

B_5H_8 .⁴ This isomerization, when catalyzed in the vapor phase by $(CH_3)_2NB_2H_5$, does not depend upon transfer of BH_3 groups, for only 4% of a sample of 1- $CH_3B_5H_8$ isomerized during a one-boron B^{10} - B^{11} exchange with $(CH_3)_2NB_2H_5$ at 100°. This and other boron isotopic exchanges will be described more fully elsewhere.

For the volatility of 2- $CH_3B_5H_8$ (m.p. -55°, $\log P = 6.889 + 1.75 \log T - 0.0065T - 2212/T$ (accuracy as in Table II; example, 19.0 mm. at 0°); thus it is roughly half as volatile as 1- $CH_3B_5H_8$ (34 mm. at 0°).⁵

Infrared Spectra. The infrared peaks shown in Table III were recorded accurately by the Beckman IR7 instrument. After each frequency (cm^{-1}) the relative intensity $k = (100/P) \log I_0/I$ (path 10 cm.; pressure P in mm. at 25°) is given in parentheses. Assignments are omitted because they would be either obvious or controversial.

(4) T. P. Onak, *J. Am. Chem. Soc.*, **83**, 2584 (1961).

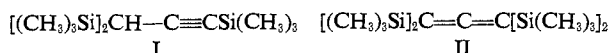
(5) G. E. Ryschkewitsch, *et al.*, *Inorg. Chem.*, **2**, 891 (1963).

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The Tetralithium Derivative of Propyne and Its Use in Synthesis of Polysilicon Compounds

Sir:

Polymetalation of 1-alkynes has been observed recently in several laboratories. Eberly and Adams have reported the reaction of 1-butyne with excess alkyl-lithium reagent to form a dilithium derivative.¹ We find that propyne reacts with *n*-butyllithium in hexane to form a tetralithium compound, C_3Li_4 , perhaps admixed with some C_3Li_3H . Derivatization of the poly-lithiated propyne with trimethylchlorosilane leads to a mixture consisting mostly of the tri- and tetrasilyl derivatives I and II.



In a typical experiment propyne (10.4 g., 0.20 mole) was added slowly to 500 ml. of 1.6 *M* *n*-butyllithium in hexane, and the red-brown solution was heated to reflux for 16 hr. During this time butane was fractionated from the mixture through a short column, a total of 3.5 equiv. being recovered. Trimethylchlorosilane (135 ml., 1.0 mole) was then added and the mixture was refluxed again for 16 hr., after which time 150 ml. of 1,2-dimethoxyethane was added and refluxing was continued for an additional 2 hr. The precipitated lithium chloride was filtered off and the solvents were removed by distillation. The residue was separated by fractional distillation under vacuum, yielding 27 g. of I (b.p. 80–85°, 19 torr) and 17 g. of II (b.p. 119–121°, 19 torr) (50 and 25%, respectively, based on propyne). *Anal.* Calcd. for $C_{12}H_{28}Si_3$ (compound I): C, 56.21; H, 11.01; Si, 32.80; mol. wt., 256. Found: C, 56.36; H, 10.88; Si, 32.89; mol. wt., 256.² Calcd.

(1) K. C. Eberly and H. E. Adams, *J. Organometal. Chem.*, **3**, 165 (1965).

(2) Molecular weights by mass spectroscopy using a C.E.C. Model 21-101C spectrometer with an inlet temperature of 200°.

for $C_{15}H_{36}Si_4$ (compound II): C, 54.77; H, 11.04; Si, 34.19; mol. wt., 328. Found: C, 54.22; H, 11.37; Si, 34.71; mol. wt., 328.²

In an experiment in which 6 equiv. of *n*-butyllithium was used for each equivalent of propyne, 3.85 equiv. of butane was recovered after 2-hr. reflux, indicating that the propyne was almost completely converted to the tetralithium derivative. Further refluxing for an additional 16 hr. led to the evolution of no more butane. Unchanged *n*-butyllithium was still present after this time, as shown by the isolation of 1.2 equiv. of *n*-butyltrimethylsilane (along with compounds I and II) upon derivatization with trimethylchlorosilane.

Compound I was identified as 1,3,3-tris(trimethylsilyl)propyne by its infrared and n.m.r. spectra. It shows a strong infrared band at 2180 cm^{-1} ($C\equiv C$ stretch)³ and no absorption in the region diagnostic for acetylenic C-H stretching (near 3300 cm^{-1}).³ The proton n.m.r. spectrum shows sharp resonances at τ 8.98, 9.90, and 9.92, with relative intensities 1:18:9, respectively, in agreement with the proposed structure. Thermolysis or photolysis effected substantially complete conversion of I to its allenic isomer 1,1,3-tris(trimethylsilyl)allene, which was separated by preparative gas chromatography. This isomer, which also had an analysis in agreement with the formula $C_{12}H_{28}Si_3$, had no infrared absorption in the acetylenic region, but showed a weak band at 3160 cm^{-1} (allenic C-H) and a strong band at 1910 cm^{-1} ($C=C=C$ antisymmetric stretching).⁴ The n.m.r. spectrum showed resonances at τ 5.90 (allenic H), 9.90, and 9.93 in the ratio 1:18:9.

The properties of the tetrasilyl derivative II show that it must also have an allenic structure. It shows no acetylenic C-C stretching absorption in the infrared but exhibits a strong band at 1890 cm^{-1} in the allenic region. The proton n.m.r. spectrum contains only a single sharp peak at τ 9.90.

Compound I is also somewhat acidic, reacting with *n*-butyllithium to form a monolithium derivative, which is converted to II in high yield upon treatment with trimethylchlorosilane. Isomerization from the acetylenic to the allenic structure could take place during formation of the lithium compound, but it seems more likely that it occurs during the reaction with trimethylchlorosilane. The formation of the unknown tetrakis(trimethylsilyl)propyne would be strongly hindered sterically, and so condensation with the fourth trimethylsilyl group may take place only after isomerization to the allenic form. Using similar arguments based on steric effects, Gilman and Aoki have explained the formation of poly(triphenylsilyl)acetylenes and -allenes, by different but related reactions.⁵

Polyolithiation appears to be a general reaction for 1-alkynes bearing α -hydrogen atoms. 1-Butyne, 1-hexyne, and 1-octyne have all been observed to form polyolithium derivatives. When 1-butyne is treated with excess *n*-butyllithium followed by trimethylchlorosilane under conditions similar to those described above, a mixture of the two isomers 1,1,3-tris(trimethylsilyl)-1,2-butadiene and 1,3,3-tris(trimethyl-

(3) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen and Co., London, 1958, pp. 58, 59.

(4) J. H. Wotiz and D. E. Marcuso, *J. Org. Chem.*, **22**, 207 (1957); L. J. Bellamy, *ref. 3*, pp. 61, 62.

(5) H. Gilman and D. Aoki, *J. Organometal. Chem.*, **2**, 44 (1964).

silyl)-1-butyne is obtained. The nature of the intermediate lithium compounds formed from 1-alkynes and their utility for the synthesis of other organometallic and organic derivatives are now under investigation.

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Book Reviews

Comparative Biochemistry. A Comprehensive Treatise. Volume VII. Edited by MARCEL FLORKIN, Department of Biochemistry, University of Liege, Liege, Belgium, and HOWARD S. MASON, University of Oregon Medical School, Portland, Ore. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1964. xix + 476 pp. 16 × 23.5 cm. \$15.00, registered; \$13.00, subscription.

Volume VII is the last volume in the series on "Comparative Biochemistry" edited by Professors M. Florkin and H. S. Mason. The pattern of this volume is similar to that of the earlier ones. The book, titled "Supplementary Volume," contains xix plus 476 pages. It contains an author index and a subject index, plus a topical subject index covering Volumes I through VII. The reviews in this volume number five.

The first chapter, titled "Expressions of the Pentose Phosphate Cycle," is by N. G. Pon. The comparisons drawn emphasize mainly the detailed knowledge of the cycle as it is manifest in various organisms and in various tissues of mammals, which represent roughly one-half of the species which have been studied. The treatment in higher plants concerns the reductive pentose phosphate cycle and the oxidative pentose phosphate cycle. In the Closing Remarks, Pon focuses on the difficult question of assigning degree of primitiveness to these metabolic pathways.

In Chapter 2, P. W. Kent reviews "Chitin and Mucosubstances." Much of this chapter is devoted to an elucidation of the chemical structure of chitin. Distribution and biosynthetic pathways are also reviewed, as are the relationships to mucosubstances.

In Chapter 3, Ernest Schoffeniels discusses "Cellular Aspects of Active Transport." This subject benefits particularly from the comparative, *i.e.*, evolutionary scrutiny, and our understanding of bioevolution may conversely be aided by more penetrating comprehension of the mechanisms of action at the cell boundary. Also valuable is the presentation of data and interpretation of amino acid transport by a representative of the Belgian school which has studied these phenomena extensively. The treatment in this chapter leaves unsolved the many questions resting upon the decision of whether transport is a function of enzymic activities in the membrane or is explainable on a simpler basis. For some the choice is no longer a matter of interpretation but one of a firm premise; Schoffeniels' chapter provides some moderating influence.

In Chapter 4, W. C. Young reviews "The Hormones and Behavior." This, the shortest of the chapters, presents a treatment which is somewhat general in nature. No tables or figures are included.

Chapter 5 on "The Comparative Biochemistry of Antibiosis and Antibiotics" is by Maurice Welsch. The presence of the words Antibiosis and Antibiotics in the same title calls to mind that, while Pasteur seems to have discovered antibiosis, his known bias for vitalistic concepts would have interfered with a search for antibiotics, the chemical principles of the phenomenon of antibiosis. One wonders if so many decades would have intervened between the discovery of antibiosis and the discovery of antibiotics if a mechanist had been responsible for the former. In the 20 years of the era of antibiotics much knowledge has been accumulated on

these typically atypical substances. Welsch treats them in a comparative mode, and as derivatives of salient classes of metabolites. The author has thought deeply about the definition of antibiotic and chooses finally to regard them as structurally diverse substances having selective toxicity. Many chemists will be interested to learn of the extent to which mechanisms of action of the most used antibiotics have been identified.

Many of the reviews in this series are of high quality. The editors are, now that this treatise is complete, to be congratulated for their monumental accomplishment. The thousands of biochemists who contributed to the areas of knowledge which are reviewed should be congratulated for their labors of detail. When one peruses or reads this treatise, he will be led to conclude that biochemistry, as a body of scientific knowledge, has attained a large measure of maturity. Also, this court record supporting Kluyver's principle of "the unity of biochemistry" is an overwhelming document which itemizes Baldwin's concept of a "common, fundamental chemical ground plan" and extends Darwin's comment on "... all living things have much in common, in their chemical composition ..."

In a phrase, the biochemistry of various organisms is a comparison much more than it is a contrast, and this appraisal of the facts strengthens the faith that our fullest understanding of life will ultimately rest basically on knowledge such as that first published in chemical journals.

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Polycyclic Hydrocarbons. Volumes 1 and 2. By E. CLAR, University of Glasgow, Scotland. Academic Press Inc., Ltd., Berkeley Square House, Berkeley Square, London W1, England. 1964. 16 × 24 cm. Vol. 1: xxvii + 487 pp. \$18.00. Vol. 2: lvii + 487 pp. \$21.50.

The second edition of Eric Clar's "Aromatische Kohlenwasserstoffe" was published in 1952, ten years after the appearance of his first edition. In 1952 it still appeared possible that the magnificent Elsevier's "Encyclopedia of Organic Chemistry" would continue to be published and would cover systematically and continuously the chemistry of the polycyclic hydrocarbons. Unfortunately, Elsevier's Encyclopedia was discontinued and it was necessary to rely on Beilstein with its limitations or hope that some knowledgeable and energetic author would continue Clar's admirable earlier work. How fortunate then, especially for readers of English, to have Clar himself, twelve years after the publication of the second edition of his German book, write these valuable treatises on polycyclic hydrocarbons.

Volume 1 is divided into two parts: Part I is devoted to what Clar calls "Kata-Annellated Hydrocarbons." Volume 2 is a