during part of this work is gratefully acknowledged. This work was supported by grants from the U. S. Public Health Service (Grant No. 3 R01 GM07262-07S1 PC), the Health Research Council of the City of New York (Grant No. U-1530), and the American Cancer Society (Grant No. P-476).

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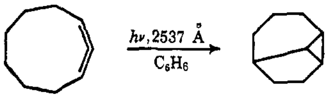
The Photolytic Conversion of an Allene to a Cyclopropylidene. The Photolysis of 1,2-Cyclononadiene[1]

Sir:

The ring opening of cyclopropylidenes to allenes is an efficient process. For example, the carbenoid species formed by the treatment of 9,9-dibromobicyclo[6.1.0]-nonane with methyllithium[2] gives 1,2-cyclononadiene in 81% yield.

The reverse of this process has been treated theoretically[3] but has not been observed experimentally. The first excited singlet and the lowest triplet states of allenes are both expected to have the substituents on the terminal carbon atoms of the allenic bond coplanar[4] which is the correct molecular geometry for closing to the cyclopropylidene. We have investigated the photolysis of 1,2-cyclononadiene, a compound in which the strain imposed by the ring should facilitate ring closure.

The benzene-sensitized photolysis of 1,2-cyclononadiene in vapor phase[5] at 2537 Å yields one major product, tricyclo[3.3.0.0^{2,9}]nonane (I). The structure of I was assigned on the basis of the identity of spectra and of chromatographic behavior with that of an independently synthesized sample.[6] The nmr spectrum[7] (CCl_4) consisted of four unresolved multiplets at τ 7.4, 8.2, 8.6, and 9.2. The ir spectrum showed an absorption band at 3045 cm^{-1}; the mass spectrum[7] had a parent peak at *m/e* 122 and a fragmentation pattern similar to that of *cis*-hydrindan, but displaced by two mass units. The synthetic product and the photoproduct had identical glpc retention times on three columns.[8]



I

Compound I did not hydrogenate over 10% palladium on carbon in ethanol but under more drastic conditions (Pt, HOAc, $HClO_4$) yielded two products (*m/e* 124). One of these was identified as *cis*-hydrindan by glpc retention times and mass spectra.

The most reasonable pathway for the formation of I is the closing of the allene to the cyclopropylidene and subsequent transannular insertion of this species into the C–H bond. Such transannular insertions are known to occur in medium-ring carbenoid reactions.[9] At very low conversions (0.1%), a plot of % conversion *vs.* time gives a straight line, indicating that I is a primary product. At higher conversions (~10%) polymer formation is noticeable. The quantum yield for the formation of I was 0.17, based on a benzene-*cis*-2-butene actinometer.[10]

The benzene-photosensitized isomerization of olefins is generally assumed[11] to proceed by energy transfer from the first triplet state of benzene to give the antiplanar triplet of the olefin. If the allene photosensitization occurs by this path, it must be a nonvertical excitation, since transfer from benzene $^3B_{1u}$ (85 kcal)[12] to give planar triplet allene (~100 kcal)[4] is endothermic and therefore unlikely. Energy transfer from the $^1B_{2u}$ or the $^3E_{1u}$ states[13] seems improbable because of the short lifetimes of these states and the relatively high efficiency of the observed photosensitization. Since only 63% of the light absorbed by benzene produces the triplet state,[14] and if the sole energy transfer mode is triplet–triplet, then the actual conversion of excited allene to I is 28%.

We conclude, then, that most probably the triplet allene is either formed in its planar configuration[15] or is quickly deactivated to that state by collision. This molecular arrangement is suitable for closing to the cyclopropylidene, but Borden[3] has predicted on the basis of orbital symmetry considerations that this conversion should not occur in either a concerted conrotatory, disrotatory, or nonrotatory fashion. Closing from the first excited singlet allene can be excluded by similar arguments.

If the triplet allene is prevented from closing to the cyclopropylidene, the most reasonable remaining path for its disappearance is a radiationless transition to a planar, and therefore highly vibrationally excited, ground electronic state. This species, at the instant of its formation, is also suitably arranged for closure to the cyclopropylidene, and this closure appears to be symmetry allowed by a nonrotatory process. This crossing from one energy surface to another in "multi-

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[1] This research was supported by the National Aeronautics and Space Administration.

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[3] W. T. Borden, *Tetrahedron Letters*, 447 (1967).

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[5] Benzene/allene = 0.5, total pressure ~9 mm.

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[7] The nmr and mass spectrometers were purchased with funds supplied by the National Science Foundation.

[8] Retention times relative to 1,2-cyclononadiene: 10% Carbowax 20M (80°), 0.7; 15% TCEP (100°), 0.68; and 10% QF-1 (50°), 0.82.

[9] A. C. Cope and S. S. Hecht, *J. Am. Chem. Soc.*, **89**, 6920 (1967).

[10] M. Tanaka, M. Kato, and C. Sato, *Bull. Chem. Soc. Japan*, **39**, 1423 (1966).

[11] R. B. Cundall and P. A. Griffiths, *Trans. Faraday Soc.*, **61**, 1968 (1965).

[12] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, p 332.

[13] The idea of energy transfer from the $^3E_{1u}$ state is attractive because a vertical excitation to give the antiplanar triplet allene is both energy and spin allowed. However, since the $^3E_{1u}$ and $^3B_{1u}$ states are separated by only ~15 kcal (G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1966, p 350), the lifetime of the $^3E_{1u}$ state is not expected, *a priori*, to allow time for efficient energy transfer. This possibility cannot be eliminated, particularly since a suggestion of just such an energy transfer from the second triplet of anthracene has appeared: R. S. H. Liu and J. R. Edman, *J. Am. Chem. Soc.*, **90**, 213 (1968).

[14] W. A. Noyes, Jr., and D. A. Harter, *J. Chem. Phys.*, **46**, 674 (1967).

[15] Calculations indicate that the excited allene is slightly bent (165°) out of planarity, but that the minimum is shallow: R. Hoffman, *Tetrahedron*, **22**, 521 (1966).

dimensional hyperspace"[16] might favorably compete with collisional deactivation to the strained ground-state allene. If this suggested reaction pathway is accurate, we would expect the singlet excited allene also to give the cyclopropylidene, but we have not yet been able to verify this expectation.

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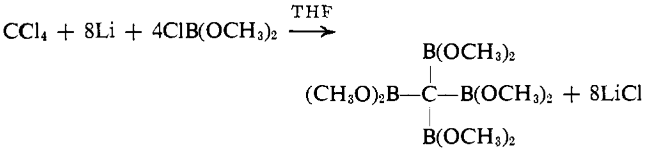
A Methanetetraboronic Ester

Sir:

We wish to report the synthesis of compounds having three and four boronic ester groups attached to one carbon atom. Although *gem*-diboronic acids and esters[1-3] and *gem*-diborylalkanes[4] are well known, attempts to prepare 1,1,1-triboryl compounds by hydroboration of an ethynylboron compound have failed.[5] Our successful method is based on the tetrasilylmethane synthesis by Merker and Scott[6] and includes some modifications similar to those used by Gilman and Smith[7] for tetrasilylsilanes. Much trial and error was required to adapt this synthesis to boron.



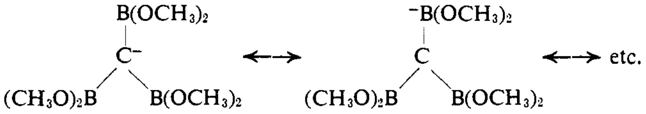
1

$$CCl_4 + 8Li + 4ClB(OCH_3)_2 \xrightarrow{THF} C[B(OCH_3)_2]_4 + 8LiCl$$

Dimethoxyboron chloride (3.4 mol) was freshly prepared by adding 236.5 g of trimethyl borate dropwise to 133.5 g of boron trichloride stirred at $\sim -70°$. This was mixed with 125 g (0.8 mol) of carbon tetrachloride and 300 ml of trimethyl borate, and the mixture was added dropwise under argon to a vigorously stirred suspension of 90 g ($\sim$6.4 g-atoms) of 50% lithium dispersion in hexane (Foote Mineral Co.) in 1.2 l. of tetrahydrofuran and 300 ml of trimethyl borate kept at $-50°$ ($\pm 5°$) by means of a Dry Ice–acetone bath. The reaction is highly exothermic and the addition required about 2 hr. The mixture was allowed to warm slowly to $-20°$, then heated to reflux for 30 min. (*Caution!* If unreacted lithium remains, sudden exothermic reaction beyond the capacity of a reflux condenser may occur on warming. We encountered this problem when smaller amounts of tetrahydrofuran were used. Immediate application of a cooling bath always controlled the reaction, but an unattended reaction once opened itself to the air and caught fire spontaneously.) The mixture was cooled to 0° and filtered to remove the lithium chloride, which was rinsed with ether. The filtrate was concentrated and distilled rapidly under vacuum, and the crude octamethyl methanetetraboronate (**1**) was redistilled: bp 70–90° (0.1 mm); mp $\sim$70–75°; no impurities evident in the infrared; 125 g (50%). An analytical sample was recrystallized from methanol and sublimed, mp 76–78°; *Anal.* Calcd for $C_9H_{24}B_4O_8$: C, 35.61; H, 7.97; B, 14.25. Found: C, 35.55; H, 8.11; B, 14.01.

We have used variations of this method to prepare hexamethyl methanetriboronate, $HC[B(OCH_3)_2]_3$, mp $\sim$45°, hexamethyl phenylmethanetriboronate, $C_6H_5C[B(OCH_3)_2]_3$, mp $\sim$35°, tetramethyl methanediboronate, $CH_2[B(OCH_3)_2]_2$, bp 24–27° (0.1 mm), and tetramethyl phenylmethanediboronate, $C_5H_5CH[B(OCH_3)_2]_2$, bp 50–54° (0.1 mm), to be reported in detail later.

Octamethyl methanetetraboronate (**1**) appears stable indefinitely in neutral methanol. With 0.1–0.2 equiv of sodium methoxide, little change occurs in 0.5 hr but most of the compound is degraded to methanediboronic ester in a day, according to nmr observations. One equivalent of methylmagnesium bromide in tetrahydrofuran converts the tetraboronic ester **1** to tris(dimethoxyboryl)methide ion (**2**). Refluxing the solution of **2** with benzyl bromide for 12 hr followed by oxidation of the high-boiling residue with hydrogen peroxide yielded a small amount of phenylacetic acid and 20% of dibenzyl ketone as the 2,4-dinitrophenylhydrazone, both verified by infrared comparison with authentic samples. Parallel behavior of 1,1-diborylalkanes has been reported.[4] We did not verify the presence of another probable degradation product, phenylacetaldehyde. We are working on the development of this alkylation into a synthesis of new types of carbon-functional boronic esters.



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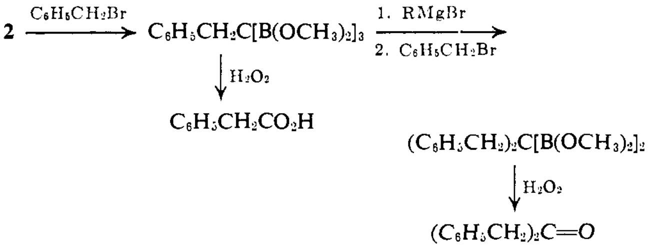

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[8] (a) Alfred P. Sloan Foundation Fellow. (b) We thank the National Science Foundation, Grant GP 6069, and the National Cancer Institute, U. S. Public Health Service Grant CA-05513-07, for financial support.

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A Valence Tautomer of a *cis*-15,16-Dihydropyrene

Sir:

The *trans*-15,16-dihydropyrenes, which have recently been reported,[1-4] are a unique addition to non-