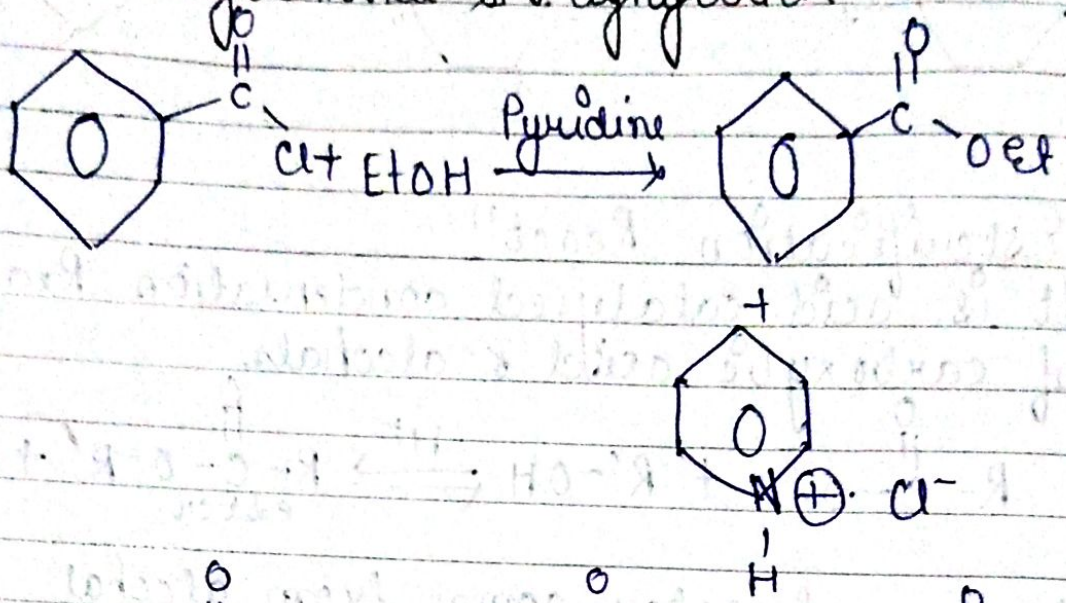
this reactⁿ is popularly known as Fischer estrification.



Mechanism of Esterification

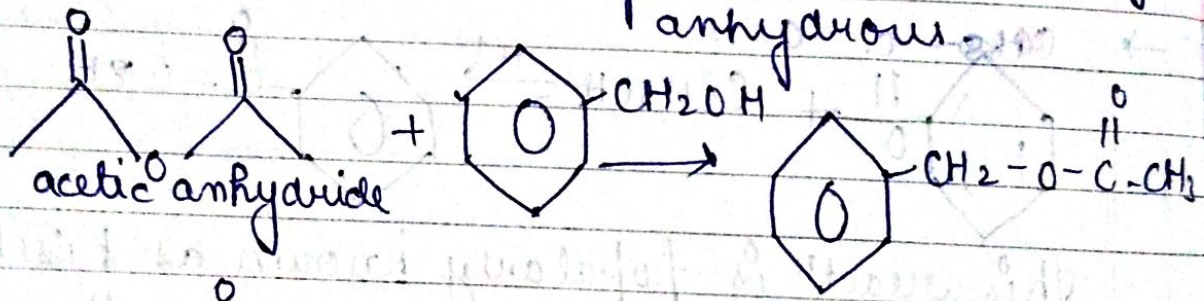


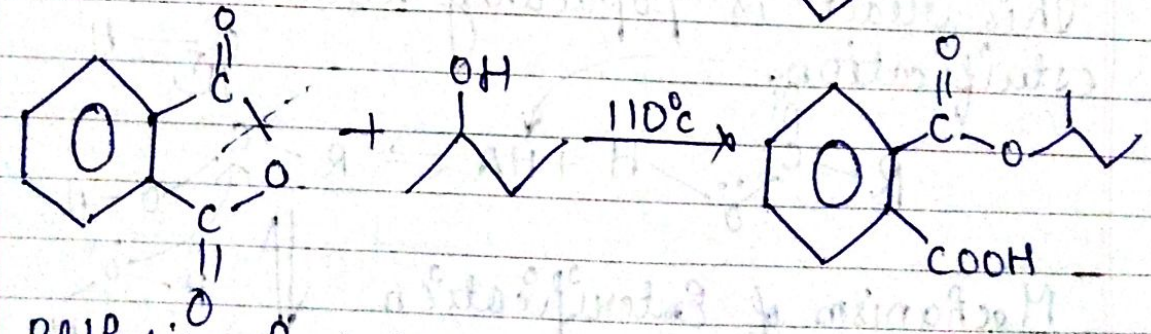
ester can also be synthesis by ester derivat like acyl chloride & dyhydride.



* $CH_3-C(=O)-O-H + H-O-C(=O)-CH_3 \rightarrow CH_3-C(=O)-O-C(=O)-CH_3$ acetic anhydri

→ removal of water gives anhydrous





Phthalic anhydride.