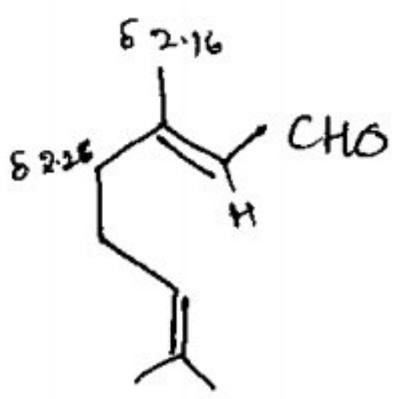
$(C_{10}H_{16}O)$ CITRAL



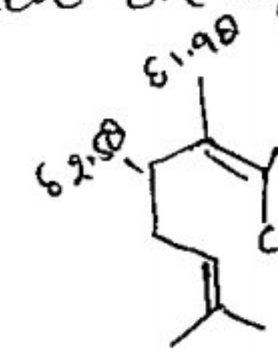
citral a or
E or trans
geranial
semicarbazone = 164°c
b.p = 117–119°c / 20 mm

⇒ A cyclic monoterpenoids

⇒ Citral an optically inactive monoterpene aldehyde, occurs widely in lemon grass oil.

⇒ It is isolated as its crystalline monobisulphite which on hydrolysis regenerates citrols.

⇒ b.p. = 224–228°c.



citral b or
Z or cis
or
neral
b.p 118–119°c/20mm
semicarbazone = 171°c

CONSTITUTION :-

⇒ Its molecular formula is $C_{10}H_{16}O$, has been obtained by usual procedure.

⇒ Citral has two carbon-carbon double bond as shown by following reaction.

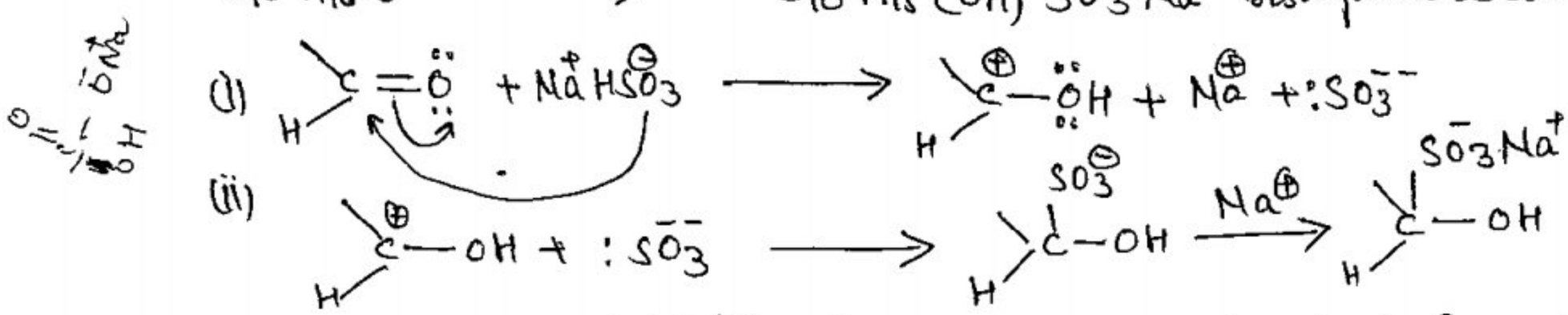
$$C_{10}H_{16}O \xrightarrow{2Br_2} C_{10}H_{16}OBr_4 \qquad C_{10}H_{16}O \xrightarrow{2H_2\,(Pd)} C_{10}H_{20}O$$

citral — citral tetrabromide — Tetrahydrocitral

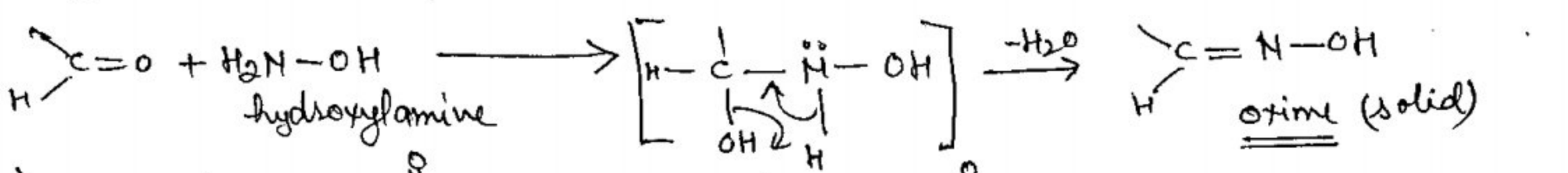
Thus $\left[\begin{matrix} C=C \\ \\ C=C \end{matrix}\right]$ may be present in aldehyde

⇒ Nature of oxygen :- The oxygen present in citral is in the form of a carbonyl group since it forms a bisulphite derivative, an oxime, a semicarbazone and a red 2,4 dinitrophenylhydrazone.

$$C_{10}H_{16}O \xrightarrow{Na^+HSO_3^-} C_{10}H_{15}(OH)SO_3^-Na^+ \text{ bisulphite adduct}$$

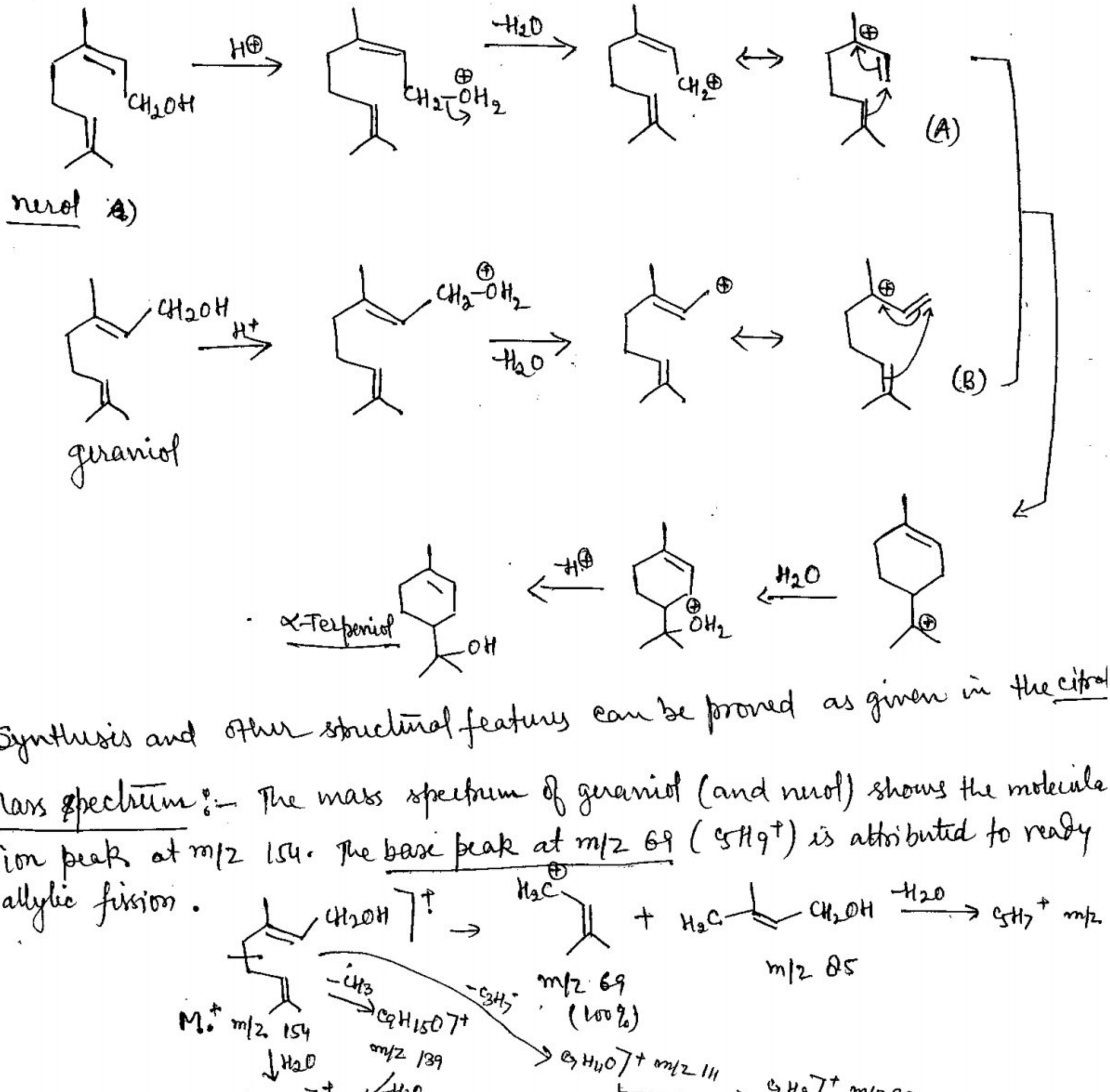


(S is more nucleophilic than O, a C–S bond is formed in the adduct)



Thus these reactions suggests that oxygen is as in carbonyl group

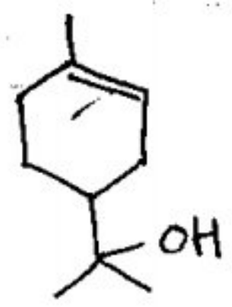
configuration of geraniol relative to nerol has been further proved by the fact that nerol undergoes acid-catalysed cyclisation to a α-terpineol nine time faster than geraniol. The large difference in the rates is explained by proximity effect. In the intermediate carbocation (A), the carbon atom bearing the positive charge and carbon-carbon double bond involved in the cyclisation are sufficiently close. On the other hand, in the case of geraniol there is a lag before the intermediate carbocation B can assume the configuration B. Thus nerol must have the CH_2OH group cis to the main chain of the molecule



Synthesis and other structural features can be proved as given in the citral

Mass spectrum :- The mass spectrum of geraniol (and nerol) shows the molecule ion peak at m/z 154. The base peak at m/z 69 ($C_5H_9^+$) is attributed to ready allylic fission.

(C10H18O) α- TERPINEOL



⇒ α- Terpineol (m.p 35°C), an optically-active monoterpene alcohol, occurs naturally both as (+) forms in oils of petil grain and neroli and as (-) form in camphor and cajuput oils.

⇒ It is a solid

Constitution and Structure:-

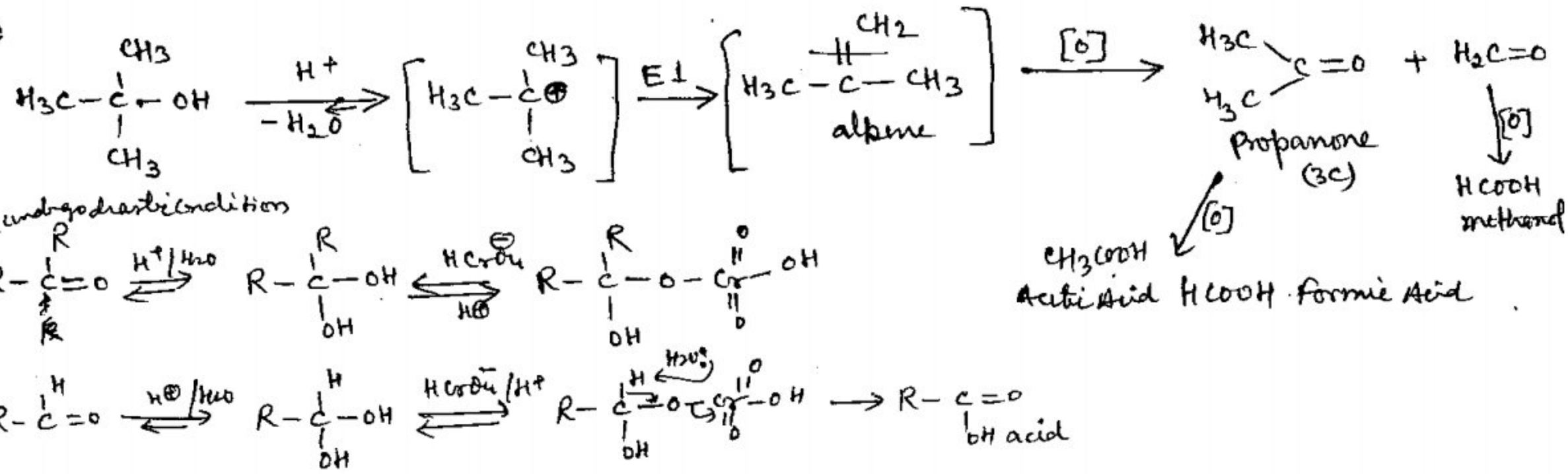
⇒ The molecular formula, determined by the usual methods, is $C_{10}H_{18}O$.

⇒ It has only one double bond because only one mole of bromine and hydrogen are adsorbed during bromination and hydrogenation for each α-terpineol.

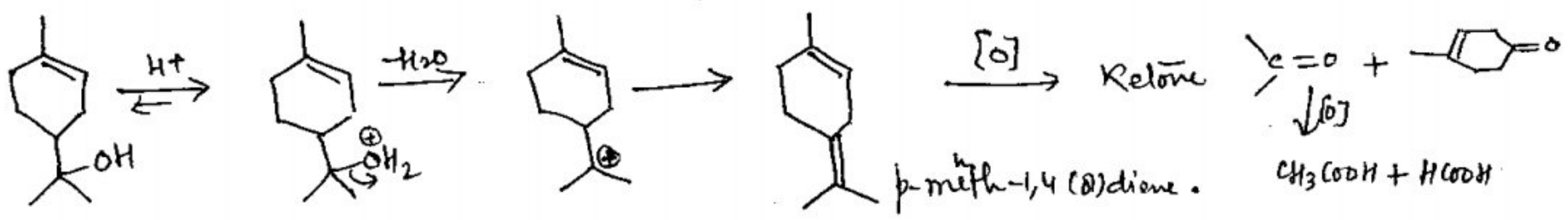
$$C_{10}H_{20}O \xleftarrow{H_2(Pt)} C_{10}H_{18}O \xrightarrow{Br_2} C_{10}H_{18}Br_2O$$

Dihydroterpineol ← α-Terpineol → dibromo α-terpineol

⇒ The Nature of oxygen: was found as a tertiary alcoholic group because it does not give aldehyde or ketone on mild oxidation. Because if primary alcoholic group, then, on oxidation it gives aldehydes with the same no. of carbon which on further oxidation will give a carboxylic acid with the same no. of carbon, but it is not actually found with α-Terpineol. If secondary it would give a ketone with the same no of carbon atom as a original alcohol. But it is also not true with the α-Terpineol. Thus, when α-Terpineol was oxidised under acidic condition (drastic) formation of alkene will take place with same no. of carbon ~~which~~ The alkene will go further oxidation and produces a ketone and other derivatives with a lesser no. of carbon atom than parent alcohol.



Mechanism of oxidation on t-OH



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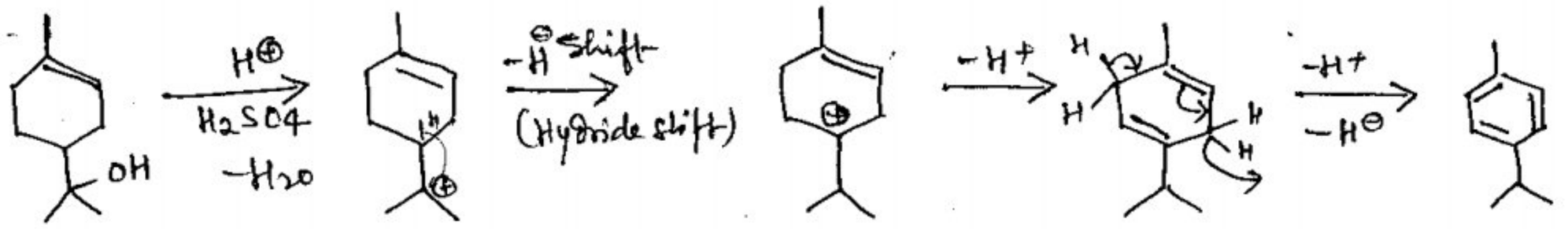
⇒ If it is fully saturated hydrocarbon ~~then it follows~~ which corresponds to the $C_{10}H_{20}$, which corresponds to monocyclic monoterpene alcohol ($C_nH_{2n}O$)

⇒ When treated with concentrated sulfuric acid, α-terpineol gives some p-cymene which indicates that it belongs to p-menthane group.



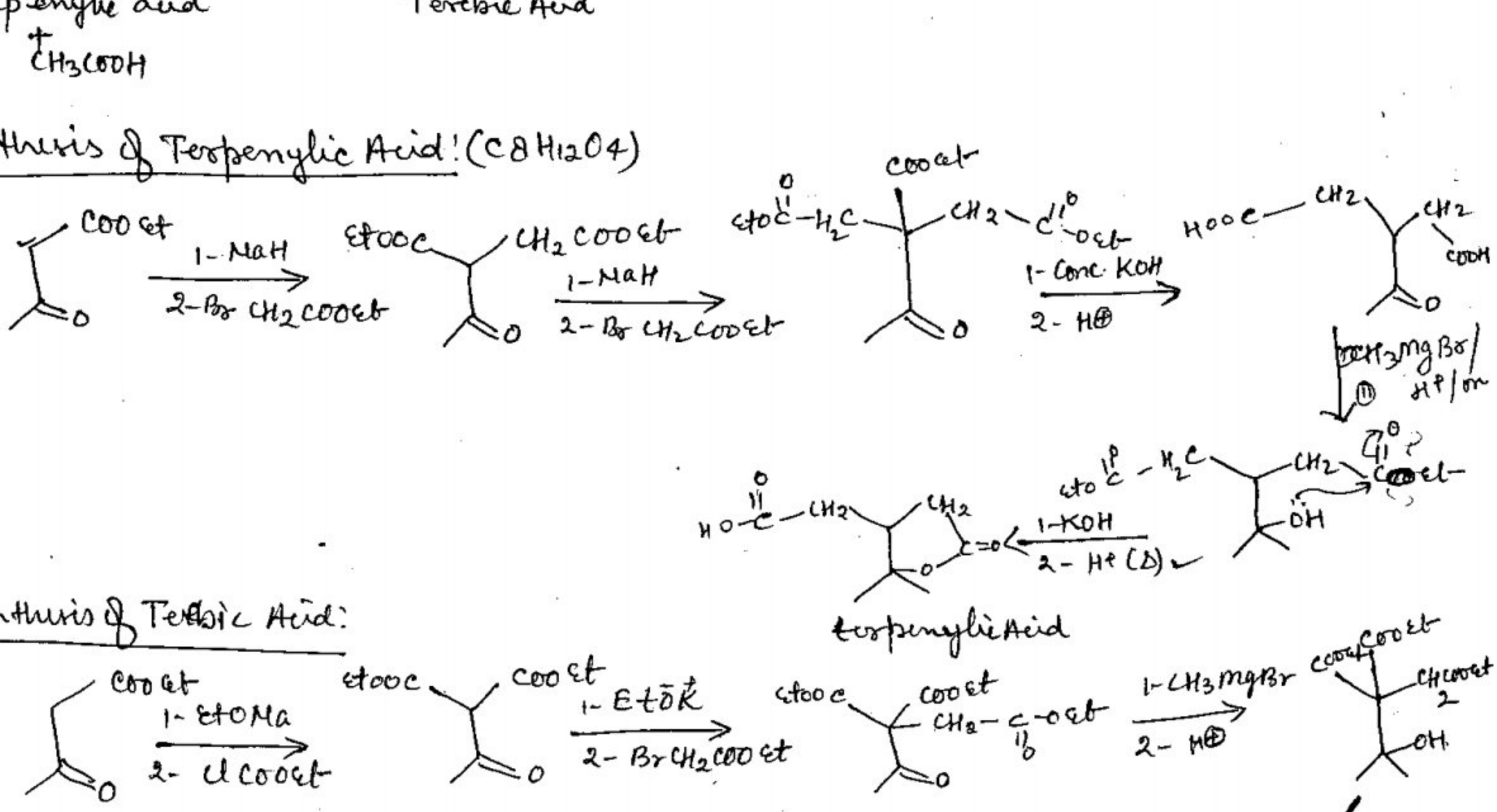
⇒ Thus we can say that α-Terpineol is probably p-menthane with one double bond and a tertiary alcoholic group.

The following sequence of oxidation experiments proves the structure of α-Terpineol.

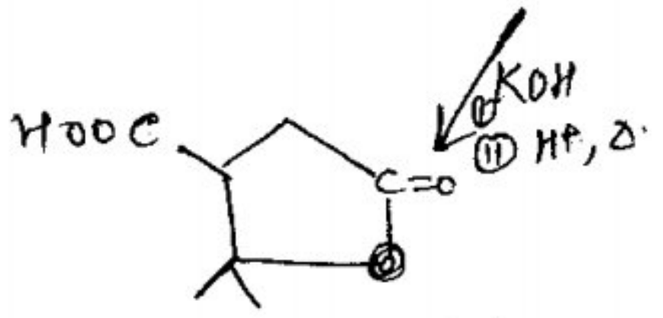
$C_{10}H_{18}O$ (α-Terpineol) $\xrightarrow[KMnO_4]{1\%\ \text{alkaline}}$ $C_{10}H_{20}O_3$ (A trihydric alcohol) $\xrightarrow{CrO_3}$ $[C_{10}H_{18}O_4]$ (A Ketohydroxy acid) $\xrightarrow{-H_2O}$ $C_{10}H_{16}O_3$ (Keto lactone) $\xrightarrow[KMnO_4]{\text{alkaline, warm}}$

$C_8H_{12}O_4$ (Terpenylic acid + CH_3COOH) $\xrightarrow[\Delta]{KMnO_4}$ $C_7H_{10}O_4$ (Terebic Acid)

Synthesis of Terpenylic Acid: ($C_8H_{12}O_4$)



Synthesis of Terbic Acid:



DBE Rule: (A) ① $DBE = x + 1 - \frac{y}{2}$ for C_xH_y $\quad C_6H_6 = 6+1-\frac{6}{2} = 4$ $\quad SO_3 = 1, 0$

② divalent atom, then (S, O, etc) ignore it, $C_3H_8O_2 = 3+1-\frac{8}{2} = \underline{0}$

③ If halogens are there, then $C_xH_yH_z = x+1-\frac{y+z}{2}$, like $C_{10}H_7Br$,

$10+1-\frac{7+1}{2} = 11-4 = 7$

④ trivalent atom like N, P, then it must be subtracted.

$x+1-\frac{y-z}{2}$, $C_{12}H_{12}N_2 = 12+1-\frac{12-2}{2} = 13-5 = \underline{8}$

No. of N atom present odd, molecular weight always will odd.

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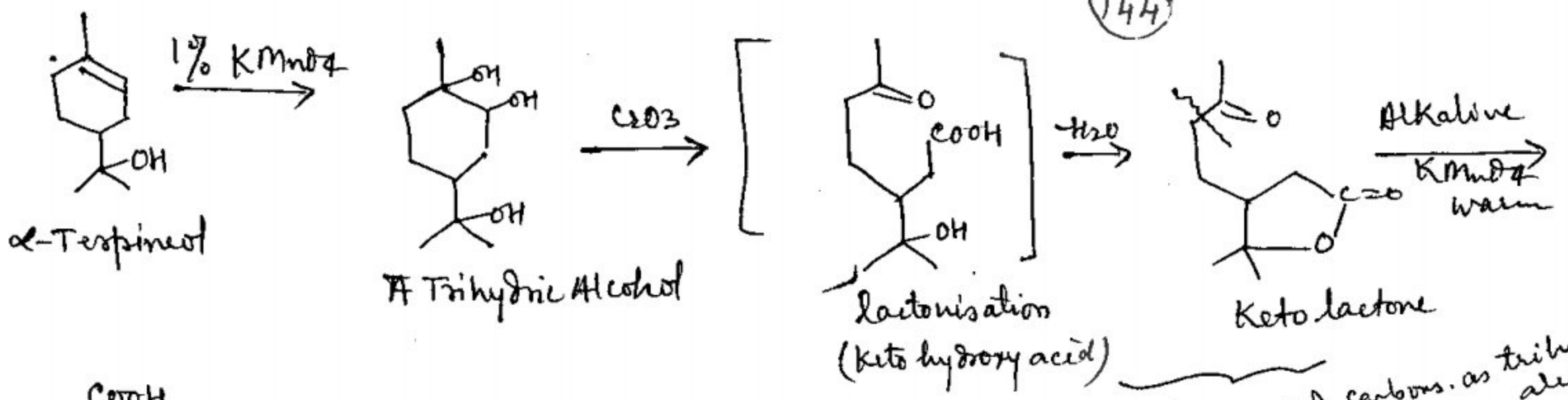
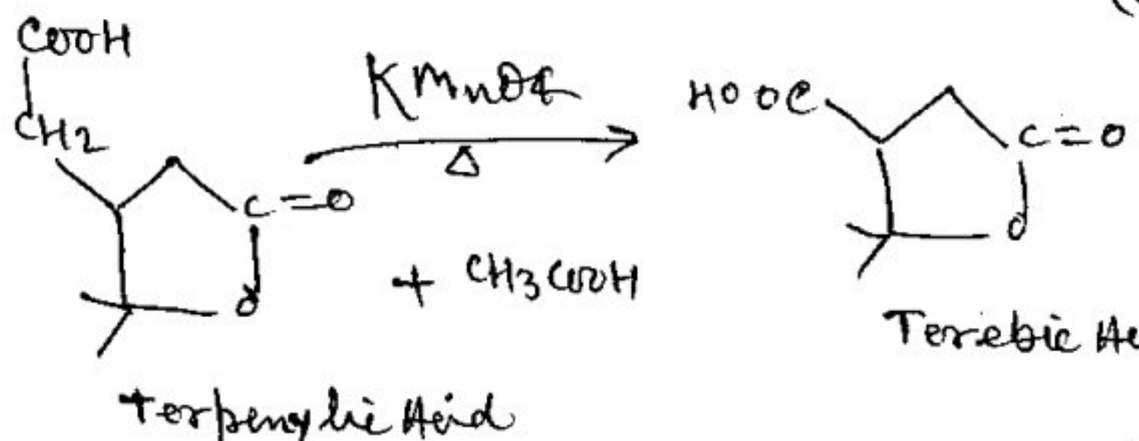
Thus all the transformation can be explained on the basis of following structure of α-Terpineol.

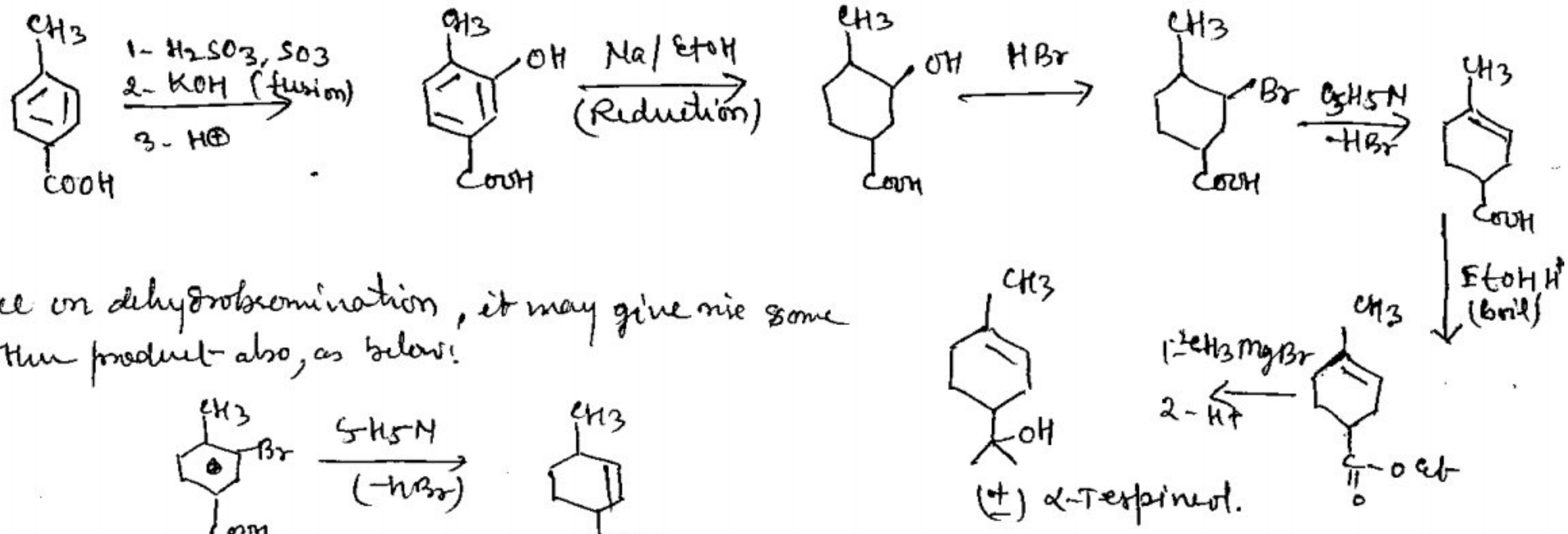




A Trihydroxy alcohol is a product of hydroxylation of the double bond giving three hydroxyl groups including the original one. This on further oxidation with CrO_3 gives a lactone of monocarboxylic acid and since it is readily formed from keto hydroxy acid, it is most probably a γ-lactone. Since keto hydroxy acid and keto lactone have the same no. of carbon atoms as trihydric alcohol have. Thus fissioned double bond must belong to the ring. The formation of acetic acid on oxidation of keto lactone with warm alkaline $KMnO_4$ indicates that the keto lactone is a methyl ketone and terpenylic acid is the lactone of monohydroxy dicarboxylic acid. Further, oxidation of terpenylic acid gives its lower homologue terebic acid which is also a lactone of monohydroxy dicarboxylic acid.

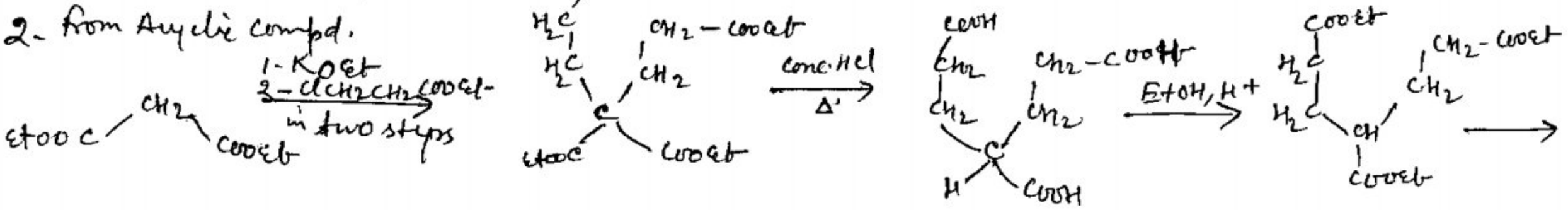
⇒ Synthesis of α-Terpineol will prove its structure:

1:



Since on dehydrobromination, it may give rise some another product also, as below:

2- From Acyclic compd.



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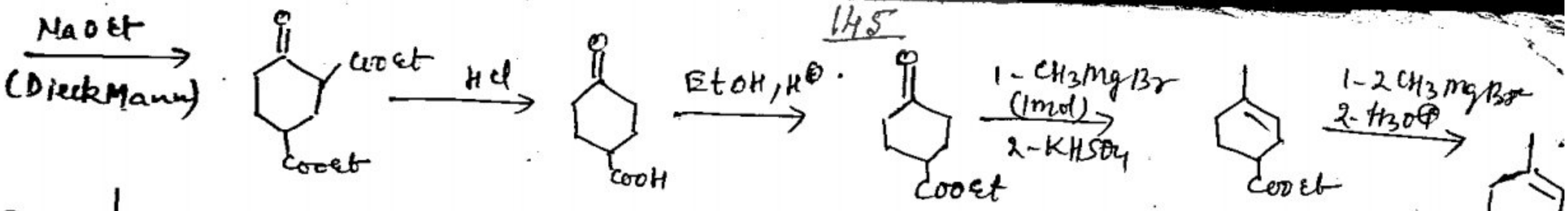

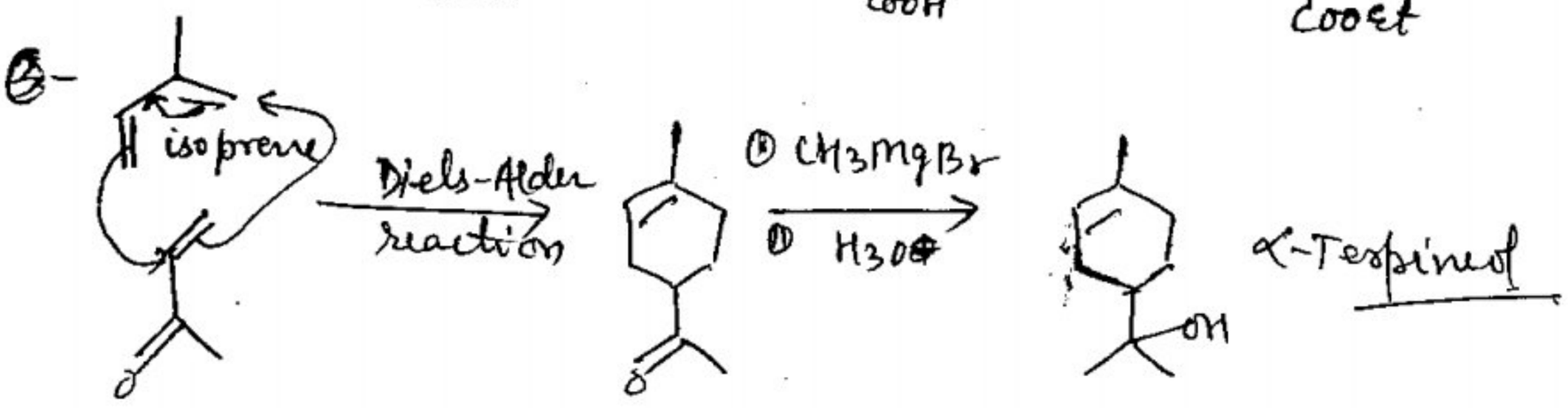

Methyl vinyl Ketone

In this method also a ~~another~~ possibility of formation of another product.