magnetic species contains only one cobalt atom. The observed g value, namely 2.026, indicates that the species is a peroxy radical,[7] but its unequivocal identification of molecular geometry would require esr studies using oxygen-17. When helium is bubbled through the solution for 15 sec immediately after the oxygenation, no signal is detected, indicating the reversibility of the oxygen addition process.

The esr signal of the freshly oxygenated solution decays with time, accompanied by an increase in optical density in the region 300–400 mμ. This optical absorption corresponds to the binuclear complexes where oxygen is bridging two cobalt complexes.[8] The disappearance of the esr signal is attributed to bimolecular termination between the peroxy cobalt radical and the paramagnetic chelated cobalt atom.

The esr signal for the peroxy cobalt radical with polyethylenimine as the ligand decays with first-order kinetics with a half-life of 3 min, whereas with other low-molecular-weight ligands the decay was much more rapid. Since the cobalt atom and the peroxy radical are attached to the polymer, the likelihood of their encounters is thereby reduced. Decreasing the pH stabilizes the radical due to electrostatic repulsion arising from protonation of the amine groups. Below pH 5.6, however, the metal complexation is reduced, hence the esr signal is decreased. The esr signal is also suppressed when salt is added to the solutions. Thus addition of KCl to the concentration of 0.3 M wipes out the signal, apparently due to suppression of the electrostatic repulsion between these polyelectrolyte ligands.

(7) B. R. McGarvey and E. L. Tepper, *Inorg. Chem.*, **8**, 498 (1969).

(8) S. Yamada, Y. Shimura, and R. Tsuchida, *Bull. Chem. Soc. Jap.*, **26**, 72 (1953).

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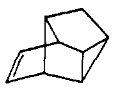
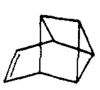
Methyl Tetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene-4-carboxylate

Sir:

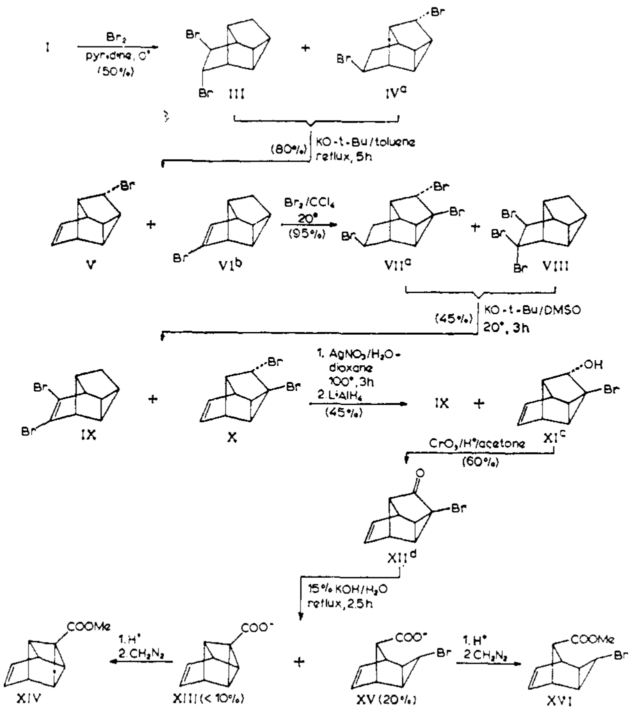
General interest in valence isomers $(CH)_{2p}$[1,2] and our own interests in tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-enes (I)[3] have caused us to attempt the conversion of a derivative of I into a structure containing the closely related (CH) skeleton of the as yet unsynthesized $(CH)_8$ isomer tetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene (II).[4] To achieve this goal we chose the pseudo-Favorskii reaction of bridgehead α-bromo ketones, which has served so well in the synthesis of cubane and other cage compounds.[9]


I


II

Bromo ketone XII was prepared by a series of addition–elimination reactions starting with I[10] (Chart I).

Chart I



[a] Configuration at C-5 assigned on mechanistic grounds only. [b] Purified by fractional distillation: bp 80–83° (18 mm); nmr (τ, CCl_4) 4.03 (d,d, 3 and 1 cps), 7.38, 7.87, 8.15–8.68. [c] Separated from IX by chromatography on alumina: nmr (τ, CCl_4) 3.95, 5.97 (d, 2 cps), 6.60, 7.10, 7.65 (OH). 8.15, 8.25. [d] Though isolated as a single peak on vpc, ir and nmr indicated that an unknown contamination was present (±25%): ir (cm^{-1}, CCl_4) 1775 and 1757; nmr (τ, CCl_4) 3.80, 6.58, 6.78, 7.62–8.20; mass: 212/210, 211/209, 184/182, 131, 103, 102, 77.

Important steps were: (1) bromination of I in pyridine, which gave predominantly unrearranged dibromide III;[11] (2) introduction of the bridgehead bromine *via*

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(1) Compilation of possible structures $(CH)_{2p}$: A. T. Balaban, *Rev. Roum. Chim.*, **11**, 1097 (1966).

(2) Whereas $(CH)_{10}$ isomers and their interconversions have received much attention, similar activities in the $(CH)_8$ field have only recently been reported: (a) J. Meinwald and H. Tsuruta, *J. Amer. Chem. Soc.*, **91**, 5877 (1969), and references given therein; (b) H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969).

(3) G. W. Klumpp, *Recl. Trav. Chim. Pays-Bas*, **87**, 1053 (1968).

(4) So far, 4,5-diphenylbenzotetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene, obtained by photoreaction between naphthalene and tolane, appears to be the only derivative of II that has been prepared.[5,6]

(5) W. H. F. Sasse, *Austr. J. Chem.*, **22**, 1257 (1969), and earlier papers by the same author.

(6) Other attempts to synthesize the carbon skeleton of II have failed: 8-carbenatricyclo[3.2.1.0^{2,4}]octane gave bicyclo[3.3.0]octa-1,6-diene as the main product;[7] 3-carbenatricyclo[3.2.1.0^{2,4}]oct-6-ene, supposed to be an intermediate in the gas-phase irradiation of norbornadiene and carbon suboxide, produced C_8H_8, which most probably is *endo*-6-ethynylbicyclo[3.1.0]hex-2-ene.[8] After this communication had been submitted for publication, the report of R. G. Bergman and V. J. Rajadhyaksha on *endo*-6-ethynylbicyclo[3.1.0]hex-2-ene (*J. Amer. Chem. Soc.*, **92**, 2163 (1970)) became available to us. Since then comparison of ir spectra has established the identity of the compounds from both laboratories. We are grateful to Professor Bergman for sending us copies of the spectra of *exo*- and *endo*-6-ethynylbicyclo[3.1.0]hex-2-ene.

(7) P. K. Freeman and D. G. Kuper, *Diss. Abstr. B*, **28**, 109 (1967).

(8) G. W. Klumpp and P. M. van Dijk, unpublished results.

(9) *Cf.* references given by K. V. Scherer, Jr., *Tetrahedron Lett.*, 5685 (1966).

(10) Prepared by the method of T. J. Katz, J. C. Carnahan, Jr., and R. Boecke, *J. Org. Chem.*, **32**, 1301 (1967).

(11) Bromination of I in all other solvents studied gives largely rearranged dibromide IV. It is interesting to note that amine or ammonium perbromides, which are probably the active species on bromination in pyridine, have found wide application in selective bromination of ketones,[12] but have seldom been used with olefins,[12,13] despite several promising reports.[14] We are currently studying the nature of this reaction.

(12) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, pp 855, 966 ff.

(13) P. B. D. De La Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, Amsterdam, 1966; however, see also L. Kaplan, H. Kwart, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **82**, 2341 (1960).

the known homocyclopropylcarbinyl rearrangement of 8-tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonyl cations[15] in step VI → VII.

In contrast to many other α-bromo ketones[9] formation of XIII is not the favored process if XII is treated with base. The title compound XIV is a minor product and must be separated by vpc from XVI and several other by-products of unknown structure. This may reflect the high strain of II and its derivatives as well as the unfavorable stereoelectronic situation, the bromine, which has to be substituted, being bound to a cyclopropane ring.[16]

Assignment of structures XIV and XVI is based on mode of formation and on spectroscopic evidence: XIV, molecular ion at m/e 162.0680 (calcd for $C_{10}H_{10}O_2$: 162.0681), other strong peaks at m/e 77, 102, and 103 (base peak); also, m* 103 → 77 (calcd: 57.56; obsd: 57.5) indicates loss of acetylene;[19] nmr (τ, CCl_4) 3.98 (2 H, triplet, $|J|$ = 2 cps, A_2 part of a degenerate A_2X_2 absorption pattern), 6.25 (2 H, multiplet), 6.40 (3 H, singlet, methoxyl), 7.23 (3 H, multiplet, $\Delta\nu_{1/2}$ = 5 cps). Decoupling of the 7.23 signal causes the 6.25 signal to collapse into a triplet, which is the X_2 counterpart of the olefinic triplet. Decoupling of the 6.25 signal (H-1 and H-6) transforms both signals at 3.98 and 7.23 into singlets. This shows that XIV is a norbornene derivative with C_s symmetry[20,21] and that the carbomethoxy group is attached to C-4:[23] ir (cm^{-1}, CCl_4) 3060, 1713, 1440, 1390, 1261, 1247, 1195, 1178, 1107, 1085. The absorption of the carbonyl group at relatively low wave number proves the cyclopropyl conjugation:[24] XVI, mp 107–108°; no molecular ion; strong peaks at m/e 183.9803 ($C_{10}H_{11}BrO_2 - COOCH_3$), 163.0752 ($C_{10}H_{11}BrO_2 - Br$), 131, 103 (base peak), 77; nmr (τ, CCl_4) 3.53 (2 H, triplet, $|J|$ = 1.8 cps), 6.33 (3 H, singlet, methoxyl), 6.56 (2 H, broad singlet, H-1 and H-5), 6.64 (1 H, triplet, $|J_{23}|$ = 1.7 cps, H-3), 8.10 (1 H, broad singlet, H-8), and 8.52 (2 H, doublet of doublets, $|J_{23}|$ = 1.7 cps and $|J|$ = 1 cps, H-2 and H-4). The configurations at C-3 and C-8 follow unequivocally from the coupling and shielding pattern:[25,26] ir (cm^{-1}, CCl_4) 3060, 1736, 1435, 1239, 1225, 1034, 725, 694.

Our work on the synthesis and chemistry of tetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-enes is being continued.

Acknowledgment. The authors are greatly indebted to Dr. J. W. de Haan and Mr. L. M. J. van de Ven, Technical University, Eindhoven, for measuring the 100-Mcps nmr spectrum of XIV and for carrying out the spin decoupling experiments and to the Koninklijke/Shell-Laboratorium, Amsterdam, for generous gifts of norbornadiene.

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(14) K. W. Rosenmund and W. Kuhnhenn, *Ber.*, **56**, 1262 (1923), and earlier references cited by these authors.

(15) (a) P. K. Freeman and D. M. Balls, *Tetrahedron Lett.*, 437 (1967); (b) R. M. Coates and J. L. Kirkpatrick, *J. Amer. Chem. Soc.*, **90**, 4162 (1968).

(16) The Haller–Bauer type cleavage, which has also been observed on other attempted pseudo-Favorskii reactions,[17] prevails even more if XII is treated with KOH–THF at 0°. It is also predominating with dihydro-XII. One other reason for this preference may be that cyclopropyl anions are more stable than other cyclanyl anions.[18]

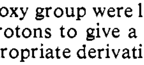
(17) K. V. Scherer, Jr., R. S. Lunt, III, and G. A. Ungefug, *Tetrahedron Lett.*, 1199 (1965).

(18) *Cf.* P. G. Gassman, J. T. Lumb, and F. V. Zalar, *J. Amer. Chem. Soc.*, **89**, 946 (1967).

(19) There is a close resemblance between the mass spectra of XIV and methyl cyclooctatetraenecarboxylate, even at low IP (9 eV). At 9 eV m/e 102 is the most intense peak besides the molecular ion.

(20) E. I. Snyder and B. Franzus, *J. Amer. Chem. Soc.*, **86**, 1166 (1964).

(21) Isomeric structures with C_s symmetry, *i.e.*, those derived from i, are considered unlikely on the basis of published nmr data on bicyclo[3.2.0]hept-6-enes[22] and because their formation is rather improbable mechanistically.



(22) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).

(23) If the carbomethoxy group were located on C-5 one would expect the three cyclopropyl protons to give a broad absorption pattern, as is observed with I and appropriate derivatives of I.[3,10]

(24) Methyl tricyclo[2.2.0.0^{2,6}]hexane-1-carboxylate absorbs at 1706 cm^{-1} (J. Meinwald and J. K. Crandall, *J. Amer. Chem. Soc.*, **88**, 1292 (1966)), methyl 4-chlorobicyclo[2.2.0]hexane-1-carboxylate at 1735 cm^{-1} (W. G. Dauben, J. L. Chitwood, and K. V. Scherer, Jr., *ibid.*, **90**, 1014 (1968)).

(25) C. W. Jefford and W. Wojnarowski, *Tetrahedron*, **25**, 2089 (1969), report similar values of J_{23} in *anti*-3-halo-*exo*-tricyclo[3.2.1.0^{2,4}]octanes.

(26) The exo–syn relation between cyclopropane ring and carbomethoxy group follows from the 1-cps splitting observed for H-2 and H-4 (probably long-range coupling with H-8) and from the strong shielding exerted by the cyclopropane ring on H-8.[27,28]

(27) H-7 of methyl bicyclo[2.2.1]hepta-2,5-diene-7-carboxylate[29] absorbs at τ 6.98. For examples and relevant literature on the use of long-range coupling and diamagnetic anisotropy as probes into tricyclo[3.2.1.0^{2,4}]octane stereochemistry, *cf.* G. W. Klumpp, A. H. Veefkind, W. L. De Graaf, and F. Bickelhaupt, *Justus Liebigs Ann. Chem.*, **706**, 47 (1967).

(28) The relatively low-field resonance of H-3 may be a case of steric deshielding: M. A. Battiste and M. E. Brennan, *Tetrahedron Lett.*, 5857 (1966).

(29) G. W. Klumpp, and F. Bickelhaupt, *ibid.*, 865 (1966).

(30) To whom correspondence should be addressed.

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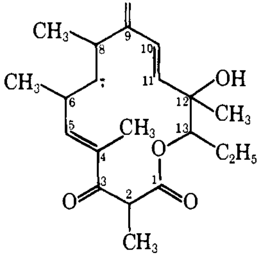
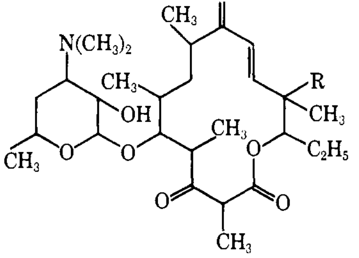
The Structure of Kromycin

Sir:

In a recent report[1] it was proposed that kromycin, the anhydro aglycone hydrolysis product of the macrolide antibiotic, pikromycin, has structure **1** and that pikromycin (**2**) is a hydroxylated narbomycin (**3**). Earlier views[2,3] had regarded pikromycin as a 12-membered ring analog of methymycin[4] rather than the 14-membered ring structure (**2**). We now report an X-ray diffraction study of kromycin that fully corroborates structure **1** and provides a detailed configurational description of the molecule.



1



2, R = OH
3, R = H

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(1) H. Muxfeldt, S. Schrader, P. Hansen, and H. Brockmann, *J. Amer. Chem. Soc.*, **90**, 4748 (1968).

(2) H. Brockmann and R. Oster, *Chem. Ber.*, **90**, 605 (1957).

(3) A. Anliker and K. Gubler, *Helv. Chim. Acta*, **40**, 1768 (1957), and preceding paper.

(4) C. Djerassi and J. A. Ederick, *J. Amer. Chem. Soc.*, **78**, 2907, 6390 (1956).