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THE SYNTHESIS OF (±)-DICTYOPTERENE A

K. C. Das and Boris Weinstein

Department of Chemistry, University of Washington, Seattle 98105

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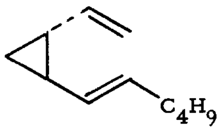
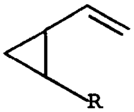
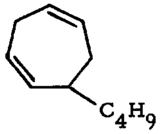
A novel hydrocarbon (+)-dictyopterene A or trans-1-(trans-1-hexenyl)-2-vinylcyclopropane (I) has been isolated from the essential oil of algae belonging to the genus *Dictyopteris*.[1] We here outline a simple preparation of the racemate of I.



(I)



(II) R= -COCl
(III) R= -CHO
(IV) R= $-CH{=}CHC_4H_9$



(V)

Ethyl diazoacetate was added to 1,3-butadiene to form ethyl 2-vinyl cyclopropanecarboxylate, which after hydrolysis, followed by treatment with thionyl chloride, gave the known acyl chloride (II).[2] The reduction of II by lithium tri-t-butoxyaluminum hydride[3] afforded the unstable aldehyde (III) [bp 44°/15 mm; 2,4-dinitrophenylhydrazone, mp 146°] . Next, Wittig reaction of III with the ylid of n-pentyltriphenylphosphonium bromide[4] in the presence of n-butyl lithium in ether at 10° yielded a colorless liquid (IV) [bp 70°/15 mm] , possessing a characteristic "odor of the sea". Gas-chromatographic analysis (polyethylene-glycol succinate or Apiezon L) of IV revealed the existence of four components (2:48:2:48). The initial major peak must be the undesired cis, trans-IV, since the remaining major peak possessed the same retention time as authentic I. The residual minor peaks probably correspond to cis, cis- and trans, cis-IV. A preparative separation then afforded (±)-I, identical with the natural product on the basis of ir, nmr, and mass spectroscopy comparisons.

The assignments were confirmed in the following manner - refluxing a xylene solution of IV produced a rapid disappearance of the first major peak with a simultaneous slower growth of the second major peak, followed in turn by a gradual dimunition. These results are accommodated in a mechanism whereby cis, trans-IV undergoes a facile Cope rearrangement to furnish the valence isomer 7-butyl-cis, cis-cyclohepta-1,4-diene (V).[5] Simultaneously, the cyclopropane ring of cis, trans-IV can open via an allylic diradical intermediate to generate additional trans, trans-IV. The observed thermal rearrangement offers an easy method for removing the undesired isomers found in crude IV. We have noted that the mass spectrum of I is essentially identical with V; this fact suggests I undergoes a related isomerization prior to ionization in the heated inlet system of the mass spectrometer.

Finally, the biosynthesis of dictyopterene A may involve methyl group transfer from methionine to a polyunsaturated fatty acid precursor, followed by cyclization and decarboxylation steps.

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