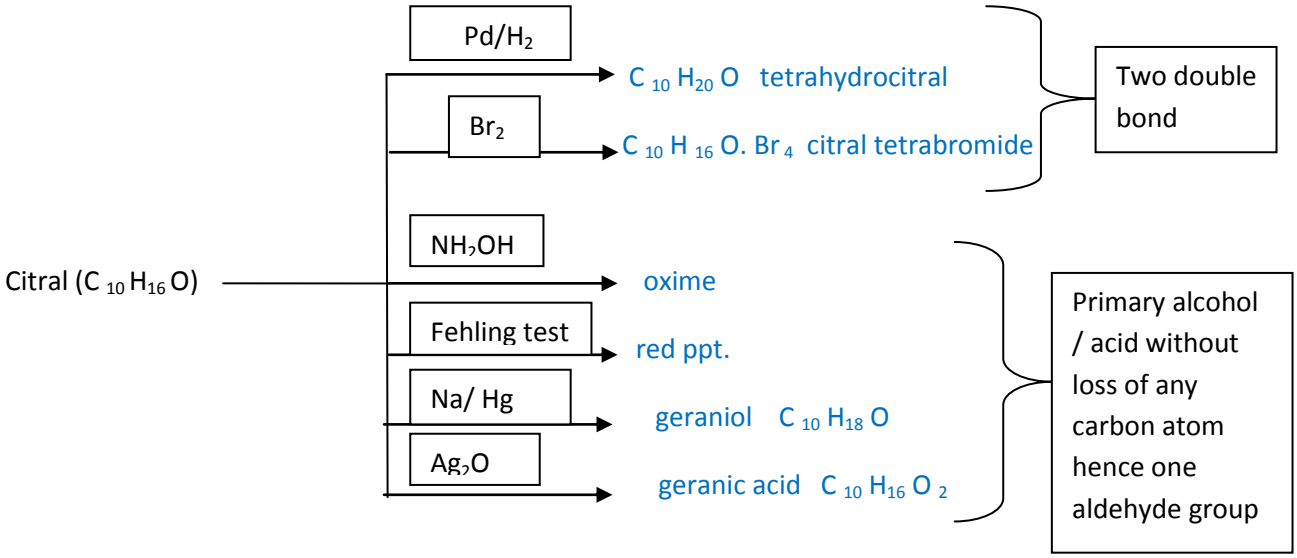
Citral

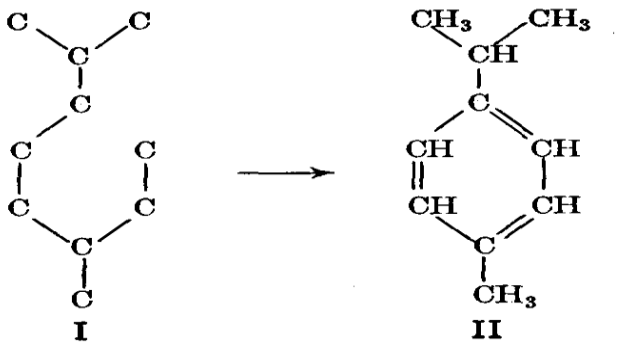
- Acylic monoterpenoid
- Used for the synthsisis of β-ionone which is frequently used in perfumery
- Optically inactive oil with lemon like smell
- Principle source is lemon grass oil which has 60-80% of citral
- Isolated as its crystalline bisulphate product which on hydrolysis gives citral back.

Constitution/ structural elucidation

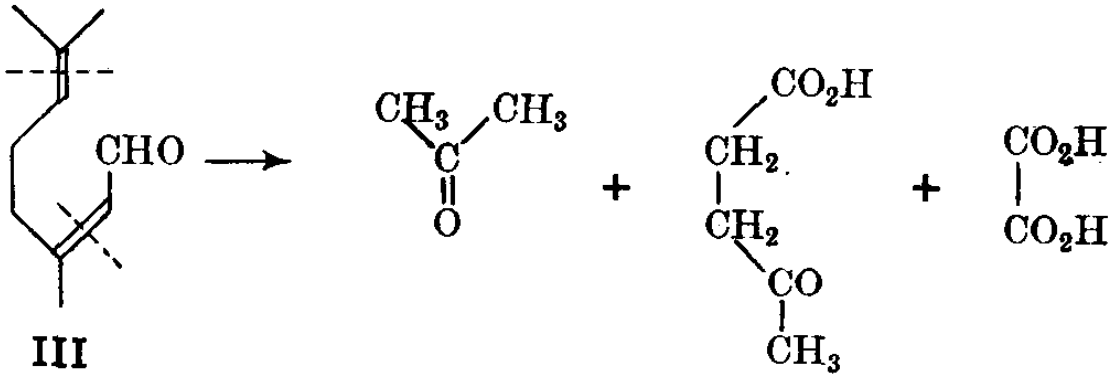
- Molecular formula $C_{10}H_{16}O$



- Presence of two double bond and an aldehydic group led to $C_{10}H_{22}$ corresponding to the general formula for acyclic compound (C_nH_{2n+2}). So, citral must be acyclic compound.
- Citral on heating with potassium hydrogen sulphate gives a well known aromatic compound p-cymene and thus, C – skeleton and hence the relative positions of the alkyl groups viz. methyl and isopropyl

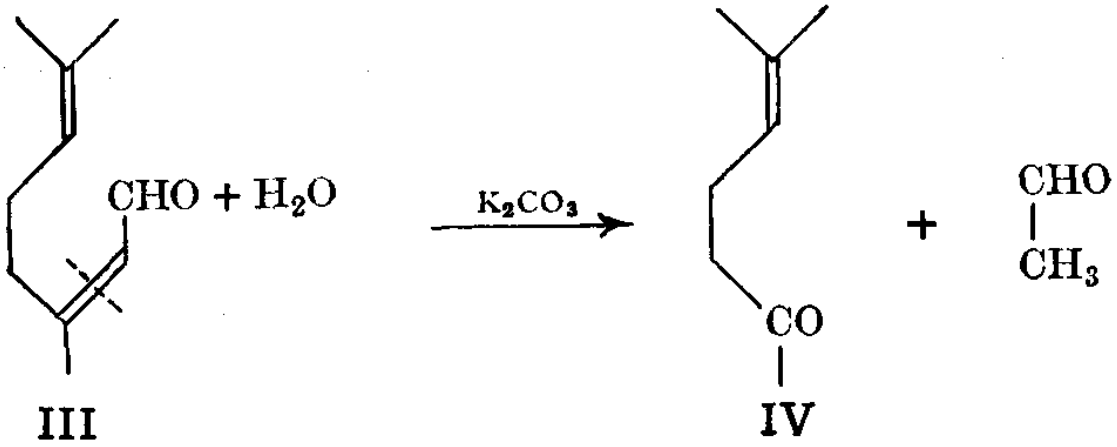


- I indicate skeleton of citral and II indicate cymene.
- On heating with sodium bisulphate citral forms mono as well as di- bisulphate addition products which indicates that one of the double bond is conjugated with >C=O group
- Oxidation with alkaline Potassium permanganate followed with chromic acid forms acetone, oxalic acid and laevulic acid



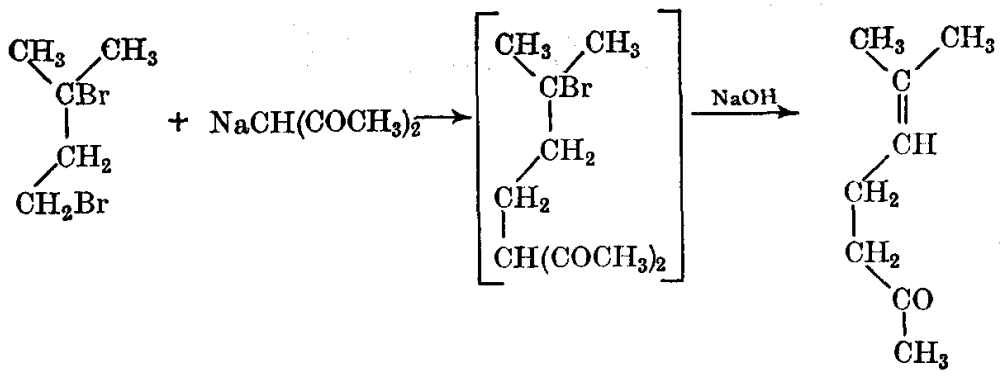
III

- With potassium carbonate it forms 6-methyl hept-5-en-2one and acetaldehyde which indicate α,β-unsaturated oxo compound.

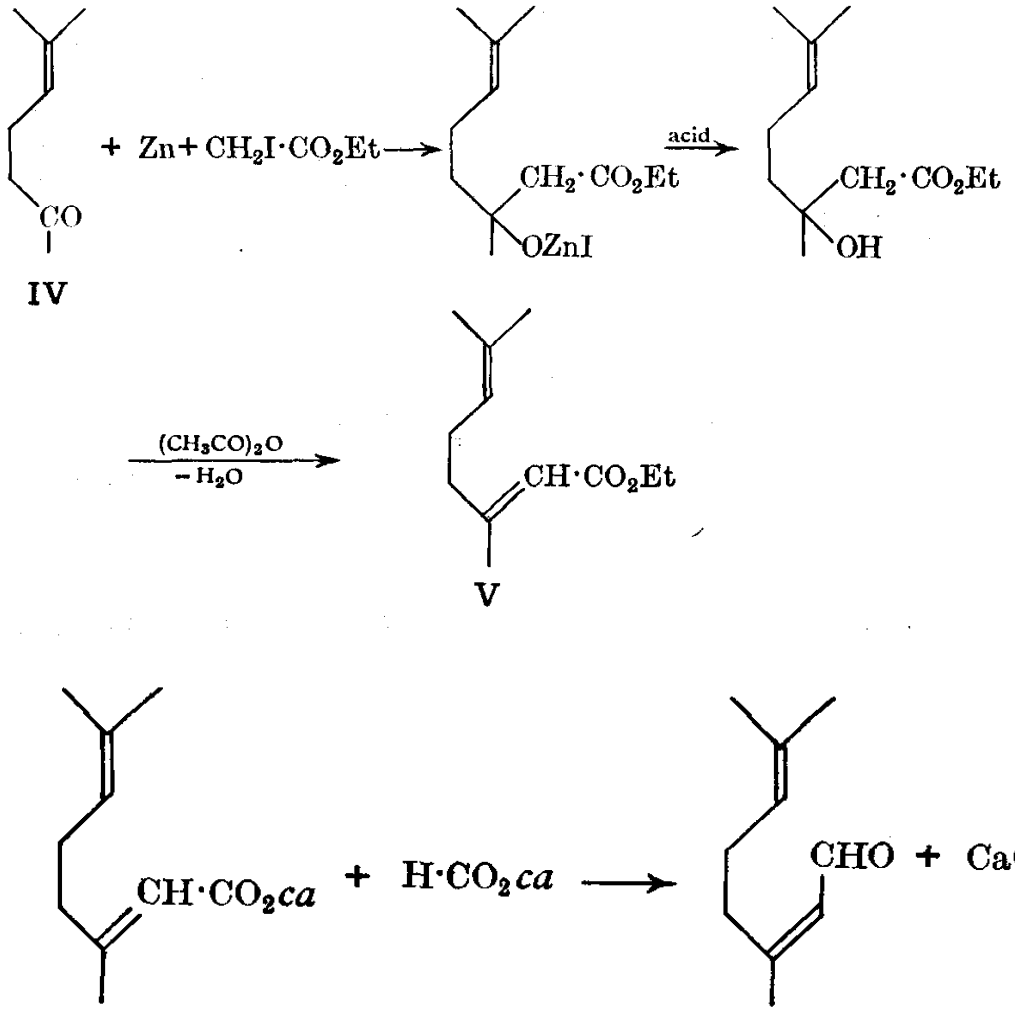


III IV

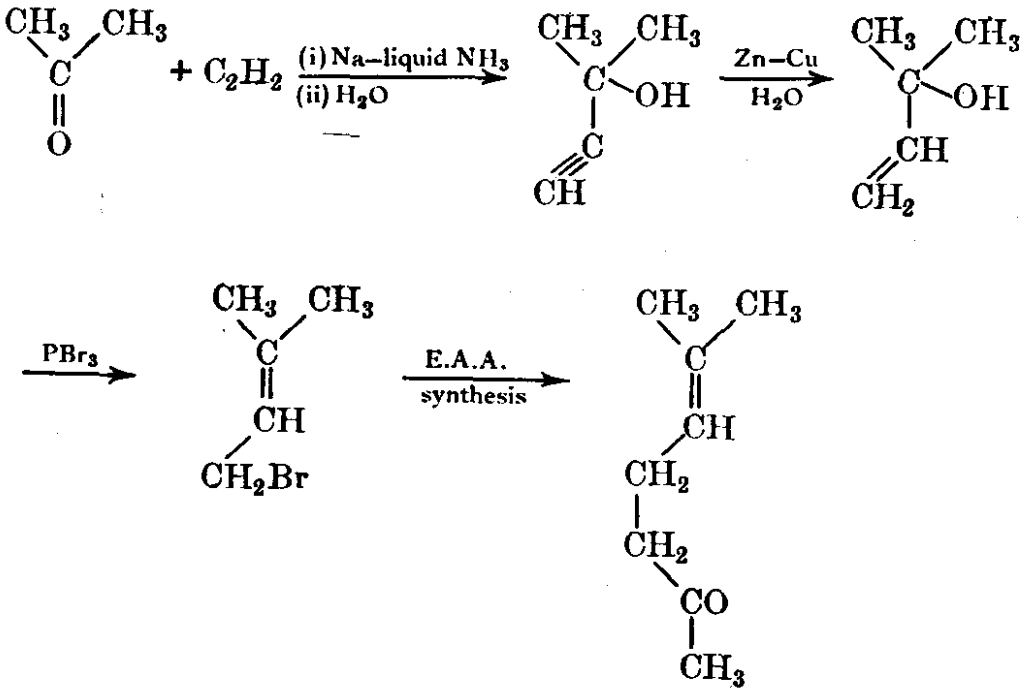
- IV gives acetone and laevulic acid on ozonolysis
- Further the structure was confirmed by its synthesis (Barbier and Bouveault) (1896)

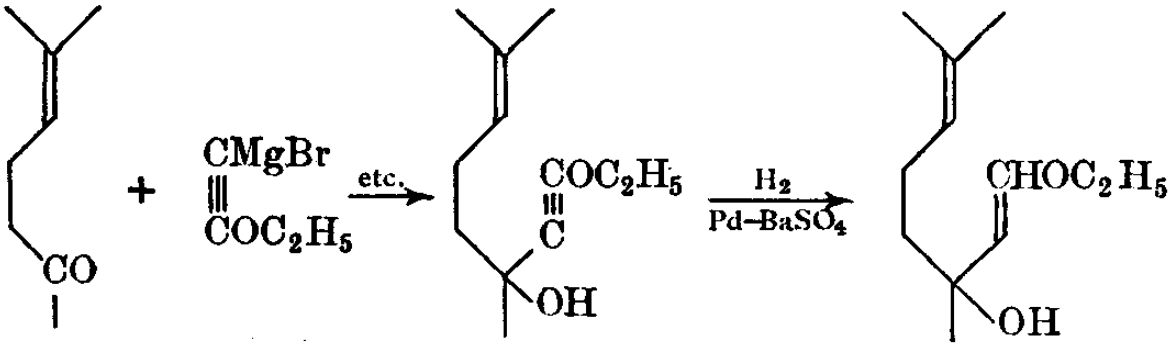


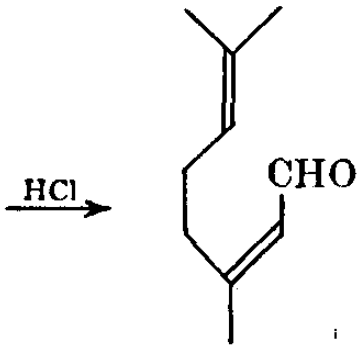
- Synthesis:
  (i) Barbier and Bouveault (1896) converted methylheptenone IV into geranic ester V (reformatsky reaction) & Tiemann (1898) geranic ester to citral (distilling mixture of geranic acid and formic acid)



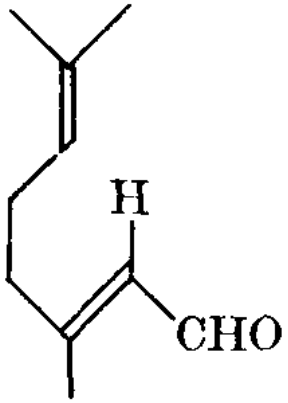
(ii) Arens and Van Drop (1948)



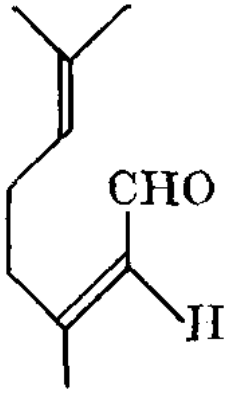




- Citral shows two types of geometrical isomerism-cis and trans

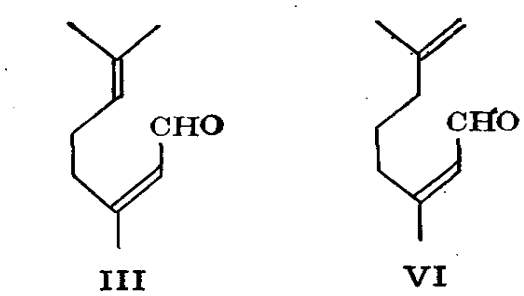


trans-form;
citral-*a*;
geranial



cis-form;
citral-*b*;
neral

- Grignard etal. on ozonolysis yields some amount of formaldehyde which shows double bond at the isopropenyl terminal. Thus two position for double bond at the mentioned terminal. (Shown below)



III VI

- So, one can say citral consists of 4 constituents 2 geraniols and 2 nerols.

Bibliography

- Chemistry of Organic Natural Products Vol. 1 O. P. Agarwal
- I.L. Finar, Organic Chemistry Vol. II

Questions :

1. Deduce the structure of citral by degradative method.
2. Deduce the structure of citral by synthesis method.
3. What will happen if citral undergoes:
   (a) ozonolysis
   (b) oxidation with alk. $KMnO_4$. Followed by chromic acid
   (c)reacts with potassium carbonate

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