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SYNTHESES IN THE CADINANE SERIES:

SYNTHESIS OF (±)-CADINENE DIHYDROCHLORIDE

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AN important group of sesquiterpenes belongs to the cadinene group, which is fairly widely distributed in nature. Several dienes (cadinenes, $C_{15}H_{24}$) and mono olefinic t-alcohols (cadinols, $C_{15}H_{26}O$) fall under this category[1,2]. The absolute configuration of compounds of this series has been recently determined[2,3,4] and is shown for the diketone (I), a degradation product of ε-cadinene[5] (II). It appeared to us that the diketone (I) represents the key substance for syntheses in the cadinane group, and this communication describes, first a total synthesis of (±)-4-isopropyl-*trans*-decalin-1,6-dione (I), and then its conversion into (±)-cadinene dihydrochloride (III).

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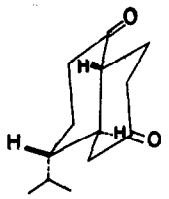
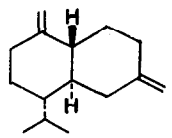
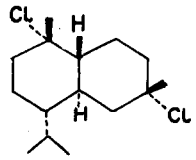


I



II



III

Birch reduction of 4-isopropyl-6-methoxy-tetralone (IV)[6,7] with sodium in liquid ammonia-ethanol gave a highly variable yield (20-70%) of the alcohol (V; b.p. 135-137°/0.6 mm, n_D^{26} 1.5260; no maximum in the 220-300 mμ region; 2:4-dinitrophenyl hydrazone,[8] red needles from acetic acid, m.p. 185°). However, consistent 60-65% yields of V could be obtained by first reducing the tetralone (IV) to 4-isopropyl-6-methoxy-tetralol (VI) by $LiAlH_4$ and then subjecting this crude tetralol to Birch reduction as above. Oxidation of V to the ketone (VII) proved quite elusive; with pyridine-chromic acid[9] or activated manganese dioxide[10] the tetralone (IV) was quantitatively regenerated. Oppenauer oxidation of V with aluminium isopropoxide in acetone-toluene[11] under essentially identical conditions gave either VII (yield 80-90%; b.p. 138-140°/0.6 mm, n_D^{29} 1.5280; λ_{max}^{EtOH} 238 mμ, ε 6900, 241 mμ, ε 7000; dioxime, m.p. 215-217°; bis-2,4-dinitrophenylhydrazone, m.p. 198-199°) or VIII (yield 80-90%; b.p. 130-134°/0.5 mm, n_D^{26} 1.5620; λ_{max}^{EtOH} 339 mμ, ε 9300) or a mixture of both. Attempted separation of VII and VIII on a column of alumina (Basic/I) led to complete isomerization

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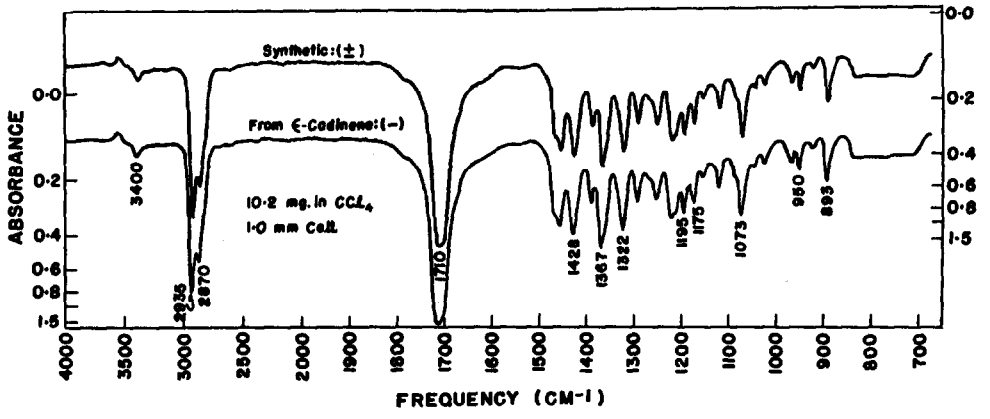

FIG. 1.

105-106°. This compound has been prepared from natural (±)-δ-cadinen,[12,13] and an authentic sample (m.p. 105-106°) did not depress the m.p. of the synthetic material and both exhibited identical infra-red spectra.

Acknowledgments - The authors wish to place on record their sincere gratitude to Professor F. Sorm and Professor M.D. Sutherland for generous samples of (-)-diketone and (±)-cadinene dihydrochloride respectively. We are also grateful to Professor D.K. Banerjee for evincing keen interest in this investigation.

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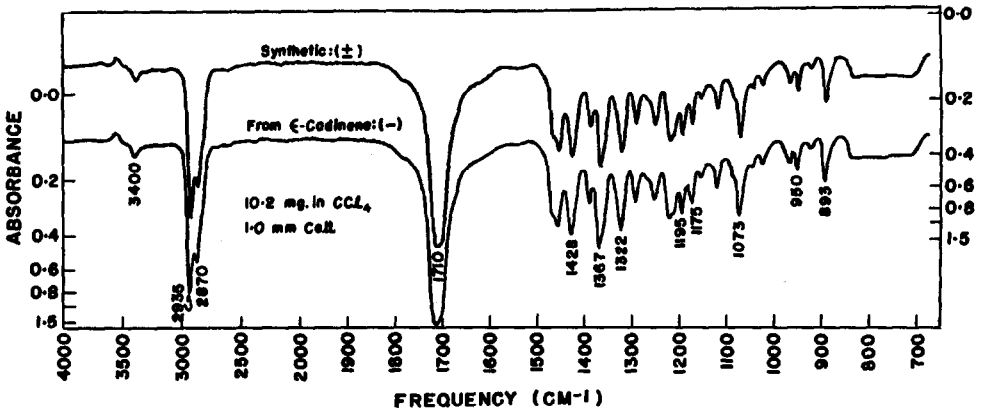

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