(16) P. v. R. Schleyer, G. W. Van Dine, V. Schöllkopf, and J. Paust, *J. Am. Chem. Soc.*, **88**, 2868 (1966).
(17) T. M. Su, W. F. Sliwinski, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **91**, 5386 (1969).
(18) Such distortions are abundantly reflected in the spectra and chemistry of homobullvalenone; cf. ref 6a.
(19) F. A. L. Anet, *J. Am. Chem. Soc.*, **86**, 458 (1964).
(20) Neither can 3^+ be less than ca. 2.5 kcal/mol more stable than 4^+ to explain the exclusive formation of **8**.
(21) The observations reported here are in marked contrast to results obtained upon ionization of **8** in superacid which gives only rearrangement: M. J. Goldstein and S. A. Kline, *J. Am. Chem. Soc.*, **95**, 935 (1973).

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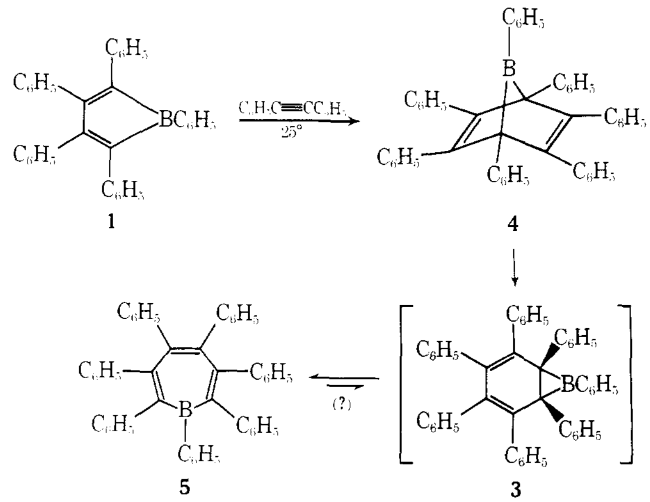
The Synthesis of Heptaphenylborepin via the Thermal Rearrangement of Heptaphenyl-7-borabicyclo[2.2.1]heptadiene[1]

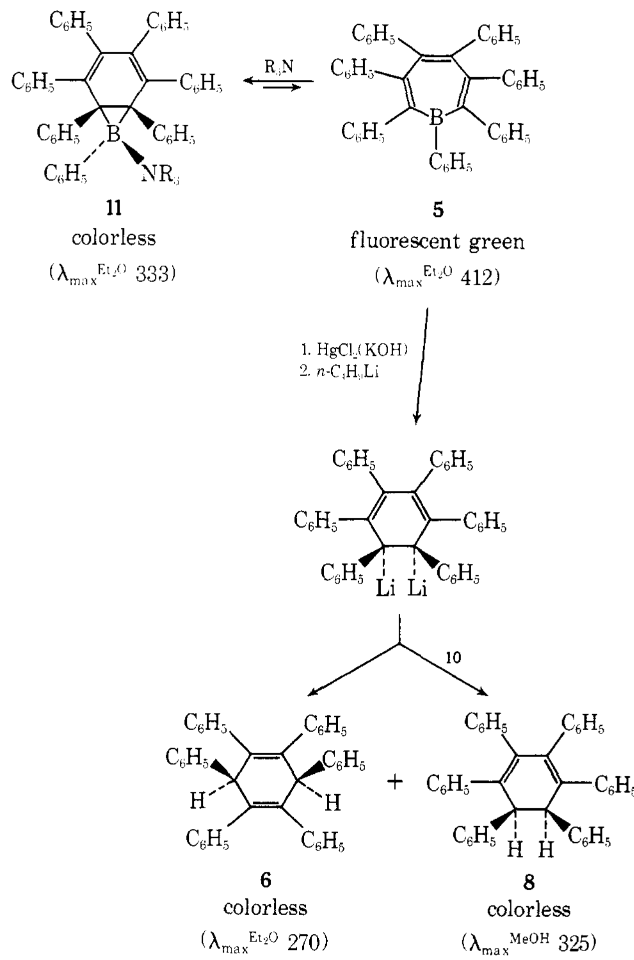
Sir:

From considerations of its covalent radius and electronegativity, an sp^2-hybridized boron atom would be expected to form cyclic conjugated systems with sets of sp^2-hybridized carbons.[2] Such boracyclopolyenes might display Hückel-aromatic or -antiaromatic character, depending upon the total number of π electrons. Thus, the recently prepared phenylborabenzene anion[3] and pentaphenylborole[4] represent nonfused, monocyclic examples of aromatic and antiaromatic boracarbocycles, respectively. Synthesis of other boracarbocycles has been limited to benzo-fused systems, such as the 3-benzoborepin,[5] dibenzoborepin,[6] and boraanthracene[7,8] systems, where the benzo annelation tends to obscure the unique electronic character of the boron ring.[9] Up to the present, the attempted syntheses of nonfused borepin and borirene rings have met with repeated failures, and only a circumstantial case can be made for the formation of the latter nucleus in solution.[2,10,11] Therefore, we are now pleased to report the synthesis of the first nonfused borepin, heptaphenylborepin (**5**), by a smooth [1,3] suprafacial sigmatropic rearrangement of heptaphenyl-7-borabicyclo[2.2.1]heptadiene (**4**), followed by a reversible, disrotatory ring-opening of intermediate **3** (Scheme I).

Scheme I



Scheme II



Thus, stirring a partial suspension of pentaphenylborole (**1**, 4.87 mmol[4]) and diphenylacetylene (**2**, 5.0 mmol) in 25 ml of toluene at 20–25° until the dark blue-green color of **1** had disappeared, followed by dilution with 75 ml of ethyl ether and filtration, gave a 60% yield of colorless **4**, mp 210° dec ($\lambda_{max}^{Et_2O}$ (ϵ): 318 (10,000)).[12] The structure of **4** follows from its spectral and analytical data, as well as from its acetolysis with hot glacial acetic acid to yield the previously identified *cis*-hexaphenyl-1,4-dihydrobenzene (**6**).[4] Now, heating **4** (2.23 mmol) in 30 ml of refluxing toluene for 24 hr, removing most of the toluene in vacuo, and diluting the residue with ethyl ether provided an 84% yield of fluorescent greenish yellow heptaphenylborepin (**5**).[13] Alternatively, the toluene solution obtained by allowing the borole **1** to react with the acetylene **2** could be heated directly to give **5** in an 82% yield. The solid borepin **5** was only slowly oxidized in air, but its solutions were rapidly attacked.

The structure assignment of the borepin **5** is based both upon its spectroscopic and chemical properties (Scheme II). Its electronic spectrum exhibited peaks at $\lambda_{max}^{Et_2O}$ (ϵ) 412 (6100), 342 (8080), 276 (22,700), and 245 (28,000), while the infrared spectrum had strong characteristic bands at 1590, 1240–1300, 770, 750, 740, 705, and 695 cm^{-1}. Pyridine forms an almost colorless complex with **5** that dissociates in warm toluene solution, but whose infrared spectrum lacks strong absorptions in the region of 1250–1350 cm^{-1}, present in uncomplexed **5** and generally considered characteristic of the conjugated heptaphenyltropenium ion ring.[14] Gaseous ammonia instantly discharges the green color of **4** and yields a complex with the following electronic spectrum: $\lambda_{max}^{Et_2O}$ (ϵ) 333 (8070), 265 (sh, 8700), and 243 (25,200). Chemical degradation of **5** by heating with acetic or propionic acid at reflux was slow and incomplete. On the other hand, **5** was smoothly mercurideboronated[15] by heating with an excess of mercuric chloride, lithium chloride, and potassium hydroxide in a THF–MeOH solvent mixture. The crude, dried organomercury product **7** was directly subjected to a mercury-lithium exchange by treating with an excess of *n*-butyllithium. Hydrolysis of the resulting dark green solution yielded 40% of a solid **8** that proved to be *cis*-1,2-dihydrohexaphenylbenzene,[16] together with 16% of **6** and 8% of hexaphenylbenzene (**9**). The structure of **8** follows from the following: (a) heating **8** with *N*-bromosuccinimide in CCl_4 gave **9** in 86% yield; (b) its NMR (CCl_4), 4.42 (s, 2) and 6.8 (m, 30), whereas the *cis*[4]- and *trans*[17]-1,4-dihydrohexaphenylbenzenes display their benzylic protons at 4.67 ppm and the reported[18] *trans*-1,2-dihydrohexaphenylbenzene has its corresponding peak at 4.0 ppm; (c) its electronic spectrum has λ_{max}^{MeOH} 325 (10,300), whereas the known trans isomer has its long-wavelength peak at $\lambda_{max}^{CH_3CN}$ 312 (10,700); and (d) **8** melts almost completely at 150–152°, but then resolidifies and melts finally at 192–195° (trans mp 180–182°). The isolation of **8** and **6** as the principal hydrolysis products seems to be best interpreted as a disrotatory ring closure of the 1,6-dimercurio- or dilithiohexatriene resulting from **5**. The ring-closure product (e.g., the dilithio product **10**) would then be protonated, with or without allylic rearrangement, to yield **6** and **8**, respectively. In any case, the spectral *and* chemical data strongly support the conclusion that the fluorescent green boron derivative obtained by heating **4** must consist, in whole or in part, of molecules possessing the borepin structure **5**, rather than the 7-borabicyclo-[4.1.0]heptadiene structure (**3**). The ultraviolet spectrum of **3** would be expected to resemble that of **8**, and hence the long-wavelength band of the green solid ($\lambda_{max}^{Et_2O}$ 412) would be unexplained. However, it may very well be that coordination complexes of **5** with Lewis bases, such as R_3N, OH^-, or Bu^- do actually assume the bicyclo structure shown in **3**, as may be the case for **11**. The observed λ_{max} for **11** is in better agreement with that of **8**, than with that reported for 1,6-diphenyl-1,3,5-hexatriene[19] ($\lambda_{max}^{C_6H_6}$ 358).

Although no definite information can be obtained on the coexistence of both valence isomers **3** and **5** for the heptaphenyl-substituted system, a study of the hexa-*p*-tolyl-substituted system has been rewarding. Thus, 1-phenyl-2,3,4,5-tetra-*p*-tolylborole was synthesized from the corresponding stannole and then was treated with di-*p*-tolylacetylene to form the Diels–Alder adduct analogous to **4**.[20] Heating the latter compound in toluene yielded the fluorescent green presumed 1-phenyl-2,3,4,5,6,7-hexa-*p*-tolylborepin (**12**): mp 276–281° dec; $\lambda_{max}^{Et_2O}$ (ϵ) 425 (5210), 345 (sh, 7810), 280 (sh, 23,100), and 249 (30,500). However, in toluene-d_8 at 25° **12** shows six distinct methyl signals of approximately equal intensity; raising the temperature to 57° causes two of these signals to coalesce. At temperatures above 113° in bromobenzene two more signals coalesce, leaving four methyl peaks. These results suggest that the borepin **12** is in equilibrium either with a nonplanar form or with its bicyclo valence isomer **13**, having a structure similar to **3**.

Whether planar borepins **5** and **12** are in equilibrium with nonplanar structures like **3**, as has been surmised for certain substituted tropenium salts,[14] is the focus of our continuing NMR and X-ray crystallographic investigations.[21]

Finally, it is noteworthy that the long-wavelength absorption of heptaphenylborepin at 412 nm bears a marked similarity to that of several heptaphenyltropylium salts, such as the bromide, fluoroborate, and perchlorate, which absorb at 405 nm in acetonitrile.[22] The other maxima of these salts at 250 (90,000) and 283 nm (17,000) also compare favorably with those of borepin **5** at 245 and 276 nm, respectively. The correspondence in electronic spectra supports the isoelectronic relationship between this borepin and its aromatic carbocyclic counterpart.

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References and Notes

(1) Part XIII of the series, "Rearrangements of Organometallic Compounds", as well as part IV of the series, "Boraaromatic Systems" (previous part: *J. Am. Chem. Soc.*, **97**, 895 (1975).
(2) J. J. Eisch and L. J. Gonsior, *J. Organomet. Chem.*, **8**, 53 (1967).
(3) A. J. Ashe III, and P. Shu, *J. Am. Chem. Soc.*, **93**, 1804 (1971).
(4) J. J. Eisch, N. K. Hota, and S. Kozima, *J. Am. Chem. Soc.*, **91**, 4575 (1969).
(5) A. J. Leusink, W. Drenth, J. G. Noltes, and G. J. M. van der Kerk (*Tetrahedron Lett.*, 1263 (1967)) synthesized *B*-phenylbenzo[*d*]borepin and, for the first time, adduced electronic and NMR spectral evidence for the aromatic delocalization of the benzoborepin ring.
(6) E. E. van Tamelen, G. Brieger, and K. G. Untch (*Tetrahedron Lett.*, **8**, 14 (1960)) synthesized *B*-hydroxydibenzo[*b,f*]borepin for the first time and isolated the compound as its ethanolamine derivative. However, no spectral data were reported on the uncoordinated dibenzoborepin itself, so that no conclusion could be drawn on the involvement of the boron $2p_z$ orbital in the possible aromatic character of the borepin ring. The possibility for aromaticity in a borepin was recognized at least as early as 1958 and quantum mechanical calculations gave support to such expectations (cf. M. E. Vol'pin, *Russ. Chem. Rev.* (*Engl. Transl.*), **29**, 129 (1960), for leading references).
(7) R. van Veen and F. Bickelhaupt, *J. Organomet. Chem.*, **30**, C51 (1971).
(8) P. Jutzi, *Angew. Chem.*, **83**, 912 (1971).
(9) The differing effects of phenyl-substitution vs. benzo annelation on the electronic spectra of borole derivatives are marked: highly purified pentaphenylborole is a deep blue-green solid[4] ($\lambda_{max}^{C_6H_5CH_3}$ 567 nm), while *B*-phenyldibenzo[*b,d*]borole is yellow (λ 405 nm). Cf. R. Köster, G. Benedikt, W. Fenzl, and K. Reinert, *Justus Liebigs Ann. Chem.*, **702**, 197 (1967).
(10) Cf. D. Sheehan (Doctoral Dissertation, Yale University, 1964, University Microfilms, Ann Arbor, Mich.) for a splendid account of masterly attempts.
(11) J. J. Eisch, K. Tamao, and R. J. Wilcsek, *J. Am. Chem. Soc.*, **97**, 895 (1972).
(12) Analysis of **4** as its pyridine complex (mp 250°, dec). Anal. Calcd for $C_{53}H_{40}BN$: C, 90.75; H, 5.71. Found: C, 90.54; H, 5.63.
(13) This compound melted at 233–236°. Anal. Calcd for $C_{48}H_{35}B$: C, 92.61; H, 5.66. Found: C, 92.58; H, 5.75. Both **4** and **5** gave strong parent peaks with the proper $^{10}B/^{11}B$ ratios in their mass spectra at 70 eV.
(14) M. A. Battiste, *J. Am. Chem. Soc.*, **93**, 4101 (1961).
(15) J. B. Honeycutt, Jr., and J. M. Riddle, *J. Am. Chem. Soc.*, **82**, 3051 (1960).
(16) Anal. of **16**: Calcd for $C_{42}H_{32}$: C, 93.99; H, 6.01. Found: C, 93.93; H, 5.92. MS (70 eV): parent peak at 536.
(17) R. Breslow and P. Dowd, *J. Am. Chem. Soc.*, **85**, 2729 (1963).
(18) M. A. Battiste, *Chem. Ind.* (*London*), 550 (1961).
(19) K. W. Hausser, R. Kuhn and A. Smakula, *Z. Phys. Chem., Abt. B*, **29**, 384 (1935); 1,4-diphenyl-1,3-butadiene displays its corresponding maximum at 334 nm (cf. those maxima of **8** and **11**).
(20) All the corresponding tolyl analogs of the stannole, **1**, **4**, and **5** gave satisfactory elemental and mass spectral analyses.
(21) Joint crystallographic studies underway with Professor Galen D. Stucky of the Department of Chemistry, University of Illinois at Champaign/Urbana.
(22) Personal communication by Professor M. A. Battiste of unpublished data from the doctoral dissertation of T. J. Barton, University of Florida, 1968.

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The Structure of Crotofolin A, a Diterpene with a New Skeleton

Sir:

The identification of the cocarcinogenic principles of *Croton tiglium* L. (Euphorbiaceae) as esters of the diterpene phorbol has stimulated considerable interest in the chemistry of this genus.[1,2] Although various diterpenes have been isolated from *Croton* these are of the commoner skele-