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.

(16) P. Seybold and M. Gouterman, *Chem. Rev.*, **65**, 413 (1965).

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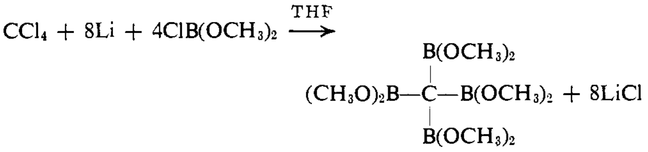
A Methanetetraboronic Ester

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.



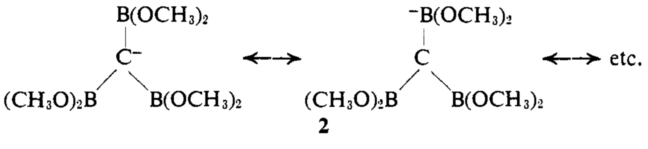
$$CCl_4 + 8Li + 4ClB(OCH_3)_2 \xrightarrow{THF} (CH_3O)_2B\text{—}\overset{\displaystyle B(OCH_3)_2}{\underset{\displaystyle B(OCH_3)_2}{C}}\text{—}B(OCH_3)_2 + 8LiCl$$

1

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 ∼−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 (∼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° (±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 ∼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 ∼45°, hexamethyl phenylmethanetriboronate, $C_6H_5C[B(OCH_3)_2]_3$, mp ∼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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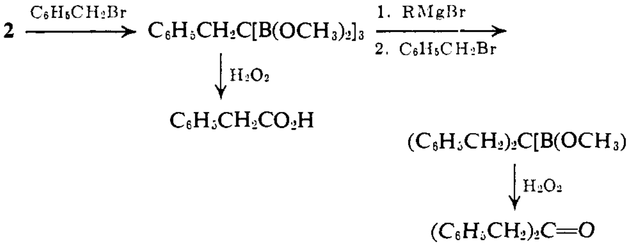

[8] (a) Alfred P. Sloan Foundation Fellow. (b) We thank the National Science Foundation, Grant GP 6069, and the National Cancer Institute, U. S. Public Health Service Grant CA-05513-07, for financial support.

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[1] D. S. Matteson and J. G. Shdo, *J. Org. Chem.*, **29**, 2742 (1964).

[2] D. S. Matteson and T. C. Cheng, *J. Organometal. Chem.* (Amsterdam), **6**, 100 (1966).

[3] D. J. Pasto, J. Chow, and S. K. Arora, *Tetrahedron Letters*, 723 (1967).

[4] G. Zweifel and H. Arzoumanian, *ibid.*, 2535 (1966); *J. Am. Chem. Soc.*, **89**, 291 (1967).

[5] (a) K. Peacock, Ph.D. Thesis, Washington State University, 1964, p 56; (b) G. Zweifel, personal communication, 1967.

[6] R. L. Merker and M. J. Scott, *J. Org. Chem.*, **29**, 953 (1964); **28**, 2717 (1963); *J. Am. Chem. Soc.*, **85**, 2243 (1963).

[7] H. Gilman and C. L. Smith, *J. Organometal. Chem.* (Amsterdam), **6**, 665 (1966).

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

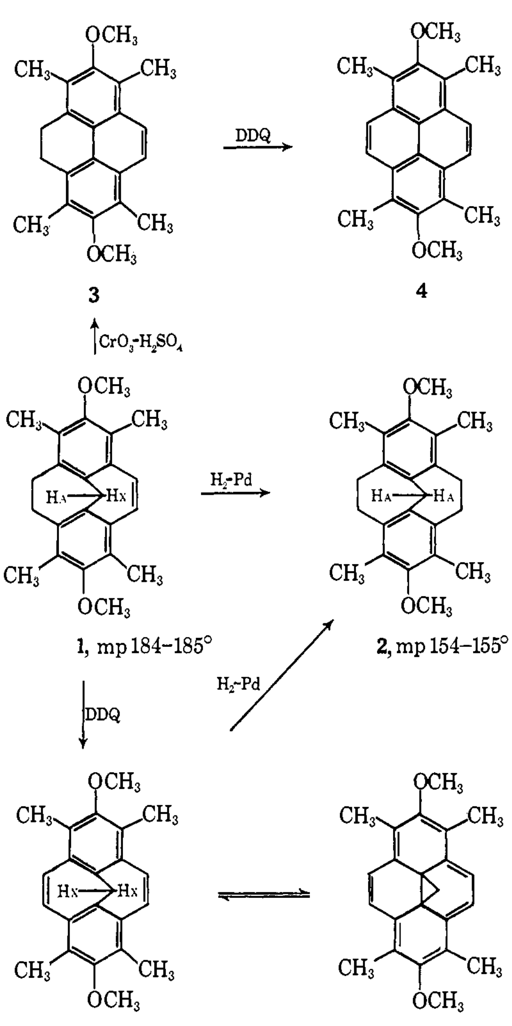
Sir:

The *trans*-15,16-dihydropyrenes, which have recently been reported,[1-4] are a unique addition to nonbenzenoid aromatic chemistry since these are the first of such entities to possess substituents contained entirely within the cavity generated by a planar π-electron periphery. It is known[5] that these *trans*-15,16-dihydropyrenes photoisomerize to *trans*-[2.2]-metacyclophane-1,9-diene valence tautomers, which revert to the original dihydropyrenes in a dark reaction.

Attention has turned to the preparation of either a 15,16-dihydropyrene possessing *cis* geometry at the central bond, or the corresponding valence tautomer thereof, and recently the synthesis of 8,16-oxido-*cis*-[2.2]metacyclophane-1,9-diene, the tautomer of pyrene *cis*-15,16-epoxide, was disclosed.[6] We wish to communicate the preparation of the 8,16-methano-*cis*-[2.2]metacyclophane-1,9-diene **5**, the valence tautomer of the 15,16-methano-*cis*-15,16-dihydropyrene **6**.

The synthesis of dimethyl- and hexamethyl-*trans*-15,16-dihydropyrenes involves an unusual oxidation of the corresponding 5,13-dimethoxy-*trans*-[2.2]metacyclophane,[1,3] giving a bisdienone which contains what eventually becomes the 15,16-dihydro linkage in these 14π systems. Since it appeared that the same synthetic approach could be followed as an entry into the *cis* series, the methano[2.2]metacyclophanes **1** and **2**, which possess the required *cis* or *syn* arrangement of aromatic rings, were prepared.[7] Oxidation of **1** with chromium trioxide[1,3,4] gave, with loss of the methano bridge, the 4,5-dihydropyrene **3**, mp 257-258°, 40% [$\lambda_{\max}^{\text{cyclohexane}}$ 222 mμ (ε 35,700), 264 (45,700), 272 (51,000), 292 (14,550), 304 (14,900), 317 (18,500), 330 (1090), 347 (1630), and 364 (1860); τ_{TMS}(CDCl$_3$): singlets at 2.17 (2, -CH=CH-), 6.23 (6, OCH$_3$), 6.85 (4, -CH$_2$CH$_2$-), 7.35 (6, -CH$_3$), and 7.55 (6, -CH$_3$)].[8] Similar oxidations of **2** have yielded more complex mixtures which include carbonyl-containing components; further attempts to oxidize **1** or **2** with iodine–silver perchlorate[9] or bromide[10] have yielded mixtures which also are currently under investigation.

However, treatment of the monoolefin **1** with freshly purified dichlorodicyanoquinone (DDQ) in hot toluene produced mixtures which contained starting material **1** and the diolefin **5** as main components. Chromatography, which was followed by long-wavelength ultraviolet light, of such mixtures in methylene chloride on silica gel produced a rose-red fluorescing fraction of **5** followed with no separation by a blue fluorescing band of **1**. Collection of the entire first fraction yielded mixtures (60:40 and 75:25 **5**:**1**, as assayed by nmr) which corresponded to yields of 15-26% of **5**. Careful rechromatography followed by sublimation at 110° (0.1 mm) and recrystallization from methanol yielded **5**, mp 217-219° [$\lambda_{\max}^{\text{cyclohexane}}$ 214 mμ (ε 56,800), 241 (47,300), 259 (47,000), and 324 (13,700); τ_{TMS} (CDCl$_3$): singlets at 2.59 (4, -CH=CH-), 6.35 (6, -OCH$_3$), 7.52 (2, -CH$_2$-), and 7.70 (12, -CH$_3$); $\nu_{\max}^{\text{KBr}}$: other than slightly increased absorption at 1575 and 1625 cm^{-1}, the infrared spectrum of **5** was quite similar to that of **1**]. Comparison of the nmr spectra of **5** and **1**[7] shows clearly the loss of the A$_2$B$_2$ multiplet (τ 6.75, -CH$_2$CH$_2$-) and AX quartet (τ 5.95 and 7.70, -CH$_A$H$_x$) of **1** and a doubling in intensity at τ 2.59 and equivalency of the methano protons at τ 7.52 in **5**. Strong diamagnetic shielding[11] of these protons (H$_X$ in **5** as well as H$_X$ in **1**) by the neighboring ethylenic orbitals produces a shift to higher field of 1.16 ppm over the methano protons (H$_A$) in **2**.[7] Mass spectral analysis[12] of **5** shows the correct molecular weight, M$^+$ 332 (87% of base peak), in addition to major fragmentations at M$^+$ − 14 (26%), M$^+$ − 15 (100%), and M$^+$ − 30 (23%). The last two fragmentations are tentatively assigned to loss of methoxyl



3

4

1, mp 184-185°

2, mp 154-155°

5, mp 217-219°

6

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(1) V. Boekelheide and J. B. Phillips, *J. Am. Chem. Soc.*, **89**, 1695 (1967).

(2) J. B Phillips, R. J. Molyneux, E. Sturm, and V. Boekelheide, *ibid.*, **89**, 1704 (1967).

(3) V. Boekelheide and T. Miyasaka, *ibid.*, **89**, 1709 (1967).

(4) H. B. Renfroe, L. A. R. Hall, and J. Gurney, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Paper O-184. A detailed manuscript has been submitted for publication.

(5) H. R. Blattman, D. Meuche, E. Heilbronner, R. S. Molyneux, and V. Boekelheide, *J. Am. Chem. Soc.*, **87**, 130 (1965). A detailed account of the photoisomerization of both dimethyl- and hexamethyl-*trans*-15,16-dihydropyrenes will be published later.

(6) B. A. Hess, Jr., A. S. Bailey, and V. Boekelheide, *ibid.*, **89**, 2746 (1967).

(7) H. B. Renfroe, J. A. Gurney, and L. A. R. Hall, *ibid.*, **89**, 5304 (1967).

(8) Satisfactory analyses were obtained for all compounds. Infrared spectra were taken with KBr disks and are consistent with assigned structures. Nmr spectra were obtained in deuteriochloroform on a Varian A-60A using TMS as an internal standard.

(9) T. Sato, E. Yameda, Y. Okamura, T. Amada, and K. Hata, *Bull. Soc. Chem. Japan*, **38**, 1049 (1965).

(10) N. L. Allinger, B. U. Gorden, S. Hu, and R. A. Ford, *J. Org. Chem.*, **32**, 2272 (1967).

(11) R. C. Cookson, T. A. Crabbe, J. J. Frankel, and J. Hudec, *Tetrahedron Suppl.*, **7**, 355 (1966), and references cited therein.

(12) The author is indebted to Dr. Paul Nicolson of these laboratories for mass spectra which were obtained on a C.E.C. Model 21-103C instrument using a heated inlet operating at 225°.

methyls; loss of the bridging methano group, though not intense, is relatively more important in **5** (26%) than in **1** (19%) or **2** (18%).

Mixtures of **5** and **1** from initial column chromatography of the dehydrogenation reaction were assayed quantitatively by nmr and subjected to catalytic hydrogenation in absolute ethanol using 10% palladium on charcoal. After absorption of the calculated amount of hydrogen for the mixture, the only product which could be isolated was the saturated metacyclophane **2** (90%). Conversely, dehydrogenation of **2** with DDQ gave mixtures of **1**, **5**, and **2**, although in much lower yields.

In solutions and in the solid state **5** demonstrates under ultraviolet light a bright reddish and yellow fluorescense, respectively, while crystals or solutions of **1** show a moderate blue fluorescence. This observation, the noted shift to lower field of the comparable protons, and increased ultraviolet absorption in the series **2** → **1** → **5** suggest that the ethylene bridges of **5** and **1** experience a definite conjugation with the aromatic rings. Idealized models constructed from the Dreiding set show the planar aromatic rings forming an angle at the methylene bridge of 75° in **2** and 85° in **5**, and indicate that the ethylenic orbitals are set at an angle of 45° with the benzenoid orbitals, thereby providing sufficient overlap for conjugation.[13] Although the bond angles, bond distances, and deformation of the aromatic rings, if any, can only be known from a detailed X-ray analysis, such models are believed to show the over-all geometry of these molecules reasonably well.[14]

The data presented here show clearly that **5** is the structure of the dehydrogenation product of **1** and that spontaneous reorganization to **6** does not occur. Indeed, none of our data suggests the presence of any of **6** due to equilibration with **5**. However, isomerization of **5** to **6** is currently being explored both photochemically and thermally. Initial pyrolysis experiments carried out on micro samples of **5** in sealed ampoules under nitrogen indicate the formation of a new material (mp 277–279°) at 250 ± 5° which has an ultraviolet absorption spectrum essentially identical with that of **4**, mp 278–280° [$\lambda_{\max}^{\text{cyclohexane}}$ 243 mμ (ϵ 41,750), 253 (56,200), 265 (12,150), 276 (26,250), 288 (47,100), 318 (4530), 332 (12,200), 348 (30,350), 367 (43,400), and 388 (1500); τ_{TMS} ($CDCl_3$): singlets at 1.90 (4, $-CH{=}CH-$), 6.14 (6, OCH_3), and 7.19 (12, CH_3)], the DDQ dehydrogenation product of **3**. These spectra are very similar to published absorption spectra of pyrenes.[15] This observation might indicate that **5** is converted to **4** possibly (though not necessarily) by isomerization to **6**, which loses the methano bridge irreversibly to give the pyrene **4**. A more detailed investigation is in progress.

$$\begin{tikzcd} 5 \arrow[r, "250°"] & {[6]} \arrow[r, "-CH_2"] & 4 \\ & 3 \arrow[ur, "DDQ"'] & \end{tikzcd}$$

Since **5** is recovered on pyrolysis at temperatures below 250°, the $M^+ - CH_2$ fragmentation in its mass spectrum (225°) must be due to electron-impact rather than thermal fragmentation.

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[13] See L. L. Ingraham in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., pp 482–483.

[14] Professor V. Boekelheide has informed the writer of an X-ray crystallographic analysis by Dr. A. Hanson of 8,16-oxido-*cis*-[2.2]-metacyclophane, which shows only slight deformation of the aromatic rings. We are appreciative of stimulating discussions with Professor Boekelheide pertaining to this research.

[15] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957.

Factoring of the Isotropic Shift in Paramagnetic Cobalt(II) Complexes[1]

Sir:

One of the major problems in interpreting the isotropic shift of paramagnetic complexes involves factoring out the pseudocontact contribution to the observed shifts so that the contact contribution can be obtained. The latter is related to the spin density at a proton. An approximation that has been used[2–5] in interpreting the shifts of the diadducts of nickel(II) and cobalt(II) acetylacetonates (acac) is that the mechanisms of spin delocalization are identical for the two metal ions, varying only in magnitude. The observed shifts in the $Ni(acac)_2$ adducts are assumed to be caused by the contact interaction. When there is more than one proton in the ligand, the ratio of the shifts of the various protons in the nickel(II) complex would equal those in the cobalt(II) complex in the absence of a pseudocontact contribution in the latter. The discrepancy in the ratios is attributed to the pseudocontact contribution. Knowing the geometric factor and assuming that the ratios for the contact contribution are the same in cobalt(II) and nickel(II), the total isotropic shift in the cobalt complex can then be factored into the contact and pseudocontact contributions.

We were very much concerned about the assumption that the ratios and hence the spin delocalization mechanisms are identical in six-coordinate cobalt(II) and nickel(II) complexes[2–4] such as those having O_h, D_{4h}, and D_3 symmetry. Cobalt(II) has unpaired spins in the "d" orbitals pointing in between the ligands which are capable of π bonding and nickel(II) does not; hence one would expect different mechanisms. We report here isotropic shifts for $Co(bipy)_3{}^{2+}$ and $Ni(bipy)_3{}^{2+}$ (bipy = bipyridine) which conclusively prove that the mechanisms for spin delocalization are different for the two metal ions and invalidate the factoring procedure,[2–4] based on the assumption that they are equivalent at least for this system. It also makes suspect the assumption[6] that the mechanisms are alike in the D_3 complexes $Co(acac)_3{}^-$ and $Ni(acac)_3{}^-$ and weakens the general application of this assumption to six-coordinate cobalt(II) and nickel(II) complexes. The measured shifts are reported in Table I.

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[1] Abstracted in part from the Ph.D. Thesis of M. L. Wicholas, University of Illinois, 1967.

[2] W. D. Horrocks, Jr., R. C. Taylor, and G. N. LaMar, *J. Am. Chem. Soc.*, **86**, 3031 (1964).

[3] R. W. Kluiber and W. D. Horrocks, Jr., *ibid.*, **87**, 5350 (1965).

[4] R. W. Kluiber and W. D. Horrocks, Jr., *ibid.*, **88**, 1399 (1966).

[5] J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

[6] W. D. Horrocks, Jr., R. A. Fischer, J. R. Hutchinson, and G. N LaMar, *J. Am. Chem. Soc.*, **88**, 2436 (1966).