CHAPTER V

A NEW SYNTHESIS OF (+) β-BISABOLENE
β- Bisabolene, a monocyclic sesquiterpene hydrocarbon occurs widely in essential oils, especially in bergamot oil (83,84), carrot oil (85) and Rhizomes of petasites officinalis Moench (86). The formulations (XXXVa), (XXXV) and (XXXVb) have been assigned to the three isomers α, β and γ-bisabolene respectively (87).

The carbon skeleton of the molecule is established by its complete hydrogenation to bisabolane (A) (83,88) whereby three moles of hydrogen are absorbed which indicates the presence of three double bonds in the molecule.
The presence of three ethylenic linkages is further confirmed by the observation that bisabolene gives a trihydrochloride derivative, structure of which has been supported through synthesis (89). These unsaturated linkages are not conjugated since bisabolene shows no marked exaltation in molecular refraction nor does it absorb in the normal ultraviolet region (90).

Sorm and coworkers (83) have established the presence of methylenic group in \( \beta \)-bisabolene (XXXV) on the basis of IR absorption studies.

Using sodium and ethanol in liquid ammonia \( \beta \)-bisabolene (XXXV) has been prepared by reduction of lanceol (69). Simultaneously two syntheses (91,92) of the hydrocarbon (XXXV) have been reported from the same intermediate compound \( \alpha \)-methyl- \( \delta \)-keto- \( \delta \)-(4-methyl- \( \Delta^3 \)-cyclohexenyl)- \( \Delta^2 \)-hexene (C), by taking advantage of the Wittig reaction (81) for the creation of methylenic bond in bisabolene skeleton. The formation of the compound (C) was reported by Manjarrez and Guzman (92) by the action of acid chloride of 4-methyl-1-
carboxy-\(\Delta^3\)-cyclohexene (D) with Grignard reagent from 1-bromo-4-methyl-\(\Delta^3\)-pentene (E) in the presence of cuprous chloride.

Again, the synthesis of the intermediate compound (C) by Vig et al (91) starts from 4-methyl-1-acetyl-\(\Delta^3\)-cyclohexane (F). The ketone (F) was treated with diethyl carbonate in the presence of sodium hydride to afford (G). The \(\beta\)-keto-ester (G) on condensation with 3-methyl-\(\Delta^2\)-butenyl bromide...
(prepared by addition of hydrogen bromide to isoprene) afforded (H), which on alkaline hydrolysis followed by decarboxylation yielded the required compound (C).

In the present studies another synthesis of the hydrocarbon (XXXV) is accomplished by employing the Wittig olefin synthesis (81) for the fixation of isopropylidene bond.

The procedure for the preparation of aldehyde \( \gamma \)-methylene- \( \gamma \)-(4-methyl-\( \Delta^3 \)-cyclohexenyl) butanal (XVIII) has already been described in the synthesis of \( \tau \) lanceol (Chapter II, p. 28). It was submitted to Wittig reaction (81), with isopropyltriphenylphosphonium iodide in dimethyl sulphoxide in presence of sodium hydride. This furnished \( \alpha \)-methyl- \( \varepsilon \)-methylene- \( \varepsilon \)-(4-methyl-\( \Delta^3 \)-cyclohexenyl)-\( \Delta^2 \)-hexene (XXXV) in 68 per cent yield. Direct comparison with \( \beta \)-bisabolene obtained from \( \alpha \)-methyl- \( \varepsilon \)-keto- \( \varepsilon \)-(4-methyl-\( \Delta^3 \)-cyclohexenyl)-\( \Delta^2 \)-hexene (C) (91) showed identical IR...
spectra. The identity of synthetic product (XXXV) with the natural hydrocarbon was further established by the comparison of its IR characteristic absorption bands (69) at 1650, 890 (terminal methylene), 1460, 1380 (C-CH₃) and 815 (triply substituted double bond) cm⁻¹. IR spectrum graph of the hydrocarbon (XXXV) is given with that of (+) Lanceol at the end of the second chapter.