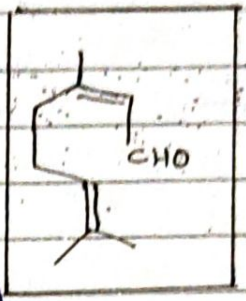
Date

Expt. No. **Terpenoids.** Page No. 7

Citral :-



- It is acyclic monoterpenoids
- It is optically inactive
- It is occured in lemon grass oil (essential oil) by 60-80%.
- It is pale yellow liquid having strong lemon like smell
- B.P - 228°C
- λmax - 238 nm

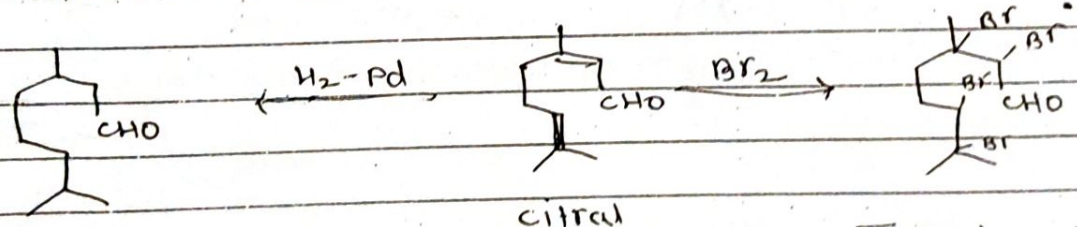
Gr. M.F. $C_{10}H_{22}$ indicate [Gattner] acyclic comp.

Constitution :-

- M.F :- $C_{10}H_{16}O$

1) Presence of two double bonds :-

As citral adds two molecules of hydrogen and Bromine. This shows that citral contains ~~two~~ two double bonds.



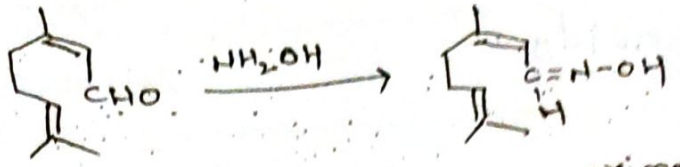
Tetrahydro citral — citral — Tetrabromide citral

2) Presence of an aldehyde group :-

with hydroxylamine citral forms oxime. indicates that presence of oxo group

Tollens reagent

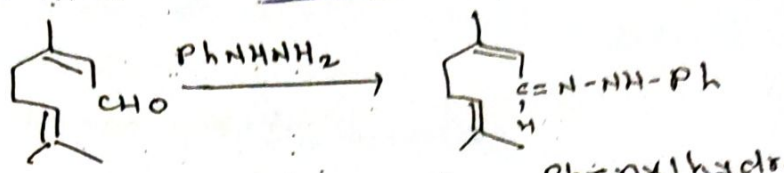
Teacher's Signature :



citral

oxime derivative.

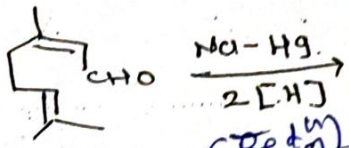
~~With Ph~~ with Phenylhydrazine, it form phenyl hydrazone indicates that the presence of oxo group



citral

Phenylhydrazone derivative

citral on Redn with sodium amalgam yields geraniol indicates that presence of an aldehyde group.

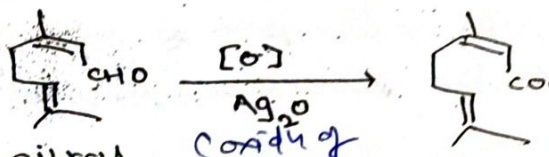


citral

(Reduction of C=O gr.)

geraniol

citral oxidised with Ag_2O gives acid which is same no. of carbon atoms indicates that presence of oxo gro



citral

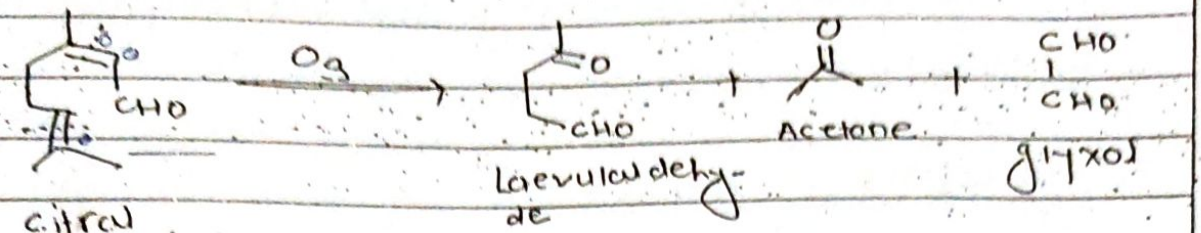
(oxidn of carbonyl gr.)

geranic acid.

citral reduce fehling soln also conforms that presence of oxo group.

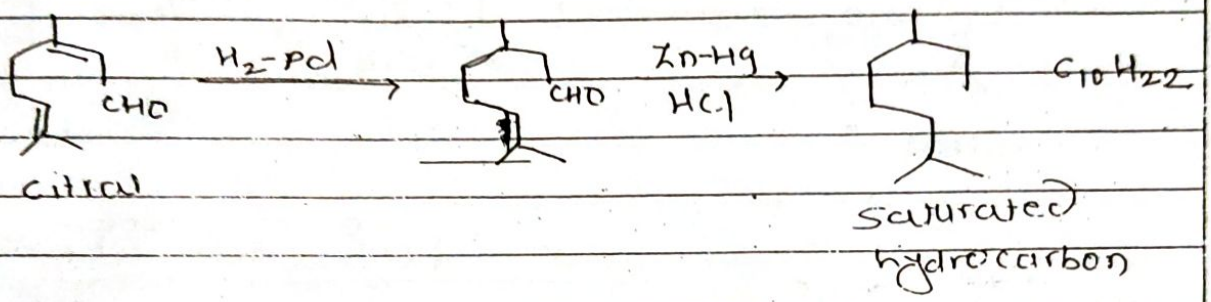
3) Citral as an acyclic compound :-

citral on ozonolysis yields acetone, glyxal and loevwoldehyde indicates that the presence of acyclic compound due to loss of carbon atom



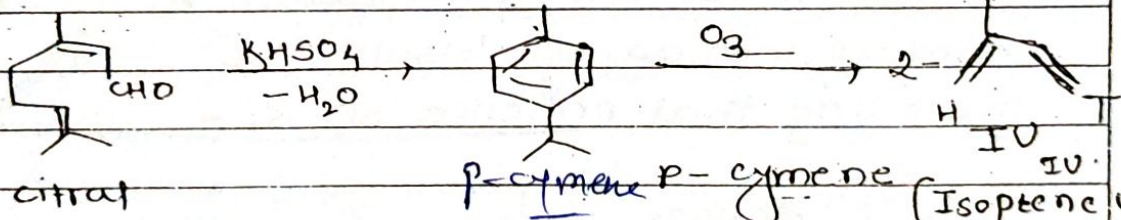
citral forms saturated hydrocarbon having M.F $C_{10}H_{22}$ which corresponds to the general formula C_nH_{2n+2} for acyclic compound.

Thus citral must be acyclic compound.

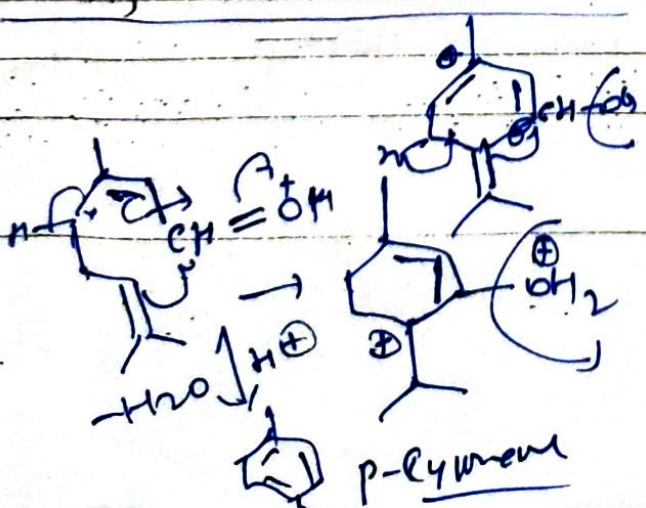


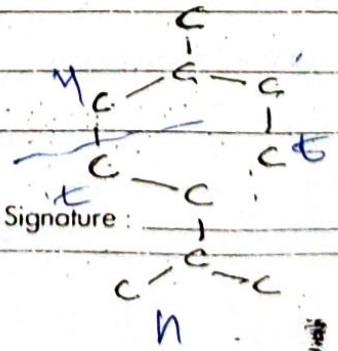
c) <u>C-skeleton of citral</u> :-

when citral is heated with pot. hydrogen sulphate it cyclise to form p-cymene.



formation of p-cymene it is then ozonolysis gives two IU. which are joined to head to Tail arrangment Indicates that <u>the presence of C-skeleton in citral.</u>



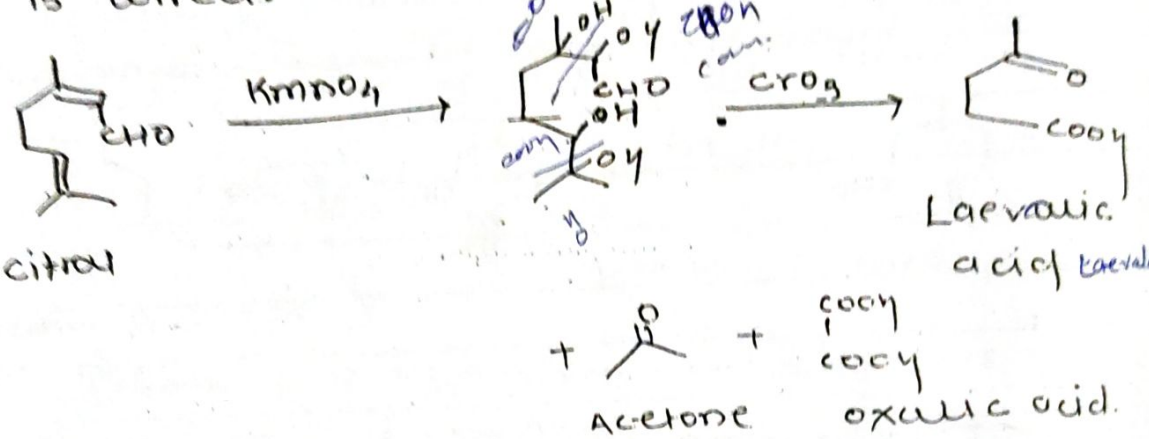


Teacher's Signature :

The formation of p-cymene also reveals that the relative position of methyl and isopropyl groups in citral.

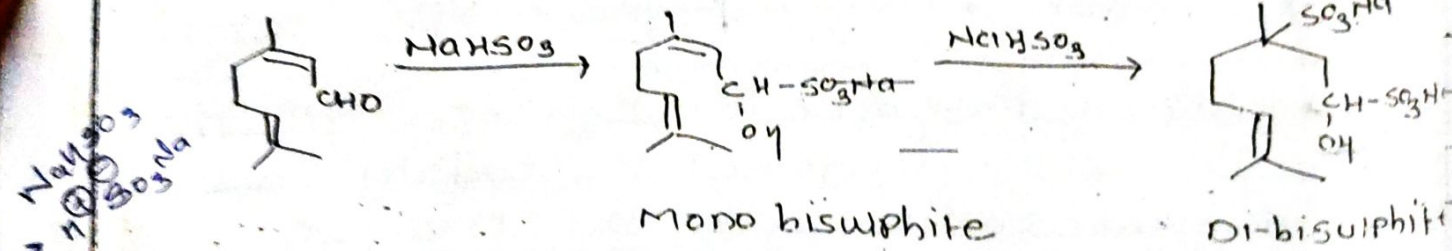
5) Structure of citral :-

citral on oxidation with $KMnO_4$ followed by CrO_3 yields oxalic acid, Acetone, laevulic acid. This indicates that the Analysis of structure of citral is correct.



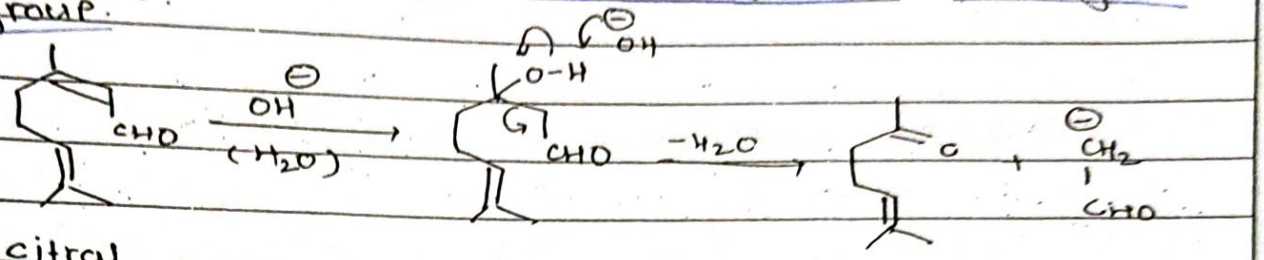
6) Confirmation of citral structure :-

citral on treatment with sodium bisulphate gives mono as well as di-bisulphite. addn product. indicating that presence of α, β- unsaturated aldehyde



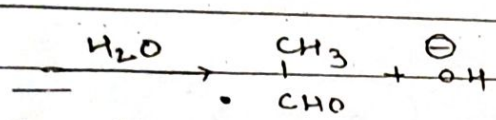
Also UV-spectra α, β- unsaturated group λ_{max} 323

Citral on boiling with aqueous NaOH yield 6-methyl hept-5-en-2-one and acetaldehyde. This reaction indicates that the presence of α,β-unsaturated aldehydic group.

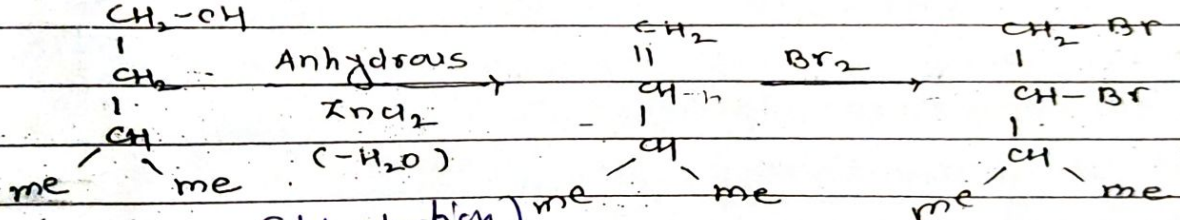


citral

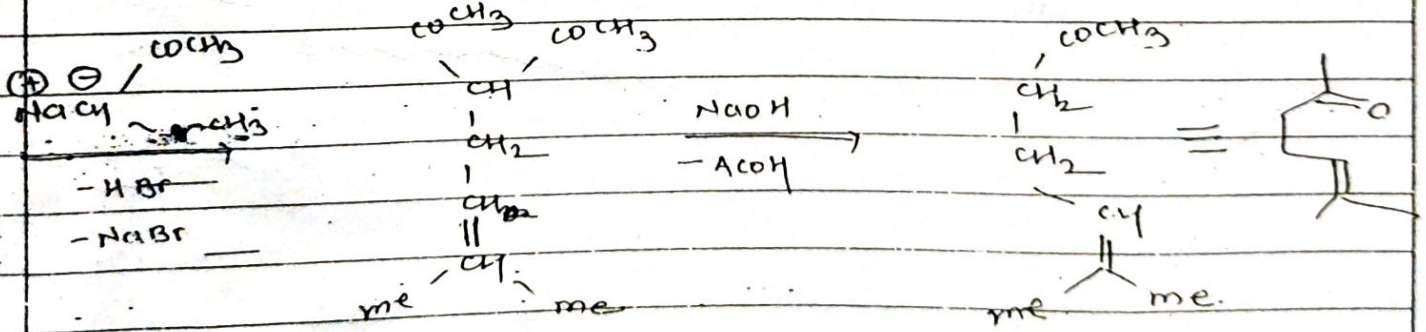
6-methyl hept-5-en-2-one.



Synthesis of methyl heptenone :-



3-methyl 1-butanol



methyl heptenone.

Teacher's Signature :

$BrCH_2COOEt + Zn \xrightarrow{Et_2O} BrZn[CH_2-\overset{\ominus}{C}-OEt \leftrightarrow CH_2=\overset{\ominus}{C}-OEt]$

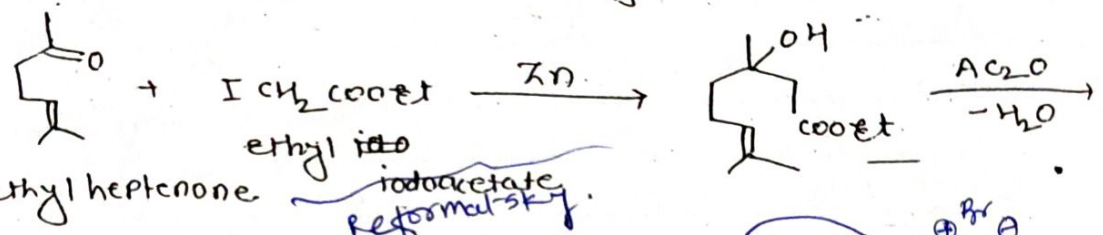
$\equiv BrZn\overset{\oplus}{C}H_2COOEt$

The structure of citral also confirmed by the synthesis of methyl heptenone.

When 3-methyl-1-butanol which is dehydrated follow by the addition of bromine to yield the product that on further condensation with sodium salt of acetyl acetone followed by hydrolysis yield methyl ~~heptan~~ heptenone.

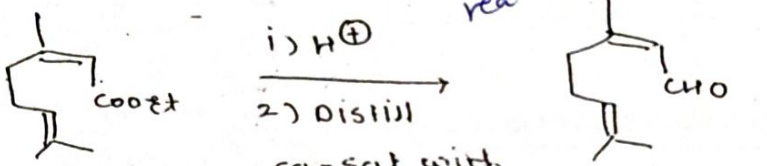
Synthesis :-

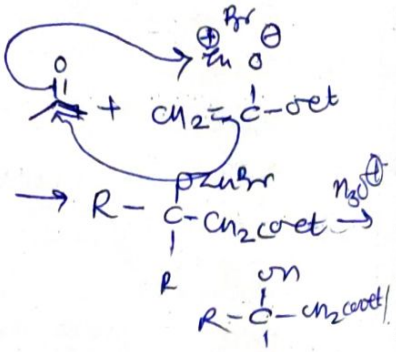
1) Barbier-Bouveault-Tiemann's synthesis :-



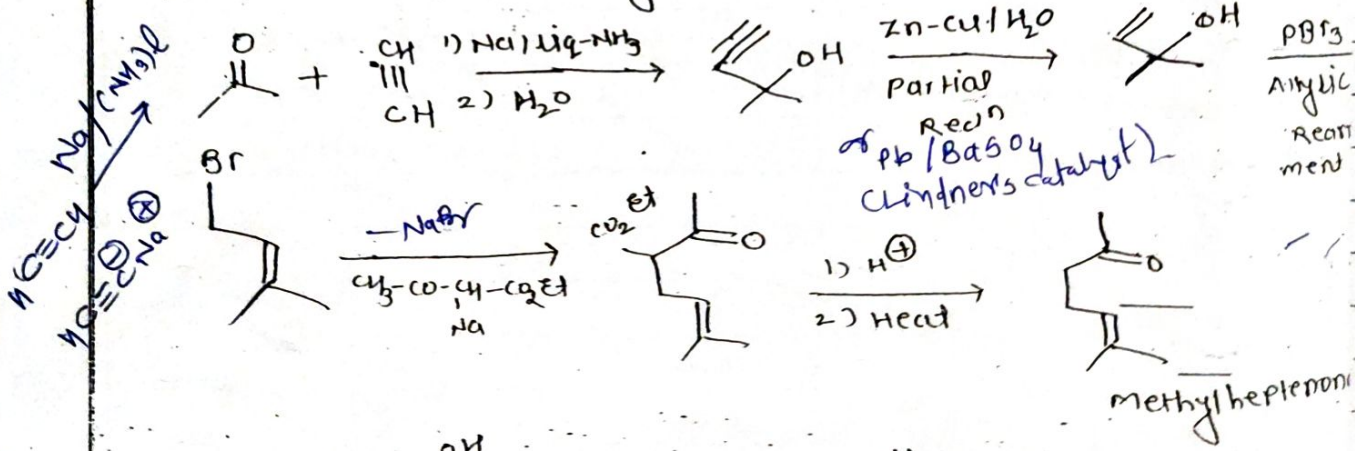
Methyl heptenone

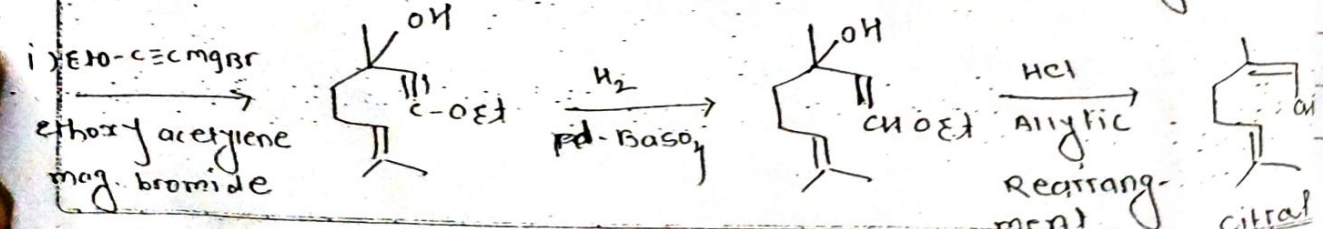
Reformatsky reaction.



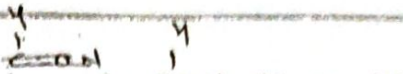


2) Arens-van Dorp's synthesis :-



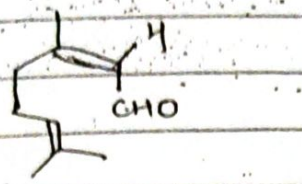


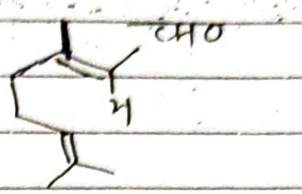
Date

Expt. No.  Page No. 13

semicarbazone

* Stereochemistry of citral :-





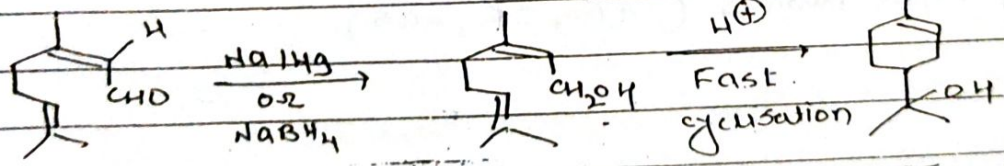
cis-(or Z) citral; citral-b
Neral
B.P - 117-118°C.

Trans-(or E) citral, citral a
Geranial
B.P - 118-119°C

The existance of the two isomeric citrals in natural citral has been confirmed by chemically due to the formation of two different semicarbazones ($H_2N-NH-CO-NH_2$) and trans-citral on reduce gives geraniol and cis-citral on reduce gives Nerol.

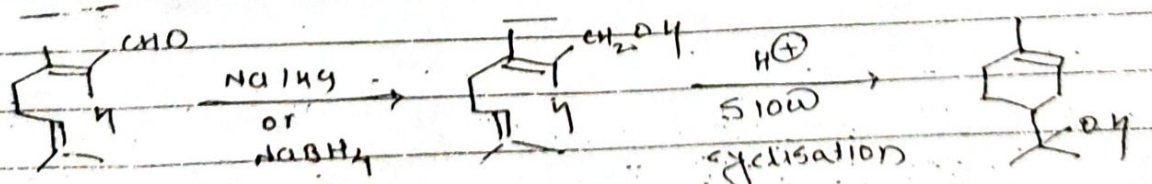
cyclisation :-

The rate of cyclisation of Neral is nine times greater than the geranial due to $\overset{|}{C}=O$ group is nearer to the $-\overset{|}{C}H$ group in citral



Neral

α-Terpineol



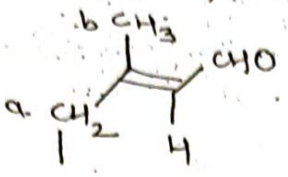
Geranial

α-Terpineol.

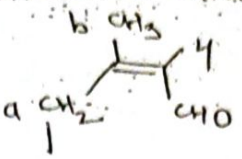
Teacher's Signature :

~~Spectroscopic~~ spectra:-

The configuration, have been confirmed by the NMR spectra of citral-a and citral-b in $CDCl_3$



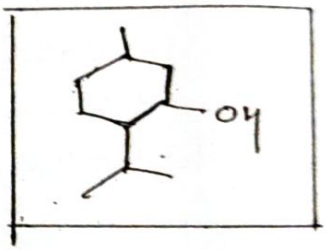
citral-a



citral-b

Isomer of citral	CH_2 (a)	CH_3 (b)
1) citral-a	τ - 7.76	τ - 7.84
2) citral-b	τ - 7.42	τ - 8.02

* Menthol :-



- It is optically active
- It is naturally occurring in levo(-) rotatory in peppermint oil. (पुदीना)
- It is monocyclic mono terpenoids.
- M.P - 43°C.
- It is used in antiseptic and anaesthetics, sedative.
- 4 pairs of enantiomers
- 8 optically active isomers (+R, 3R, -4S).

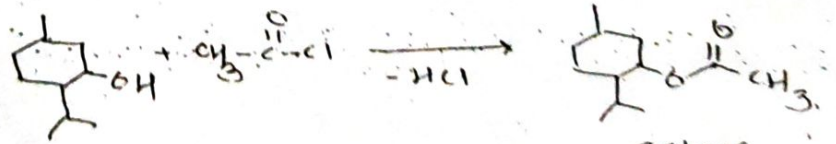
Constitution:-

- M.F - $C_{10}H_{20}O$

1) Presence of hydroxyl group:-

- menthol forms esters readily with Acid chloride

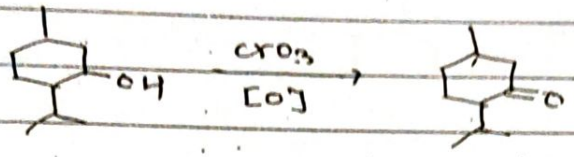
• indicates that the presence of hydroxyl group



menthol

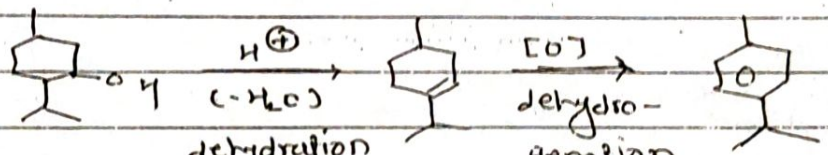
esters.

- The oxidation of menthol gives ketone, menthone. indicates that the hydroxyl group in menthol 2° in nature.



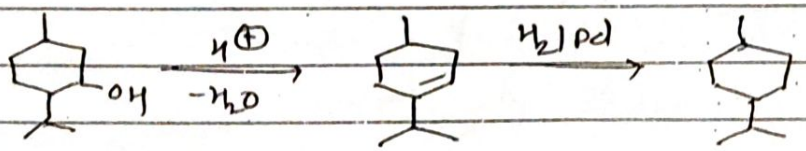
② Presence of C-skeleton :-

On dehydration followed by dehydrogenation menthol gives p-cymene indicates that presence of p-cymene skeleton



p-cymene.

Also menthol contain p-menthane skeleton suchas,



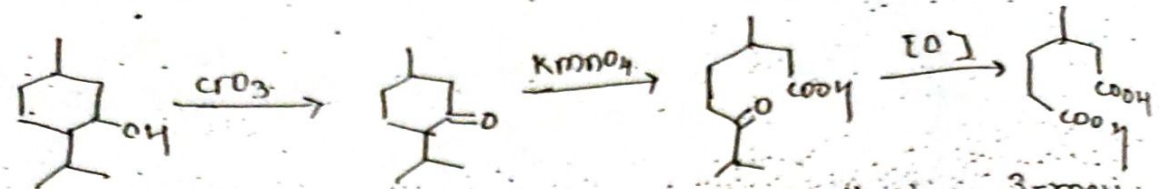
p-menthane

③ Oxidation product of menthol :-

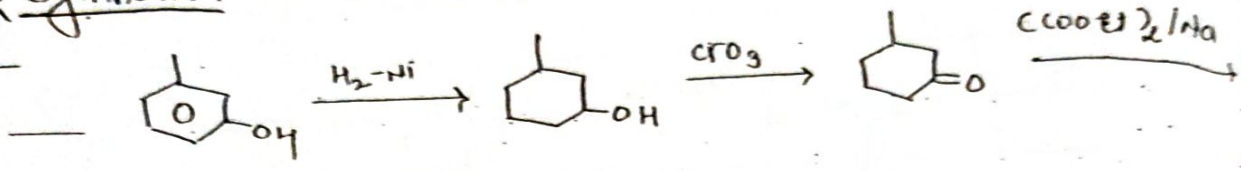
When menthol is oxidised to give menthone then is oxidised with KMnO4 gives ketomenthylic acid and this also compound oxidised to give 3-methyl adipic acid.

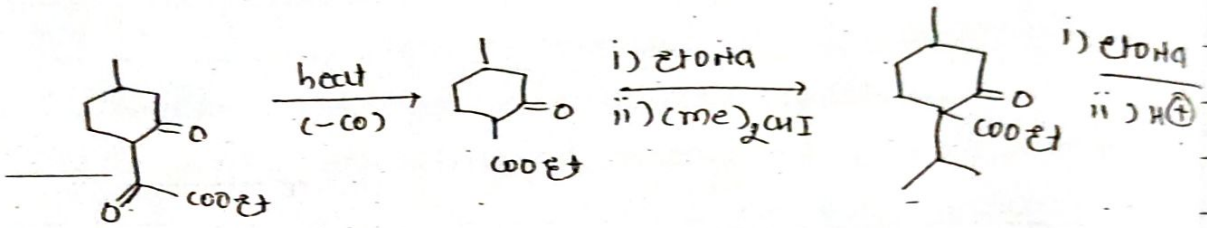
This indicates that the structure of menthone which is oxidation product of menthol.

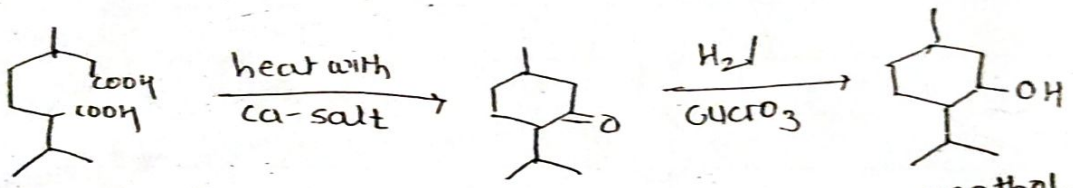
Teacher's Signature :



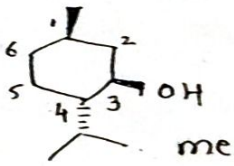
* **Synthesis:-**







* **Stereochemistry:-**



menthol.

menthol contains 3- dissimilar chiral centers 1, 3 & 4

∴ No. of optical isomers - $2^n = 2^3 = 8$

Eight optically active forms are possible theoretically. The configurations are known such as

* Horizontal line represents cyclohexane ring.

Expt. No. _____ Date _____

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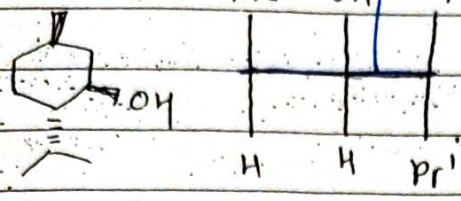
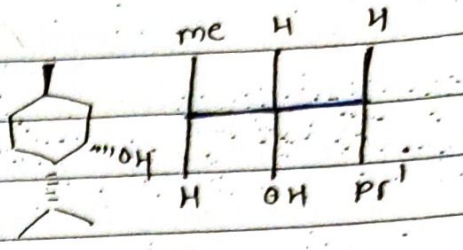
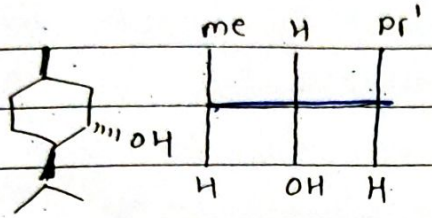
line shows Cyclohexane Ring

i) 

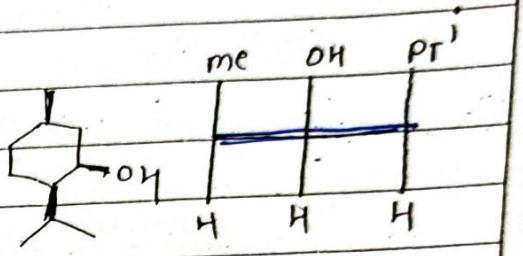
menthol

ii) 

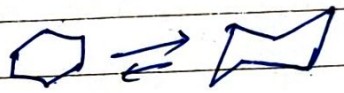
neomenthol

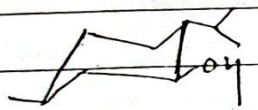
iii) 

isomenthol

iv) 

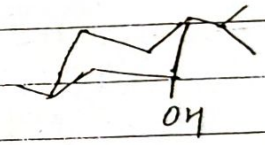
Neoisomenthol

Conformation studies :- 

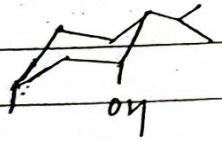


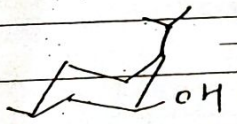
menthol

isomenthol



neomenthol



or 

neoisomenthol.

By the above structures the rate of esterification of equatorial hydroxyl group is faster than the axial hydroxyl group. Thus rate order

menthol > isomenthol > neoisomenthol > neomenthol.

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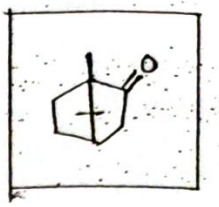
* Camphor :-



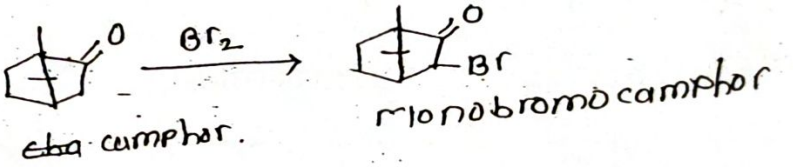
1) It is optically active
2) It is occures in camphora; cinnamonum.
3) It is highly proportion present in trunck
4) monocyclic monoterpenoids.
5) It is solid having m.p - 180°c.

Constitution :-

- M.F :- $C_{10}H_{16}O$

1) Saturated system :-

Camphor reacts with Bromine, Nitrosyl chloride gives monobromocaphor, monochlorochamphor but it is does not gives dibromo or any addition product This indicates that the presence of camphor is saturated

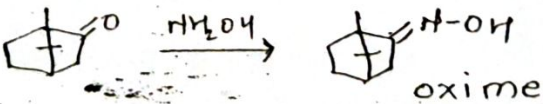


ebba camphor. monobromocamphor

2) presence of Keto group :-

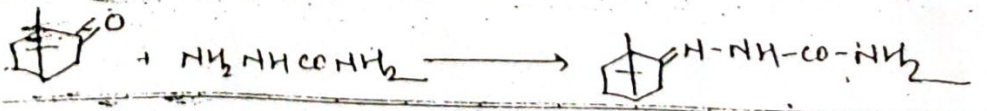
presence of cyclic Ketone indicates that following facts.

1) It forms oxime with hydroxylamine



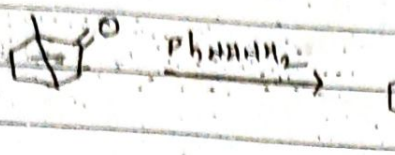
oxime

2) It forms semicarbazone with semicarbazide



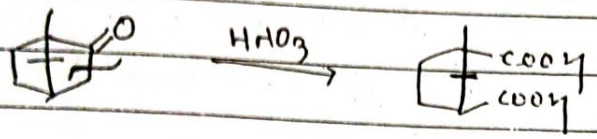
semicarbazone.

3) It forms phenylhydrazone with phenylhydrazine.

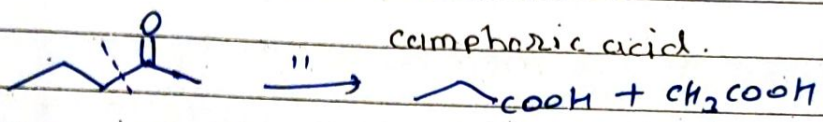


phenylhydrazone.

4) When camphor is oxidised with nitric acid gives camphoric acid without loss of any carbon atom indicates that presence of cyclic Ketone.

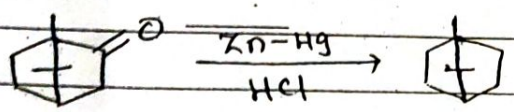


camphoric acid.



5) <u>presence of Bicyclic system :-</u>

when camphor reduced with Zn-Hg/HCl gives saturated hydrocarbon of camphor is camphane.



$DB.E = C+1-\left(\frac{H+X-N}{2}\right)$

$C_{10}H_{16}O$ camphane $C_{10}H_{18}$

$DBE = 2$

Thus above saturated hydrocarbon of camphor has DBE = 2 indicates that camphor is Bicyclic system.

6) <u>presence of $-CH_2-CO-$ group :-</u>

when bengaldehyde reacts with camper inpresence of base having active methylene group to give

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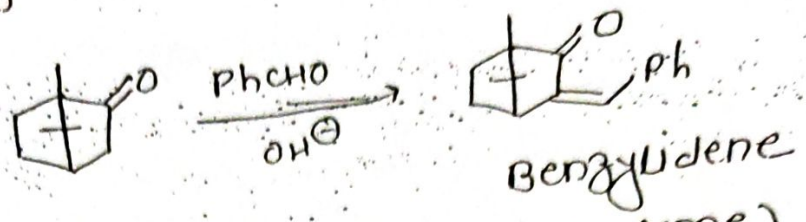
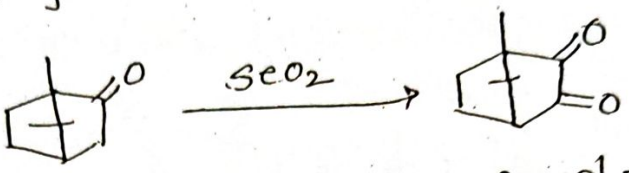
benzylidene. indicates that presence of $-CH_2CO$ group Ex



Benzylidene (chalcone).

Also indicates that presence of $-CH_2CO$ group by following reaⁿ



Camphor quinone.

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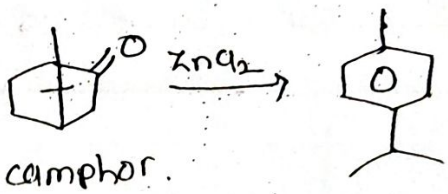
5) <u>presence of six membered ring :-</u>

When camphor is heated with $ZnCl_2$ to p-cymene This indicates that presence of six-membered ring in camphor.

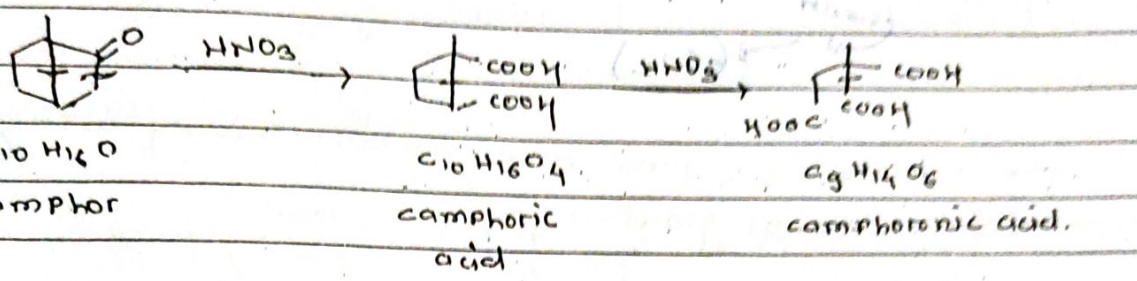


camphor. p-cymene.

- <u>Nature of carbon skeleton in camphor :-</u>

When camphor is oxidised with nitric acid it crystaline dibasic acid camphoric acid $C_{10}H_{16}O_4$ As camph acid possess same no. of carbon atoms as camphor. it means that keto group must be present in one of rings of camphor. Thus camphor is saturated bicyc system then one of ring is breakdown and another is as it is. It means that camphoric acid is mon compound

When camphoric acid is further oxidised with Nitric acid gives camphoronic acid.

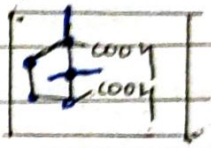


$C_{10}H_{16}O$ — camphor

$C_{10}H_{16}O_4$ — camphoric acid (I)

$C_9H_{14}O_6$ — camphoronic acid. (II)

* Structure of camphoric acid :-



- M.F :- $C_{10}H_{16}O_4$
- It is saturated dicarboxylic acid
- Presence of cyclic system :- ← DBE = 1

camphoronic acid (II) possess three methyl groups Thus camphoric acid also possess three methyl groups Then M.F can be written as,

$(CH_3)_3 C_5H_5(COOH)_2$ C_5H_{10}

$3 + 5 + 2 = 10$

The parent hydrocarbon of camphoric acid is C_5H_{10} by using general formula C_nH_{2n}

DBE = 1

on the basis of DBE = 1 camphoric acid is monocyclic compound.

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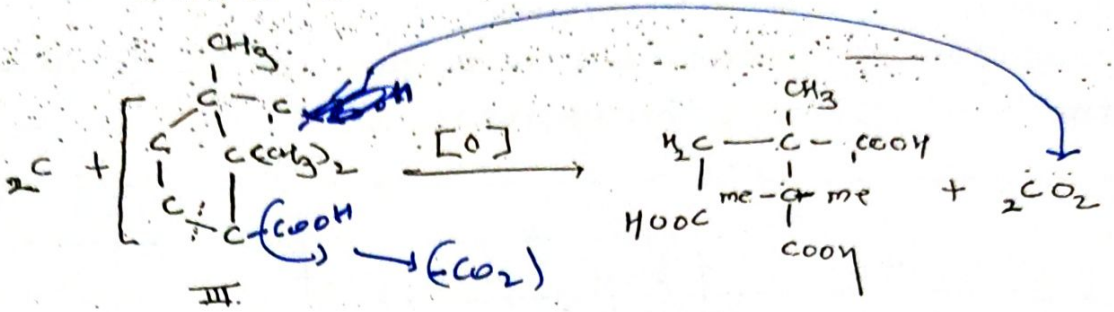
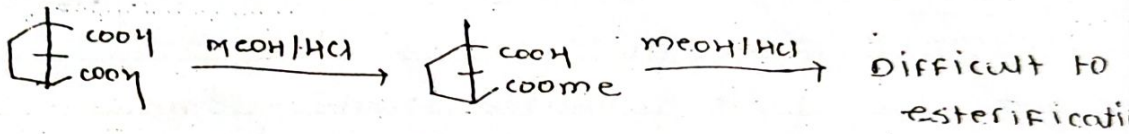
oxidation of camphoric acid to camphoronic acid may be written as



III.

The skeleton (III) plus one carbon having arrangement with two carboxyl group

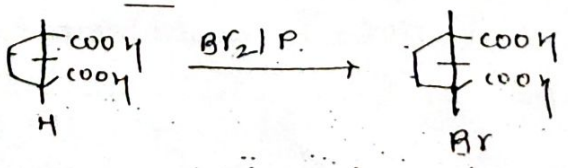
— Nature of carboxyl groups in camphoric acid :-



Monoester derivative.

As camphoric acid able to form monoester readily but it forms diester with difficulty, this indicates that two carboxyl groups are not similar. i,e one of the primary or secondary and another is tertiary

But camphoric acid forms monobromo derivative is only possible when one of the carboxyl groups is secondary



monobromo derivative

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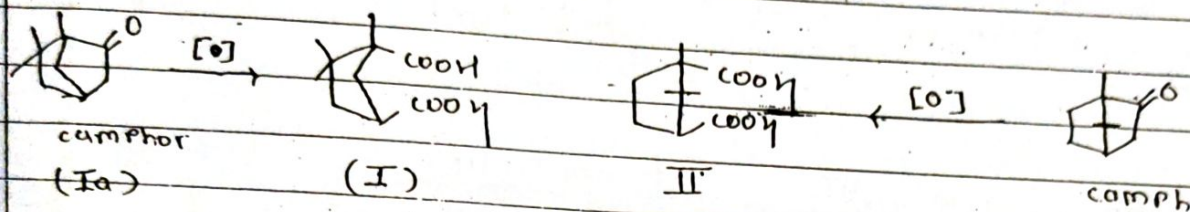
- Position of carboxyl groups :-

The cyclopentane ring of camphoric acid is opened to give camphoronic acid, one carbon atom is readily lost. Thus camphoric acid has two types of structure can drawn

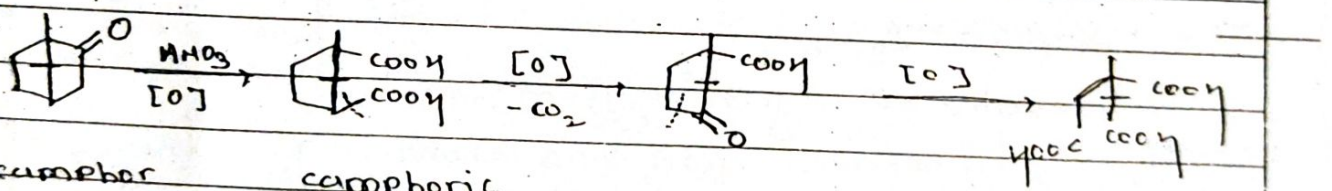


camphor (Ia) (I) II camphor (IIa)

since the two carboxyl groups are produced from the $-CH_2CO-$ group in camphor

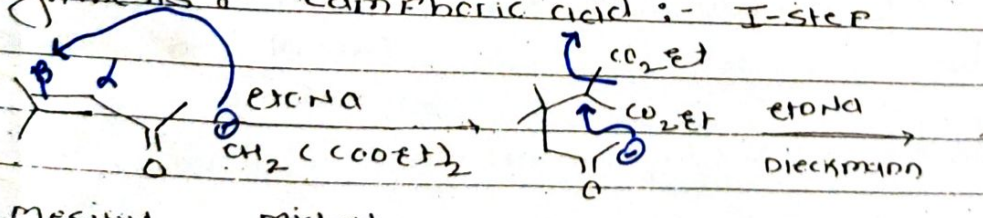
Thus starting compound of (I) is contain six-membered ring and geminal dimethyl group. But structure (Ia) can not form p-cymene skeleton.

Thus the structure of (II) are obey's all facts. so structure II and IIa are correct.



camphor camphoric acid. camphoronic acid

Synthesis :- camphoric acid :- I-step



Mesityl oxide Michal addn etona Dieckmann

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