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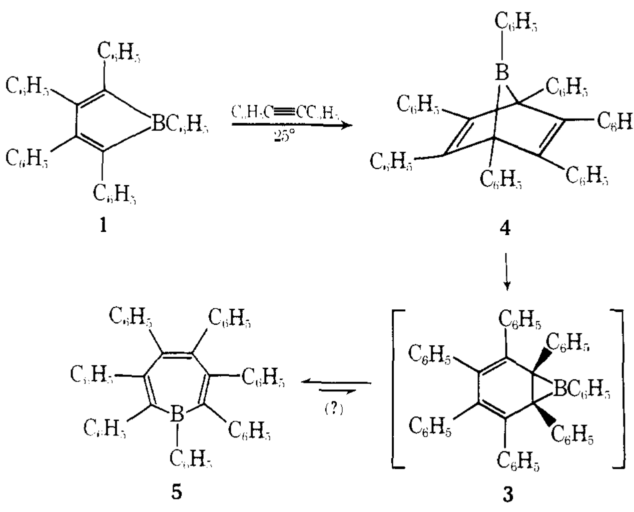
The Synthesis of Heptaphenylborepin via the Thermal Rearrangement of Heptaphenyl-7-borabicyclo[2.2.1]heptadiene[1]

Sir:

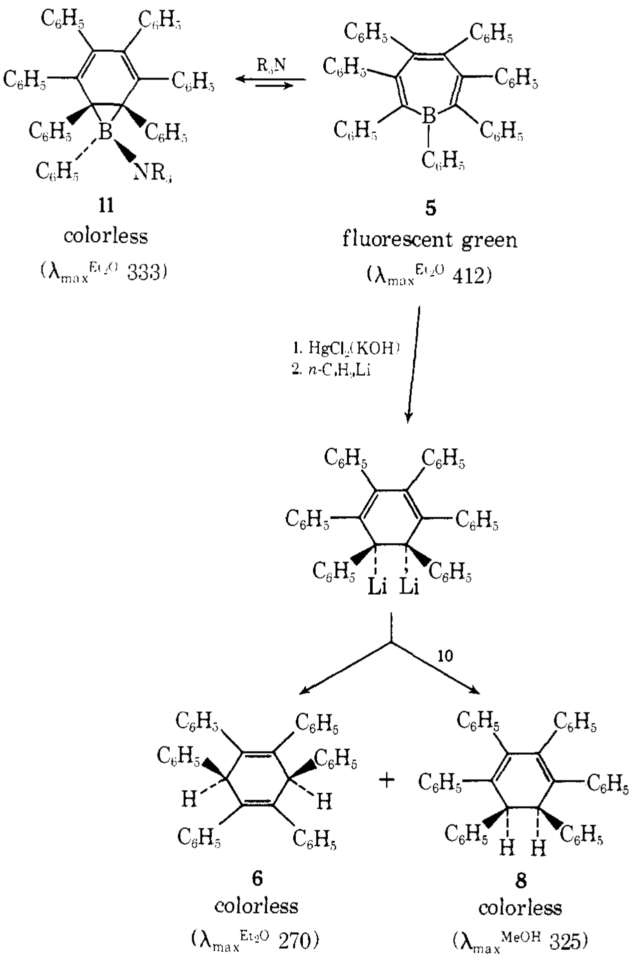
From considerations of its covalent radius and electronegativity, an sp^2-hybridized boron atom would be expected to form cyclic conjugated systems with sets of sp^2-hybridized carbons.[2] Such boracyclopolyenes might display Hückel-aromatic or -antiaromatic character, depending upon the total number 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).

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.

Scheme I



Scheme II



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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(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.
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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-