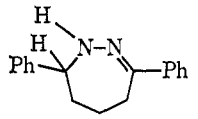
Imine oxaziridine structure **8** is especially ruled out by the spectroscopic data[14] as well as the observed chemistry of **6**. The $LiAlH_4$ and thermal reactions as well as the unusual stability of **6** in acid are inconsistent with the expected properties of an oxaziridine structure.[3,16]

The remarkable thermal stability of **6** (12-hr half-life in refluxing diglyme) and its inability to revert thermally to **3** are consistent with the qualitative predictions of Woodward and Hoffmann for systems such as this.[17]

The formation of the four-membered-ring azoxy compound from this photolysis of an azine monoxide represents the *first authentic example* of an electrocyclic, ring-forming reaction in a diazabutadiene system. No analogous reactions of cyclic or acyclic azines have thus far been able to be detected.

Acknowledgment. We are pleased to acknowledge support of this work by the Petroleum Research Fund (Grant No. 3521-A1,4), administered by the American Chemical Society, and by the Research Corporation.

(14) The uv spectrum of compound i,[15] which is a reasonable model



i

λ_{max} 290 mμ (ε 5370)

structure for **8**, is inconsistent with the observed uv spectrum of compound 6.

(15) C. G. Overberger and J. G. Lombardino, *J. Am. Chem. Soc.*, 80, 2317 (1958).

(16) For a summary of oxaziridine properties see E. Schmitz, "Dreiringe Mit Zwei Heteroatomen," Springer-Verlag, Berlin, 1967.

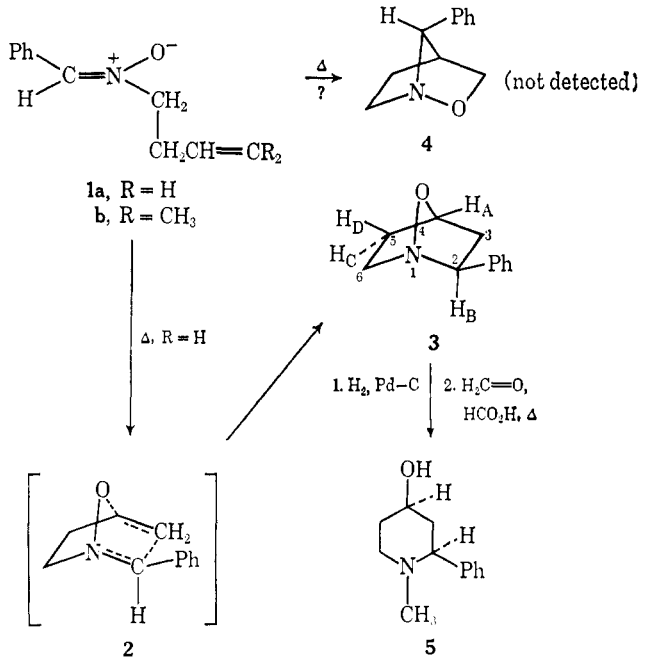
(17) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1, 17 (1968).

William R. Dolbier, Jr., W. Michael Williams
Department of Chemistry, University of Florida
Gainesville, Florida 32601
Received February 25, 1969

exo-2-Phenyl-1-aza-7-oxabicyclo[2.2.1]heptane, a Novel Heterobicyclic Ring System

Sir:

The present paper reports the synthesis of the title compound by a new mechanisticly significant mode of intramolecular 4 + 2 cycloaddition of a nitrone to a double bond. Slow fractional distillation, or refluxing in xylene (10% w/v) for 24 hr, of N-1-buten-3-yl-*anti*-benzaldoxime (**1a**)[1-3] afforded a basic product (bp 88–92° (0.005 mm), 72%) from which was isolated a crystalline picrate (mp 139–140°, $CHCl_3$, 87.3%).[2] Treatment of the picrate with aqueous sodium carbonate gave a colorless liquid isomer of **1a**.[2,7] The ir spectrum



of this material indicated no olefin absorption and lacked the characteristic nitrone bands at 1585 and 1150 cm^{-1}.[8] The nmr spectrum (100 MHz) showed two low-field hydrogens expected of structure **3** but not of **4**. A broad triplet at δ 4.88 (J = 4.8 Hz) is assignable to H_A which should be coupled nearly equally to the *exo* hydrogens at C_3 and C_5 and negligibly to the *endo* hydrogens.[9] The expected doublet of doublets for H_B is observed at δ 3.80 (J = 5.2, 8.0 Hz). A 13-line multiplet centered at δ 2.99 is assigned to the methylene hydrogens at C_6 since this is not coupled to H_A or H_B according to spin-decoupling experiments. The eight-line multiplet centered at δ 1.56 is assigned to H_C (*endo*-C_5) since this signal collapses to a broad doublet ($J \sim 11$ Hz) and a broad quartet ($J \sim 11$, 7.5 Hz) when the δ 2.99 multiplet is irradiated at its center and at the center of its low-field half, respectively. A first-order approximation assuming coupling constants summarized in Table I is remarkably similar (eight lines allowing for superpositions) to the observed pattern for H_C.

Table I. Summary of Coupling Constants (in Hertz) in Bicyclo[2.2.1]heptanes

	Bicyclo[2.2.1]-heptanes[9]	3[a,b]
$J_{endo-endo}$	8.9	8.0
$J_{endo-exo}$	2.3	5.2
J_{A-exo}	~4	4.8
J_{A-endo}	~0	~0
J_{CD}	12.0[9c]	~11

[a] Assumed equal to line spacings. [b] Sign not implied.

Final confirmation of structure **3** and *exo*-C_2 stereochemistry came from hydrogenolysis (Pd–C) followed by methylation with formaldehyde and formic acid to

(1) Prepared in 42% yield by alkylation of the sodium salt of *anti*-benzaldoxime[4,5] with 1-iodo-3-butene.[6]

(2) Satisfactory microanalyses have been obtained for all new compounds reported herein.

(3) Bp 105–107° (0.01 mm); $\nu_{max}^{CHCl_3}$ 3060, 2950, 1640, 1585, 1150, 993, 943, 920 cm^{-1}; nmr^{DMSO-d_6} (δ ppm, TMS) 8.32 (2 H, m), 7.88 (1 H, s), 7.42 (3 H, m), 6.25–6.50 (3 H, m), 4.03 (2 H, t, J = 7Hz), 2.65 (2 H, m, J = 7 Hz).

(4) E. Buehler, *J. Org. Chem.*, 32, 265 (1967).

(5) E. F. Schoenewaldt, R. B. Kinnel, and P. Davis, *ibid.*, 33, 4270 (1968).

(6) L. Kaplan, *Chem. Commun.*, 754 (1968).

(7) Bp 90° (0.005 mm); $\nu_{max}^{CHCl_3}$ 2960, 1490, 1450, 1280, 995, 875, 830 cm^{-1}; mol wt (osmometric in benzene) 173, 176 (calcd 175.22).

(8) J. Thesing and W. Sirrenberg, *Chem. Ber.*, 92, 1748 (1959).

(9) See: (a) J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.*, 85, 2514 (1963), for coupling constants in some bicyclo[2.2.1]heptane derivatives; (b) F. A. Anet, *Can. J. Chem.*, 39, 789 (1961); (c) R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron Suppl.*, 7, 355 (1966).

cis-1-methyl-2-phenyl-4-piperidinol (**5**). The degradation amino alcohol was identical according to infrared spectra and mixture melting point with an authentic sample of **5**.[2,10,11]

The bridged bicyclic isoxazolidine (**3**) is the first reported example of the 1-aza-7-oxabicyclo[2.2.1]-heptane ring system.[13] Intramolecular additions of nitrones to unconjugated olefins in alkyl or cycloalkyl groups attached to the nitrone carbon atom led to bridged[14] and fused[15] bicyclic isoxazolidines. Intramolecular addition of a nitrone to an alkenyl group attached to the nitrone nitrogen atom as in the present study uniquely places both hetero atoms at the one-atom bridge and bridgehead positions.

Inspection of Dreiding models of nitrone **1a** indicates that significant σ overlap between O and C_4 and C_2 and C_3 in transition state **2** cannot develop simultaneously unless the latter assumes product-like geometry. A concerted pathway[16] for the formation of **3** is proposed although arguments in favor of a stepwise, diradical mechanism for 1,3-dipolar cycloaddition reactions have recently been made.[17] Geometric restrictions on the transition state **2** make this reaction an ideal case for study of kinetic solvent effects as a probe for transition-state geometry and other points of argument. The high orientational selectivity of this reaction argues strongly against the intervention of one of the four possible and closely similar diradicals (Firestone mechanism).[18] Preferential formation of **3** rather than **4** by a concerted pathway may be due to steric destabilization of the transition state for formation of the latter. Nitrone **1b** gives no isoxazolidine under conditions which cyclize **1a** in high yield, indicating again that steric affects play an important role in this mode of cyclization. Experiments are in progress to determine the scope and mechanistic significance of this type of intramolecular cycloaddition reaction as well as the chemical and physical properties of the new heterobicyclic ring systems produced.[19]

(10) Prepared by $LiAlH_4$–$AlCl_3$ reduction[12] of the previously reported, but incompletely characterized,[2] 1-methyl-2-phenyl-4-piperidone: K. Hohenlohe-Oehringen, *Monatsh.*, **94**, 1222 (1963).

(11) Mp 87–88° (sublimed); $\nu_{max}^{CHCl_3}$ 3346, 2930, 2780, 1450, 1370, 1150, 1055, 1017, 979 cm^{-1}; nmr^{CDCl_3} (100 MHz, δ ppm, TMS) 7.28 (5 H, finely split singlet), 3.84 (1 H, 7 of 9 lines, J = 11, 4.5 Hz), 3.09 (3 H, 11 lines), 2.67 (1 H, s), 2.11 (3 H, s), 2.06 (4 H, complex).

(12) This reduction gives equatorial cyclohexanols with >99% stereoselectivity: E. L. Eliel and M. N. Rerick, *J. Am. Chem. Soc.*, **82**, 1367 (1960).

(13) A 5,6-benzo analog of **3** is reportedly formed by a 2 + 4 cycloaddition of N-phenylmaleimide to 3,4-benzisoxazole: C. D. Nenitzescu, E. Cioranescu, and L. Birladeanu, *Comm. Acad. Rep. Populare Romine*, **8**, 775 (1958); *Chem. Abstr.*, **53**, 18003 (1959).

(14) N. A. LeBel, G. M. J. Slusarczuk, and L. A. Spurlock, *J. Am. Chem. Soc.*, **84**, 4360 (1962).

(15) N. A. LeBel, M. E. Post, and J. J. Whang, *ibid.*, **86**, 3759 (1964).

(16) R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968).

(17) R. A. Firestone, *ibid.*, **33**, 2285 (1968).

(18) Suggested by a referee.

(19) This work was generously supported by the Department of Chemistry, Saint Louis University. Support from National Science Foundation Grant No. GP-8510 for the 100-MHz nmr spectrometer is gratefully acknowledged.

William C. Lumma, Jr.
Department of Chemistry, Saint Louis University
Saint Louis, Missouri 63156

Received February 12, 1969

Book Reviews

Acetylenic Compounds. Preparation and Substitution Reactions. By THOMAS F. RUTLEDGE, Atlas Chemical Industries, Inc., Wilmington, Del. Reinhold Book Corp., 430 Park Ave., New York, N. Y. 1968. xvii + 342 pp. 16 × 23.5 cm. $20.00.

This book is the first of two on the chemistry of acetylenic compounds. In it the preparation, substitution reactions, and some uses of these compounds are discussed. The second book, by the same author, promised for early publication, will cover the preparation of allenic compounds as well as addition reactions involving acetylenic and allenic bonds.

The author admits at the outset the impossibility of comprehensive coverage in two medium-length books of recent progress in the chemistry of acetylenic and allenic compounds. Instead he sets as his objective "to include enough details of the most important reactions of all kinds of acetylenic compounds to furnish interested chemists with a good background and with leads into the pertinent literature." He accomplishes this objective very well. The "informative writing" style adopted is clear and surprisingly readable. Critical evaluation of the material presented is seldom attempted, but the literature of the last 10–15 years is covered quite completely. Although it is stated that "mechanisms are emphasized," this emphasis consists mainly of reasonable mechanistic formulations of a number of the reactions discussed. Physical organic chemical investigations to establish these mechanisms are seldom presented; indeed it is often true that none has been carried out.

The organization of the book is excellent and arrangement of references convenient. A brief chapter on physical (bond lengths, molecular radii, solubility) and chemical properties (acetylenes as H-bonding acids or bases, intermolecular association, donor capacity, structure, and acidity) is followed by an all-too-brief chapter on experimental aids. Explosive hazards are mentioned wherever appropriate throughout the book, but especially here; the section is rather incomplete and the hazards of certain compounds (*e.g.*, diacetylene) appear to be underemphasized. Treatment of purification, detection, analysis, and identification is extremely brief (*e.g.*, the one reference of glpc of acetylenes is good, but others should be cited). Useful references to ir spectra of acetylenes are given, and the section on nmr is well done. The chapter on preparation of acetylenic compounds by elimination reactions, while short, is a gold mine of references presented in a clear and usable fashion.

The first of two long chapters on reactions of acetylenic compounds discusses replacement of acetylenic hydrogen by other elements. Orderly division into six sections involves progression through the groups of the periodic table. The reader should be aware that coverage is incomplete. For example, under laboratory conditions it is often more convenient to prepare sodium acetylide by passage of acetylene into liquid ammonia as sodium is being dissolved in the solvent, yet this is not mentioned. Alkylation of sodium acetylide in liquid ammonia, often better than alkylation in organic diluents, is not discussed. Iodoacetylene and diiodo-