Thus the results support the conclusion that the carbonylation of perhydro-9b-boraphenalene proceeds cleanly to product perhydro-9b-phenalenol. This represents the first member of a new class of derivatives, characterized by having the central carbon atom carrying a functional group supported by three rings with common sides, which we propose to call "tercyclanols,"[15] etc. Even more important, this development establishes the practicality of this new approach to the synthesis of complex polycyclic derivatives. Certainly the simple formation of three carbon–carbon bonds in a single operation offers major promise for the synthesis of new, interesting structures. We continue to explore the potentialities of this new synthesis.

[15] We are exploring the chemistry of these unusual derivatives (work in progress with W. C. Dickason).

[16] Postdoctorate research associate on a grant supported by the National Institutes of Health (ROI-GM 10937).

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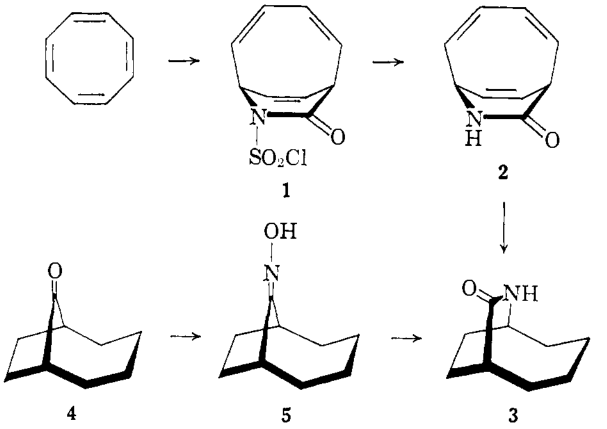
Received August 3, 1967

A Synthesis of the Azabullvalene System[1]

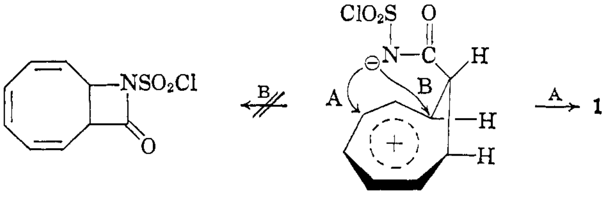
Sir:

Characterization of molecules with fluctuating bonds has advanced rapidly in recent years due chiefly to the capability of nmr spectroscopy to study fast reactions which produce no net chemical change.[2] A unique member of this class of molecules is bullvalene wherein fast and reversible valence isomerization results in complete scrambling of all the carbon atoms (1,209,600 interconvertible permutations).[3,4] In this communication, we wish to describe an exceptionally facile synthetic entry into the azabullvalene (azatricyclo[3.3.2.0^{2,8}]deca-3,6,9-triene) system. The subsequent report[5] deals with the intriguing temperature-dependent nmr spectrum of a monomethoxy derivative.

First, slow addition of chlorosulfonyl isocyanate to cyclooctatetraene[6] in the absence of solvent at 50° led in 73% yield to an N-(chlorosulfonyl) lactam (**1**), mp 85–86.5°.[7,8] Reduction of **1** proceeded smoothly (98% yield) with thiophenol and pyridine in acetone at 0°[9] with loss of the chlorosulfonyl group to produce C_9H_9NO (**2**), mp 139–140°.[7] The structure of this lactam (**2**) was deduced from its spectral parameters[10] [$\nu_{\max}^{\mathrm{CHCl_3}}$ 1685 cm^{-1}, $\lambda_{\max}^{\mathrm{CH_3CN}}$ 266 mμ (ϵ 3100), very little change upon addition of acid, $\delta_{\max}^{\mathrm{CDCl_3}}$ 3.63 (multiplet, 1 H, >CHC(=O)–), 4.07 (multiplet, 1 H, >CHNH–), 5.93 (multiplet, 6 H, vinyl protons), and 8.07 (broad singlet, 1 H, >NH)[11]] and by its catalytic reduction with the absorption of six atoms of hydrogen to **3**, mp 157°.[7,12] Independent synthesis of **3** was effected from the known bicyclo[4.2.1]nonan-9-one (**4**).[13] Oximation of the carbonyl group and subsequent Beckmann rearrangement of the resulting oxime **5** produced **3** in very low yield as the sole characterizable product.



With the secure establishment of structure **2** comes the realization that the formation of **1** represents a unique example of 1,4 cycloaddition to cyclooctatetraene.[14] Likewise, it appears to be the first example of conjugate addition for the chlorosulfonyl isocyanate reagent.[15] A possible mechanistic rationale for the



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[1] Unsaturated Heterocyclic Systems. XXXII. For paper XXXI, see L. A. Paquette and D. E. Kuhla, *Tetrahedron Letters*, in press.

[2] For a recent review, consult G. Schröder, J. F. M. Oth, and R. Merenyi, *Angew. Chem. Intern. Ed., Engl.*, 4, 752 (1965).

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

[4] G. Schröder, *Chem. Ber.*, **97**, 3140 (1964).

[5] L. A. Paquette, T. J. Barton, and E. B. Whipple, *J. Am. Chem. Soc.*, **89**, 5481 (1967).

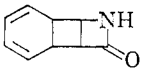
[6] We wish to thank Badische Anilin und Soda Fabrik for a generous gift of cyclooctatetraene.

[7] Satisfactory elemental analyses were obtained for all new compounds.

[8] On one occasion the chlorosulfonyl isocyanate–cyclooctatetraene mixture exploded violently ~1 hr after the completion of addition. Due to the approximate time of the explosion (3 AM), no witnesses were present; however, the extensive distribution of broken glass and black tar in the laboratory suggests that proper safety precautions should be enforced in the execution of this experiment.

[9] R. Graf, *Ann.*, **661**, 111 (1963).

[10] These data effectively removed the following logical alternative structures from consideration.



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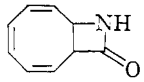

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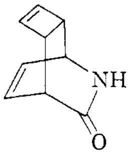
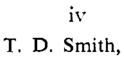


iii

[11] A satisfying nmr parallel is found in the spectra of the 2-pyridone photodimers: L. A. Paquette and G. Slomp, *J. Am. Chem. Soc.*, **85**, 765 (1963).

[12] The possible formation of ii under these conditions was further denied by the independent synthesis of iv (mp 76°) from chlorosulfonyl isocyanate and cyclooctene: Farbwerke Hoechst A.-G., Netherlands Patent Application 6,504,300; *Chem. Abstr.*, **64**, 8135 (1966).



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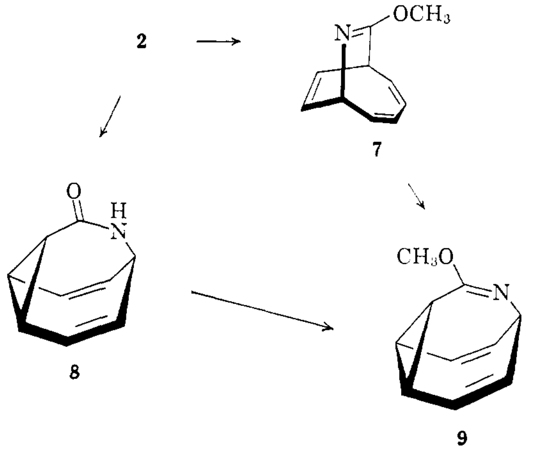
[13] C. D. Gutsche and T. D. Smith, *J. Am. Chem. Soc.*, **82**, 4067 (1960). We are indebted to Professor Gutsche for a generous sample of ketone 4.

[14] To our knowledge, only four examples (all radical in nature) of 1,4 addition to cyclooctatetraene are known: α-cyanoisopropyl radicals, J. L. Kice and T. S. Cantrell, *J. Am. Chem. Soc.*, **85**, 2298 (1963); difluoramino radicals, T. S. Cantrell, *J. Org. Chem.*, **32**, 911 (1967); cyanonitrene, A. G. Anastassiou, *J. Am. Chem. Soc.*, **87**, 5512 (1965); dinitrogen tetroxide (as ·NO_2), H. Shechter, J. J. Gardikes, T. S. Cantrell, and G. V. D. Tiers, *ibid.*, **89**, 3005 (1967).

[15] The addition of chlorosulfonyl isocyanate to derivatives of 1,3-butadiene reportedly results in open-chain amide formation: H. Hoffmann and H. J. Diehr, *Tetrahedron Letters*, 1875 (1963).

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, $-\mathrm{OCH_3}$ 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.

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(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.

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Received July 27, 1967

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-

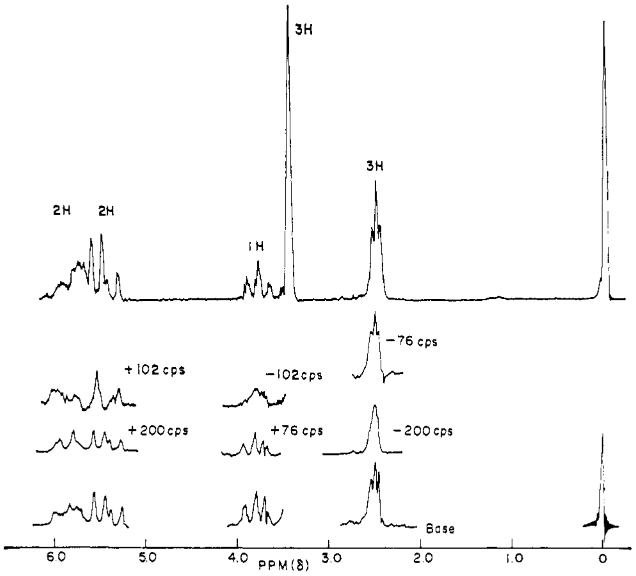
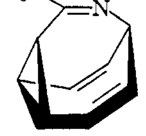


Figure 1. Upper curve: nmr spectrum of methoxyazabullvalene (I) in CCl₄ solution at ~38°. Lower section: spin decoupling (~38°) of I in CS₂ solution; values indicate the relative location of the applied stationary radiofrequency.



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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 CS₂, δ 3.40; in CCl₄, 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).