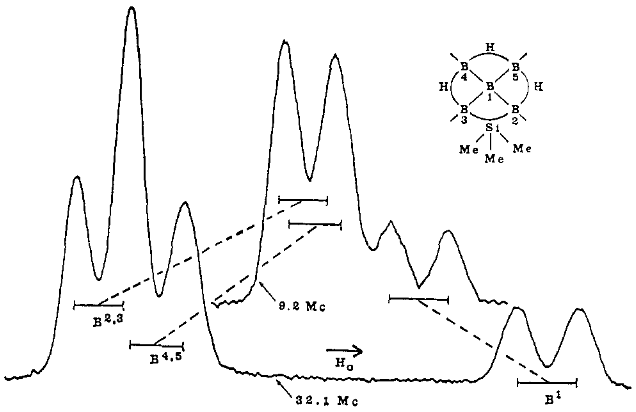


Figure 1. The ^{11}B nmr spectra of μ-Si(CH$_3$)$_3$B$_5$H$_8$ at 32.1 and 9.2 Mc. The assignments, chemical shifts (ppm from $BF_3 \cdot O(C_2H_5)_2$), and coupling constants (cps in parentheses) are: B^{2,3}, 8.5 (145); B^{4,5}, 13.2 (158); B^1, 48.0 (179).

The higher field doublet in this group has a chemical shift and coupling constant very nearly the same as that of B_5H_9 and has therefore been assigned as arising from B^{3,4}. The lower field doublet, arising from B^{2,3}, has a coupling constant somewhat smaller than usual, probably as a result of bonding of those boron atoms to the bridge silyl group. The 100-Mc ^{1}H nmr spectrum of μ-(CH$_3$)$_3$SiB$_5$H$_8$ agrees with the ^{11}B spectrum. Integration of the bridge and terminal hydrogen regions gives values which agree with those calculated, assuming five terminal and three bridge hydrogens.

Isomerization of μ-(CH$_3$)$_3$SiB$_5$H$_8$ to 2-(CH$_3$)$_3$SiB$_5$H$_8$ occurs at room temperature in the presence of dimethyl ether. After 1 day, 94% of the starting material was recovered as the 2 isomer, identified by its mass spectrum (which is indistinguishable from that of the bridge isomer) and by its ^{11}B and ^{1}H nmr spectra. Integration of the ^{1}H nmr spectrum agreed with that calculated, assuming four bridge and four terminal hydrogen atoms.

Bromination of μ-(CH$_3$)$_3$SiB$_5$H$_8$ occurs rapidly at room temperature to produce 1-Br-μ-(CH$_3$)$_3$SiB$_5$H$_7$ in moderate yield. A single crystal X-ray study of this compound is presently under way in the laboratory of Professor Lawrence F. Dahl.

The bonding in the silicon bridge of μ-(CH$_3$)$_3$SiB$_5$H$_8$ can be viewed as similar to that suggested for the carbon bridge in dimeric trimethylaluminum.[4] Thus a three-center two-electron bond is probably formed using sp^3 orbitals from the silicon and the two adjacent boron atoms. There appear to be no previous examples of compounds in which silicon atoms are thought to participate in electron-deficient bonding.

Several other preliminary investigations suggest that trialkylgermanium and -tin halides react with LiB$_5$H$_8$ in the same manner as trimethylsilyl chloride to produce the corresponding bridged pentaborane(9) derivatives. There is no evidence as yet, however, for the existence of stable pentaborane(9) derivatives having carbon bridges between boron atoms.

Further studies of group IV bridged boron hydride derivatives are in progress and will be published shortly.

Acknowledgments. The authors wish to thank Dr. Jerry E. Dobson and Arthur O. Clause at Indiana University for the 9.2-Mc ^{11}B nmr spectra. This work was supported in part by a grant from the National Science Foundation. The nmr instrumentation was provided in part by an institutional grant from the National Science Foundation.

(4) P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, 21, 986 (1953).

Donald F. Gaines, Terry V. Iorns
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received May 25, 1967

Additions and Corrections

The Donor Properties of Pyrophosphate Derivatives. III. A Colorless Copper(II) Complex [*J. Am. Chem. Soc.*, **88,** 5465 (1966)]. By MELVIN D. JOESTEN and JAMES F. FORBES, Department of Chemistry, Southern Illinois University, Carbondale, Illinois 62903.

In Table III the experimental magnetic moments should be expressed as an average magnetic moment/metal ion. This results in values of 2.04, 2.04, 5.24, and 5.24 BM for [Cu(OMPA)$_2$][CuBr$_4$], [Cu(OMPA)$_2$][CuCl$_4$], [Co(OMPA)$_3$][CoBr$_4$], and [Co(OMPA)$_3$][CoCl$_4$], respectively. The calculated magnetic moments/metal ion from the spin-only formula are 1.73 BM for Cu(II) and 3.88 BM for Co(II).

On Hydroxyalkylcobaloximes and the Mechanism of a Cobamide-Dependent Diol Dehydrase [*J. Am. Chem. Soc.*, **89,** 143 (1967)]. By G. N. SCHRAUZER and R. J. WINDGASSEN, Shell Development Company, Emeryville, California.

On page 147, the side heading in the first line should read: Degradation of β-Hydroxy-*n*-propylpyridinatocobaloxime.

Catalytic Reactions Involving Azomethines. VIII. Water and Alanine Catalysis of the Transamination of 3-Hydroxypyridine-4-aldehyde by Alanine [*J. Am. Chem. Soc.*, **89,** 2090 (1967)]. By DAVID S. AULD and THOMAS C. BRUICE, Department of Chemistry, University of California at Santa Barbara, Santa Barbara, California 93106.

Equation 12 should read as follows

$$k_{\mathrm{I}} = \frac{(k'_{\mathrm{H_2O},3}a_{\mathrm{H}}{}^3 + k_{\mathrm{H_2O},3}a_{\mathrm{H}}{}^2 + k_{\mathrm{H_2O},1}K_{\mathrm{S^+}}a_{\mathrm{H}})\left(\dfrac{KK_{\mathrm{PCHO^+}}K_{\mathrm{PCHO}}K_{\mathrm{AH}}K_{\mathrm{AH_2}}[\mathrm{H_2O}]}{K_{\mathrm{S}}K_{\mathrm{S^+}}}\right)}{\left[\left(\dfrac{K_{\mathrm{PCHO^+}}}{K_{\mathrm{B}}} + 1\right)a_{\mathrm{H}}{}^2 + K_{\mathrm{PCHO^+}}(K_{\mathrm{Z}} + 1)a_{\mathrm{H}} + K_{\mathrm{PCHO^+}}K_{\mathrm{PCHO}}\right](a_{\mathrm{H}}{}^2 + K_{\mathrm{AH_2}}a_{\mathrm{H}} + K_{\mathrm{AH}}K_{\mathrm{AH_2}})} \tag{12}$$

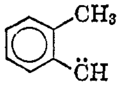
Catalytic Reactions Involving Azomethines. IX. General Base Catalysis of the Transamination of 3-Hydroxypyridine-4-aldehyde by Alanine [*J. Am. Chem. Soc.*, **89,** 2098 (1967)]. By DAVID S. AULD and THOMAS C. BRUICE, Department of Chemistry, University of California at Santa Barbara, Santa Barbara, California 93106.

At the bottom of eq 7 the following definition should be added.

$$k_{\mathrm{B},3}' = k_{\mathrm{B},3}/K_{\mathrm{SH^+}}$$

The Vacuum Ultraviolet Photochemistry of *o*-Xylene [*J. Am. Chem. Soc.*, **89,** 2367 (1967)]. By HAROLD R. WARD, Metcalf Chemical Laboratories, Brown University, Providence, Rhode Island 02912.

In the first group of structure drawings on page 2371, the bottom structure of the group should be

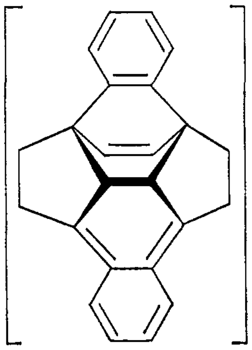


New Heteroaromatic Compounds. XXV. Studies of Salt Formation in Boron Oxyacids by ^{11}B Nuclear Magnetic Resonance [*J. Am. Chem. Soc.*, **89,** 2408 (1967)]. By MICHAEL J. S. DEWAR and RICHARD JONES, Department of Chemistry, The University of Texas, Austin, Texas 78712.

In Table I the value of δ_{EBT} for 10-hydroxy-10,9-borazarophenanthrene (I) in EtOH should read -29.3 ppm and not -36.8 ppm as indicated.

Dibenzoequinene. A Novel Heptacyclic Hydrocarbon from the Photolysis of [2.2]Paracyclonaphthane [*J. Am. Chem. Soc.*, **89,** 2770 (1967)]. By HARRY H. WASSERMAN and PHILIP M. KEEHN, Department of Chemistry, Yale University, New Haven, Connecticut 06520.

On page 2771 formula III should be



III

Book Reviews

Indole Alkaloids, An Introduction to the Enamine Chemistry of Natural Products. By W. I. TAYLOR, CIBA Pharmaceutical Company. Pergamon Press, Inc., 44-01 21 St., Long Island City, N. Y. 1966. xi + 148 pp. 13 × 19.5 cm. $4.50.

This book represents a lucidly written introduction to the chemistry of indole alkaloids. It skims the surface of the large field of present-day research therein and thus only whets the appetite of the potential scholar in the field. Its strength lies in its compactness, but its weakness derives from its potential appeal to only a limited reading audience. While the book may be of aid to the beginning graduate student entering the field of alkaloid research, it is too cursory a test to be of value to the advanced worker and loses in competition with exhaustive review books, *e.g.*, Manske's "The Alkaloids."

While thus of limited value in research, the book is also unlikely to score well in teaching. This is no fault of the author who makes a valiant attempt to make the chemistry of indole alkaloids appear alive, but rather reflects the subtle requirements of teaching the chemistry of natural products. Properly presented, a university course on the chemistry of natural products can be the high point of a graduate student's career, reviewing, strengthening, and collating his knowledge of organic chemistry, acquainting him with related scientific disciplines, and opening to him vast vistas of new research ideas. Improperly taught, such a course can be extraordinarily stale and can be the most effective means of making physical-organic chemists (or even less respectable chemists) out of budding young natural-products scientists. One of the drabbest methods of presentation of an organic natural products course is in the form of a survey of the field ("taxonomic chemistry"). Perhaps the most refreshing and forever-changing mode of delivery of such a course (with different, never repeating contents every year) is in terms of rigorous, critical analyses of recent research data of a limited number of natural products of chemical significance. Fortunately no book is needed nor can any be written for such a special topics course.

While the book had extraordinarily few mistakes (*e.g.*, page 30, line 17, "... molecule..." should read "... molecular..."), it does incorporate some flaws that are worthy of correction. For example, Chart 3.2 shows the detailed mechanism of the intriguing, thermally induced unravelling of akuammicine (the mechanism of the migration of the ethylidene double bond into the piperidine ring is portrayed meaninglessly by an arrow in the fourth formula), but omits the mechanistic details of the perhaps most interesting chemical change in the last step(s). The discussion of stereochemistry on pages 68–70 represents a slight rewriting of history. [The stereochemical problems were not resolved by the total synthesis of ajmalicine (since it, as the earlier degradation of the alkaloid, had proceeded through the potentially stereochemically ambiguous 19-ketone), but rather by complete degradation of tetrahydroalstonine and correlation of the degradation products with those of ajmalicine (omitted in the book) as well as by the "measurement of rates of alkylation and the proton topology deduced from nuclear magnetic resonance spectra" (cited in the book).]

The past few years have seen a growing expansion of the market of scientific books accompanying the logarithmic increase of publications in scientific journals. Sometimes the books have been of value in chemical research, although often they are reviews which more advantageously (especially for the scientists' pocketbooks) could find space in review journals. More frequently they occupy