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SYNTHESIS OF (±)-GRANDISOL FROM (+) Δ^2-CARENE : AN APPLICATION OF PHOTO-INDUCED VINYLCYCLOPROPANE REARRANGEMENT[+]

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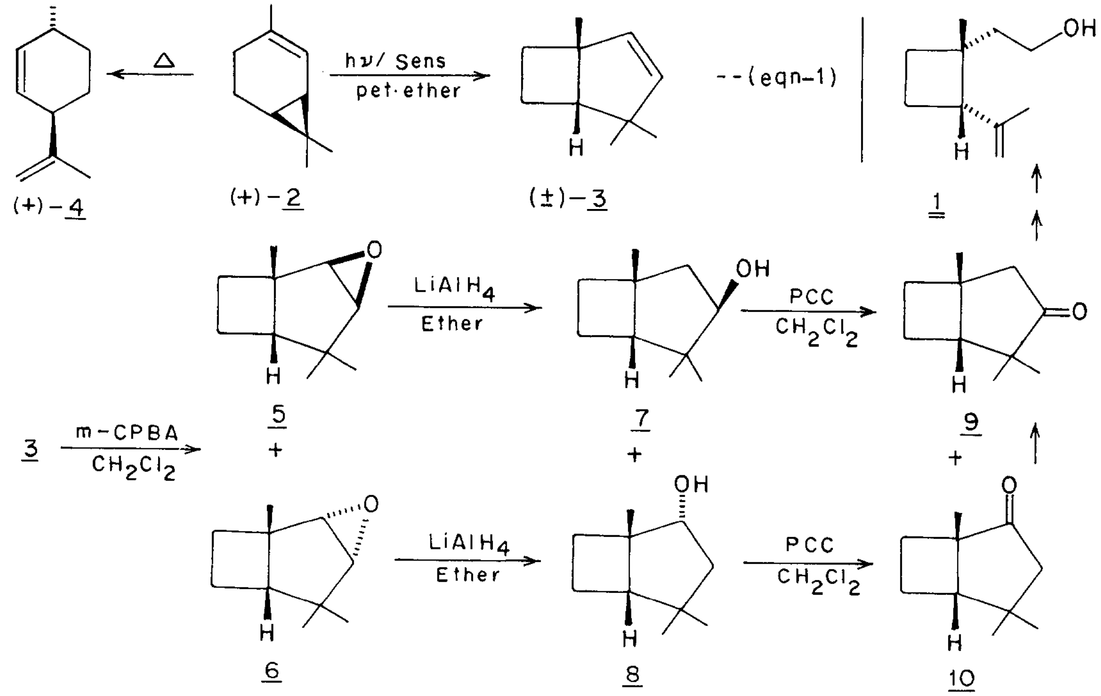
SUMMARY: A new synthesis of (±) - Grandisol from (+) Δ^2-carene involving the photo-induced vinylcyclopropane rearrangement (VCR) as the key step is described.

Grandisol 1 is the most important component of male Boll Weevil sex pheromone[1] and has been the subject of many synthetic investigations[2]. These include both non-photochemical and photochemical approaches. Of the latter, only [2+2] photocycloaddition has been so far utilised for the construction of cyclobutane ring[2].

We have shown recently[3] that bicyclo[4.1.0]heptene derivatives undergo VCR only under photo-sensitized conditions furnishing bicyclo[3.2.0]heptene systems. The present communication provides an example of the first synthetic application of photo-induced VCR[4] transforming readily accessible Δ^2-carene[5] into (±)-1 in good yield. The key step in our approach (scheme) is the conversion of (+)-2 into the crucial intermediate (±)-3. It is noteworthy that thermolysis of (+)-2 is reported[6] to furnish exclusively (+)-4 by a 1,5-sigmatropic rearrangement (eqn-1)



Scheme[13]

Toluene-sensitized photolysis[7] of (+)-2 in petroleum ether (bp 40-60°) solution afforded essentially (60% yield) a bicyclic hydrocarbon which was characterized as 3[8] on the basis of its spectral data [^{1}H NMR ($CDCl_3$) 5.38 (s, 2H), 1.90-2.19 (m,1H), 1.56-1.87 (m, 4H), 1.16 (s, 3H), 0.97 (s, 3H) and 0.94 (s, 3H)]. This assignment was further supported by its ^{13}C NMR spectrum which displayed two singlets (53.1, 47.8), three doublets (139.9, 135.9, 53.9), two triplets (31.0, 18.5) and three quartets (31.3, 26.4, 21.9). This hydrocarbon furnished a mixture (GLC) of epoxides 5 (70%) and 6 (30%) on reaction with m-chloroperbenzoic acid in good yield (80%). The stereochemistry of the oxirane ring is tentative and is based on the expected preferential attack[9] of the peracid from the more exposed exo-face of the cis-fused[3] bicyclic system of 3. The mixture of secondary alcohols 7 and 8 obtained by the LAH reduction (80% yield) of epoxides when subjected to oxidation with PCC in methylene chloride furnished the corresponding ketones 9 (70%) and 10 (30%) in high yield. The identity of these ketones was established by comparison of their spectral data with those of authentic samples[10]. Since the ketone 9 has already been independently converted to (±)-1 by Wenkert[11] and Ayer[12], the preparation of 9 constitutes a formal synthesis of (±)-Grandisol.

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7. A solution of 0.03 M each of (+)2 and toluene in 500 ml of pet. ether was irradiated with a 450 watt high pressure Hg Hanovia lamp using a vycor filter for 40-50 hours in an immersion well apparatus.
8. The product 3 was optically inactive; the mechanistic implications of this result will be communicated separately.
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10. The ketones 9 and 10 were separated by preparative glc (column FFAP 30%, 160°, 70 ml/min.) The authors are indebted to Prof.W.A.Ayer for providing the PMR and IR spectra of 9 for comparison.
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12. W.A.Ayer and L.M.Browne, Can.J.Chem., 52, 1352 (1974); These authors employ ketone 10 as a precursor to 9 in their synthesis of 1.
13. In the reduction of epoxides, the competing minor process leading to the epimers of 7 and 8 is not included in the scheme.

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