CHAPSO, which is in contrast to the pronounced effects of Tb^{3+} on NaTC aggregation. This is consistent with our lanthanide-induced ^1H NMR shift studies, which indicate that the association constant for Tb^{3+}-CHAPSO is much smaller than that for Tb^{3+}-NaTC.[16]

Fluorescence anisotropy of BkF in CHAPSO (Figure 5) showed a small increase in the presence of Tb^{3+} in the 13-14 mM CHAPSO region. As shown in the figure, uncertainty in the anisotropy values is in the range of ±0.003-0.004 at concentrations of CHAPSO above 10 mM. The increase in the viscosity of the probe microenvironment probably results from association of Tb^{3+} with CHAPSO micelles. Structural changes in the aggregate upon binding of the metal cation, which were indicated for NaTC, may be occurring for CHAPSO as well, despite the absence of cmc effects.

Conclusions

These studies indicate that metal cations can lower the cmc and increase the size of NaTC aggregates in aqueous solution. Trivalent cations show the greatest effect, while the smallest effects are observed with univalent Na^+. Other factors besides metal cation charge are also important: Tb^{3+} shows greater effects than Al^{3+}, suggesting that the larger and relatively softer acid Tb^{3+} is more strongly associated with the soft-base sulfonate groups on the hydrophilic NaTC tail than is the harder Al^{3+} ion. The microenvironment of the BkF probe is most viscous in the presence of Tb^{3+}, again suggesting a stronger binding and structural rigidity for NaTC aggregates with Tb^{3+} than with the other cations. The results suggest a 1:4 metal cation to NaTC binding stoichiometry above the cmc, which is consistent with other reports.[13,20] Scattered light intensity shows that the largest NaTC aggregates form in the presence of Tb^{3+}, followed by $Al^{3+} > Mg^{2+} > Na^+$, NaTC alone. The counterion of the metal salt appears to have no effect on the cmc behavior of NaTC.

In contrast to NaTC, CHAPSO is relatively insensitive to the metal cations. No significant cmc effects are observed, although the viscosity of the BkF microenvironment is slightly higher in the presence of Tb^{3+}. The absence of strong metal cation effects on CHAPSO aggregation is consistent with the nonionic behavior reported for zwitterionic bile salt derivatives.[23,24]

Acknowledgment. This work was supported by the United States Department of Energy (Grant No. DE-FG05-88ER13931).

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Photochemistry of Tetraarylborate Salts (Ar_4B^-): Formation of 2,5,7,7-Tetraphenyl-7-boratabicyclo[4.1.0]hepta-2,4-diene (a Boratanorcaradiene) by Irradiation of (*p*-Biphenylyl)triphenyl Borate

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Abstract: Irradiation of tetramethylammonium (*p*-biphenylyl)triphenylborate with UV light gives three isomeric boratanorcaradiene anions by a process analogous to the di-π-methane rearrangement of hydrocarbons. One of the boratanorcaradienes, tetramethylammonium 2,5,7,7-tetraphenyl-7-boratabicyclo[4.1.0]hepta-2,4-diene (**1**), was isolated as a deep red crystalline solid, and its structure was determined by X-ray crystallography. Borate **1** is a fluxional compound at room temperature; an electrocyclic rearrangement exchanges the two boron-bound phenyl groups. A mechanism for the photochemical rearrangement of (*p*-biphenylyl)triphenylborate is proposed, and the structural, chemical, and physical properties of **1** are discussed.

Williams and co-workers were the first to report a systematic study of the photochemistry of tetraarylborates.[1] They found that irradiation of sodium tetraphenylborate in oxygen-free aqueous solution produces 1-phenyl-1,4-cyclohexadiene in nearly quantitative yield. Under these conditions, the ultimate boron-containing product is the sodium salt of diphenylborinic acid. The mechanism of this unusual rearrangement was investigated by means of labeling experiments. These studies showed that the new carbon-carbon bond is formed intramolecularly between carbon atoms originally bound to boron. Photolysis of deuterium-labeled potassium dimesityldiphenylborate in water-containing dimethoxyethane (DME) solution gives a triarylborane. The substitution pattern observed in this product led Williams and co-workers to propose a reaction mechanism that proceeds through the formation of the bicyclic borate-containing intermediate(s) shown in Scheme I.

Scheme I

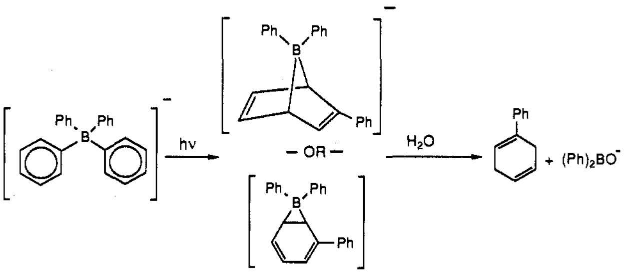
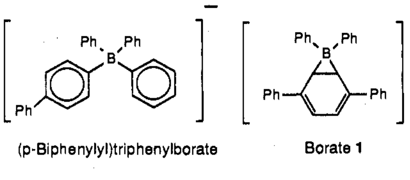


Chart I



(p-Biphenylyl)triphenylborate

Borate 1

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(1) Williams, J. L. R.; Grisdale, P. J.; Doty, J. C.; Glogowski, M. E.; Babb, B. E.; Maier, D. P. *J. Organomet. Chem.* **1968**, *14*, 53. Williams, J. L. R.; Grisdale, P. J.; Doty, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 4538. Williams, J. L. R.; Doty, J. C.; Grisdale, P. J.; Regan, T. H.; Happ, G. P.; Maier, D. P. *J. Am. Chem. Soc.* **1968**, *90*, 53. Grisdale, P. J.; Babb, B. E.; Doty, J. C.; Regan, T. H.; Maier, D. P.; Williams, J. L. R. *J. Organomet. Chem.* **1968**, *14*, 63. Grisdale, P. J.; Williams, J. L. R.; Glogowski, M. E.; Babb, B. E. *J. Org. Chem.* **1971**, *36*, 544.

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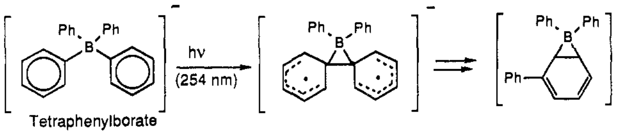
In 1975, Eisch and co-workers reported that photolysis of sodium tetraphenylborate in oxygen-free DME or THF solution gives diphenylborene anion (Ph_2B^-) by loss of biphenyl in competition with the direct formation of arylborohydrides.[2,3] However, our subsequent study of the irradiation of tetraphenylborate showed[4] that its primary photochemical reaction is formation of one of the bridged-borate intermediates considered by Williams.

Herein we report the first isolation and characterization of a boratanorcaradiene anion of the kind postulated by Williams and co-workers to be formed in the photolysis of tetraarylborates.[5] Irradiation of tetramethylammonium (*p*-biphenylyl)triphenylborate in oxygen-free acetonitrile solution gives tetramethylammonium 2,5,7,7-tetraphenyl-7-boratabicyclo[4.1.0]hepta-2,4-diene (**1**; Chart I). Borate **1** is a stable, deep red compound that is characterized by ^1H, ^{11}B, and ^{13}C NMR spectroscopy and by X-ray crystallography. The ^1H NMR spectrum of borate **1** shows that it is a fluxional compound; at room temperature a degenerate rearrangement interconverts the two boron-bound phenyl groups.

Results

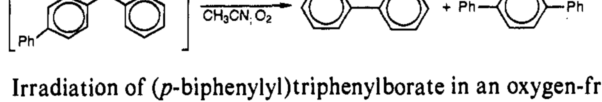
Irradiation of sodium tetraphenylborate in oxygen-free acetonitrile or THF solution gives one major primary product that was identified by ^1H and ^{11}B NMR spectroscopy as tetramethylammonium 2,7,7-triphenyl-7-boratabicyclo[4.1.0]hepta-2,4,-diene. However, despite numerous efforts, we were unable to isolate this compound in a form suitable for certain characterization by X-ray crystallography.[4] Mechanistic studies indicated that irradiation of tetraphenylborate initiates a process related to the well-known di-π-methane rearrangement of hydrocarbons,[6] eq 1. On this basis, we reasoned that irradiation of (*p*-biphenylyl)triphenylborate would give borate **1**, which, by virtue of its higher symmetry, we hoped, would be isolable in crystalline form.



Tetraphenylborate

(1)

(1) Photolysis of (*p*-Biphenylyl)triphenylborate. The UV-vis absorption spectrum of tetramethylammonium (*p*-biphenylyl)triphenylborate in acetonitrile solution shows a maximum at 272 nm (ϵ_{max} = 22 600 M^{-1} cm^{-1}) that is characteristic of biphenyl derivatives. Its ^{11}B NMR spectrum shows a single resonance at δ -6.76. Irradiation of (*p*-biphenylyl)triphenylborate at 254 nm in oxygen-saturated acetonitrile solution gives biphenyl (18%) and *p*-terphenyl (82%), eq 2. Observation of these products signals operation of the di-π-methane-like reaction with rearrangement of the biphenylyl group dominating migration of a phenyl group by a ratio of ca. 5:1.



(2)

Irradiation of (*p*-biphenylyl)triphenylborate in an oxygen-free acetonitrile solution at 0 °C gives a blood red photolysis mixture. The ^{11}B NMR spectrum of this solution immediately after the irradiation shows two new peaks at δ -26.6 and -27.2 in a ratio of ca. 1:1 (Figure 1a). This ratio does not stay constant. At 30 °C, the intensity of the resonance at δ -27.2 decreases according to a first-order rate law ($t_{1/2}$ = 115 min) simultaneously with an increase in the intensity of the peak at δ -26.6. After 6 h at 30 °C, the intensities of the two peaks reach a ratio ca. 5:1 (Figure 1b) and are constant thereafter.

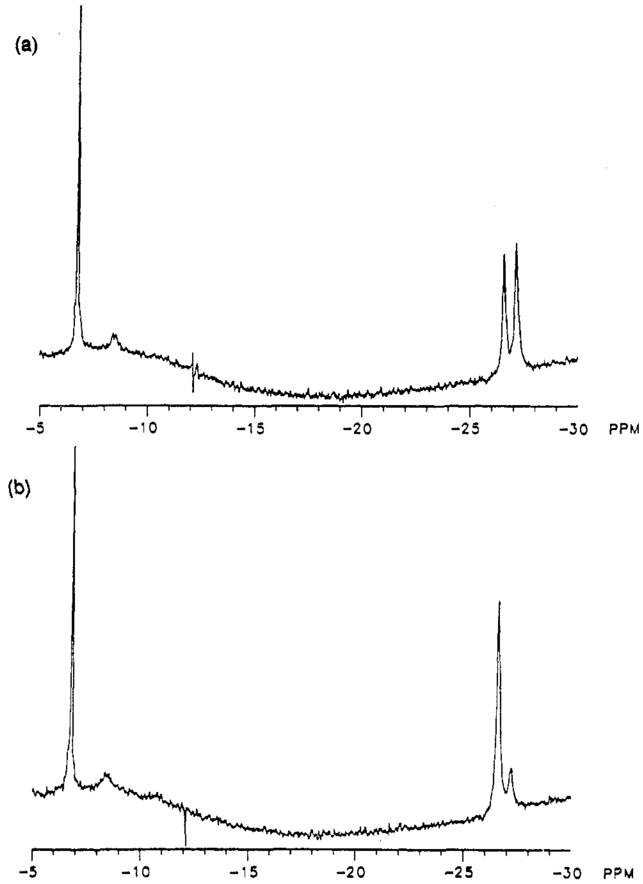


Figure 1. 96-MHz ^{11}B NMR spectrum of: (a) a solution of (*p*-biphenylyl)triphenylborate (1.20×10^{-2} M in CD_3CN) following irradiation at 254 nm; (b) same solution as (a) after 6 h at 30 °C.

Related behavior is observed when the photolysis of (*p*-biphenylyl)triphenylborate is monitored by ^1H NMR spectroscopy in CD_3CN solution. Immediately after irradiation, the NMR spectrum of the reaction mixture shows resonances for three products (the chemical shift data are given in the Experimental Section). However, after the sealed solution was heated at 70 °C for 2 h, one product had completely disappeared, the second had increased by the amount corresponding to the disappearance of the first, and the resonances of the third product were unchanged.

These findings show that irradiation of (*p*-biphenylyl)triphenylborate leads to three primary photoproducts. Two of these (^{11}B NMR δ -26.6, -27.2) account for 80% of the consumed starting material; they are formed by migration of the biphenylyl group and give *p*-terphenyl when they react with oxygen. The third (^{11}B NMR δ -27.2) is formed by migration of a phenyl group; it gives biphenyl when it reacts with oxygen. One of the products (^{11}B NMR δ -27.2) formed by migration of the biphenylyl group is thermally unstable. It rearranges completely to its isomer with ^{11}B NMR absorption at δ -26.6. Thus, the irradiation of (*p*-biphenylyl)triphenylborate followed by thermal isomerization gives two products in a ratio of 5:1.

The major product from photolysis of tetramethylammonium (*p*-biphenylyl)triphenylborate following thermal isomerization of the photolysis mixture was isolated in 30% yield as dark red, almost black, needles. Elemental analysis shows that it is isomeric with the starting material. Its ^{11}B NMR spectrum in acetonitrile solution shows a single resonance at δ -26.6. The UV-vis spectrum of the photoproduct at room temperature in acetonitrile solution (Figure 2) shows a UV band at 294 nm (ϵ_{max} = 19 900 M^{-1} cm^{-1})

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(2) Eisch, J. J.; Tamao, K.; Wilcsek, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 895.

(3) The route for formation of diphenylborene anion has recently been reconsidered: Eisch, J. J.; Boleslawski, M. P.; Tamao, K. *J. Org. Chem.* **1989**, *54*, 1627. However, reinvestigation of these claims has shown them to be ambiguous: Boyatzis, S.; Wilkey, J. D.; Schuster, G. B. *J. Org. Chem.* **1990**, *55*, 4537.

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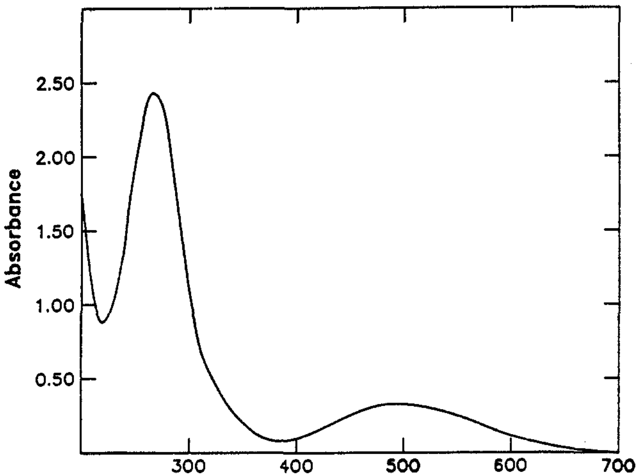


Figure 2. UV–vis absorption spectrum of **1** (1.3×10^{-4} M) in acetonitrile solution.

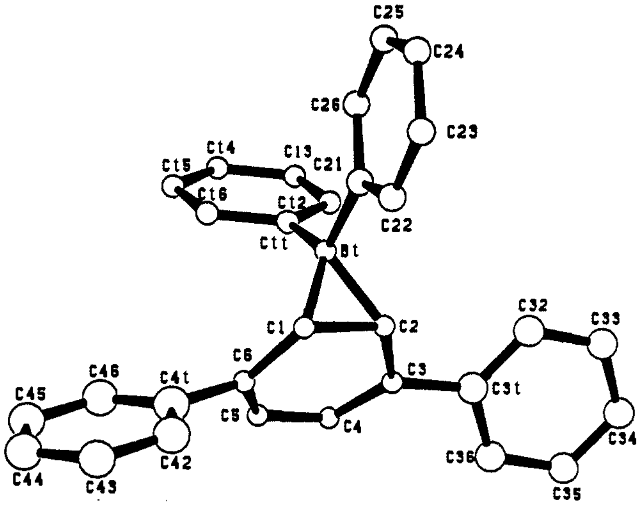
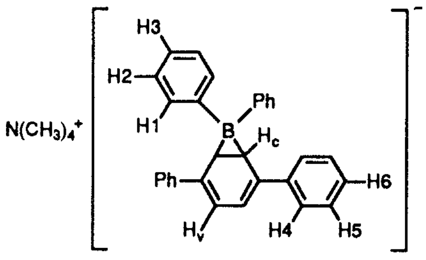


Figure 3. Structure of boratanorcaradiene anion **1** determined by X-ray crystallography. The tetramethylammonium cation is not shown. Key bond lengths and angles: **B**1–C1 = 1.60 (5), C1–C2 = 1.58 (5), C2–C3 = 1.45 (5), C3–C4 = 1.40 (5), C4–C6 = 1.46 (5) Å; ∠C1B1C2 = 60 (2), ∠B1C1C2 = 59 (2)°.

Table I. Correlation of ^1H and ^{13}C NMR Resonances of **1** from HETCOR Experiment



1

^{13}C NMR (δ)	assignment	^1H NMR (δ)
37.2 (br)	CH_c	1.39 (s, 2 H)
55.5	NCH_3	2.74 (s, 12 H)
112.9	CH_v	5.55 (s, 2 H)
122.0	CH_3	6.68 (t, J = 7.2 Hz, 2 H)
126.4	CH_2	6.81 (t, J = 7.2 Hz, 4 H)
125.6	CH_6	7.03 (t, J = 7.5 Hz, 2 H)
135.5 (br)	CH_1	7.10 (d, J = 7.0 Hz, 4 H)
128.1	CH_5	7.17 (t, J = 7.5 Hz, 4 H)
126.6	CH_4	7.69 (d, J = 7.5 Hz, 4 H)

and a visible band at 510 nm (ϵ_{max} = 2500 M^{-1} cm^{-1}). Significantly, the intensity ratio of these two bands is essentially unchanged when the spectrum is recorded in glassy 2-methyltetrahydrofuran at 77 K. This observation rules out the possible presence of two rapidly equilibrating species, one of which is responsible for the color of the solution.

The ^1H NMR spectrum of the isolated photoproduct in CD_3CN at room temperature shows a tetramethylammonium peak at δ 3.01, two sharp singlets (δ 1.29, 5.57), each representing two hydrogens, and six multiplets accounting for the 20 aromatic hydrogens. The ^{13}C NMR spectrum of the photoproduct in THF-d_8 shows peaks for only nine unique carbon atoms.[7] Two of these (δ 37.1 and 135.5) are broadened by coupling to the boron atom. We presume that the resonances of the unprotonated carbon atoms are not observed in this spectrum, and therefore, the carbons with resonance at 135.5 are assigned to β positions with respect to boron.

The chemical and spectroscopic data indicate that the major product obtained from photolysis of (*p*-biphenylyl)triphenylborate is boratanorcaradiene **1**. This conclusion was proven by X-ray crystallography.[8] Figure 3 shows the structure of the borate and gives some key bond angles and lengths. Within experimental error, the borate-containing ring is an equilateral triangle inclined at an angle of 104° with respect to the four nearly coplanar diene carbon atoms. The six-membered ring is twisted; C2 is ca. 24 (5)° above the diene plane. Surprisingly, the unit cell contains two unique anions. Furthermore, neither anion is symmetric about the plane containing the boron and bisecting C1–C2 and C4–C5. These slight asymmetries, both within each borate and between the borate anions, are attributed to crystal-packing forces.

(2) Triplet Sensitization of (*p*-Biphenylyl)triphenylborate. The sensitizer employed for investigation of the reactions of triplet (*p*-biphenylyl)triphenylborate must meet several requirements. First, the triplet energy of the sensitizer must be greater than that of the borate. The latter value is certainly less than 66 kcal/mol, which is the triplet energy of biphenyl itself.[9] Second, the sensitizer must absorb in a unique spectral region of lower energy than the borate. This will ensure exclusive excitation of the sensitizer and avoid complications caused by singlet–singlet energy transfer. Third, the sensitizer must be a relatively difficult compound to reduce. We have shown previously that single-electron transfer from tetraphenylborate to easily reduced sensitizers results in reaction of the former to form biphenyl.[4] For these reasons, we chose *N*-phenylcarbazole as the sensitizer. Its triplet energy is reported to be 69.6 kcal/mol,[10] its singlet energy is 82.6 kcal/mol, and its singlet lifetime is only 6.9 ns in acetonitrile solution.[11] The reduction potential of *N*-phenylcarbazole is presumed to be lower than −2.00 V vs SCE in DMF solution,[12] and therefore, its triplet state is unlikely to react with (*p*-biphenylyl)triphenylborate by a single-electron transfer mechanism.

Irradiation of *N*-phenylcarbazole at 350 nm in the presence of (*p*-biphenylyl)triphenylborate in nitrogen-saturated acetonitrile solution gives borate **1** as the sole primary product detected by ^{11}B NMR spectroscopy. None of the other isomeric borates formed during the direct irradiation of (*p*-biphenylyl)triphenylborate could be detected in this experiment. Irradiation of (*p*-biphenylyl)triphenylborate alone at 350 nm gives no reaction. The yield of borate **1** formed in the triplet-sensitized reaction never rises above ca. 20% due to its competitive absorption with *N*-phenylcarbazole at 350 nm. Irradiation of borate **1** leads to its decomposition.

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(7) (a) Gragg, B. R.; Layton, W. J.; Niedenzu, K. *J. Organomet. Chem.* **1977**, *132*, 29. (b) Marks, T. J.; Shimp, L. A. *J. Am. Chem. Soc.* **1972**, *94*, 1542.

(8) A description of the structure determination is given in ref 5. A complete report of the crystal structure determination is available as supplementary material to that paper.

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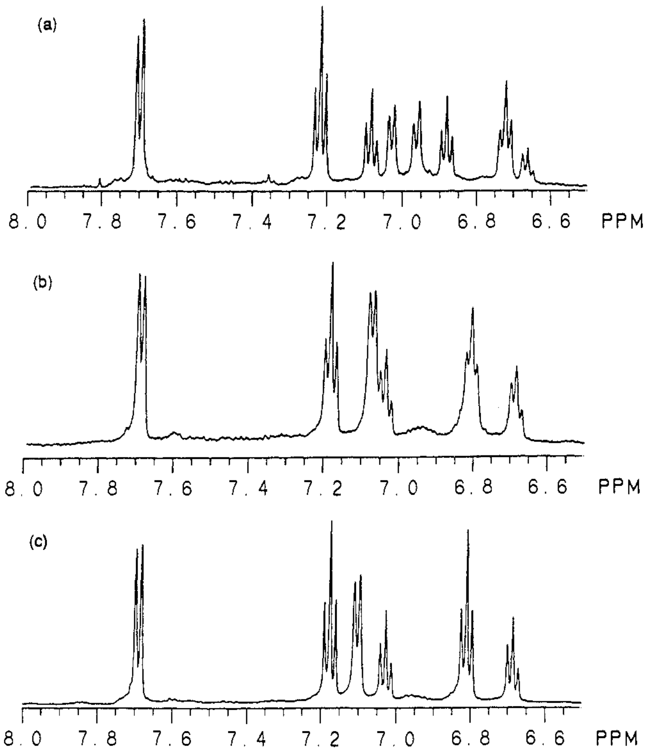

Figure 4. 500-MHz ^{1}H NMR spectrum of **1** in THF-d_8: (a) −80; (b) −5; (c) 20 °C.

(3) Chemical and Physical Properties of Tetramethylammonium 2,5,7,7-Tetraphenyl-7-boratabicyclo[4.1.0]hepta-2,4-diene (1). With the structure of borate **1** clearly established, it is possible to assign uniquely many of the resonances in its ^{1}H and ^{13}C NMR spectra. This was accomplished by comparison of the ^{1}H and ^{13}C NMR spectra in THF-d_8 with a (^{1}H, ^{13}C) HETCOR 2-D NMR experiment.[13] The results allow unambiguous assignment of all ^{1}H resonances, as well as all ^{13}C resonances for proton-bearing carbon atoms. The assignments are summarized in Table I. The broadening of the ^{13}C resonance at δ 135.5 due to coupling with boron allows differentiation of the phenyl groups bound to the boron atom from those bound to carbon atoms.

One peculiar fact evident from the ^{1}H NMR spectrum of borate **1** is that there is only one group of resonances for the phenyl groups attached to the boron atom. It is apparent from the structure of **1** that these groups should be inequivalent. We examined the temperature dependence of the ^{1}H NMR spectrum of **1** in THF-d_8 to resolve this dilemma.

The aromatic regions of the ^{1}H NMR spectra (500 MHz) of borate **1** in degassed THF-d_8 recorded at 20, −5, and −80 °C are shown in Figure 4. The spectrum at 20 °C shows relatively sharp resonances for the six two-proton multiplets assigned in Table I. Three of these multiplets begin to broaden when the temperature is lowered to −5 °C; the other three multiplets as well as the two singlets (not shown) for H$_c$ and H$_v$ (see Table I) are unaffected by the decrease in temperature. Further cooling results in additional broadening until at −80 °C these broadened peaks once again sharpen into resolved multiplets. The ^{1}H NMR spectrum of borate **1** recorded at −80 °C shows the presence of two distinct phenyl groups bound to the boron atom. The correlation of the ^{1}H NMR resonances of **1** at 20 and −80 °C are summarized in Table II. There are no additional changes in the spectrum when the temperature is lowered below −80 °C.

These experiments reveal operation of a rapid, degenerate thermal rearrangement that exchanges the phenyl groups of borate **1** that are attached to the boron atom. Further examination of this rearrangement as well as consideration of the thermodynamic parameters derived from the coalescence temperature (−20 °C at 500 MHz) will be detailed in the Discussion.

Table II. Correlation of ^{1}H NMR Resonances of **1** at 20.0 and −80.0 °C

δ (20.0 °C)	δ (−80.0 °C)
1.39 (s, 2 H)	1.29 (s, 2 H)
2.74 (s, 12 H)	2.89 (s, 12 H)
5.55 (s, 2 H)	5.57 (s, 2 H)
6.68 (t, 2 H)	6.72 (t, J = 7.2 Hz, 1 H) 6.66 (t, J = 7.5 Hz, 1 H)
6.81 (t, 4 H)	6.88 (t, J = 7.2 Hz, 2 H) 6.72 (t, J = 7.2 Hz, 2 H)
7.03 (t, 2 H)	7.08 (t, J = 7.2 Hz, 2 H)
7.10 (d, 4 H)	7.03 (d, J = 7.0 Hz, 2 H) 6.96 (d, J = 7.5 Hz, 2 H)
7.17 (t, 4 H)	7.22 (t, J = 7.5 Hz, 4 H)
7.69 (d, 4 H)	7.71 (d, J = 8.0 Hz, 4 H)

The temperature dependence of the ^{11}B NMR spectrum of borate **1** in CD$_3$CN was also examined. There is no change in the chemical shift when the solution is cooled to −40 °C, but a significant broadening of the resonance is noted. Similarly, heating the solution to 60 °C causes only a sharpening of the ^{11}B resonance of **1**. These effects are attributed to the temperature dependence of the quadrupolar relaxation of the ^{11}B nucleus rather than to a thermal rearrangement.

Finally, in the attempt to help explain the unexpected deep red color of borate **1** and as an aid to the description of its reaction with oxygen, we tried to determine its oxidation potential. Cyclic voltammetry in degassed acetonitrile solution containing tetrabutylammonium perchlorate as a supporting electrolyte shows an irreversible oxidation wave (sweep rate 50 v/s) for **1** at −0.8 V vs SCE. Thus, borate **1** is a powerful reducing agent.

Discussion

(1) Mechanism of the Direct and Triplet-Sensitized Irradiation of (*p*-Biphenylyl)triphenylborate. The direct irradiation of (*p*-biphenylyl)triphenylborate gives three isomeric primary products. One of these is unambiguously identified as boratanorcaradiene **1** by its spectroscopic properties and, finally, by X-ray crystallography. The structures of the two remaining products are assigned on the basis of their chemical and spectroscopic properties and by reference to the well-known di-π-methane rearrangement pathway. We designate the analogous process the di-π-borate rearrangement since this reaction has been shown to operate generally when a tetravalent boron anion replaces the "methane" carbon atom.[14-16]

The di-π-borate rearrangement of (*p*-triphenylyl)triphenylborate gives rise to three isomeric boratanorcaradiene products. These are shown in Scheme II along with a possible mechanism for their formation. Irradiation of (*p*-triphenylyl)triphenylborate at 254 nm generates two singlet excited states: a higher energy state localized primarily on one of the phenyl groups and the lowest energy state localized primarily on the biphenylyl group. If the reaction to form bridged biradical intermediate **4** is faster than internal conversion of the upper state, then this two-state hypothesis may accommodate phenyl to phenyl group coupling leading, ultimately, to borate **3** and biphenylyl to phenyl group coupling that results in formation of borates **1** and **2**. The cleavage of one of the two equivalent carbon–boron bonds in **4** regenerates a phenyl group, and subsequent bond formation leads to unobserved intermediate borate **6**. The postulated [1,5] sigmatropic shift of **6** is exothermic by virtue of the extension of conjugation and leads to the observed boratanorcaradiene **3**. A related path leads to boratanorcaradienes **1** and **2**. Biphenylyl to phenyl group coupling generates bridged biradical intermediate **5** where the two

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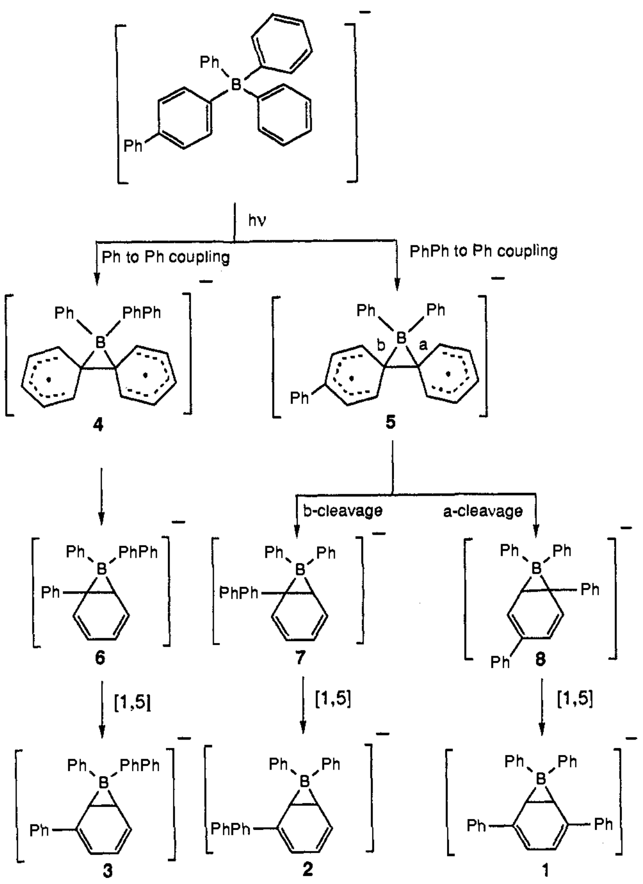
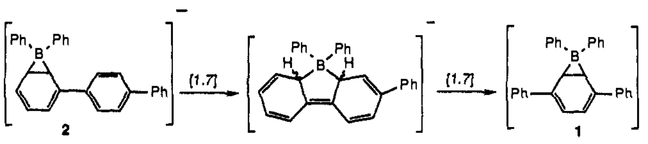
Scheme II



Scheme III



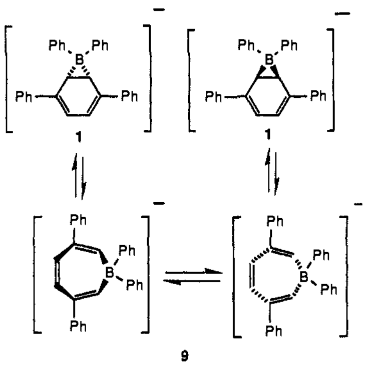
carbon–boron bonds are inequivalent. Cleavage of the bond labeled a gives unobserved borate **8** and, after a [1,5] shift, boratanorcaradiene **1**. On the other hand, cleavage of the bond labeled b leads ultimately to formation of **2**. With the data available, the mechanism outlined in Scheme II cannot be distinguished from one where concerted [1,2] sigmatropic shifts from the excited singlet state(s) of (*p*-biphenylyl)triphenylborate give borates **6**, **7**, and **8** directly.

The results of the triplet-sensitization experiments can be accommodated by the mechanism postulated in Scheme II. Triplet *N*-phenylcarbazole is sufficiently energetic to form only the lowest triplet state of (*p*-biphenylyl)triphenylborate so only biphenylyl to phenyl group coupling products are obtained. Similarly, it is likely that the spin state of biradical intermediate **5** will influence the selection of bond a or bond b for cleavage. Alternatively, if the di-π-borate rearrangement in the direct irradiation proceeds by the concerted [1,2] shift path, the triplet-sensitized reaction may proceed through the mechanism shown in Scheme II with only the route through **5** and **8** to **1** active.

(2) Thermal Conversion of Borate 2 to Borate 1. Isomerization of **2** to **1** can occur by a number of thermally allowed routes. However, the overall reaction can be described as two [1,7] sigmatropic rearrangements as shown in Scheme III. As no intermediates are detected by NMR spectroscopy, there is no direct evidence to support a specific pathway. The driving force to the isomerization is presumably the extension of conjugation of the π system that occurs when the two phenyl groups are at the terminal positions of the 1,4-diene.

(3) Degenerate Thermal Rearrangement of Borate 1. It is clear from analysis of the temperature dependence of the ^{1}H NMR spectrum of borate **1** that at room temperature in solution it undergoes a rapid degenerate thermal rearrangement. This process exchanges the two phenyl groups bound to boron without simultaneously exchanging the hydrogen atoms on the cyclohexadiene-like ring. Sigmatropic rearrangements cannot produce this unique equivalence. However, electrocyclic ring opening of **1** to 1,1,3,6-tetraphenylboratepine (**9**) followed by boat–boat interconversion of **9** and subsequent ring closure can fulfill the experimental requirements. This path is outlined in Scheme IV. The related interchange of C7 substituents of norcaradienes has also been rationalized by this process.[17]

Scheme IV



The experimental data do not permit discrimination between the exchange mechanism outlined in Scheme IV from one where heterolytic carbon–boron bond cleavage generates a cyclohexadienyl-like anion. We consider the latter route to be much less likely since bond cleavage and the formation of a high energy content intermediate are not compensated by bond formation.

With assumption of the exchange mechanism of Scheme IV, the relative energies of borates **1** and **2** may be estimated from the NMR spectral data. The coalescence of the boron-bound phenyl group resonances occurs at −20 °C and implies that **9** can be no more than ca. 10 kcal/mol higher energy than **1**. Similarly, since no resonances attributable to **9** (or to anything else other than **1**) can be detected in the ^{1}H or ^{11}B NMR spectra of **1** up to 60 °C, we estimate that **9** must be at least 3 kcal/mol higher energy than **1**.

(4) Optical and Electrochemical Properties of Borate 1. We were surprised to discover that boratanorcaradiene **1** is a highly colored compound. Similarly substituted norcaradienes are colorless substances with absorptions only in the UV spectral region.[18] To address this feature, ab initio molecular orbital calculations on the parent (unsubstituted) boratanorcaradiene anion were carried out with use of GAUSSIAN 86 series of programs and a 3-21G basis set.[19] For comparison purposes, calculations at the same level were performed on norcaradiene itself.

The molecular orbital calculations on boratanorcaradiene anion satisfactorily reproduce the geometry of borate **1** obtained from the solution of the crystal structure. They also reveal that the HOMO of **1** is formed from combination of the diene Ψ_2 orbital with the appropriate Walsh-like orbital of the three-membered boron-containing ring. Significantly, the HOMO of norcaradiene has precisely the same nodal properties as are calculated for the boratanocaradiene anion. However, the energy of the hydrocarbon HOMO is considerably lower than that obtained for the borate.

The findings of the calculations may be used to explain the absorption spectrum of **1** and its electrochemical behavior. Boratanorcaradiene and norcaradiene are isoelectronic and appear also to be nearly isostructural. The difference, of course, is that

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the borate has one fewer nuclear proton than the hydrocarbon. Consequently, there is a smaller attractive potential for the electrons of the former, and its corresponding orbitals are of higher energy. It is reasonable to expect that the effect of decreasing nuclear charge will diminish with distance from the nucleus. On this basis, the difference in energy of the LUMO of boratanorcaradiene anion and norcaradiene will be less than for their HOMOs.[20] Thus, the lowest energy absorption bhand of the borate is expected to occur at lower energy than the corresponding band of the hydrocarbon. These considerations also account for the remarkably low oxidation potential of **1**.

Conclusions

Irradiation of tetramethylammonium (*p*-biphenylyl)triphenylborate with UV light causes a di-π-borate rearrangement and formation of three isomeric boratanorcaradienes. One of these is thermally unstable and isomerizes to tetramethylammonium 2,5,7,7-tetraphenyl-7-boratabicyclo[4.1.0]hepta-2,4-diene (**1**). Borate **1** is a red, crystalline solid. Its structure was determined by means of X-ray crystallography. In solution at room temperature, **1** is a fluxional compound. An electrocyclic rearrangement causes rapid equilibration of the boron-bound phenyl groups without concomitant exchange of the hydrogen atoms bound to the cyclohexadiene-like ring.

Experimental Section

General Procedures. Photolyses were performed in a Rayonet photochemical reactor, Model RPR-100, equipped with 254- or 350-nm lamps. ^{1}H NMR spectra were recorded on Varian Associates XL-200 or General Electric QE 300-, NT 360-, or GN 500-MHz FT-NMR spectrometer. ^{11}B chemical shifts are referenced to $BF_3{\cdot}Et_2O$ (δ 0.0), with negative values assigned to higher field resonances, and were recorded on a GE QE-300NB spectrometer at 96 MHz. ^{13}C NMR spectra were recorded on General Electric GN-300NB or GN-500-MHz FT-NMR spectrometer. UV–vis absorption spectra were recorded on a Perkin-Elmer Model 552 spectrophotometer. Conversion of borates was monitored by reversed-phase HPLC on a Perkin-Elmer Series 2 liquid chromatograph with LC-75 spectrophotometric detector with use of a 25-cm Alltech CN column from Alltech Associates and 30:70 acetonitrile/water as eluant. Elemental analyses were performed by the Microanalysis Laboratory, Department of Chemistry, University of Illinois. Manipulation of the air-sensitive borate **1** was accomplished in a Vacuum Atmospheres Co. Model HE-553 Dri Lab equipped with an AV-1 Auto Vac and a Dri Train Model 40-1 inert gas purifier. *N*-Phenylcarbazole (Aldrich) was recrystallized from ethanol prior to use. Diethyl ether, tetrahydrofuran, and THF-d_8 were distilled from sodium immediately prior to use. Acetonitrile and CD_3CN were distilled from calcium hydride immediately prior to use.

Tetramethylammonium (*p*-Biphenylyl)triphenylborate. 4-Bromobiphenyl (10.4 g, 44.6 mmol) in 80 mL of dry THF was cooled to −78 °C under nitrogen. *n*-Butyllithium (1.5 M in hexane, 20 mL, 30 mmol) was added dropwise with stirring. The mixture was stirred for 40 min, during which time 4-biphenylyllithium precipitated as a white solid. Triphenylborane (5.95 g, 24.6 mmol) in 20 mL of THF was added dropwise, and the solution was stirred at −78 °C for 1 h. The mixture was warmed to room temperature, the solid dissolved, and the solution was stirred for 24 h. The reaction mixture was concentrated in a stream of dry nitrogen and diluted with 10 mL of benzene and 10 mL of a saturated aqueous solution of $N(CH_3)_4Br$. The resulting white solid was collected by vacuum filtration and washed with ether. Recrystallization from acetonitrile/methanol yielded 10.8 g (23 mmol, 92%) of tetramethylammonium (*p*-biphenylyl)triphenylborate: ^{1}H NMR (CD_3CN) δ 3.02 (s, 12 H), 6.85 (t, 3 H), 7.01 (t, 6 H), 7.22–7.39 (m, 13 H), 7.58 (d, 2 H); ^{11}B NMR (CH_3CN) δ −6.76 (s); λ_{max} (CH_3CN) 272 nm (log ϵ 4.4). Anal. Calcd for $C_{34}H_{36}NB$: C, 86.98; H, 7.73; N, 2.98; B, 2.30. Found: C, 86.68; H, 7.57; N, 2.97; B, 2.07.

Photolysis of Tetramethylammonium (*p*-Biphenylyl)triphenylborate Followed by ^{1}H NMR Spectroscopy. Into a 5-mm NMR sample tube was placed 0.5 mL of a 6.7×10^{-3} M solution of (*p*-biphenylyl)triphenylborate in CD_3CN. The sample was freeze–pump–thaw degassed (four cycles, 5×10^{-6} mm), and the tube was sealed. The sample was irradiated at 254 nm and examined by ^{1}H NMR spectroscopy at irradiation times of 0, 1.5, 5, 20, and 60 min. After 60 min of irradiation, the ^{1}H NMR spectrum of the deep red solution revealed an ~50% conversion of starting borate and the presence of three boratanorcaradiene photoproducts. The products were identified by the chemical shifts and splitting patterns of their vinyl hydrogen resonances. For (**1**): boratacyclopropyl hydrogens δ 1.28 (s), vinyl hydrogens 5.56 (s). For (**2**): vinyl hydrogens δ 4.99 (dd, J_1 = 6 Hz, J_2 = 9 Hz), 5.47 (d, J = 6 Hz), 6.23 (dd, J_1 = 6 Hz, J_2 = 9 Hz). For (**3**): vinyl hydrogens δ 4.99 (dd, J_1 = 6 Hz, J_2 = 9 Hz), 5.41 (d, J = 6 Hz), 6.23 (dd, J_1 = 6 Hz, J_2 = 9 Hz). Afterward, the sealed tube was heated at 70 °C for 2 h. The ^{1}H NMR spectrum then revealed the disappearance of the resonances of **2** accompanied by an increase in intensity of the resonances of **1**. The resonances of **3** were unchanged. The ^{11}B NMR spectrum of this sample showed a major product resonance at δ −26.6 (**1**) and minor resonances at −27.2 (**3**).

Photolysis of (*p*-Biphenylyl)triphenylborate Followed by ^{11}B NMR Spectroscopy. Approximately 3 mL of a 1.20×10^{-2} M solution of the borate in CD_3CN was placed in a 10-mm NMR sample tube. The sample was freeze–pump–thaw degassed (four cycles, 10^{-6} mm), and the tube was sealed. The ^{11}B NMR spectrum before irradiation showed the presence of the starting borate (δ −6.76) and no other resonances. The sample was placed in a quartz cooling vessel containing ice–water and irradiated at 254 nm for 2 h. The ^{11}B NMR spectrum of this deep red solution revealed an approximately 45% conversion of starting borate. In addition, new resonances at δ −26.6 and −27.2 were observed in a ratio of 1:1. Thereafter, the NMR probe was maintained at 30 °C for a period of 6 h by use of the variable-temperature controller. During this time, ^{11}B NMR spectra were recorded every 15 min, 2.5 min of which was required for data acquisition. After 6 h, the ratio of product resonances was 5:1. The 24 spectra thus obtained were analyzed in the following manner. A Lorentzian line shape was assumed for each peak, and the peak height of each product resonance was normalized by the peak height of the stating borate, which is inert under these conditions. The resulting data were plotted versus time. Within experimental error, both the decay of the δ −27.2 resonance and the growth of the δ −26.6 resonance are first order and occur with the identical rate constant $k = 1.0 \times 10^{-4}\ s^{-1}$. These data, along with the ^{1}H NMR spectra, allowed the unambiguous correlation of ^{1}H and ^{11}B resonances.

Photolysis of (*p*-Biphenylyl)triphenylborate in the Presence of Oxygen. A 2-mL volume of a 5.8×10^{-3} M solution of the borate in CH_3CN was placed in a 1-cm quartz cell. The sample was purged with oxygen and irradiated at 254 nm for 2 h with stirring. A measured quantity of naphthalene was added to the exhaustively irradiated yellow sample as internal standard, and the sample was diluted with CH_3CN to a known volume. Analysis of the sample by gas chromatography revealed the formation of biphenyl (18%) and *p*-terphenyl (82%), identified by comparison of GC retention times and mass spectra of authentic samples: biphenyl, M^+ 154; *p*-terphenyl, M^+ 230.

Preparation and Isolation of 1. Typical Procedure. An acetonitrile solution of (*p*-biphenylyl)triphenylborate (100 mL, 2.0×10^{-2} M) was placed in a 250-mL quartz round-bottom flask containing a magnetic stir bar. The flask was fitted with a septum, and the sample was purged with nitrogen for 30 min. The flask was placed in a Rayonet reactor and irradiated at 254 nm for 2 h with stirring. The nitrogen atmosphere was maintained throughout the photolysis. Analysis of such solutions by ^{11}B NMR spectroscopy indicates an approximately 70% conversion of starting borate. Further irradiation does not improve the yield of **1** but results, instead, in its photochemical decomposition.

Workup of the photolysis mixture was accomplished in a drybox no less than 24 h after photolysis to ensure that equilibrium between the products had been established. The separation scheme was devised to take advantage of the differing solubilities of the various components of the mixture. First, the solution was concentrated in vacuo with gentle heating to a volume of ~5 mL. The mixture was filtered to remove *p*-terphenyl, which is only slightly soluble in acetonitrile, and the filtrate was evaporated to dryness. The resulting solid was digested with ~5 mL of warm THF and filtered to remove starting borate, which is insoluble. The filtrate was evaporated to dryness, and the resulting solid was recrystallized from acetonitrile/ether. Several recrystallizations were required to obtain **1** that was sufficiently free from other borates and oxidation products. Pure **1** was obtained as dark purple (almost black) needles: ^{1}H NMR (CD_3CN) δ 1.29 (s, 2 H), 3.01 (s, 12 H), 5.57 (s, 2 H), 6.80 (t, J = 7.5 Hz, 2 H), 6.90 (t, J = 7.5 Hz, 4 H), 7.04 (d, J = 7.0 Hz, 4 H), 7.16 (t, J = 7.8 Hz, 2 H), 7.29 (t, J = 7.8 Hz, 4 H), 7.70 (d, J = 7.0 Hz, 4 H); ^{13}C NMR (CD_3CN) δ 36.7 (br), 56.5, 112.9, 123.2, 126.9, 127.3, 129.0, 135.6 (br); ^{11}B NMR (CD_3CN) δ −26.6 (s); λ_{max} (CH_3CN) 294 nm (log ϵ 4.3), 510 (3.4). Anal. Calcd for $C_{34}H_{36}NB$: C, 86.98; H, 7.73; N, 2.98; B, 2.30. Found: C, 86.50; H, 7.62; N, 3.10; B, 2.05.

Variable-Temperature ^{11}B NMR Spectroscopy. Approximately 3 mL of a solution of **1** in CD_3CN was placed in a 10-mm NMR sample tube. The sample was freeze–pump–thaw degassed, and the tube was sealed.

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^{11}B NMR spectra were recorded while the variable-temperature controller was used to maintain the desired probe temperature. Spectra were obtained at the following temperatures (observed Lorentzian line width): +60 °C (21 Hz), +40 °C (25 Hz), ambient (30 Hz), −40 °C (80 Hz). Neither the resonance frequency of **1** (δ −26.6) nor the symmetry of the peak was observed to change with either heating or cooling of the sample.

(^1H, ^{13}C) HETCOR Spectroscopy of 1 in THF-d_8. A sample of **1** in THF-d_8 was placed in a 5-mm NMR sample tube. The sample was freeze–pump–thaw degassed and the tube sealed. A HETCOR experiment was performed. From the ^1H, ^{13}C, and 2-D NMR data, the assignments shown in Table I were made. The carbon resonances at δ 37.2 and 135.5 are broadened due to coupling to boron.

Variable-Temperature ^1H NMR Spectroscopy of 1. A solution of **1** in THF-d_8 (0.5 mL) was placed in a 5-mm NMR sample tube. The sample was freeze–pump–thaw degassed, and the tube was sealed. The temperature of the NMR probe was regulated by use of the variable-temperature controller, and ^1H NMR spectra were obtained at the following temperatures: 20.0, −1.0, −5.0, −10.0, −15.0, −20.0, −25.0, −30.0, −40, −50, −60, −70, −80, −90, −100 °C. When the solution was cooled to −5.0 °C, the resonances assigned to the phenyl groups attached to boron (7.10, 6.81, 6.68) began to broaden. Further cooling resulted in additional broadening until at −80 °C these broadened peaks once again sharpened into multiplets. At −80 °C, the ^1H NMR spectrum showed the presence of two unique phenyl groups attached to boron. All other resonances were unaffected by cooling, except for minor changes in chemical shift. No further change in the appearance of the spectrum was observed upon cooling below −80 °C. Table II summarizes the observed changes.

The triplet at δ 6.81 was chosen for the calculation of kinetic and thermodynamic parameters since it appeared in a relatively clean region of the spectrum and split symmetrically upon cooling (6.88, 6.72 at −80.0 °C). The coalescence temperature of this resonance was determined to be ca. −20 °C.

Cyclic Voltammetry of 1 in Acetonitrile. A solution of **1** in acetonitrile containing tetrabutylammonium perchlorate as supporting electrolyte was oxidized with use of a glassy carbon electrode and a platinum counter electrode. An irreversible oxidation peak was observed at E_p −1.06 ± 0.02 V vs $Ag/AgNO_3$. Ferrocene was subjected to the cyclic voltammetry conditions as a standard. The reversible oxidation of this species occurred at 0.072 V under these conditions.

Triplet Sensitization of (*p*-Biphenylyl)triphenylborate with *N*-Phenylcarbazole Followed by ^{11}B NMR Spectroscpy. A 3-mL volume of an acetonitrile solution of *N*-phenylcarbazole (1.29×10^{-2} M) and **4** (1.11×10^{-2} M) was placed in a 10-mm NMR sample tube. The tube was fitted with a septum, and the sample was purged with nitrogen for 5 min. The sample was irradiated at 350 nm under nitrogen and monitored periodically by ^{11}B NMR spectroscopy. After 10 min of irradiation, the ^{11}B NMR spectrum revealed an ~10% conversion of starting borate and the presence of a single product at δ −26.6 (i.e., borate **1**). After 30 min of irradiation, ~20% of the starting borate had reacted.

A solution of (*p*-biphenylyl)triphenylborate (1.11×10^{-2} M) treated in the same manner showed no reaction after 10 min of irradiation.

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Photochemistry of Alkynyl-, Alkenyl-, and Cyclopropyl-Substituted Borate Salts: The Di-π- and Cyclopropyl-π-borate Rearrangements

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Abstract: The photochemistry of potassium triphenyl(phenylethynyl)borate (**1**), tetramethylammonium triphenyl(*trans*-β-styryl)borate (**2**), and cesium phenyl(2-phenylcyclopropyl)dimethylborate (**3**) was studied. When irradiated with UV light, these compounds undergo rearrangements to generate potassium 1,1,2,3-tetraphenylboratirene (**4**), tetramethylammonium *trans*-1,1,2,3-tetraphenylboratirane (**5**), and (unisolated) cesium 1,1-dimethyl-2,4-diphenylboratetane (**6**), respectively. The mechanism of these reactions appears to be similar to the di-π-methane and cyclopropyl-π-methane routes for the analogous hydrocarbons. The effect of borate structure on the efficiency of these reactions was analyzed. Additionally, the chemical and physical properties of the small-ring borates were probed.

The first systematic investigation of the photochemistry of organic borates was carried out by Williams and co-workers.[1] Subsequent studies confirmed their suggestion that a formal [1,2] sigmatropic rearrangement of a phenyl group leads to intermediates containing a bridging borate group. In particular, we showed that irradiation of tetramethylammonium tetraphenylborate gives 2,7,7-triphenyl-7-boratabicyclo[4.1.0]hepta-2,4-diene.[2] Similarly, we isolated and characterized by X-ray crystallography the bridged borate formed by irradiation of tetramethylammonium (*p*-biphenylyl)triphenylborate.[3] In 1975, Eisch and co-workers suggested that a related rearrangement occurs when lithium triphenyl(phenylethynyl)borate is irradiated with UV light.[4] In more recent work, this group reported the successful isolation and characterization of triarylborirenes formed by a [1,2] aryl group rearrangement when diaryl(arylethynyl)boranes are irradiated in donor-containing solvents.[5]

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