

Presented by

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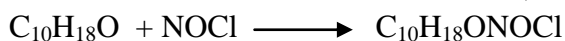
α -terpineol

1.1 Introduction

- Monocyclic monoterpenoid (because elucidation of its structure clarified and confirmed the structure of several other mono terpenoids)
- Optically active
- Crystalline solid
- Mp. 37-38⁰C
- B.pt. 220⁰C
- Found either free of or as its esters in various essential oils
- d-form found in oils of petitgrain and neroli, l- form in camphor oils and dl-forms in cajuput oil
- extensively used in preparation of lilac perfumes and lilac scented soaps

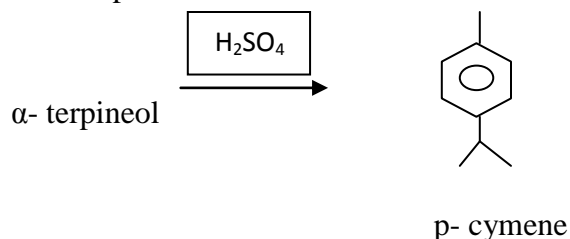
1.2 Constitution

- molecular formula C₁₀H₁₈O
- α -terpineol reacts with Bromine water and nitrosyl chloride to form dibromide and nitrosochloride respectively

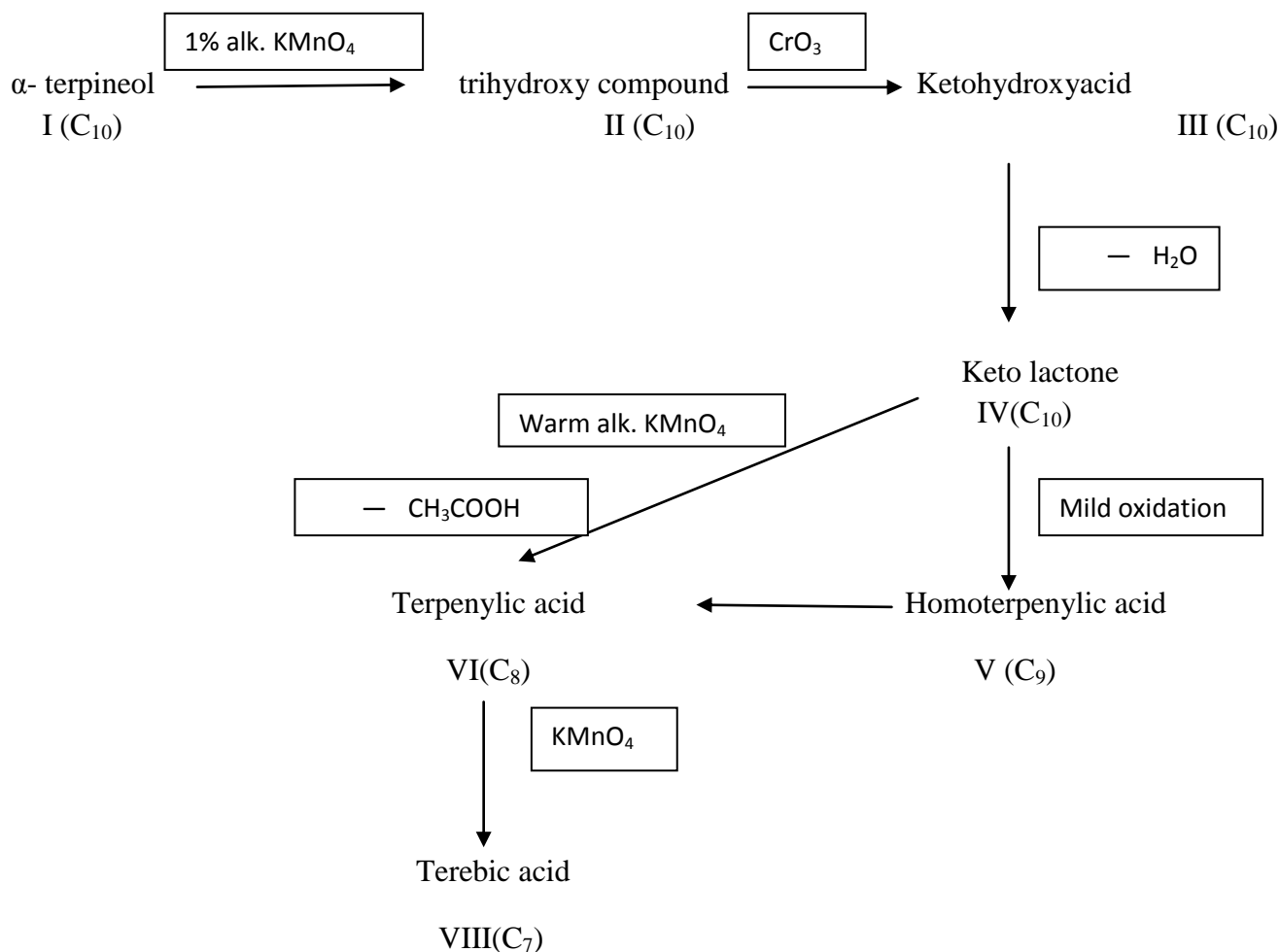


The above two reaction confirms one unsaturation means one C-C double bond

- the oxygen atom is found to be present as tertiary alcohol
- above three points suggest that the molecular formula is fully saturated hydrocarbon of α -terpineol to be C₁₀H₂₀ which corresponds to the molecular formula C_nH_{2n}, of a monocyclic compounds. Hence, α -terpineol must be monocyclic.
- On heating with sulphuric acid, α -terpineol gives p-cumene, indicates the p-cymene skeleton is present in α -terpineol.

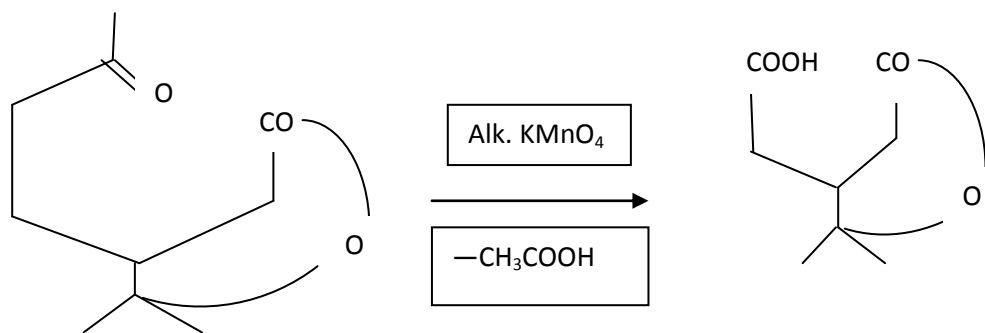


- From the above point, it is clear that α -terpineol is p-menthane (fully saturated p-cymene) with a double bond and a tertiary alcoholic group. The latter two functions may be established by Wallch work (1893, 1895). Wallach degraded α -terpineol having C₁₀ to a well known C₇ acid, the terebic acid
- The series of degradation of α -terpineol are as follows:



From the above set of oxidation degradation reactions following results were obtained:

- (i) The conversion of I to II by means of alk. KMnO₄ (Baeyer's reagent) indicates conversion of double bond to hydroxylated compounds. The oxidation from II to IV with same number of carbon atoms indicates double bond should be inside the ring because had it been present outside the ring the oxidation products i.e. III and IV would have lesser carbon atoms.
- (ii) Since compound III is found to possess a keto, a hydroxyl and a carboxylic acid group and it is not isolated it must be easily lactonisable hydroxyl acid. This means either a γ or δ -hydroxy acid. Now, as the synthetic γ -keto lactone is found to be identical with the compound IV the latter must be a γ -keto lactone. The nature of compound IV as a lactone is proved by its neutral nature which on alkaline hydrolysis gives keto-hydroxy acid III.
- (iii) The formation of acetic acid as by-product on oxidation of ketolactone IV to terpenylic acid VI indicates that the IV must contain a group of the type of -COCH₃ i.e. IV is a lactone with -COCH₃ group. IV compound was identified and further proved by its synthesis as homoterpenylmethyl ketone, so its oxidation to terpenylic and terebic acids may be represented below:

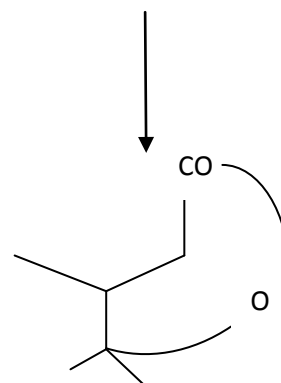


Terpenylic acid, VI

Homoterpenyl methyl ketone, IV

C₁₀

C₈

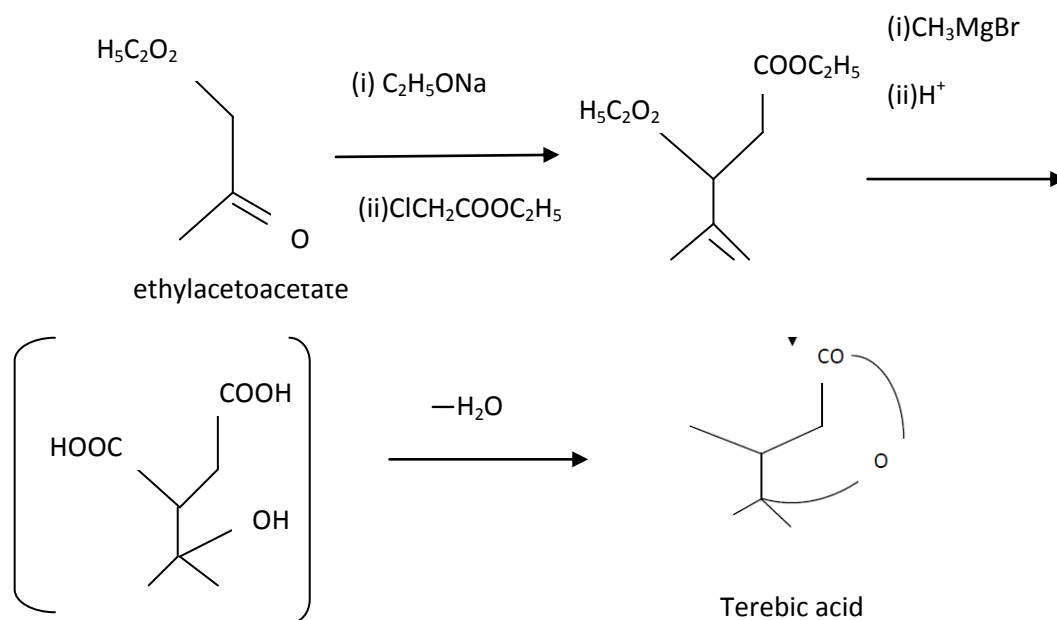


Terebic acid, VII

C₇

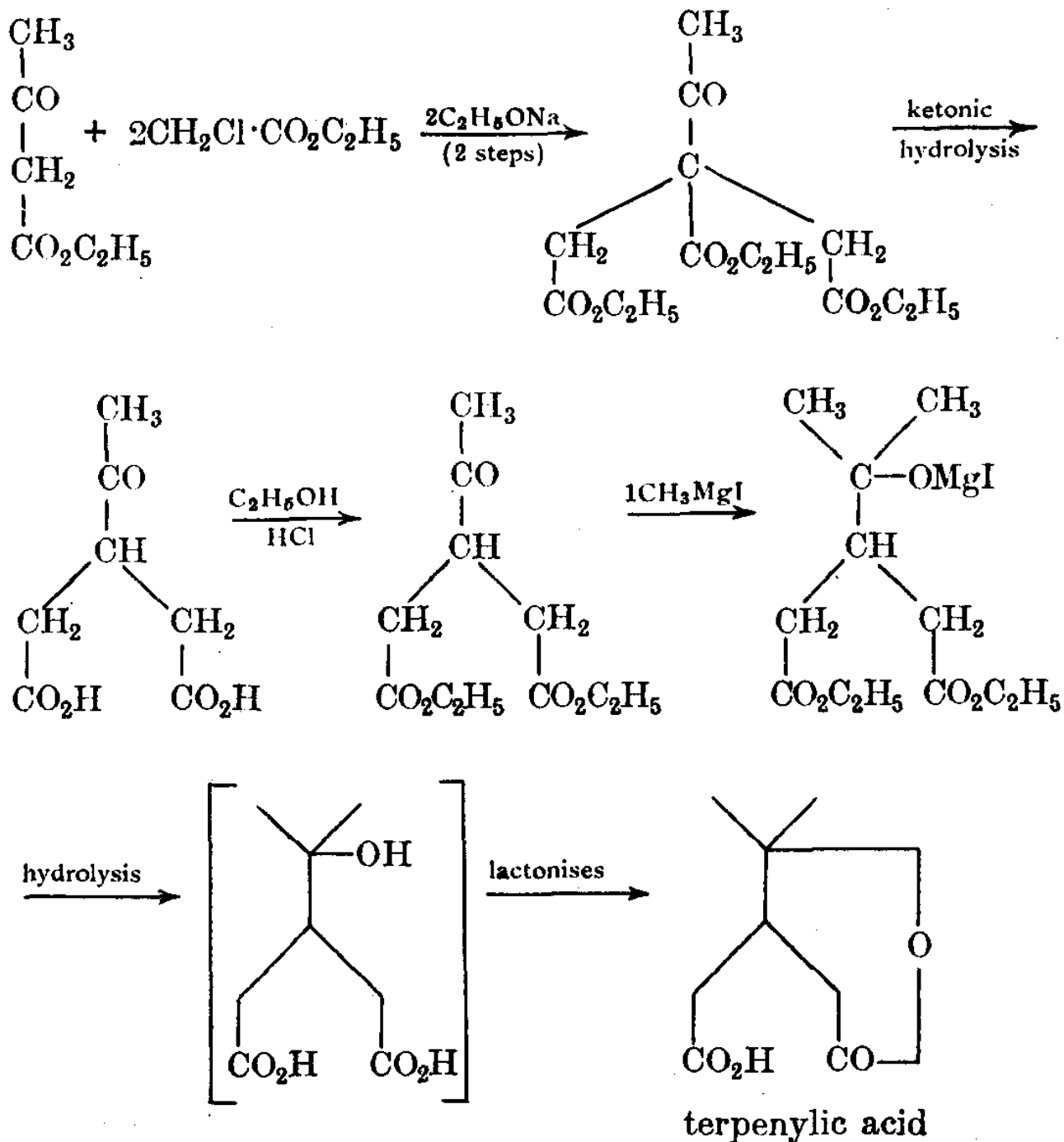
- The structure of terebic, terpenylic and homotrpenylic acids have been proved by their synthesis:

Synthesis of terebic acid:

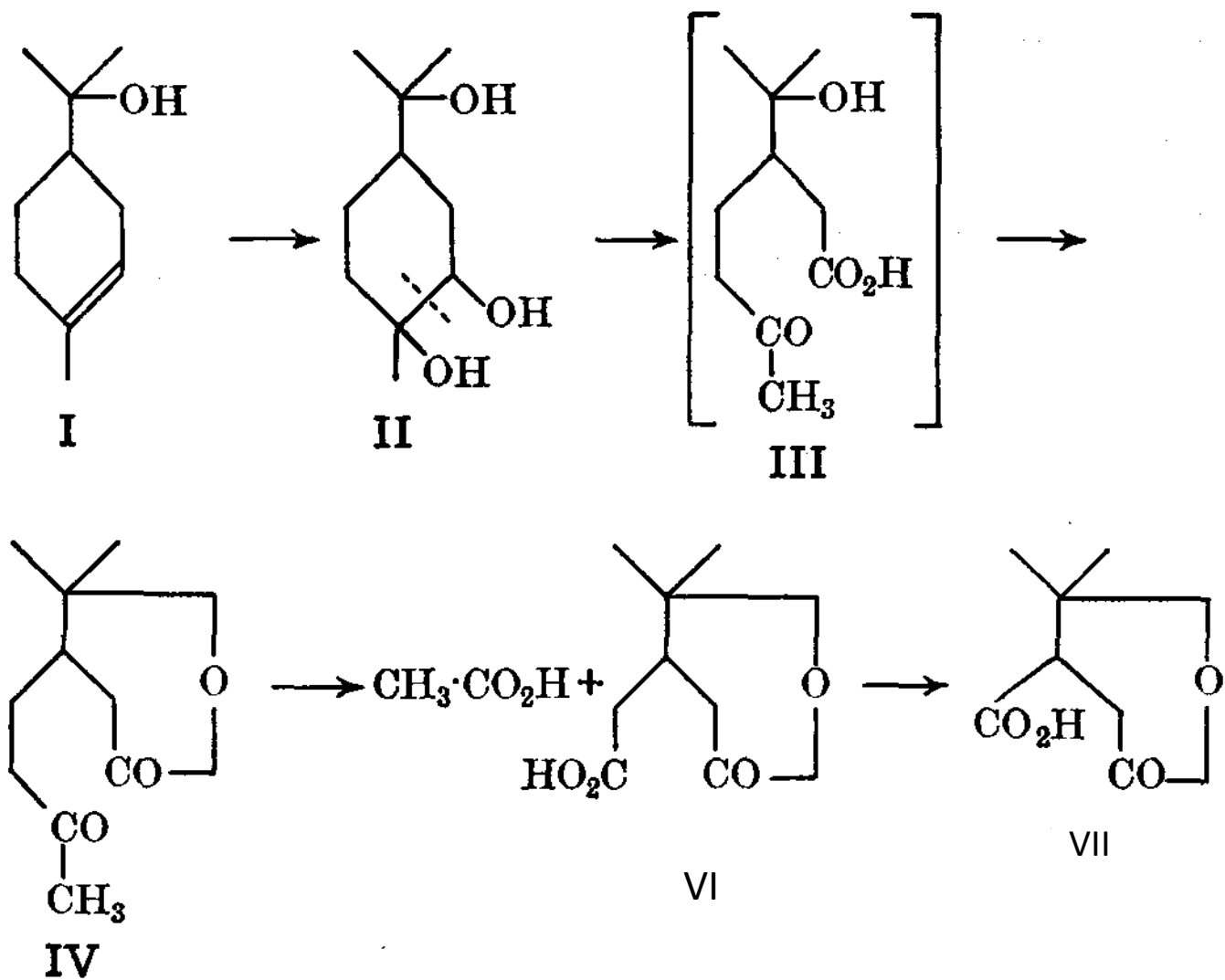


Synthesis of terpenylic acid

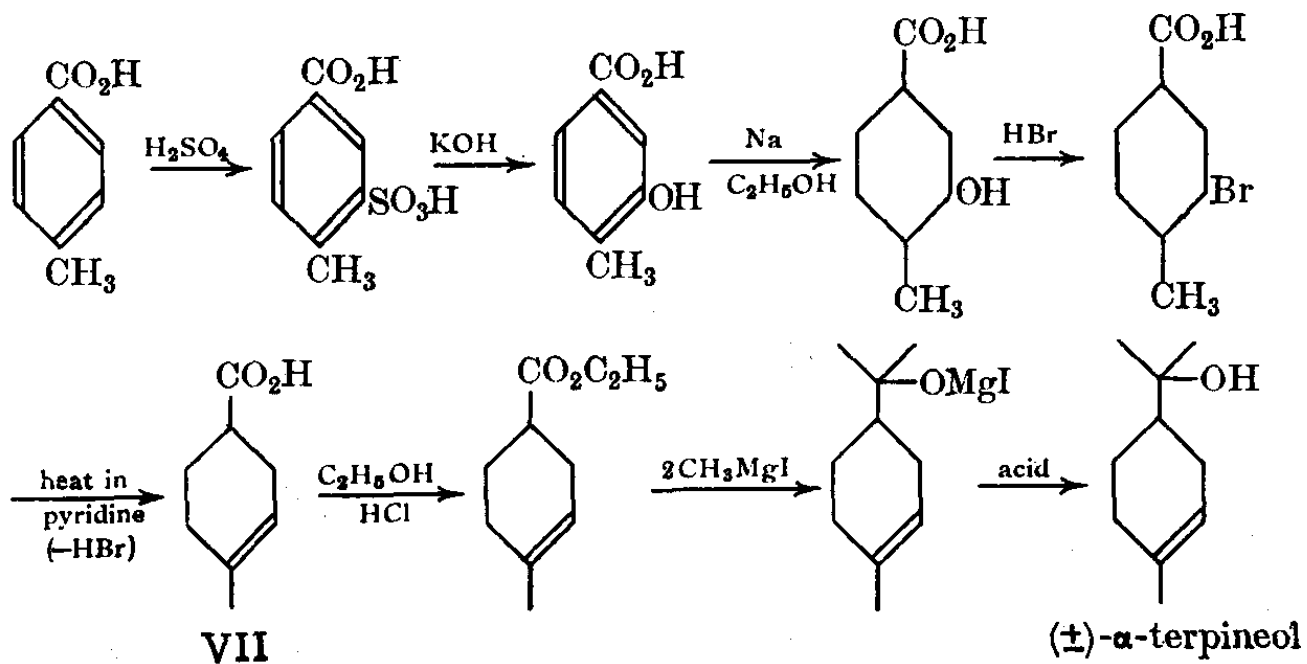
Terpenylic acid, m.p. 90°.



- On the basis of the above structure of terebic acid, homoterpenylic acid and homoterpenyl methyl ketone and the above set of oxidation, α terpineol may be formulated as I which explains all the reactions:



- The structure is further confirmed by its synthesis:
 (i) Perkin junior (1904)



(ii) Alder and Vogot synthesis

A much simpler synthesis of α -terpineol has been carried out by Alder and Vogt (1949); this makes use of the Diels-Alder reaction, using isoprene and methyl vinyl ketone as the starting materials

