Formation of the 2-Azabicyclo[3,3,1]non-1-ene System

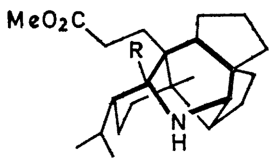
By MASAAKI TODA and YOSHIMASA HIRATA
(*Chemical Institute, Nagoya University, Chikusa, Nagoya, Japan*)
and SHOSUKE YAMAMURA*
(*Faculty of Pharmacy, Meijo University, Showa-ku, Nagoya, Japan*)

Summary The 2-azabicyclo[3,3,1]non-1-ene system has been formed from methyl homosecodaphniphyllate.

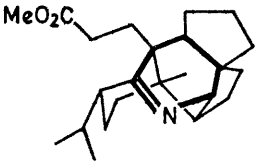
THE structure of methyl homosecodaphniphyllate (I), an alkaloid of *Daphniphyllum macropodum* Miq., has been established by *X*-ray analysis, together with its chemical and spectral data.[1]† The alkaloid (I) contains the 2-azabicyclo[3,3,1]nonane system as well as the 2-azabicyclo [2,2,2]octane system.

We describe the formation of the 2-azabicyclo[3,3,1]non-1-ene system, an unusually stable anti-Bredt's-rule imine (II).

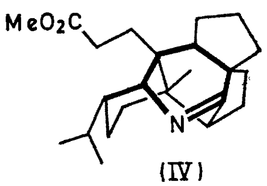
When treated with lead tetra-acetate in dry benzene at room temperature for 1 h, the alkaloid (I) afforded an oxidation product (II), m.p. 96—98°; $C_{23}H_{35}O_2N$; *m/e* 357 (M^+), which showed no NH absorption band in its i.r. spectrum, and which was re-converted into the starting material (I) on treatment with sodium borohydride at room temperature for 1 h. Catalytic hydrogenation of the imine (II) over PtO_2 in methanol (room temp., 1 h) also afforded (I) in quantitative yield, indicating that no rearrangement of the carbon skeleton took place in the course of oxidation of (I) with lead tetra-acetate. Furthermore, treatment of (II) with an excess of sodium cyanide in dimethylformamide (90—100°, 3 h) afforded a cyano-compound (III), *m/e* 384 (M^+), ν_{max} ($CHCl_3$) 2240 and 1735 cm^{-1}. Surprisingly, however, acetylation of (III) with acetic anhydride–pyridine (room temp., overnight) gave not the corresponding *N*-acetyl derivative, but the imine (II).



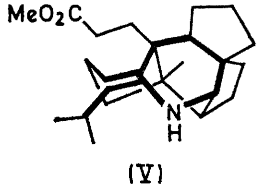
(I) R = H
(III) R = CN



(II)



(IV)



(V)

The easy formation of the imine (II) may be attributed to the following. (i) The cyano-compound (III) has the boat conformation of its 2-azabicyclo[3,3,1]nonane system fixed by a part of the 2-azabicyclo[2,2,2]octane system. (ii) The strain energy must be increased by the formation of the imine, whereas steric repulsions between the cyano-group and the other substituents in (III) can be relieved. On the basis of the above chemical properties and the spectral data [*m/e* 357 (M^+), ν_{max} ($CHCl_3$) 1600 cm^{-1} and δ 4·24 p.p.m. (1H, d, *J* 3·5 Hz, N–C–*H*)], the structure of the oxidation product must be (II), containing the 2-azabicyclo[3,3,1]-non-1-ene system. The structure (IV), which contains the

---

† The structure of the *N*-bromoacetyl derivative of (I) has been determined by *X*-ray analysis. The result will be reported in detail.

2-azabicyclo[2,2,2]oct-1-ene system, can be ruled out on steric grounds, and the enamine structure (V) can be ruled out since the oxidation product has no NH absorption band in its i.r. spectrum (in KBr or $CHCl_3$), and no signals corresponding to an NH group can be observed in the n.m.r. spectrum.

Recently, the synthesis and chemistry of the anti-Bredt's-rule olefin bicyclo[3,3,1]non-1-ene have been reported in detail.[2] The olefin's spectral properties are normal,[2] whereas the imine (II) has an i.r. absorption band at 1600 cm^{-1}, which can be assigned to C=N absorption usually observed in the region of higher wave-number (1690—1640 cm^{-1}).[3] The imine (II) shows an abnormal u.v. spectrum [λ_{max} (MeOH) 210 nm (ϵ 3300)] which has not yet been explained.

We thank the National Institutes of Health, U.S.A., for support of this work.

(*Received, September 2nd,* 1970; *Com.* 1474.)

---

[1] H. Irikawa, M. Toda, S. Yamamura, and Y. Hirata, *Tetrahedron Letters*, 1969, 1821.

[2] J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, 1970, **92**, 948; J. R. Wiseman and W. A. Pletcher, *ibid.*, p. 956.

[3] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, p. 267.