Organometallics 1990, *9*, 2342-2349

Thermal Generation and Transformation of the Borepin Ring System: A Paradigm of Pericyclic Processes[1]

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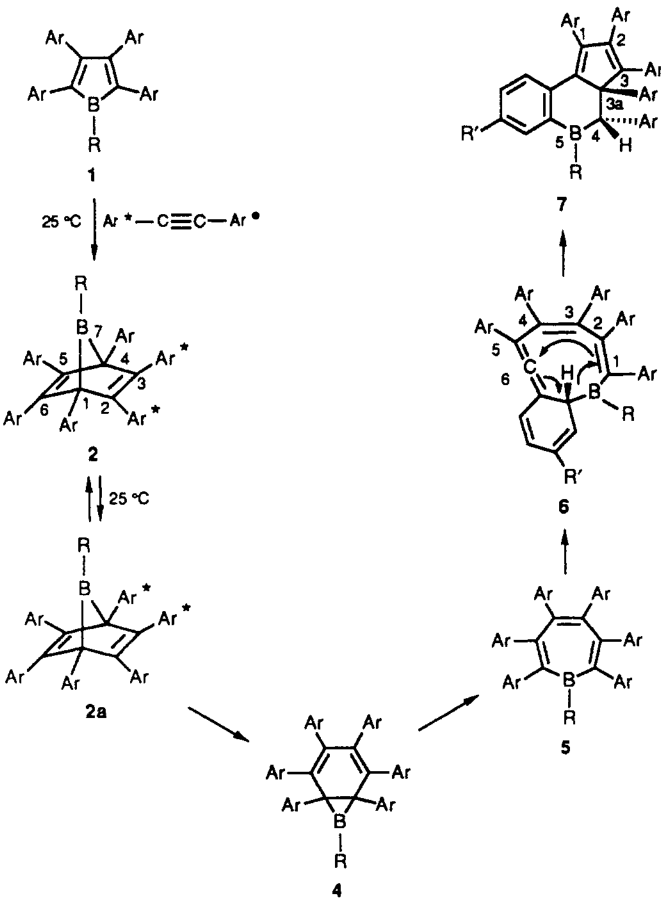
Received February 14, 1990

Almost 15 years ago the synthesis of the borepin ring system was reported to result from the interaction of an alkyne with the highly reactive borole ring and the occurrence of an unusual sequence of skeletal rearrangements. In this manner, both heptaphenylborepin and 1-phenyl-2,3,4,5,6,7-hexa-*p*-tolylborepin were prepared as bright yellow solids, whose chemical degradation by successive treatment with $HgCl_2$, *n*-butyllithium, and H_2O yielded a mixture of the *cis*-1,2-dihydrohexaarylbenzenes and the hexaarylbenzenes. The isolation of these hydrocarbons was consistent with the cleavage of the carbon–boron bonds of the borepins and the disrotatory electrocyclic ring closure of the resulting (*E*,*Z*,*E*)-1,3,5-hexatrienes. Further heating of these borepins leads to electronic and NMR spectral changes which show that all the six *C*-aryl substituents become nonequivalent and that an isomer of the borepin has now been formed. These fluorescent green compounds undergo protodeboronation with glacial acetic acid to yield 5-benzyl-1,2,3,4,5-pentaarylcyclopentadienes. X-ray crystallographic analysis of the isomer formed from 1,2,3,4,5,6,7-heptaphenylborepin shows it to be 1,2,3,3a,4,5-hexaphenyl-5-bora-3a,4-dihydro-5*H*-benz[*e*]indene. That the tricoordinate boron in the latter is conjugated with the cyclopentadiene ring is shown by the hypsochromic spectral shift caused by coordination with amines. The overall conversion of borole to this isomer of borepin involves a remarkable sequence of pericyclic reactions: a Diels–Alder cycloaddition, 1,3-sigmatropic suprafacial rearrangements of the resulting 7-borabicyclo[2.2.1]heptadiene, a 1,6-disrotatory electrocyclic ring opening to the borepin, a 1,3-sigmatropic ring expansion to a boracyclononatetraene, and a final ring-closing ene reaction yielding the 5-bora-3a,4-dihydro-5*H*-benz[*e*]indene system. The role of the unoccupied $2p_z$ orbital on boron in facilitating these rearrangements and in influencing the spectral properties of the unsaturated boracarbocycles involved is discussed in terms of Hückel molecular orbital theory.

Introduction

Almost 15 years ago we reported that the borepin ring system could be synthesized by the interaction of an alkyne with a borole and the ensuing sequence of skeletal rearrangements (Scheme I: 1 → 5).[2] Starting with a [4 + 2] Diels–Alder cycloaddition[3] and proceeding via [1,3]-suprafacial, sigmatropic rearrangements (2 → 2a → 4),[4] a 1,6-disrotatory electrocyclic ring opening of the 7-borabicyclo[4.1.0]heptadiene (4 → 5) provided the borepins 5 as bright yellow solids.[5] The structures of the borepins (5: R = Ph, Me) obtained were assigned on the basis of spectral properties (^1H NMR, IR, UV, and MS), elemental analysis, and chemical degradation. For example, treatment of heptaphenylborepin (5: R, Ar = Ph) with a sequence of $HgCl_2$, *n*-butyllithium, and finally H_2O yielded *cis*-1,2-dihydrohexaphenylbenzene (40%), *cis*-1,4-dihydrohexaphenylbenzene (16%), and hexaphenylbenzene (8%). Direct treatment of borepin 5 (R = Me, Ar = Ph) with methyllithium and then H_2O also yielded (*E*,*Z*,*E*)-1,2,3,4,5,6-hexaphenyl-1,3,5-hexatriene. These degradation products are consistent with the formation of (*E*,*Z*,*E*)-1,3,5-hexatriene intermediates from the borepin ring and the disrotatory electrocyclic ring closure of such open-chain trienes under the reaction conditions.

Scheme I



In subsequent studies, however, we obtained indications that the borepin ring system is not the ultimate, most stable product of such thermal rearrangements.[6] Prolonged heating of heptaphenylborepin, for example, led to a color change from canary yellow to chartreuse green. The ^1H NMR spectrum changed in overall appearance, and a new sharp singlet appeared at 4.17 ppm (1 proton). The mass spectrum of this product now lacked a peak at *m*/*e* 534, which in the original borepin signals the facile loss of the ^{11}B–Ph fragment. Further investigation of these observations has led to the discovery of yet another re-

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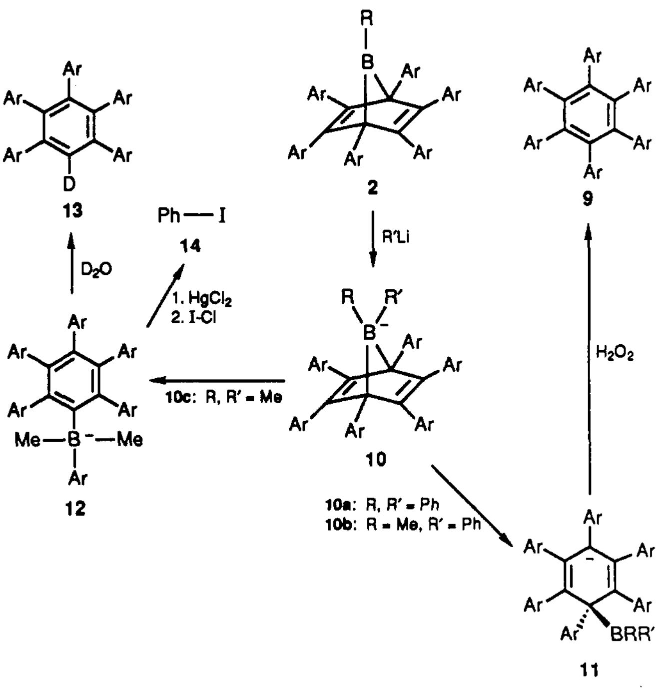
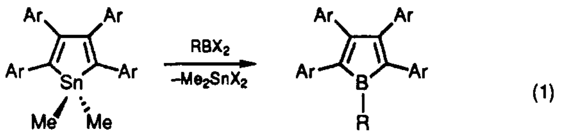
Scheme II



markable rearrangement of such aryl-substituted borepins. Accordingly, we are finally able to present an overall view of the series of rearrangements that generate and isomerize the borepin nucleus (Scheme I).

Results

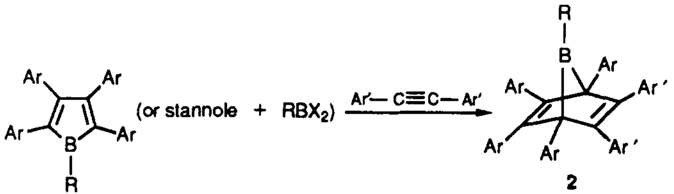
Synthesis and Diels–Alder Reactions of Boroles 1. The various 2,3,4,5-tetraphenyl- and 2,3,4,5-tetra-*p*-tolylboroles 1 employed in this study could be readily generated from the corresponding stannoles by treatment with the appropriate boron halide (eq 1). Details on this synthesis and the spectral properties of the isolated boroles have already been published.[3] Therefore, for the Diels–Alder reaction of the boroles with the diarylacetylenes, it was shown that the preformed borole need not be isolated but could be generated from the stannole in the presence of the acetylene. The blue boroles reacted very rapidly with the acetylene, and the blue color of the toluene solution of 1 faded after a reaction time of several minutes at 25 °C. The colorless Diels–Alder adducts 2 could be isolated pure in over 80% yield (eq 2).[4]



(1)

1a: R, Ar = Ph
b: R = Ph, Ar = *p*-Tol
c: R = Me, Ar = Ph
d: R = Cl, Ar = Ph

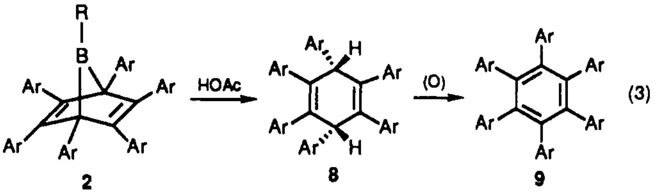
R = Ph, Me, Cl; X = Cl, Br



1 2 (2)

Since diarylacetylenes rank as relatively unreactive dienophiles, the rapidity of this Diels–Alder reaction points to the high reactivity of the borole as a diene and hence as an antiaromatic ring from the standpoint of Hückel molecular orbital theory.[7]

Chemical Degradation and Rearrangement of 7-Borabicyclo[2.2.1]heptadienes 2. Protodeboronation of these Diels–Alder adducts with glacial acetic acid produces *cis*-1,4-dihydrohexaarylbenzenes 8 and, if adventitious oxidation is not avoided, the hexaarylbenzene 9 as well (eq 3).



2 8 9 (3)

Alternatively, the boron bridge in such adducts can be cleaved with organolithium reagents and the product then hydrolyzed with H_2O or oxidized with H_2O_2. The outcome of this cleavage reaction depends upon the nature of the substituent R in 2 and on the R group in the organolithium reagent (Scheme II). In each case, it can be assumed that RLi forms the tetraorganoborate complex 10 with 2 and that 10 undergoes ring opening to 11 (vivid green color of the reaction solution). However, where R and R' = methyl, 11 undergoes a further 1,2-aryl shift from carbon to boron with concomitant aromatization of the central ring to produce 12. Deuteriolytic and halolytic cleavages of 12 establish the presence of the proposed C–B bonds in 12.

Physical Properties of 7-Borabicyclo[2.2.1]heptadienes and Their Degenerate Rearrangement. The spectral properties of 1,2,3,4,5,6,7-heptaphenyl-7-borabicyclo[2.2.1]heptadiene (**3a**) were examined in the most searching detail. The ^1H NMR spectrum displays a central, sharp singlet of 15 protons at 7.5 ppm. Likewise, the 7-phenyl-1,2,3,4,5,6-hexa-*p*-tolyl derivative **3b** has a sharp 13-proton singlet at 7.32 ppm. The ^1H NMR spectra of **3a** and of **3b** have 10-proton and 8-proton multiplets, respectively, both above and below their central singlet resonance. Thus, the spectra are consistent with **3a** and **3b** having symmetrical boron bridges (14), rather than distorted boron bridges (15). In the latter case, the aryl protons of groups on C_2 and C_3 would differ from those on C_5 and C_6.[8]

The ^{11}B NMR absorption for **3a** lies only 5.0 ppm downfield from that for $BF_3{\cdot}OEt_2$ and thus is relatively

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(1) Bora-Aromatic Systems. 12. Part 11: Eisch, J. J.; Shafii, B.; Odom, J. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 1847.

(2) Eisch, J. J.; Galle, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 4436.

(3) (a) Eisch, J. J.; Hota, N. K.; Kozima, S. *J. Am. Chem. Soc.* **1969**, *91*, 4575. (b) Eisch, J. J.; Galle, J. E.; Kozima, S. *J. Am. Chem. Soc.* **1986**, *108*, 379.

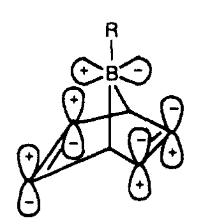
(4) Eisch, J. J.; Galle, J. E. *J. Organomet. Chem.* **1976**, *127*, C9.

(5) Subsequent to our report, 1-methyl-4,5-cyclopentenoborepin was made by the exchange of $MeBBr_2$ with the preformed 1,1-dibutyl-4,5-cyclopentostannepin; this mode of preparation is not subject to the skeletal rearrangements to which 5 is prone: Ashe, A. J., III; Drone, F. J. *J. Am. Chem. Soc.* **1987**, *109*, 1879.

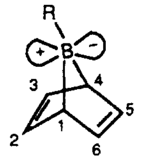
(6) An early indication of this conclusion, already mentioned in ref 2, was that samples of 1-phenyl-2,3,4,5,6,7-hexa-*p*-tolylborepin inexplicably developed an ^1H NMR spectrum, upon warming, that exhibited six separate methyl hydrogen signals. At that stage in our studies, we speculated that the borepin 5 might be in thermal equilibrium with its valence isomer 4.

(7) Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961; pp 256–304.

(8) The methyl proton signals in the ^1H NMR spectrum of **3b** occur as 6- and 12-proton singlets at 2.64 and 2.72 ppm, respectively; such signals are readily assignable as stemming from the bridgehead tolyl and bridge-situated tolyl groups. It is unlikely that the distorted bridge form 15 contributes much to the actual structure at 25 °C, especially since the allylic shifts depicted in eq 4 occur in the range of 25–100 °C.



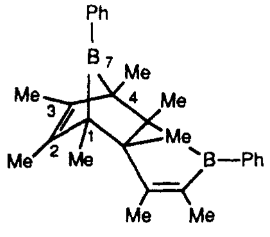
14



15

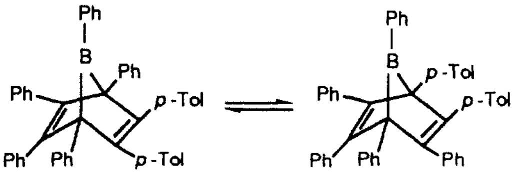
highly shielded. Complexation of **3a** with pyridine moves the ^{11}B resonance only 7.8 ppm upfield.[9] In the electronic spectrum of **3a**, the long-wavelength absorption lies at 318 nm, but its pyridine complex displays only a shoulder absorption at 275 nm. Thus, the 318-nm peak has undergone a pronounced hypsochromic shift upon coordination at the boron.[10a] Both the ^{11}B NMR and the UV observations suggest that the free $2p_z$ orbital of the sp^2-hybridized boron in **3a** overlaps with the π molecular orbitals of the vinylene bridges (**14**). Such an interaction would increase electron density at the boron and thus move its ^{11}B resonance upfield, as well as delocalize the stilbenylene π electrons and give a bathochromic UV shift.[10a]

In a recently published report,[10b] a 7-bora analogue of a norbornene system, **15a**, has been shown to exhibit interaction of the bridgehead phenylboron group with the C_2–C_3 double bond: in the X-ray crystal structure the plane defined by B_7, C_1, and C_4 makes an angle of 90.1° relative to the plane defined by C_1, C_2, C_3, and C_4, suggesting that the boron is attracted to the C_2–C_3 double bond. In the present heptaphenyl-7-boranorbornadiene system (**3**), however, there would not be any energetic advantage for the PhB group to incline itself toward the C_2–C_3 or toward the C_5–C_6 double bond, since equally effective homoconjugation with both C=C bonds can be operative in the symmetrical structure **14**.



15a

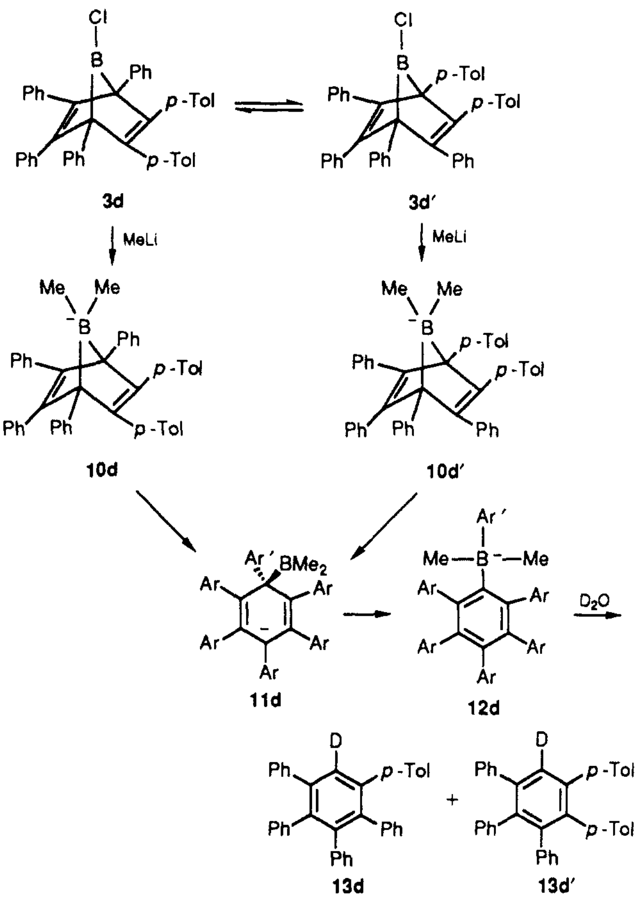
Scrutiny of the Diels–Alder adduct of pentaphenylborole (**1a**) with di-*p*-tolylacetylene revealed that a subtle, degenerate rearrangement of the Diels–Alder adduct **3e** was occurring at room temperature (eq 4). Because of the symmetry plane bisecting the vinylene bridges and the boron in **3e**, only one methyl signal would be expected in the ^1H NMR spectrum. But in fact, two methyl signals in a ratio of 2:1 at 98 °C were observed. Indeed, if isomers **3e** and **3e′** were freely interconverting and if a tolyl group attached to an sp^2-hybridized carbon would exhibit its methyl downfield from that of a tolyl group at a bridgehead, sp^3-hybridized carbon, this is exactly what the probable combinations would suggest.[11]



3e **3e′** (4)

Proof that initially formed bicyclic systems like **3e** can undergo such a facile isomerization as that depicted in eq 4 was adduced by employing the boron-bridge-cleaving rearrangement depicted in Scheme II (**3** → **10** → **12** → **13**). As is clear from Scheme II, only aryl groups at bridgeheads can undergo the pivotal 1,2-aryl shift (**10** → **12**). Accordingly, if one can show that **3e** undergoes a 1,2-tolyl shift, then **3e** must be easily interconverted into **3e′**, which would have a *p*-tolyl group at the bridgehead able to migrate.

Scheme III



With this in mind, borole **1d** was prepared and then allowed to react at 25 °C with di-*p*-tolylacetylene. The resulting adduct **3d** was treated with an excess of methyllithium to generate the tetraorganoborate **10d**. Subsequent heating at reflux (→**12d**) and hydrolysis led to the isolation of a mixture of tetraphenyl-*p*-tolyl- and triphenyldi-*p*-tolylbenzenes (**13d** and **13d′**), proof that both a 1,2-phenyl and 1,2-*p*-tolyl shift has occurred from **10d** and **10d′** (Scheme III, via **11d**). Accordingly, **3d** must have isomerized to **3d′**, so that the isomeric borate **10d′** could also be formed.

Thermal Skeletal Rearrangement of the 7-Borabicyclo[2.2.1]heptadiene System. Heating any of the colorless Diels–Alder adducts **3** over 100 °C led to the appearance of a vivid yellow and eventually a fluorescent

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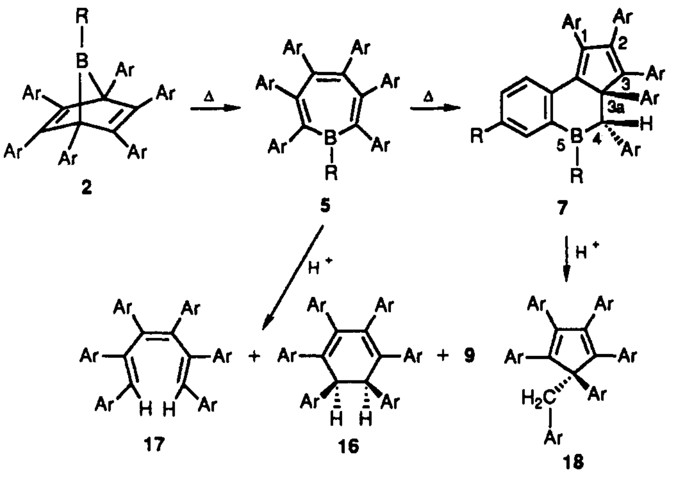
[9] We are grateful for the assistance of Professor Jerome D. Odom, Department of Chemistry, The University of South Carolina, in conducting this measurement.

[10] (a) For purposes of comparison, the structure of pyridine-complexed **3a** possesses only two unconjugated *cis*-1,2-diphenylethenediyl units (PhCH=CHPh) and would be expected to have its long-wavelength absorption near that of *cis*-stilbene. Indeed, *cis*-stilbene absorbs at 278 nm. (b) Fagan, P. J.; Burns, E. G.; Calabrese, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 2979.

[11] On the C_6 carbon skeleton of **3c**, there are four sites for tolyl groups on bridge-situated positions and two sites at bridgeheads. Thus, if probability determines the site of a tolyl group, the ratio of bridge tolyl to bridgehead tolyl would be 2:1.

Scheme IV



green color, signaling that isomerization of **3** had taken place. Chemical degradation of the isolated yellow-green product, either by protodeboronation with glacial acetic acid or by addition of methyllithium and subsequent hydrolysis (cf. eq 3) led to a mixture of *cis*-1,2-dihydrohexaarylbenzene (**16**), hexaarylbenzene (**9**), (*E*,*Z*,*E*)-1,2,3,4,5,6-hexaaryl-1,3,5-hexatriene (**17**), and 5-benzyl-1,2,3,4,5-pentaarylbenzene (**18**). These hydrocarbons would arise from the arylated borane isomers of **3**, namely the borepin (**5**) and 5-bora-3a,4-dihydro-5*H*-benz[*e*]indene (**7**) systems (Scheme IV; Ar = Ph, *p*-Tol).

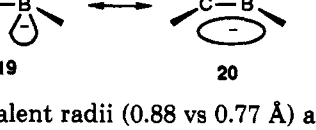
That isomer **7** was formed via isomer **5** and is thermodynamically more stable was shown by prolonging the heating period. In this way, **5** could be almost completely converted into **7**, which could then be isolated in the pure state as chartreuse green, strongly fluorescing solids. Its unusual structure could then be established by X-ray crystallography (Figure 1). It is noteworthy that addition of either ammonia or pyridine to **7** yielded colorless complexes, whose long-wavelength absorption had undergone a hypsochromic shift (415 → 330 nm).

The canary yellow component of the reaction mixture, which could not be isolated free of **7**, is assigned the structure of a borepin (**5**), because it yields a hexatriene (**17**) or its disrotatory ring-closure isomer **16** upon protodeboronation. Moreover, the mass spectrum of **5**, admixed with **7**, exhibits a prominent peak denoting the loss of the R–B fragment, a peak conspicuously absent in the mass spectrum of pure **7**.

Formation of isomer **7** or "pseudoborepin" from **2** and **5** can be monitored conveniently in the case where R = phenyl and Ar = *p*-tolyl, since the ^{1}H NMR spectrum shows the growth of the methine proton at C_4 (4.5 ppm) and the emergence of six distinct methyl singlets in the 2.6-ppm region as **7** is generated from **5** (Ar = *p*-tolyl).

Discussion

Carbon–Boron π-Bonding. Since triorganoboranes (R_3B) are isoelectronic with carbenium ions (R_3C^+), the sp^2-hybridized boron has an unoccupied 2p$_z$ orbital that can overlap with an occupied 2p orbital of an adjacent sp^2- or sp-hybridized carbon (**19** ↔ **20**). A priori, the similarities of the covalent radii (0.88 vs 0.77 Å) and Allred–Rochow electronegativities (2.01 vs 2.50) between boron and carbon suggest that such overlap should lead to π-electron delocalization, albeit less than that between two sp^2-hybridized carbon centers. Both ab initio molecular orbital calculations[12] and a variety of experimental spectroscopic measurements[13] lend a posteriori support to this hypothesis. Such p$_\pi$–p$_\pi$ conjugation is thereby concluded to make a minor contribution (about 25%) to the strength of carbon–boron bonding in such systems as phenylboranes.[14]



19 **20**

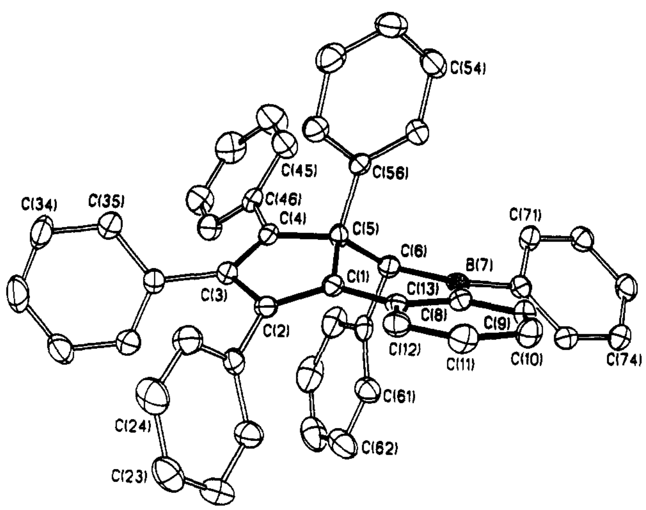


Figure 1. Molecular structure and labeling scheme for 1,2,3,3a,4,5-hexaphenyl-5-bora-3a,4-dihydro-5*H*-benz[*e*]indene, drawn without hydrogen atoms for the sake of clarity. Significant bond lengths (Å): B–C(6), 1.592 (5); B–C(8), 1.556 (5); B–C(76), 1.595 (4); C(8)–C(13), 1.426 (4); C(13)–C(1), 1.464 (4); C(1)–C(5), 1.515 (5); C(5)–C(6), 1.562 (4); C(5)–C(4), 1.523 (4); C(4)–C(3), 1.356 (5); C(3)–C(2), 1.471 (4); C(2)–C(1), 1.353 (4). Bond angles (deg): C(76)–B–C(6), 119.3 (3); C(6)–B–C(8), 117.7 (3); C(8)–B–C(76), 122.9 (3). The atom numbering employed here is only valid for this figure. Elsewhere in the text the atom numbering is that given for the structure of **7** in Scheme I.

However, incorporation of boron into a cyclic array of sp^2-hybridized carbons permits a boron center to transmit, as well as to participate in, π-electron delocalization. That certain boracyclopolyenes thereby gain significant π-electron stabilization is corroborated by both theory and experiment. For example, Schleyer and co-workers have estimated, by ab initio MO calculations at high levels of refinement, that boracyclopropene (or borirene) possesses about 75% of the resonance stabilization of the isoelectronic cyclopropenium cation.[15] Addressing themselves to physical reality, Eisch and co-workers have prepared and isolated triarylborirenes[16-18] and shown them to have remarkable stability, so long as the sp^2 hybridization of boron is maintained.[18]

Cyclic arrays of sp^2-hybridized carbon and boron need not be stabilized by π-electron delocalization. Since such monocyclic systems can be viewed as Hückel π-bonded rings, only those rings having $4n + 2$ π electrons (where $n = 0, 1, 2, 3, ...$) should display aromatic stabilization;

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[12] Guest, M. F.; Hillier, I. H.; Saunders, V. R. *J. Organomet. Chem.* **1972**, *44*, 59.

[13] Onak, T. *Organoborane Chemistry*; Academic Press: New York, 1975; pp 2–18.

[14] Rice, B.; Young, T. F.; Gonzalez Barredo, J. M. *Am. R. Soc. Esp. Fis. Quim., Ser. B* **1952**, *48*, 191.

[15] Krogh-Jespersen, K.; Cremer, D.; Dill, J. D.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 2589.

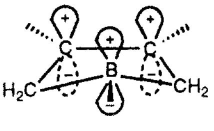
[16] Eisch, J. J. In *Advances in Organometallic Chemistry*; West, R., Stone, F. G. A., Eds.; Academic Press: New York, 1977; Vol. XVI, pp 67–109.

[17] Eisch, J. J.; Shen, F.; Tamao, K. *Heterocycles* **1982**, *18*, 245.

[18] Eisch, J. J.; Shafii, B.; Odom, J. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 1847.

those not having this number should actually be destabilized. Experimental confirmation of this Hückel corollary has been provided by the synthesis of pentaarylboracyclopentadienes (or boroles),[3,19] which proved to be highly unstable.

By extending the Hückel theory of π-electron delocalization to homoconjugation as well, one might look for manifestations of delocalization even in cyclic arrays of sp^2-hybridized carbon and boron atoms interrupted by sp^3-carbon centers (e.g. **21** $\leftrightarrow$ **22**).



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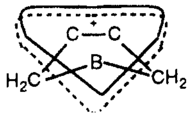

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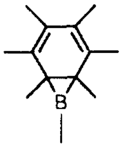

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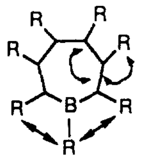
Again, by applying the Hückel $4n + 2$ π-electron criterion, the electronic spectral properties and chemical stability of the 7-borabicyclo[2.2.1]heptadiene system **3** are in accord with the operation of homoaromatic π-electron stabilization.[4,10b] A corollary of this Hückel homoconjugation theory, yet to be verified experimentally, is that 7-borabicyclo[4.1.0]heptadiene (**23**) should be homoantiaromatic and thus should be destabilized. Indeed, ab initio SCF calculations at the 6-31G* level indicate that **3** should be more stable than **23** by about 15 kcal/mol.[20]

Finally, therefore, it is evident that sp^2-hybridized boron can participate in cyclic conjugation with an array of sp^2-hybridized carbon atoms. Now, one of the most fundamental and characteristic class of reactions undergone by all-carbon polyenes is that of pericyclic reactions.[21] Accordingly, boracyclopolyenes would be expected to enter into pericyclic reactions with a facility dependent, partly at least, upon their Hückel aromatic stabilization.

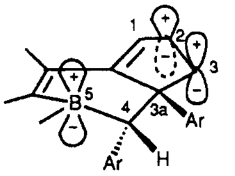
Pericyclic Reactions of Boracyclopolyenes. The chain of reactions leading from the borole ring **1** to the generation of the borepin system **5** and its ultimate transformation to the borabenzindene **7** runs its course cleanly over the temperature range of 25–110 °C. These facts are in accord with the operation of thermally facile processes that occur with the conservation of orbital symmetry, so-called thermally allowed Woodward–Hoffmann processes where bond making and bond breaking occur in a concerted manner.[22] With reference to Scheme I, the involvement of the following pericyclic reaction steps can be discerned in the formation of **7**: (1) an initial [4 + 2] cycloaddition or Diels–Alder reaction of the borole (**1** $\rightarrow$ **2**), (2) dual [1,3]-suprafacial sigmatropic shifts interconverting homoaromatic isomers of **2** and moving the boron about the C$_6$ framework (**2** $\rightarrow$ **2a**), (3) a higher energy [1,3]-suprafacial sigmatropic shift producing homoantiaromatic **4**, (4) a probably facile disrotatory ring opening of **4** to yield presumably aromatic borepin **5**, (5) another [1,3]-suprafacial sigmatropic shift to place the boron at the ortho position of the 2-aryl substituent, and (6) ring closure of **6** in a process that can be viewed as an intramolecular ene reaction (**6** $\rightarrow$ **7**), a reaction having a close orbital kinship with [4 + 2] cycloadditions.[23] Some of the foregoing steps deserve comment as to what they reveal concerning carbon–boron π bonding. First, the reaction of borole **1** with the relatively unreactive dienophile ArC≡CAr proceeds promptly to completion at 25 °C. This is consistent with the destabilization of **1** by homoantiaromaticity. Second, the isomerization of borabicyclo intermediates **2** and **4** to yield the aromatic and hence more stable borepin **5** confirms the applicability of the Hückel aromatic theory to the C$_6$B atom array. Thus, the borepin nucleus can take its place alongside the borirene and borole nuclei as systems whose properties are greatly influenced by carbon–boron cyclic conjugation. Third, although the thermal formation of borepin **5** from **2** reveals its relative stability, the fact that **5** slowly isomerizes further to **7** indicates that its aromatic stabilization is probably relatively small.[24]

Whether a ring system stabilized by delocalization will undergo further reaction clearly depends on two factors: its inherent delocalization energy and the relative accessibility of a more stabilized isomer over an activation barrier. In the case of these heptaarylborepins, both factors operate against the thermal stability of the ring system. First of all, a planar array of C$_6$B atoms generates internal bond angle strain (approaching 130°, or a 10° deviation for sp^2-hybridized atoms). This angle widening, in turn, contracts external bond angles between substituents and the ring to about 115° and brings adjacent substituents on the ring closer to each other (**24**). These effects curtail the overall stabilization of the planar borepin and thus may lower the activation energy leading to **6**.



24

internal angle 130°
external angle 115°



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Second, there is evidence that the ultimate product **7** resulting from **5** also has significant, possibly stabilizing π-electron delocalization, which may explain why it is the energy sink among isomers **2**, **4**, **5**, **6**, and **7**. Isomer **7** itself has a long-wavelength absorption of 415 nm, which is shifted to 330 nm upon coordination of an amine with the boron center. Examination of C–C and C–B bond distances in **7** makes it discernible that the boron is conjugated with the array of atoms C(8)–C(13)–C(1)–C(2)–C(3)–C(4); the C(8)–B distance of 1.556 Å and the C(8)–C(13) distance of 1.426 Å show relative shortening and lengthening, respectively, suggestive of electron delocalization. A further possible source of electron delocalization in **7** might be the bishomoconjugation or hyperconjugation through σ orbitals operating in the boroindene region, which would involve overlap of the boron 2p$_z$ orbital and that of C(3) (**25**).[25]

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(19) Not only does the borole nucleus display unusually high reactivity as a diene in a Diels–Alder reaction with the usually unreacted dienophile diphenylacetylene (eq 2) but the borole itself can also function as its own dienophile. Thus, upon prolonged standing at 25 °C, deep blue **1** dimerizes to a pale yellow adduct (Eisch, J. J.; Boleslawski, M. P. Unpublished studies, 1990).

(20) Disch, R. L.; Sabio, M. L.; Schulman, J. M. *Tetrahedron Lett.* **1983**, *24*, 1863.

(21) Gill, G. B.; Willis, M. R. *Pericyclic Reactions*; Chapman & Hall: London, 1974.

(22) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie-Academic Press: Weinheim, FRG, 1971.

(23) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556.

(24) Ab initio molecular orbital calculations suggest that the perprotio-substituted borepin would be about 26 kcal/mol more stable than 7-borabicyclo[2.2.1]heptadiene at the STO-3G(SCF) level of refinement and 38 kcal/mol at the 6-31G(SCF) level.[20] Naturally, such calculations do not take into account the destabilizing effect of vicinal, bulky substituents.

(25) A through-space overlap of the 2p$_z$ orbitals of boron and that of C(3) may be small because of the distance of separation; alternatively, some type of through-bond hyperconjugation involving the σ orbitals of the phenyls at C(3a) and C(4) may be operative: Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; pp 195–200.

In the former, less likely view, 7 could be considered as a bishomoborepin and would thereby gain in some π stabilization. In addition, 7 would be less subject to steric destabilization than 5, because adjacent aryl substituents are either out of plane from each other or are situated on a planar C_5 ring, whose sites are less compressed. In the latter view, delocalization of the π electrons in the cyclopentadienyl ring into the $2p_z$ orbital on boron might ensue over the σ orbitals of the C–phenyl bonds at C_{3a} and C_4.

Experimental Section

General Procedure and Measurements. All operations involved in the preparation, transfer, and analyses of organometallic compounds were conducted under an atmosphere of pure, anhydrous nitrogen or argon.[26] Likewise, all the solvents employed in such procedures were purified and distilled under an atmosphere of nitrogen from the following drying agents: $LiAlH_4$ for ethers and hydrocarbons and BaO for pyridine and benzonitrile.[27]

The spectral samples were prepared by published techniques,[28] and the spectra were measured with the following instruments: ^1H NMR spectra with a Varian A-60 or EM-360 spectrometer; mass spectra at the Mass Spectral Facility at Cornell University, where as Perkin-Elmer Model 270, an AEI-902, or a CEC-21-103A instrument was employed; IR spectra with a Perkin-Elmer Model 457 spectrophotometer; electronic spectra with a Cary Instrument Model 14 instrument.

Chromatographic analyses were performed with an F&M dual-column, programmed-temperature gas chromatograph (Model 720). Elemental analyses were carried out by Galbraith Laboratories, Knoxville, TN.

Starting Materials and Reagents. 1,1-Dimethyl-2,3,4,5-tetraphenylstannole, 1,1-dimethyl-2,3,4,5-tetra-*p*-tolylstannole, diphenylacetylene, and di-*p*-tolylacetylene were prepared and purified according to previously published procedures.[3b]

The requisite dichlorodimethyltin, dichlorophenylborane, and dibromomethylborane were used directly as obtained from Alfa (Ventron).

Synthesis of the 2,3,4,5-Tetraarylboroles 1. Either of the foregoing stannoles, dissolved in anhydrous, deoxygenated toluene, was treated with 1 molar equiv of dichlorophenylborane at 25 °C, in order to generate the boroles 1,2,3,4,5-pentaphenylborole (**1a**) and 1-phenyl-2,3,4,5-tetra-*p*-tolylborole (**1b**). Details concerning the preparation, the spectral properties, and both the oxidation and protoboronation of these boroles have already been published.[3b] However, those details concerning 1-methyl-2,3,4,5-tetraphenylborole (**1c**) have not been published and hence are given below.

Preparation of 1-Methyl-2,3,4,5-tetraphenylborole (1c). Treatment of 1.0 mmol of the stannole dissolved in 10 mL of anhydrous, deoxygenated toluene with 0.18 mL (2.0 mmol) of dibromomethylborane led to complete boron–tin exchange within a few minutes at 25 °C. After suitable dilution the resulting solution showed a broad maximum in the visible spectrum at 542 nm: ^1H NMR (toluene) 1.5 (s, 3 H), 6.97 (m, 10 H), 7.25 (m, 6 H), 7.55 ppm (m, 4 H).

Diels–Alder Reactions of the 2,3,4,5-Tetraarylboroles. a. Reaction of 1,2,3,4,5-Pentaphenylborole (1a) with Diphenylacetylene. A stirred blue suspension of 2.16 g (4.87 mmol) of borole **1a** in 10 mL of anhydrous, deoxygenated toluene was treated dropwise with a solution of 890 mg (5.0 mmol) of diphenylacetylene in 15 mL of toluene at 25 °C. The blue color rapidly disappeared, and the pale yellow suspension began to deposit colorless crystals of the adduct heptaphenyl-7-borabicyclo[2.2.1]heptadiene (**3a**). Collecting the crystals, washing with ether, and drying yielded 1.84 g (60%) of product, which melted at 209–210 °C (decomposition with yellowing, in a sealed, nitrogen-filled capillary): ^1H NMR ($CDCl_3$) 7.2–7.4 (m, 10 H), 7.5 (s, 15 H), 7.6–7.8 ppm (m, 10 H); UV (Et_2O) λ_{max} (ϵ) 318 nm (10000); UV of pyridine complex (THF) λ_{max} (ϵ) 248 (34700), 275 (sh) nm (14700); MS (m/e at 70 eV) 622 (4), 621 (1); IR (mineral oil) 705 (s), 725 (s), 738 (s), 765 (s), 770 (s), 789 (m), 795 (m), 1035 (m), 1080 (m), 1248 (m), 1580 (m), 1602 (s), 1634 (s) cm^{-1}. Anal. Calcd for the pyridine complex of **3a** (mp 250 °C dec): Anal. Calcd for $C_{53}H_{40}BN$: C, 90.75; H, 5.71. Found: C, 90.54; H, 5.63.

b. Reaction of 1-Phenyl-2,3,4,5-tetra-*p*-tolylborole (1b) with Di-*p*-tolylacetylene. The borole was generated in situ from the reaction of 2.80 g (5.0 mmol) of the stannole in 20 mL of pure toluene with 795 mg (5.0 mmol) of dichlorophenylborane. After a few seconds the blue color of the borole appeared, and after 30 min 1.05 g (5.1 mmol) of the acetylene was introduced. After a further 30 min the blue-green color had faded, so the solvent was removed under reduced pressure. Then, after the reaction residue was warmed in a heating bath at 60 °C in vacuo, the Me_2SnCl_2 byproduct was removed by sublimation. The residue was washed with two 25-mL portions of anhydrous diethyl ether to give 2.70 g (77%) of nearly colorless 7-phenyl-1,2,3,4,5,6-hexa-*p*-tolylbicyclo[2.2.1]heptadiene, mp >200 °C dec. An analytical sample of the pyridine complex was prepared by redissolution in toluene and the addition of 1 mL of anhydrous pyridine. The precipitated pyridine complex was recrystallized twice from an ethanol–methylene chloride mixture; mp >200 °C (yellowing and gas evolution at about 240 °C, in a sealed capillary under nitrogen). Anal. Calcd for $C_{59}H_{52}BN$: C, 90.18; H, 6.67. Found: C, 89.83; H, 6.56. The spectral properties for the uncomplexed **3b** are as follows: ^1H NMR ($CDCl_3$) 2.64 (s, 6 H), 2.72 (s, 12 H), 7.05–7.3 (m, 8 H), 7.32 (s, 13 H), 7.45–7.80 ppm (m, 8 H).

c. Reaction of 1,2,3,4,5-Pentaphenylborole (1a) with Di-*p*-tolylacetylene. The borole was generated from the reaction of 2.53 g (5.0 mmol) of the stannole in 15 mL of pure toluene with 795 mg (5.0 mmol) of dichlorophenylborane and isolated in the usual manner as a deep blue solid, yield 1.84 g (82%). It was then allowed to react as a suspension in 15 mL of fresh toluene with 845 mg (4.1 mmol) of the acetylene for 12 h at 25 °C. Rechilling to −80 °C and filtering at this temperature provided 2.30 g (86%) of the Diels–Alder adduct **3e**.

The ^1H NMR spectrum of **3e** in tetrachloroethene displayed two methyl singlets at 2.78 and 2.70 ppm, which had signal areas in a ratio that was temperature-dependent. The aromatic signals occurred as multiplets between 7.18 and 7.80 ppm, and the ratio of the aromatic signal area to that of both methyl signals was found to be 5.5:1.0, in agreement with theory. The ratio of the methyl signals at 2.78 and 2.70 ppm to each other varied from 3.0:1.0 at 47 °C to 2.0:1.0 at 98 °C. Recording the spectrum at 120 °C, in C_2Cl_4 solution at 100 MHz with signal lock on internal $C_6H_5SiMe_3$, did result in partial merging but not coalescence of the signals. From this observation it may be estimated that the site-exchange process for the methyl groups has a $\Delta G^{\ddagger}$ value that is greater than 20 kcal/mol. No yellow or green color developed during this heating process, so no skeletal isomerization to the borepin had yet taken place. The mass spectrum of **3e** displayed the parent ion at m/e 650 and the P − 1 peak in a 4:1 ratio.

d. Reaction of 1-Methyl-2,3,4,5-tetraphenylborole (1c) with Diphenylacetylene. The borole **1c** was generated in situ from 3.03 g (6 mmol) of the stannole and 0.90 mL of dibromomethylborane in 30 mL of pure toluene and in the presence of 1.42 g (8.0 mmol) of the acetylene. The solvent, Me_2SnCl_2, and excess $MeBBr_2$ were removed by warming to 50 °C under reduced pressure. The ^1H NMR spectrum ($CDCl_3$) of the Diels–Alder adduct **3c** displayed a singlet at 0.34 ppm (3 H) and a singlet with some slight structure at 6.84 ppm (30 H).

e. Reaction of 1-Chloro-2,3,4,5-tetraphenylborole (1d) with Di-*p*-tolylacetylene. This borole was generated in situ by the interaction of 5.05 g (10.0 mmol) of the stannole with an excess of boron trichloride in 50 mL of pure toluene. The acetylene (2.06 g, 10.0 mmol) was then introduced to discharge the blue color. When the mixture was warmed under reduced pressure, Me_2SnCl_2, BCl_3, and toluene were removed. This Diels–Alder adduct **3d** was then further treated as described below.

Chemical Degradation of the 7-Borabicyclo[2.2.1]heptadiene (3) System. a. Protodeboronation of the Heptaphenyl Derivative 3a. Heating a 1.00-g sample of borane **3a** with 15 mL of glacial acetic acid at reflux for 12 h under a nitrogen atmosphere, neutralizing the diluted acetic acid mixture with aqueous $NaHCO_3$, and extracting with ether permitted separation of the organic protodeboronation products. Drying the organic

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[26] Eisch, J. J. *Organometallic Syntheses*; Academic Press: New York, 1980; Vol. 2, pp 7–22.
[27] Reference 26, pp 20–26.
[28] Reference 26, pp 63–80.

extract with MgSO$_4$, evaporating the solvent, and chromatographing on an alumina column allowed the isolation of hexaphenylbenzene (35%), which was identified by mixture melting point and infrared spectral comparison with an authentic sample, and *cis*-hexaphenyl-1,4-dihydrobenzene (45%; mp 184–186 °C; UV (Et$_2$O) λ_{max} 270 nm; ^{1}H NMR (CDCl$_3$) 4.67 ppm; IR, identical with that of an authentic sample).

b. Anionic Boron Removal and Skeletal Rearrangement of the 7-Methyl Heptaphenyl Derivative 3c. Treatment of Diels–Alder adduct **3c**, generated in section d above, with 23 mmol of methyllithium in ether and 40 mL of THF caused the formation of a deep green solution. After being stirred for 20 min at 25 °C, the solution was treated with enough ethanol to discharge the color. The reaction product was crystallized by gradually distilling off THF and replacing it with ethanol. A total of 1.95 g (70%) of the hydrocarbon product was isolated; further recrystallization from an ethanol–methylene chloride mixture gave pure pentaphenylbenzene (mp 243–245 °C; ^{1}H NMR (CDCl$_3$) 6.83 (s), 6.90 (s), 7.18 (s) ppm), as demonstrated by comparison with an authentic sample.

c. Anionic Boron Removal from 3a with Aromatization. A 1.2-mmol sample of heptaphenyl-7-borabicyclo[2.2.1]heptadiene was treated with 1.2 mmol of phenyllithium in a toluene–ether mixture. Then pure 1,2-dimethoxyethane (20 mL) was slowly added as the other solvents were distilled off. Reflux for 15 h, removal of solvent, and addition of 0.5 mL of 30% H$_2$O$_2$ caused the prompt deposition of hexaphenylbenzene. The usual hydrolytic workup permitted a 73% yield of this hydrocarbon to be isolated.

d. Anionic Boron Removal and Skeletal Rearrangement of 7-Chloro-1,2,3,4-tetraphenyl-5,6-di-*p*-tolyl-7-borabicyclo[2.2.1]heptadiene (3d). Previously prepared **3d** was dissolved in 100 mL of anhydrous THF and then treated with 34 mmol of methyllithium in ether. The resulting emerald green solution was heated to reflux for 60 min and then treated with ethanol. The usual hydrolytic workup and extraction with water gave an organic layer that was dried and evaporated. The residue was subjected to column chromatography on alumina with a gradient of benzene–hexane. A total of 80% of hydrocarbons was isolated. By ^{1}H NMR and mass spectroscopy this mixture was shown to consist of tetraphenyl-*p*-tolylbenzene and triphenyldi-*p*-tolylbenzenes.

A sample of **3d** was treated with methyllithium in the foregoing manner, and a solution of mercuric chloride in methanol–water was then added. Finally, iodine chloride was introduced and the solution heated at reflux. Hydrolytic workup led to the isolation of 20% of iodobenzene.

A sample of **3d** was treated with methyllithium in the foregoing manner and the reaction mixture then quenched with D$_2$O. The usual workup gave a mixture of monodeuterated tetraphenyl-*p*-tolyl- and triphenyldi-*p*-tolylbenzenes.

Thermal Rearrangement of the 7-Borabicyclo[2.2.1]heptadiene System. a. 7-Methyl-1,2,3,4,5,6-hexaphenyl-7-borabicyclo[2.2.1]heptadiene (3c). A sample of **1c** was prepared in situ by treating a mixture of the stannole (1.16 g, 2.3 mmol) and the acetylene (445 mg, 2.5 mmol) in 20 mL of pure toluene with 2.3 mmol of dibromomethylborane for 30 min and then by removing the solvent and Me$_2$SnBr$_2$ by warming in vacuo. The almost colorless residue of **3c** was taken up in 50 mL of anhydrous, deoxygenated xylene and heated at reflux. The characteristic methyl absorption in the ^{1}H NMR spectrum at 0.34 ppm decreased with time of reflux and was replaced by new singlets at 0.74 and 0.85 ppm and principally at 1.17 ppm. Also, a new singlet grew in downfield at 3.85 ppm, whose intensity was about 15% of the signal at 1.17 ppm. The signal at 1.17 ppm is considered to be characteristic of borepin **5c**; that at 3.85 ppm is assigned to the isomer of borepin, **7c**. During the refluxing period in xylene the initially colorless solution became yellow and developed a yellow fluorescent shade with time.

The xylene solvent was evaporated from the reaction mixture in vacuo, and the residue was redissolved in 50 mL of anhydrous, deoxygenated THF. Thereupon 7.2 mmol of methyllithium in diethyl ether was added and the resulting mixture heated for 2 h at reflux. Quenching the reaction mixture with ethanol, removing the solvent in vacuo, and recrystallizing the residue by extracting and filtering with hot methylene chloride provided 0.20 g (16%) of hexaphenylbenzene. The residual organic material from the mother liquor was heated for 12 h with glacial acetic acid and after the usual neutralizing aqueous workup was chromatographed on a column of alumina. The main fraction eluting with a benzene–hexane gradient gave a mixture of hydrocarbons, 680 mg (55%), which by ^{1}H NMR spectroscopy was composed of *cis*-hexaphenyl-1,2-dihydrobenzene (singlet at 4.45 ppm) and the new hydrocarbon **17**. The latter was separated as a pale yellow solid from the mixture by repeated crystallization from an acetonitrile–methylene chloride mixture: mp 272–274 °C; ^{1}H NMR (CDCl$_3$) δ 5.89 (s, 2 H), 7.02 (s, 20 H), 7.5 (m, 4 H), 8.1 (m, 2 H), 8.75 ppm (m, 2 H); MS (*m*/*e*) 536, P. From these data, the structure of **17** can be assigned as (*E*,*Z*,*E*)-1,2,3,4,5,6-hexaphenyl-1,3,5-hexatriene.

b. Heptaphenyl-7-borabicyclo[2.2.1]heptadiene (3a). This compound was generated in situ by allowing 3.93 g (8.85 mmol) of borole **1a** to react with 1.60 g (9.0 mmol) of diphenylacetylene in 30 mL of pure toluene at 25 °C until the mixture became colorless. The mixture was then heated at reflux, during which time the solution became yellow and gradually turned a fluorescent yellow-green color. A characteristic singlet grew in the ^{1}H NMR spectrum (CDCl$_3$) of reaction samples at 4.25 ppm; after 24 h at reflux it constituted approximately 60% of 1.0 proton, if the aromatic proton signal area was taken as representing 35 protons.

Toluene was evaporated from the reaction mixture in vacuo, and the residue was digested with 10 mL of pure ether. The bright yellow powder was filtered off and then washed with dry ether at -10 °C; yield 1.18 g (84%).

That this solid was a mixture of at least two components was shown by a Soxhlet extraction procedure. The yellow solid was placed in a glass thimble having a frit of fine porosity. Extraction under nitrogen with anhydrous, deoxygenated ether led to deposition of a yellow solid in the extracting solid reservoir flask and left a residue in the thimble having a chartreuse green color.

This green component could be isolated in the pure state by repeated recrystallization from anhydrous, deoxygenated 1-chloroheptane. By X-ray crystallography (vide infra) this compound was shown to be an isomer of borepin **5a**, namely 1,2,3,3a,4,5-hexaphenyl-5-bora-3a,4-dihydro-5*H*-benz[*e*]indene (**7a**) or pseudoborepin: mp 233–235 °C; ^{1}H NMR (CDCl$_3$) 4.25 (s, 1 H), 6.25–7.50 ppm (m, 34 H); IR (mineral oil) 695 (s), 705 (s), 730 (m), 740 (m), 749 (m), 760 (s), 770 (m), 790 (m), 1550 (m), 1590 (s) cm^{-1}; UV (CH$_2$Cl$_2$) λ_{max} (ϵ) 415 (6100), 342 (8080), 276 (22700), 245 nm (28000). In contrast with the mass spectrum of borepin **5a**, pseudoborepin does not have a significant peak at *m*/*e* 534 (loss of PhB group).

The other component, 1,2,3,4,5,6,7-heptaphenylborepin (**5a**), could not be obtained in the pure state. A sample containing both the borepin and the pseudoborepin was obtained as a canary yellow solid from the ether extract of the Soxhlet procedure. When this solid is heated, it isomerizes into the pseudoborepin; thus, it does not have a true melting point. The ultraviolet spectrum of the borepin also appears to have a maximum around 410 nm witha shoulder absorption of 335 nm (Et$_2$O solution). The mass spectrum of borepin **5a** exhibits the parent ion (*m*/*e* 622) as the base peak and has a prominent peak at *m*/*e* 534 (loss of PhB group).

Although the pure borepin could not be obtained, its presence admixed with the pseudoborepin could be ascertained by chemical degradation.

c. Identification of Borepin 5a and Pseudoborepin 7a by Chemical Degradation. Prolonged heating of pure pseudoborepin **7a** with glacial acetic acid and the usual hydrolytic workup led to the isolation of 5-benzyl-1,2,3,4,5-pentaphenylcyclopentadiene (**18**) and small amounts of 1,2,3,4,5-pentaphenylcyclopentadiene. Compound **18** was identified by comparison with an authentic sample synthesized independently (vide infra).

Degradation of mixtures of borepin **5a** and its isomer **7a** can be achieved by mercurodeboronation. Thus, a mixture of the borepin isomers **5a** and **7a** (1.35 g, 2.0 mmol) was heated with a solution of 1.7 g (6.0 mmol) of mercuric chloride and 2.0 g of lithium chloride in 200 mL of THF and 40 mL of methanol. Then a solution of 2.0 g of potassium hydroxide and 1.0 g of mercuric chloride in 20 mL of methanol was introduced. After 2 h at reflux, the reaction mixture was poured into a mixture of benzene and water and the resulting suspension filtered. The benzene extract was separated, dried, and evaporated in vacuo. The residue was dissolved in anhydrous THF and the solution treated with a large excess of *n*-butyllithium. Heating the resulting mixture gave an emerald green color; after 15 min the solution was treated with methanol. The usual workup and column chromatographic separation allowed the isolation of 8% of hexaphenylbenzene (**8a**), 17% of *cis*-hexaphenyl-1,4-dihydrobenzene (**9a**), and 40% of *cis*-hexaphenyl-1,2-dihydrobenzene (**14a**), melting almost completely at 150–152 °C, resolidifying, and melting at 192–194 °C.

The structure of *cis*-hexaphenyl-1,2-dihydrobenzene can be determined from the following: (a) heating with *N*-bromosuccinimide in CCl_4 produces hexaphenylbenzene in 86% yield; (b) its ^1H NMR spectrum (CCl_4) is 4.45 (s, 2 H) and 6.8 ppm (m, 30 H), whereas the trans-1,2-, cis-1,4-, and trans-1,4-isomers have their methylene hydrogen signals at 4.0, 4.67, and 4.67 ppm, respectively; (c) its ultraviolet spectrum (MeOH) has its maximum at 325 nm (ϵ 10 300), whereas the *trans*-1,2-isomer absorbs at 312 nm (ϵ 10 700 in MeCN); (d) its mass spectrum has a parent peak at *m/e* 536; (e) it gives the correct elemental analysis for $C_{42}H_{32}$. Anal. Calcd: C, 93.99; H, 6.01; Found: C, 93.93; H, 5.92.

d. 7-Phenyl-1,2,3,4,5,6-hexa-*p*-tolyl-7-borabicyclo[2.2.1]heptadiene (3b). Heating samples of borane **3b** in refluxing toluene causes a merging of the two methyl signals to a broad signal (at 25 °C) at 2.60 ppm, as well as the growth of a singlet at 4.50 ppm. At 100 MHz and with an expanded scale, the peak at 2.60 ppm can be resolved into six distinct singlets of approximately equal intensity (at 25 °C in toluene-d_8). These signals are clearly characteristic of the tricyclic isomer of the borepin system, namely **7b**.

Synthesis of 5-Benzyl-1,2,3,4,5-pentaphenylcyclopentadiene (18). The interaction of 2.23 g (5.0 mmol) of pentaphenylcyclopentadiene with 5.5 mmol of *n*-butyllithium in 30 mL of anhydrous THF generates cyclopentadienyllithium. Addition of 6.0 mmol of benzyl bromide to the solution, 4 h of stirring, and hydrolytic workup yields crude 18. Recrystallization from ethanol yields colorless prisms: yield 2.09 g (78%); mp 185.5–186.5 °C; ^1H NMR ($CDCl_3$) 3.75 (2 H) and 6.7–7.4 ppm (30 H); mass spectrum (*m/e*): 536 (P, 92), 445 (P − 91, 100). Anal. Calcd for $C_{42}H_{32}$: C, 93.99; H, 6.01. Found: C, 93.67; H, 6.21.

X-ray Crystallographic Analysis of 7a. The photographic characterization of the unit cell of **7a**, $C_{48}H_{35}B$, found no symmetry higher than triclinic. The centrosymmetric alternative $P\bar{1}$ was confirmed by the presence of inversional symmetry. No correction for absorption was applied to the data. Crystal parameters: triclinic, $P\bar{1}$, a = 9.939 (2) Å, b = 10.530 (3) Å, c = 16.790 (4) Å, α = 78.58 (2)°, β = 85.53 (2)°, γ = 88.94 (2)°, V = 1717.1 (7) Å^3, Z = 2, μ(Mo Kα) = 0.70 cm^{-1}, D(calcd) = 1.20 g cm^{-3}. The structure was solved by direct methods, after inclusion in the starting set, reflections found to be weak links in the convergence map. All non-hydrogen atoms were refined with anisotopic thermal parameters, and all hydrogen atoms were treated as idealized (d(CH) = 0.96 Å) isotropic contributions. The phenyl rings at C(2), C(3), C(4), C(5), C(6), and B(7) were constrained to rigid, planar hexagons (d(CC) = 1.395 Å). Yellow-green crystals (0.22 × 0.22 × 0.39 mm) were examined at 295 K on a Nicolet R3m diffractometer and 5152 reflections collected at 0.710 73 Å with a graphite monochromator. The scan limits were $4 \le 2\theta \le 48°$ by the Wyckoff scan method. Of the 4971 independent reflections (R(merge) = 0.037), 3516 were observed at the $3\sigma(F_o)$ level. The refinement of the data yielded $R(F)$ = 6.59%, $R(wF)$ = 6.84%, GOF = 1.447, Δ/σ(final) = 0.026, $\Delta(\rho)$ = 0.29 e Å^{-3}, and N_α/N_γ = 9.02. All computations used SHELXTL(5.1) software (G. Sheldrick, Nicolet XRD, Madison, WI).

Acknowledgment. The support of the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant AFOSR-85-0108, and of Akzo Corporate Research America is gratefully acknowledged.

Supplementary Material Available: Tables of crystallographic data, atom coordinates, selected bond distances and angles, least-squares planes, anisotropic thermal parameters, and H atom coordinates and isotropic thermal parameters (7 pages); a table of observed vs calculated structure factors (30 pages). Ordering information is given on any current masthead page.