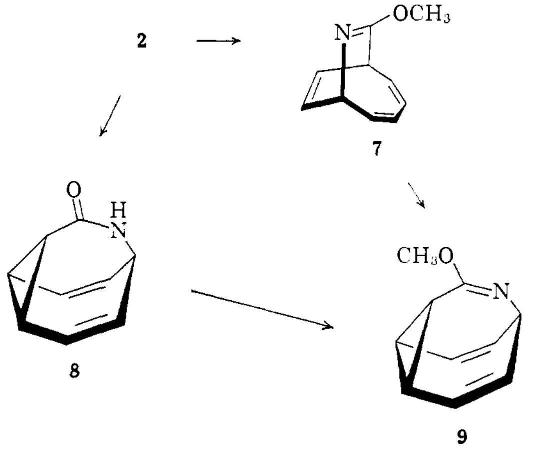
formation of **1** involves initial electrophilic attack[9] to afford the dipolar homotropylium cation **6**;[16] the rate of collapse of **6** *via* a six-centered transition state (path A) can be expected to be faster than the four-centered pathway demanded by **B**.

Exposure of **2** to trimethyloxonium fluoroborate[17] in a manner previously described[18] led to the isolation of imino ether **7**, mp 50.5–52°[7] [$\lambda_{\max}^{\mathrm{CH_3CN}}$ 271 mμ (ε 2000), $\delta_{\max}^{\mathrm{CCl_4}}$ 3.57 (singlet overlapping a multiplet, 4 H, $-OCH_3$ plus bridgehead proton), 4.30 (multiplet, 1 H, bridgehead proton), and 5.97 (complex multiplet, 6 H, vinyl protons)] in 81% yield. Irradiation of a methanol solution of **7** with an immersion-type 450-w Hanovia medium-pressure mercury arc resulted in smooth conversion (54%) to a highly crystalline photoisomer, mp 49.5–50.5°.[7] The nmr spectrum of this material and its variable temperature behavior[5] conclusively establish the structure as that of the azabullvalene derivative **9**.



In a second approach to the title system, irradiation of **2** under similar conditions led in 50% yield to **8**, $\nu_{\max}^{\mathrm{KBr}}$ 1655 and 1640 cm^{-1},[7,19,20] which was transformed in turn (92% yield) to the identical azabullvalene derivative, mp 49–50°, when treated with trimethyloxonium fluoroborate.

Extensive studies dealing with azabullvalene chemistry are in progress and will be reported subsequently.

Acknowledgment. We wish to express our gratitude to the National Institutes of Health and the Lilly Research Laboratories for their generous financial support of this work.

[16] Evidence for "inside" protonation (deuteration) of cyclooctatetraene in leading to the homotropylium cation has recently been presented: S. Winstein, C. G. Kreiter, and J. I. Brauman, *J. Am. Chem. Soc.*, **88**, 2047 (1966); S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *ibid.*, **87**, 3267 (1965); J. L. Rosenberg, J. E. Mahler, and R. Pettit, *ibid.*, **84**, 2842 (1962). For more recent work, see G. Boche, W. Hechtl, H. Huber, and R. Huisgen, *ibid.*, **89**, 3344 (1967); R. Huisgen, G. Boche, and H. Huber, *ibid.*, **89**, 3345 (1967).

[17] H. Meerwein, *Org. Syn.*, **46**, 120 (1966).

[18] L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 4096 (1964), and references cited therein.

[19] Compound **8** displayed interesting melting point behavior; when slowly heated, an analytical sample failed to melt up to 300°, except for partial softening at *ca.* 220°. A fresh sample placed in the oil bath at 250° melted completely and immediately. The thermal rearrangement of **8** is now under investigation.

[20] Conjugation between the carbonyl function and the cyclopropyl group evidently renders **8** considerably more stable than its valence-bond isomer.

[21] Alfred P. Sloan Foundation Fellow, 1965–1967.

[22] National Institutes of Health Postdoctoral Fellow, 1967.

Leo A. Paquette,[21] Thomas J. Barton[22]
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

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The Temperature-Dependent Behavior of 3-Methoxy-4-azatricyclo[3.3.2.0^{2,8}]deca-3,6,9-triene (Methoxyazabullvalene)[1]

Sir:

Previously we have reported a four-step synthesis of an imino ether (I) possessing the structural features of the remarkable bullvalene molecule.[1] In this communication we wish to present evidence for its structure and the fluxional nature of its bonds as clearly revealed by its temperature-dependent nmr spectrum.

At room temperature several features of the spectrum are discernible (Figure 1).[2] In addition to the sharp methoxyl singlet at δ 3.46,[3] a three-line pattern of relative area 3 centered at δ 2.50 arises from the three cyclopropyl hydrogen atoms in I, a more expansive three-line pattern (with obvious additional small coupling) at δ 3.80 results from the proton at the bridgehead location, and a four-proton multiplet appears in the low-field region around δ 5.7 ascribable to vinyl hydrogens. Since all cyclopropyl and vinyl protons have similar chemical shifts, one must conclude that no one of these is adjacent to the nitrogen atom, an observa-

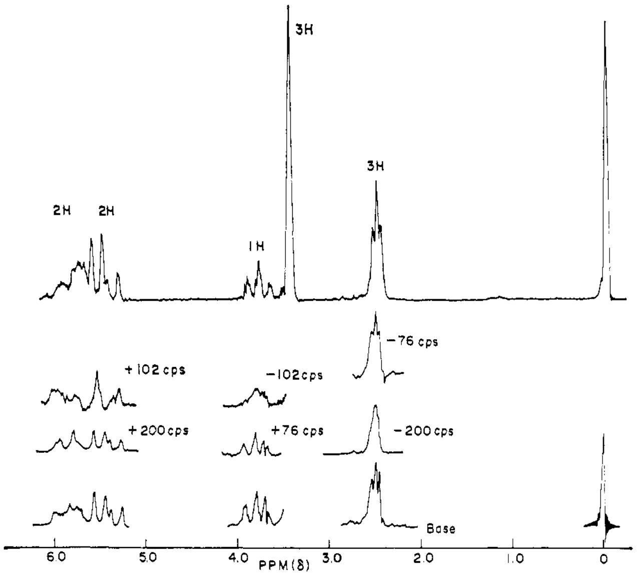
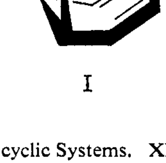


Figure 1. Upper curve: nmr spectrum of methoxyazabullvalene (I) in CCl_4 solution at ∼38°. Lower section: spin decoupling (∼38°) of I in CS_2 solution; values indicate the relative location of the applied stationary radiofrequency.



I

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[1] Unsaturated Heterocyclic Systems. XXXIII. For paper XXXII, see L. A. Paquette and T. J. Barton, *J. Am. Chem. Soc.*, **89**, 5480 (1967).

[2] The spectrum shows interesting changes below room temperature, but the essential features of the 38° spectrum remain unchanged.

[3] The role of the methoxyl group as an internal probe should be noted. From −90 to +194°, this peak remained a sharp singlet, and its chemical shift did not vary more than ±2 cps (a small solvent effect was noted: in CS_2, δ 3.40; in CCl_4, δ 3.52). The same phenomenon appears to exist in methoxybullvalene: J. F. M. Oth, R. Merenyi, J. Nielsen, and G. Schröder, *Chem. Ber.*, **98**, 3385 (1965).

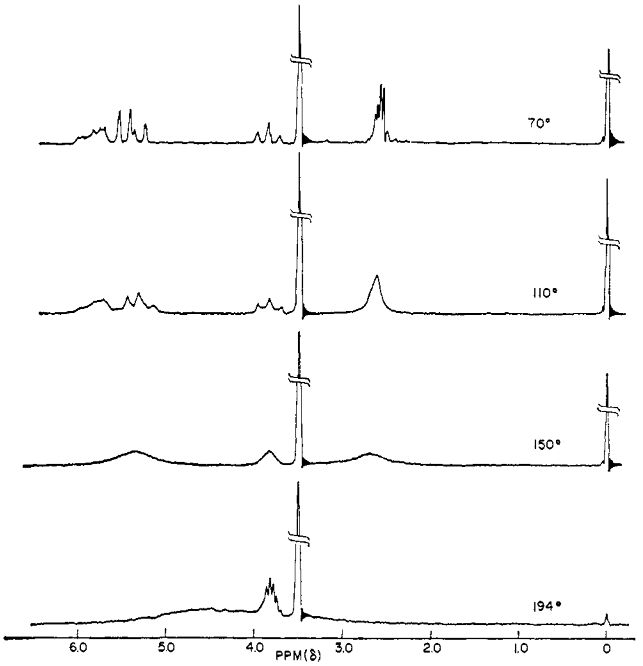
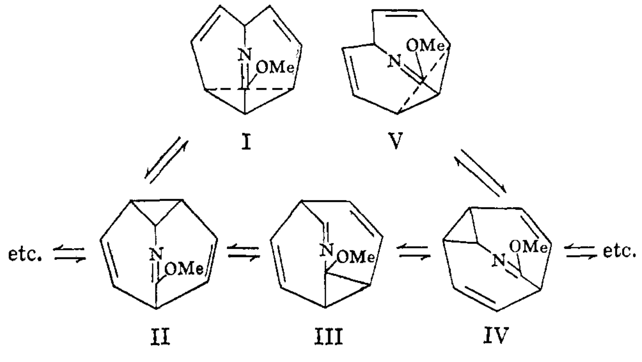


Figure 2. Nmr spectra of I in Cl$_2$C=CCl$_2$ solution at 70, 110, 150, and 194°.

tion which restricts the number of possible structures (21) to I. Spin-decoupling studies (Figure 1) demonstrated that the olefinic protons centered at $\delta \sim 5.8$ are strongly coupled to the cyclopropyl protons, whereas the protons giving the more well-resolved vinyl absorption at $\delta \sim 5.5$ interact substantially with the bridgehead proton. The bridgehead and cyclopropyl protons do not appear to be spin coupled.

When a sample of I in tetrachloroethylene solution is heated above 150° (Figure 2), the proton signals from different regions are seen to coalesce, the sole exception being the 3.8-ppm signal which, apart from coupling constants,[4] does not seem to be affected.[5]

The only averaging process that can produce this behavior is the combination of the two Cope rearrangements illustrated in I through V below. The two-step conversion of II to the equivalent structure IV amounts formally to a rotation of the inner "spoke" on the outer "rim" by $2\pi/7$ radians, it being evident that repetition of such a process would average the rim positions and exclude the spoke.[6] Each of the seven equivalent structures thus generated is connected by a second Cope rearrangement of the type I $\rightleftharpoons$ II to a more stable isomer whose structure corresponds to I, the unique proton in the averaging process thereby appearing in the bridgehead position.



The reason that such a relatively simple averaging process occurs is apparently the strong preference of the nitrogen atom for participation in a double bond. By precluding any rearrangement path that places the heteroatom in the three-membered ring, this maintains the integrity of the three skeletal atoms constituting the "spoke" above and limits the number of accessible structural arrangements to 28, seven each of types I, II, III, and seven apparently incidental ones related to III in the same way as I is to II.

Acknowledgment. We wish to express our gratitude to the National Institutes of Health and the Lilly Research Laboratories for their generous financial support of this work. We are grateful to Mr. H. Gisler for assistance in recording the spectra.

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[4] At 194° all other protons are scrambled at a rate about equal to that of the frequency separation between the vinyl and cyclopropyl regions. This is fast compared to any couplings to the bridgehead proton, so that it should appear as an eight-line pattern with the same total spread as the low-temperature triplet.

[5] When the sample is subsequently cooled to room temperature, the previous spectrum reappears without modification. The identical result was observed on returning the −90° sample to room temperature.

(6) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(7) Alfred P. Sloan Foundation Fellow, 1965–1967; author to whom inquiries should be directed.

(8) National Institutes of Health Postdoctoral Fellow, 1967.

Leo A. Paquette,[7] Thomas J. Barton[8]
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Earl B. Whipple
Union Carbide Research Institute
Tarrytown, New York 10591

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The Structure of a Dicarbonium Ion in the Crystalline State[1]

Sir:

There has been considerable controversy surrounding claims for the detection of dicarbonium ions in solution.[2,3] A report[4] of a tetraphenylcyclobutenium dicarbonium ion in solution was not substantiated by an X-ray study[5] on the crystal. More recently, Volz and Volz de Lecea[6] have reported the identification and isolation of a number of di- and tricarbonium ions as crystalline hexachloroantimonate salts. Hart and co-workers[7] have also reported studies on similar systems. As definite crystallographic evidence for the presence of a dicarbonium ion in the solid state would be of great value, we have undertaken an X-ray study of the compound reported to be I.[6] In the course of the later stages of our investigation, the crystal structure of the tetra-*p*-anisylethylene dication was described.[8]

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(1) Work supported in part by U. S. Public Health Service Grant GM 12470-03 and GM 722-05.

(2) H. Hart and R. W. Fish, *J. Am. Chem. Soc.*, **80**, 5894 (1958); **83**, 4460 (1961).

(3) R. J. Gillespie and E. A. Robinson, *ibid.*, **86**, 5676 (1964); **87**, 2428 (1965).

(4) H. H. Freedman and A. M. Frantz, *ibid.*, **84**, 4165 (1962).

(5) R. F. Bryan, *ibid.*, **86**, 733 (1964).

(6) H. Volz and M. J. Volz de Lecea, *Tetrahedron Letters*, 4675 (1966); 4683 (1966).

(7) H. Hart, T. Sulzberg, R. W. Schwendeman, and R. H. Young, *ibid.*, 1337 (1967).

(8) N. C. Baenziger, R. E. Buckles, and T. D. Simpson, *J. Am. Chem. Soc.*, **89**, 3405 (1967).