

The Transformation of Phyllocladene into a Neoatisirane System

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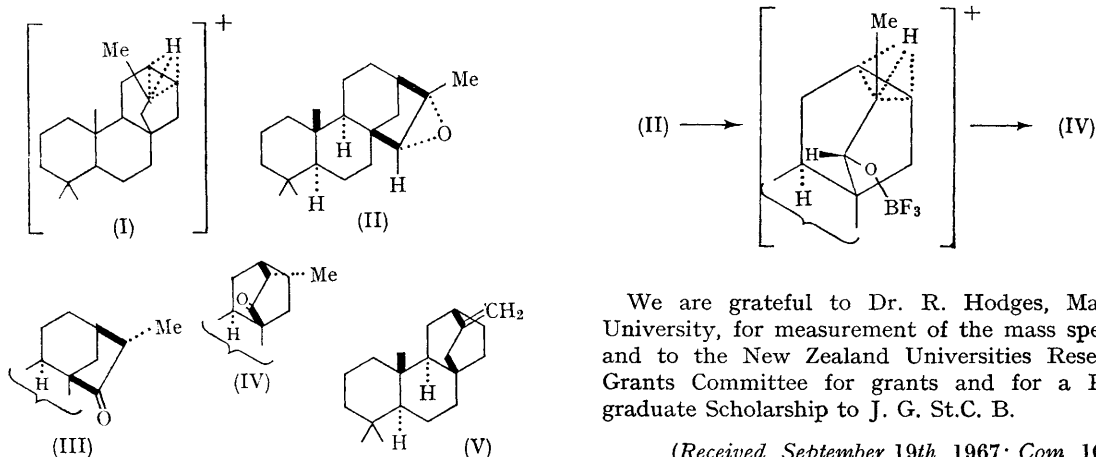
INTERCONVERSION and rearrangement of the tri-, tetra-, and penta-cyclic diterpenes have aroused particular interest in recent years, both as a means of establishing structural inter-relationships and as a model for biosynthetic pathways. A Glasgow group¹ has demonstrated the acid-catalysed conversion of the hydrocarbons (+)-stachene [(–)-hibaene], trachylobane, and kaurene into mixtures of atisirene, isoatisirene, kaurene, and isokaurene; the formation of the atisirane skeleton requiring a novel 1,3-hydride shift. Other groups² have reported the interconversion of the hibaene and kaurene systems. A key intermediate in these transformations may be the non-classical carbonium ion (I) suggested by Wenkert³ to be of biogenetic significance.

We now report the reaction of 15 α ,16 α -epoxy-phyllocladane (II)⁴ with boron trifluoride-etherate to give the known ketone (III)⁴ and, in 29% yield, a new ketone assigned the structure (IV). This is the first recorded example of the conversion of a phyllocladene derivative into a compound possessing the neoatisirane skeleton. No compounds of this class have, as yet, been found naturally, although the biogenesis of both phyllocladene and neoatisirene from isopimaradiene can be rationalised by an extension⁵ of Wenkert's hypothesis.¹ Zalkow and Oehlschlagel⁵ have recently synthesised neoatisirene (V) and the endocyclic double-bond isomer, neoisoatisirene, in 14 steps from maleopimaric acid.

The ketone (IV), C₂₀H₃₂O, had m.p. 137°,

$[\alpha]_D - 33^\circ$ with a negative Cotton effect curve, ν_{\max} 1714 cm^{-1} , δ 0.64 (20-Me), 0.80, 0.86 (18, 19-Me) and 1.05 (*d*, $J = 7$ c./sec., 17-Me). The doublet at δ 1.05 was collapsed to a singlet on double irradiation at δ 2.0. Treatment of the ketone (IV) with MeONa–MeOD gave a ketone containing one atom of deuterium (mass spectral M , 289) in which the n.m.r. signal due to the 17-methyl group appeared as a broadened singlet. The ketone (IV) did not form an ethylene ketal, an oxime, or a toluene-*p*-sulphonyl hydrazone even under forcing conditions, and was inert towards bromine in acetic acid and pyridinium

bromide perbromide. Reduction with lithium aluminium hydride gave an alcohol, $\text{C}_{20}\text{H}_{34}\text{O}$, m.p. 156–158°, $[\alpha]_D + 16^\circ$, ν_{\max} 3628 (strong, free OH) and 3460 cm^{-1} (weak, intermolecularly hydrogen-bonded OH), in which the n.m.r. signal due to the 20-methyl group appeared at δ 1.01. The ketones (III) and (IV) showed marked similarities in all their chemical and i.r., n.m.r., and mass spectral properties. This transformation can be rationalised as proceeding by the pathway outlined, involving 1,2-alkyl shifts and a 1,3-hydride shift through a non-classical ion closely related to the ion (I):



We are grateful to Dr. R. Hodges, Massey University, for measurement of the mass spectra and to the New Zealand Universities Research Grants Committee for grants and for a Post-graduate Scholarship to J. G. St.C. B.

(Received, September 19th, 1967; Com. 1004.)

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