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-

acetylene are not included, while other haloacetylenes are. The chapter is nevertheless a useful one.

The second long chapter, on ethynylation and alkynylation, is very well done. A list of earlier reviews is included and the recent literature is covered in some detail. The chapter has sections on dicarbonyl compounds in these reactions and on the Mannich reaction with acetylenes.

The final three chapters (coupling of acetylenic compounds; cyclic and macrocyclic acetylenes; acetylenic compounds as drugs) are short but present excellent reviews of these topics.

Dr. Rutledge is an industrial research chemist of long experience in the field of acetylenic compounds. His book has a flavor of the practical that is welcome; his sense of the direction that the commercial development of the field is likely to take rings true. At the same time he is familiar with the important developments throughout the field without prejudice as to their industrial potential, and he presents these developments concisely. His book should certainly be available through technical libraries not only to chemists working in the field but to all organic chemists who might want to employ this most useful class of compounds. The reactions have intriguing variety, and the book should serve as a source of new ideas. Those in the field would find it a rewarding book to own although the cost seems high.

Thomas L. Jacobs

Department of Chemistry, University of California
Los Angeles, California

BOOKS RECEIVED, *March 1969*

A. Albert Baker, Jr. "Unsaturation in Organic Chemistry." Houghton Mifflin Co., 110 Tremont St., Boston, Mass. 1968. 136 pp. $2.95.

Cornelius K. Cain, Editor-in-Chief. "Annual Reports in Medicinal Chemistry, 1967." Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1968. 374 pp. $7.95.

A. O. Fitton and R. K. Smalley. "Practical Heterocyclic Chemistry." Academic Press Inc. (London) Ltd., Berkeley Square House, Berkeley Square, London, W.1., England. 1968. 146 pp. 35 s.

John H. Holloway. "Noble-Gas Chemistry." Barnes and Noble, Inc., 105 Fifth Ave., New York, N. Y. 1968. 213 pp. $6.75.

D. A. Johnson. "Some Thermodynamic Aspects of Inorganic Chemistry." Cambridge University Press, 32 East 57th St., New York, N. Y. 1968. 224 pp. $7.50.

T. J. Mabry, Editor. "Recent Advances in Phytochemistry." Volume 1. "Proceedings of the Sixth Annual Symposium of the Phytochemical Society of North America." Appleton-Century-Crofts, 440 Park Ave. South, New York, N. Y. 1968. 437 pp. $16.50.

E. F. Mooney, Editor. "Annual Review of NMR Spectroscopy." Volume 1. Academic Press Inc. (London) Ltd., Berkeley Square House, Berkeley Square, London, W.1., England. 1968. 353 pp. $14.00.

Leo A. Paquette. "Principles of Modern Heterocyclic Chemistry." W. A. Benjamin, Inc., 2 Park Ave., New York, N. Y. 1968. 401 pp. $11.95.

G. D. Parkes, Revised and Edited by. "Mellor's Modern Inorganic Chemistry." John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1968. 1025 pp. $7.00.

C. N. R. Rao. "Ultra-Violet and Visible Spectroscopy. Chemical Applications." Plenum Publishing Corp., 227 West 17th St., New York, N. Y. 1967. 210 pp. $10.00.

Meldrum B. Winstead. "Organic Chemistry Structural Problems." Sadtler Research Laboratories Inc., 3316 Spring Garden St., Philadelphia, Pa. 1968. 258 pp. $4.95.

M. Zander. "Phosphorimetry. The Application of Phosphorescence to the Analysis of Organic Compounds." Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1968. 206 pp. $10.00.