J. Org. Chem. 1990, 55, 4537-4544

Fourier map and were included in subsequent refinements with isotropic thermal factors. Final atomic parameters are available as supplementary material. Atomic scattering factors were taken from *International Tables for X-ray Crystallography*.[17] All the computations were carried out on Mitsubishi MX-2000 and IBM-3081 GX3 computers at Shimane University.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 63628005) from the Ministry of Education, Science and Culture, Japan.

Supplementary Material Available: Tables of bond lengths and angles of **1a–c**, atomic coordinates with isotropic thermal parameters of non-hydrogen atoms, and final atomic coordinates with isotropic thermal parameters of hydrogen atoms for complexes I and II (12 pages); listing of observed and calculated structure factor amplitudes for complexes I and II (25 pages). Ordering information is given on any current masthead page.

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[17] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Photochemistry of 2,5,7,7-Tetraphenyl-7-boratabicyclo[4.1.0]hepta-2,4-diene (a Boratanorcaradiene Anion): No Evidence for Diphenylborene Anion

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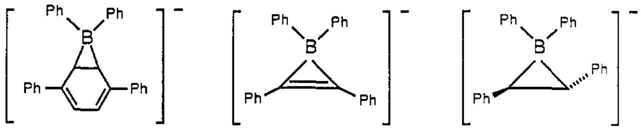
Irradiation of 2,5,7,7-tetraphenyl-7-boratabicyclo[4.1.0]hepta-2,4-diene anion (1, a boratanorcaradiene, as its potassium or tetramethylammonium salt) with UV light leads to formation of *p*-terphenyl in high yield. This observation led us to consider the possibility that diphenylborene anion (Ph_2B^-, an analogue of diphenylcarbene) might also be formed in this reaction. We designed and carried out a series of spectroscopic and chemical experiments to detect and characterize the borene. None of these experiments provides evidence for the formation of diphenylborene from this reaction. We suggest that the formation of *p*-terphenyl from the photolysis of 1 is initiated by an electron-transfer (photoionization) process. We also reexamined experiments reported earlier that were claimed to show that diphenylborene is formed from the irradiation or overirradiation of tetraphenylborate. Each of these experiments is ambiguous and cannot be relied upon to demonstrate the formation of the borene by this route.

Recently there has been considerable interest and some controversy concerning the photochemistry of tetraarylborate salts $\{M^+[Ar_4B]^-\}$. In the first experiments in this area, Grisdale and co-workers studied the photolysis of tetraphenylborate anion in protic solvents and concluded that unisolated bridged-boron intermediates are formed.[1] Later, Eisch and co-workers claimed that irradiation of tetraphenylborate anion (254 nm) in tetrahydrofuran (THF) or dimethoxyethane (DME) solution caused it to fragment to biphenyl and diphenylborene $[Ph_2B]^-$, a carbene analogue of some interest.[2] This conclusion was based on the results of a trapping experiment with diphenylacetylene and the observation that D_2 is evolved when the photolysis mixture is quenched with deuteriated acetic acid. Our reinvestigation of the photolysis of tetraphenylborate convinced us that Eisch's experiments had been misinterpreted.[3] We concluded that there was no valid experimental evidence that diphenylborene is formed from photolysis of tetraphenylborate.

Chart I



Boratanorcaradiene 1

Boratirene 2

Boratirane 3

In subsequent work, we succeeded in isolating and characterizing by X-ray crystallography the blood-red bridged-boron product (boratanorcaradiene, Chart I) formed from the irradiation of a tetraarylborate.[4] Also, we succeeded in the preparation, isolation, and characterization by X-ray crystallography[5] of the boratirene anion 2 claimed by Eisch to be the product of reaction of diphenylborene with diphenylacetylene when the irradiation of tetraphenylborate is performed in the presence of the acetylene.

In a recent paper in this Journal, Eisch and co-workers painstakingly reconsidered the experiments that led to the earlier report that diphenylborene is formed from photolysis of tetraphenylborate.[6] They are compelled by the data to modify their earlier conclusion. These workers claim now that diphenylborene is a red compound, stable in DME solution for hours, formed from the "... prolonged irradiation of the Schuster intermediate (a boratanorcaradiene)".

We report herein results from the study of the photochemistry of 2,5,7,7-tetraphenyl-7-boratabicyclo[4.1.0]hepta-2,4-diene (1, a boratanorcaradiene) and a search for facts that might substantiate a claim that its photolysis generates diphenylborene. This study provides no experimental evidence to support the conclusion that the photolysis of boratanorcaradienes generates diphenylborene either as a transient species or as a compound

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[1] (a) Williams, J. L. R.; Doty, J. C.; Grisdale, P. J.; Searle, R.; Regan, T. H.; Happ, G. P.; Maier, D. P. *J. Am. Chem. Soc.* **1967**, *89*, 5153. (b) 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. (c) 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. (d) 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. (e) Grisdale, P. J.; Williams, J. L. R.; Glogowski, M. E.; Babb, B. E. *J. Org. Chem.* **1971**, *36*, 544.

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

[3] Wilkey, J. D.; Schuster, G. B. *J. Org. Chem.* **1987**, *52*, 2117.

[4] Wilkey, J. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 7569.

[5] Kropp, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1989**, *111*, 2316.

[6] Eisch, J. J.; Boleslawski, M. P.; Tamao, K. *J. Org. Chem.* **1989**, *54*, 1627.

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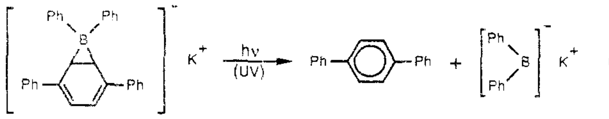
stable in DME solution for hours.

Results and Discussion

The chemical and physical properties of carbenes, silylenes, and nitrenes have been under intensive investigation for more than 50 years.[7] Thousands of experiments on these hypovalent intermediates have been carried out, and a clear description of these compounds has emerged. The parent borene (H_2B^-, isoelectronic with carbene, CH_2) has been examined by means of molecular orbital calculations and is predicted to be a bent molecule with two low-lying, nonbonding orbitals.[8] However, as will become clear, no authentic examples of a borene have ever been prepared, and the chemical and physical properties of these compounds remain completely unknown.[9]

I. Photolysis of Boratanorcaradiene (1) in "Inert" Solvents at Room Temperature. Irradiation of a degassed THF or acetonitrile solution of borate 1 (λ_{max} = 294 nm, ϵ_{max} = 19 000 M^{-1} cm^{-1} and λ_{max} = 510 nm, ϵ_{max} = 2700 M^{-1} cm^{-1}, as its potassium salt) in a Rayonet photoreactor equipped with 350-nm lamps leads to rapid consumption of the borate with formation of *p*-terphenyl. This observation led us to consider the possibility that diphenylborene might be formed from the photolysis of 1 (eq 1).



1

(1)

Analysis of the course of the photolysis of borate 1 by ^1H NMR spectroscopy shows that *p*-terphenyl is a primary photoproduct; it is formed simultaneously with the consumption of the borate. Analysis of the reaction mixture by GC and GC/MS after complete consumption of borate 1 shows that *p*-terphenyl is formed in 85–95% yield. When the photolysis of borate 1 is monitored by ^{11}B NMR spectroscopy, its disappearance is observed but no new boron-containing products are identifiable.

In contrast to its photolysis with UV light, irradiation of borate 1 in THF or acetonitrile solution with visible light ($\lambda \approx 500$ nm, Na vapor lamp) does not initiate any reaction. This finding is of particular significance when compared with results from the similar irradiation of 1 in solutions containing phenyl-substituted alkenes and alkynes as traps for the potentially formed diphenylborene.

II. Diphenylcarbene: A Spectroscopic and Chemical Model for Diphenylborene. Diphenylborene is isoelectronic and isostructural with diphenylcarbene.[10] On this basis it is reasonable to expect that the borene will be an extremely reactive substance with only transient existence under normal conditions. Accordingly, we performed a series of experiments designed to trap or detect diphenylborene based on the assumption that its chemical and spectroscopic properties might be related to that of diphenylcarbene.[11]

One of the most critical issues to be addressed in considering experiments for the chemical or spectroscopic detection of diphenylborene is the spin multiplicity of its ground state. Diphenylcarbene is a triplet, a fact which provides for its ready detection by EPR spectroscopy when it is formed in a rigid medium at low temperature.[12] However, the electronically excited singlet state of diphenylcarbene is only ca. 3 kcal/mol above the ground state.[13] Consideration of the consequences of changing the carbon atom of the carbene to the boron of the borene leads to the qualitative prediction that the energy gap between the triplet and the singlet states of the latter will be smaller than that of the former.[14] Briefly put, the nonbonding orbitals of the borene are expected to be more diffuse than those of the carbene and, therefore, electron–electron repulsion in the singlet ($^1A_1$) state of the borene will be less than for the carbene. In contrast, if the energies of the nonbonding σ- and π-orbitals of the borene are displaced approximately equally relative to that of the carbene, then the energy of the triplet ($^3B_1$) states of these compounds will be less affected by the atomic change. On this basis we considered that the ground state of diphenylborene could have either singlet or triplet spin multiplicity and designed experiments that might indicate its formation from photolysis of borate 1 in either case.

(1) Photolysis of Borate 1 at Low Temperature: EPR Spectroscopy. Frozen solutions of borate 1 in 2-methyltetrahydrofuran were irradiated in the cavity of an EPR spectrometer with visible or UV light. The spectrum of the reaction mixture was recorded from 500 to 10 000 G. No signals attributable to triplet diphenylborene are observed either at 77 K or at 8 K under any of the conditions we investigated. At the lower temperature, after extensive irradiation with UV light, the spectrum of the hydrogen atom is observed.

Interpretation of the absence of an EPR signal appropriate for triplet diphenylborene from the irradiation of 1 is problematical. This result might indicate that borate 1 does not fragment at the low temperature in a rigid medium to give diphenylborene, or that the borene is unstable chemically or photochemically under the reaction conditions, or that it has a singlet ground state. In light of the ambiguous interpretation of the EPR spectroscopic results, we undertook a series of chemical trapping experiments to probe for the formation of diphenylborene from irradiation of 1.

(2) Photolysis of Borate 1 at Room Temperature in Solutions Containing Traps for Diphenylborene. A hallmark characteristic of carbenes is their reaction with alkenes to form cyclopropanes.[11] On the assumption that borenes might behave similarly, we examined the photolysis of borate 1 in solutions containing phenyl-substituted alkenes. Boratiranes are the boron-containing three-membered-ring anionic compounds analogous to cyclopropanes that would be formed by the addition of a borene to an alkene.

We recently reported the first isolation and characterization of a boratirane.[15] Tetramethylammonium 1,1,2,3-tetraphenylboratirane (**3**) is a colorless solid that is stable in the absence of oxygen and water, stable to

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(7) *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; John Wiley and Sons: New York, 1978, Vol. 1; 1981, Vol. 2. *Reactive Molecules*; Wentrup, C., Ed.; John Wiley and Sons: New York, 1984. Tang, Y.-N. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1982; Vol. 2, p 297.

(8) Koga, T.; Kobayashi, H. *Theor.* Chim. *Acta.* (*Berl.*) **1984**, *65*, 303.

(9) In contrast, there are several reliable reports concerning the properties of neutral R-B intermediates (termed borylenes): Pachaly, B.; West, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 454. Rice, J. K.; Caldwell, N. J.; Nelson, H. H. *J. Phys. Chem.* **1989**, *93*, 3600. See, however: Calhoun, G. C.; Schuster, G. B. *J. Org. Chem.* **1984**, *49*, 1925.

(10) Nefedov, O. M.; Manakov, M. N. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 1021.

(11) Schuster, G. B. *Adv. Phys. Org. Chem.* **1986**, *22*, 311.

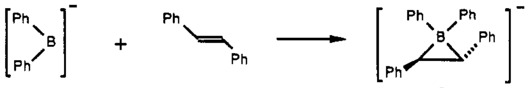
(12) Trozzolo, A. M. *Acc. Chem. Res.* **1968**, *1*, 329.

(13) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190. Griller, D.; Nazran, A. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 198. Sitzman, E. V.; Langan, J.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1984**, *106*, 1868.

(14) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485.

(15) Kropp, M.; Bhamidapaty, K.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 6252.

irradiation with 350- or 500-nm light, and readily detected by ^{11}B NMR spectroscopy. We carried out a series of experiments designed to probe for the formation of diphenylborene from irradiation of 1 based on the hypothesis that the borene would form 3 by reaction with *trans*-stilbene (eq 2).



3

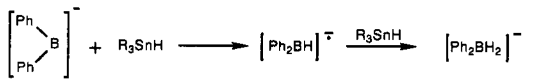
(2)

Irradiation of borate 1 in THF or acetonitrile solution containing *trans*-stilbene (5×10^{-3} to 0.05 M) with UV light leads to the consumption of 1 without any indication by ^{11}B NMR spectroscopy for the formation of 3. Analysis of the reaction mixture after complete reaction of borate 1 reveals formation of *p*-terphenyl, along with bibenzyl and a small amount of *cis*-stilbene.

Significantly, irradiation of 1 in the presence of *trans*-stilbene with visible light, conditions where the borate is unreactive in the absence of stilbene, leads to its disappearance. Analysis by ^{11}B NMR spectroscopy during the course of this reaction shows that boratirane 3 is not formed. The products from the visible-light photolysis were shown by GC/MS to be primarily *p*-terphenyl, bibenzyl, and a trace of *cis*-stilbene. Evidently, there is a reactive channel open to the lowest excited state of borate 1 in the presence of stilbene that is not available in the absence of the trapping agent. However, neither the UV or visible light irradiation of borate 1 in the presence of stilbene gives any evidence for the formation of tetraphenylboratirane 3.

If the analogy between the chemical properties of triplet diphenylcarbene and triplet diphenylborene is valid, then *trans*-stilbene might be a poor trap for the borene. It is generally known that terminal olefins, styrene for example, react much more rapidly with triplet diphenylcarbene than do internal olefins like stilbene.[11] For this reason we examined the photolysis of borate 1 in solutions containing styrene as a trap for diphenylborene. In this case the anticipated product of the reaction of the borene is 1,1,2-triphenylboratirane, an unknown compound, but one whose ^{11}B NMR spectrum and chemical properties should be closely related to those of 3. Irradiation of borate 1 with visible or UV light in solutions containing styrene led to its efficient consumption but did not give any evidence for the formation of the boratirane.

A second reaction characteristic of triplet carbenes is their abstraction of hydrogen atoms from suitable substrates.[11] We sought evidence for the formation of diphenylborene from photolysis of 1 on this basis. We assumed that triplet diphenylborene would abstract a hydrogen atom from tri-*n*-butylstannane to form diphenylborane radical anion,[16] which, in turn, might abstract a hydrogen atom from additional stannane and form diphenylborohydride, a substance readily detected by its characteristic ^{11}B NMR spectrum (eq 3). However, irradiation of stannane-containing solutions of borate 1 with visible or UV light did not give any evidence for the formation of the borohydride.



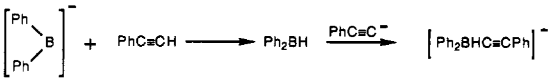
(3)

III. Search for Non-Carbene-like Behavior of Diphenylborene.

(1) Singlet Diphenylborene Should Be a Strong Base. If the ground state of diphenylborene is a singlet, the analogy between its properties and those of diphenylcarbene might not be valid. Diphenylborene is the conjugate base of diphenylborane and as such is readily predicted to be a very strong base (eq 4). In contrast, diphenylcarbene is the conjugate base of the diphenylmethyl cation and therefore is not expected to be an exceptionally strong base.

We examined the photolysis of borate 1 in the presence of phenylacetylene with the hope of detecting strongly basic singlet diphenylborene. The hypothesis is that phenylacetylene ($pK_a = 18.5$) will donate a proton to diphenylborene and form diphenylborane and the phenylacetylide anion. In a subsequent rapid step, the acetylide anion should add to the borane to form (phenylethynyl)diphenylborohydride (eq 5). Related borohydrides have been detected by ^{11}B NMR spectroscopy.[17] Alternatively, the diphenylborene might undergo a carbene-like addition to the acetylene to form triphenylboratirene anion, the three-membered-ring compound analogous to a cyclopropene (eq 6).

$$Ph_2BH \rightleftharpoons [Ph_2B]^- + H^+ \qquad (4)$$

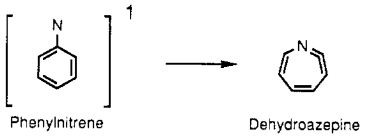


(5)

(6)

Solutions of borate 1 containing phenylacetylene are stable in the dark. Their irradiation with visible or UV light leads to efficient consumption of the borate with formation of *p*-terphenyl. However, analysis of the reaction mixture by ^{11}B NMR spectroscopy gives no evidence for formation of a borohydride or the boratirene.

(2) Phenylnitrene: An Alternative Model for the Reactions of Diphenylborene. Phenylnitrene is another well-studied hypovalent compound that is isoelectronic with diphenylborene. The ground state of phenylnitrene also has triplet spin multiplicity. However, for this compound ring expansion of the upper singlet state to give dehydroazepine competes effectively with relaxation of the nitrene to its ground triplet state[18] (eq 7). We examined the possibility that singlet diphenylborene, if it is formed from photolysis of borate 1, might undergo a related ring expansion and form *B*-phenyl-1,2-dehydroborepinate (4) (eq 8). Boripinate 4 may be regarded as a strained, boron-stabilized vinyl anion.



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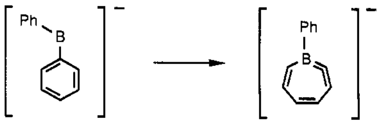

(8)

One component of our search for formation of borepinate 4 from the irradiation of borate 1 was based on the

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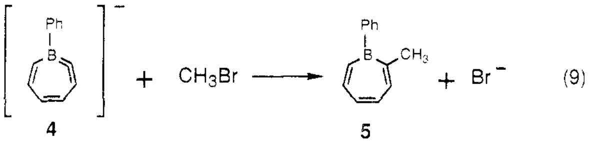
[16] Baban, J. A.; Brand, J. C.; Roberts, B. P. *J. Chem. Soc., Chem. Commun.* **1983**, 315.

[17] Brown, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 4100. We have observed $Li^+[PhBH_3]^-$ as a quartet with resonance at δ −27.

[18] Li, Y. Z.; Kirby, J. P.; George, M.; Poliakoff, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 8092.

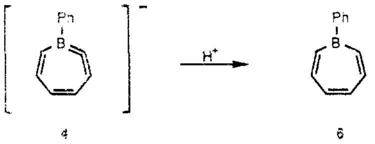
report by Rathke and Kow[19] that boron-stabilized carbanions react with alkyl bromides to give C-alkylated products. If this reaction path is followed by borepinate 4, then its reaction with methyl bromide will give *B*-phenyl-2-methylborepine (5) (eq 9). Compounds closely related to borepin 5 are known and have been carefully characterized.[20]



(9)

Borate 1 is thermally stable at room temperature in THF solution containing methyl bromide (added as a diethyl ether solution). Irradiation of this mixture at 350 nm leads to consumption of the borate. Careful analysis of the photolysis mixture by ^{1}H NMR spectroscopy reveals *p*-terphenyl and a trace of 2′-methyl-*p*-terphenyl, but no significant products with a methyl group resonance in the range predicted for borepin 5 (δ 2.1–3.3).

A second component to our search for formation of borepinate 4 from photolysis of 1 is based on the hypothesis that the borepinate will be strongly basic and might be stable in THF solution at low temperature. Protonation of 4 is expected to give *B*-phenylborepin 6 (eq 10). The 4,5-dihydro derivative of 6 has been prepared and characterized by mass spectroscopy.[21] On this basis we hoped to detect and characterize 6, which, based on the aromaticity of related compounds,[20] should be more stable than its known dihydro derivative.



(10)

A degassed solution of borate 1 in THF was prepared in one chamber of a two-chambered vessel. The second chamber contained 1 equiv of benzenesulfonic acid. The vessel was cooled to −40 °C and irradiated with 350-nm light until all of the borate was consumed. Without warming, the contents of the two chambers were mixed, and the reaction mixture was analyzed by GC/MS. The chromatogram showed *p*-terphenyl and a small amount of biphenyl but did not reveal any compounds that might be assigned to borepin 6. The solvent was removed from the sample, and the residue was analyzed by mass spectroscopy using a direct inlet technique. Again, there was no evidence for the presence of 6 in the sample.

Finally, we searched for evidence for the formation of borepinate 4 based on its expected basicity but with the assumption that it is unstable in THF at −40 °C. In this case we irradiated borate 1 in a THF solution containing *tert*-butyl bromide. The rationale in this experiment is that strongly basic borepinate will initiate E2 elimination from the tertiary halide to give borepin 6, isobutene, and potassium bromide. However, in this case too, no evidence for the presence of 6 was obtained by mass spectroscopy.

IV. An Examination of the Experiments of Eisch and Co-workers. In their recent report, Eisch and coworkers describe three experiments that are considered to confirm formation of diphenylborene from the overirradiation of sodium tetraphenylborate.[6] In the potentially most convincing experiment, diphenylacetylene was added to a solution of tetraphenylborate either before or after the borate was irradiated with 254-nm light for 24 h. Next, acetic acid (or deuteriated acetic acid) was added to the reaction solution, and the resulting mixture was analyzed for the presence of *cis*- and *trans*-stilbene. Small amounts (less than 3%) of both stilbenes were found.

Eisch argues that the observation of *cis*-stilbene among the products indicates that the reaction of diphenylborene with diphenylacetylene gives tetraphenylboratirene (2), which, on protodeborination with acetic acid, gives *cis*-stilbene. The experiment is flawed when it is performed with the acetylene present at the outset since the irradiating light will be absorbed primarily by diphenylacetylene not by tetraphenylborate.[3] However, when diphenylacetylene is added after irradiation is complete, this experiment could provide evidence for the formation of diphenylborene if this species is stable for hours at room temperature in DME solution. We repeated the postirradiation addition experiment described by Eisch in the effort to detect and characterize diphenylborene.

A DME solution of sodium tetraphenylborate in a sealed, degassed, quartz tube was irradiated at 254 nm. Since we recently succeeded[5] in the preparation and characterization by X-ray crystallography of tetraphenylboratirene, we did not treat the solution with acetic acid, but analyzed it directly by ^{11}B NMR spectroscopy for the presence of the boratirene. Figure 1A shows the ^{11}B NMR spectrum of the reaction mixture before irradiation (Ph_4B^-, δ −6.7). Figure 1B was recorded 2 h after the start of the irradiation; it shows nearly complete consumption of the tetraphenylborate with formation of the boratanorcaradiene (δ −27). The irradiation was continued until ^{11}B NMR spectroscopy showed that nearly all of the boratanorcaradiene had been consumed (an additional 5 h), the sealed sample was then opened in a drybox and freshly distilled diphenylacetylene was added to the reaction mixture. Figure 1C is the ^{11}B NMR spectrum recorded after addition of the acetylene, which causes no change in the ^{11}B NMR spectrum of the reaction mixture. In particular, there is no resonance at δ −16.1 characteristic of boratirene 2. To establish a limit for detectability of 2 and to insure its stability under the conditions of the analysis, we added a small amount of authentic tetramethylammonium boratirene to the NMR tube containing the irradiated sample and diphenylacetylene. This spectrum is shown in Figure 1D; it shows that the maximum yield of boratirene 2 that could be formed from the reaction of the putative borene with diphenylacetylene is less than 1% of the amount of starting tetraphenylborate.

In all of the experiments reported by Eisch, tetraphenylborate solutions are irradiated for 24 h before their workup and analysis. In the repetition of this experiment, we monitored the course of the irradiation by ^{11}B NMR spectroscopy. In the early stage (see Figure 1B), tetraphenylborate is converted to the boratanorcaradiene. Additional irradiation causes consumption of the boratanorcaradiene. Eventually the sample becomes a very complex mixture of overirradiation products (see Figure 1C). Of some significance is the observation that several of the overirradiation products exhibit one-bond, boron–hydrogen coupling characteristic of borohydrides.

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[20] Nakadaira, Y.; Sato, R.; Sakurai, H. *Chem. Lett.* **1987**, 1451. Ashe, A. J., III; Drone, F. J. *J. Am. Chem. Soc.* **1987**, *109*, 1879. Disch, R. L.; Sabio, M. L.; Sculman, J. M. *Tetrahedron Lett.* **1983**, *24*, 1983. Eisch, J. J.; Galle, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 4436. van Tamelen, E. E.; Brieger, G.; Untch, K. G. *Tetrahedron Lett.* **1960**, 14. Leusink, A. J.; Drenth, W.; Noltes, J. G.; van der Kerk, G. J. M. *Tetrahedron Lett.* **1967**, 1263.

[21] Herberich, G. E.; Bauer, E.; Hengesbach, J.; Kölle, U.; Huttner, G.; Lorenz, H. *Chem. Ber.* **1977**, *110*, 760.

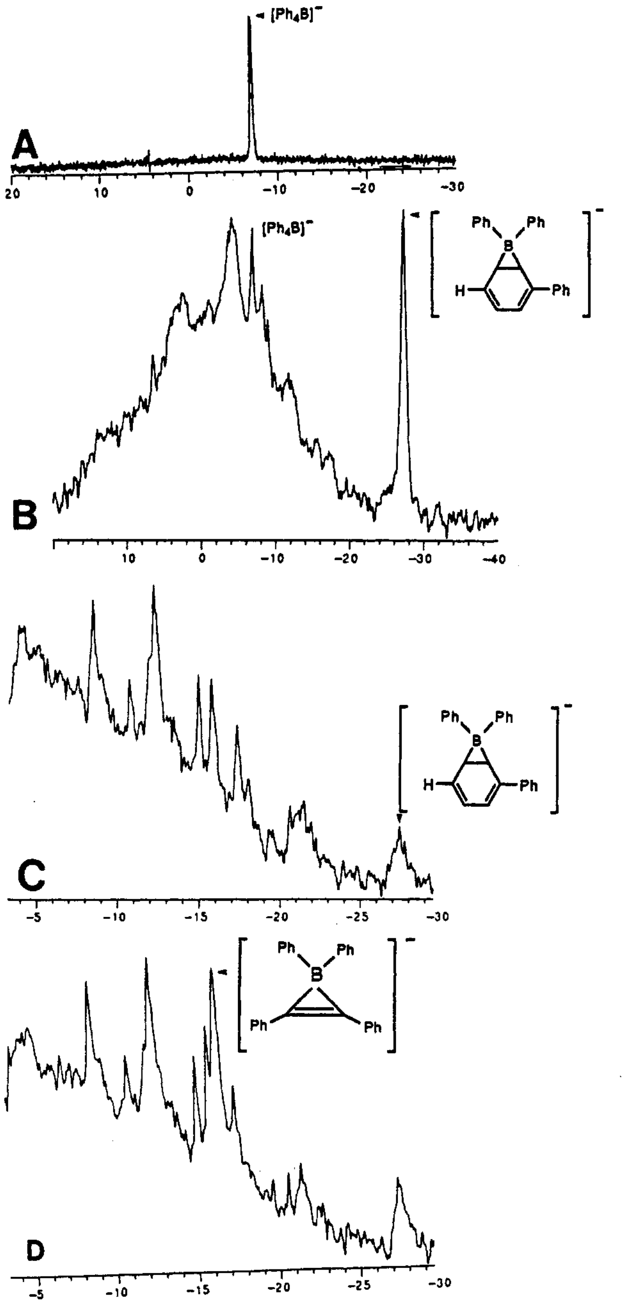

Figure 1. ^{11}B NMR spectra, recorded in sealed tubes from the photolysis of sodium tetraphenylborate in DME solution: (A) A sample of tetraphenylborate (δ -6.7) before irradiation. (B) The spectrum of the reaction mixture recorded after 2 h of irradiation; it shows boratanorcaradiene (δ −27), a small amount of unreacted tetraphenylborate, and several unknown borate-containing products. (C) A spectrum of the reaction mixture recorded following addition of diphenylacetylene to a sample of tetraphenylborate that had been irradiated for 7 h; it shows a small amount of unreacted boratanorcaradiene and several unknown borate-containing products. (D) Same as spectrum C except that tetraphenylboratirene (2, δ −16.1) equivalent to 2% of the tetraphenylborate present at the start of the photolysis has been added to the reaction mixture.

The second result claimed by Eisch to support formation of diphenylborene is that addition of acetic acid or (deuteriated acetic acid) to the photolysis solution gives hydrogen (or a mixture of H_2, HD, and D_2). Since hydrogen will be formed in the reaction of borohydrides with acetic acid, this observation can reveal nothing about the presence of diphenylborene. However, the formation of a high proportion of D_2 in the gas mixture formed when deuteriated acetic acid is added to the photolysis solution is claimed to be evidence supporting the presence of diphenylborene. No conclusive information about the structure of the hydrogen-generating intermediate is revealed by this experiment; nevertheless it, too, was repeated.

A degassed DME solution of sodium tetraphenylborate in a sealed quartz tube was irradiated at 254 nm for 24 h. After the irradiation, the sample was opened in a Vacuum Atmospherics drybox and acetic acid (or deuteriated acetic acid) was added. The proportion of H_2, HD, and D_2 in the gas mixture was determined directly by mass spectroscopy. We find that the proportion of H_2, HD, and D_2 produced in these reactions varies significantly from experiment to experiment. For example, from one photolysis a 14:71:15 ratio of H_2:HD:D_2 is found, in another the ratio is 22:55:23.

The observed variability in the hydrogen isotope ratio and the difference between our findings and those reported by Eisch may be readily explained.[22] Conforth demonstrated that exchange of hydrogen isotopes between borohydrides and weak acids which is significantly faster than the decomposition of the borohydride to give hydrogen. For example in the case where 1 mol of lithium borohydride and 3 mol of D_2O are mixed, the exchanged borohydride contains 64% deuterium. However, when 1 mol of borohydride is mixed with 0.5 mol of D_2O, the exchanged borohydride contains 13% deuterium.[22] Thus, the proportion of H_2, HD, and D_2 obtained from the reaction of deuteriated acetic acid with the borohydrides generated in the overirradiation of tetraphenylborate may simply reflect the rate of mixing of reagents (a high local concentration of DOAc would give a high proportion of D_2) and the mole ratio of "active hydride" in the reaction mixture to the amount of added deuteriated acetic acid. Since the amount of hydride present in an uncontrolled irradiation will be variable, and the rate of mixing is difficult to control, the proportion of H_2, HD, and D_2 formed will vary. Thus, it does not appear that the hydrogen isotope ratio measured in this experiment needs to be related to the presence of diphenylborene in the reaction mixture.

Finally, Eisch and co-workers report that addition of benzyl chloride to a pyridine-containing solution of overirradiated tetraphenylborate bleaches the red color of the solution and gives a complex product mixture containing the four possible phenylbenzylboranes. This result is taken to imply that diphenylborene is present in the photolysis solution. In this case, the borene is said to "couple" with the chloride and give the boranes. To aid in the interpretation of this experiment, we examined the reaction of borate 1 with benzyl chloride.

A pyridine-containing solution of 1 in DME is stable for at least 24 h, but the blood-red color of the boratanorcaradiene is bleached when benzyl chloride is added to the solution. This is an expected result since the boratanorcaradiene is a powerful reducing agent (E_{ox} = −0.8 V vs SCE, irreversible). One-electron reduction of benzyl chloride gives the benzyl radical which then, if reduced by a second equivalent of the borate, could give the benzyl anion. Thus, the reported formation of the complex mixture of phenylbenzylboranes need not be taken to indicate "coupling" of diphenylborene with benzyl chloride, but may simply be the result of reaction of the benzyl anion (or radical) with a boron-containing product from the overirradiation of tetraphenylborate.

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(22) Conforth, R. H. *Tetrahedron* **1970**, *26*, 4635. The mechanism for hydride exchange of borohydrides is of continuing interest.[23]

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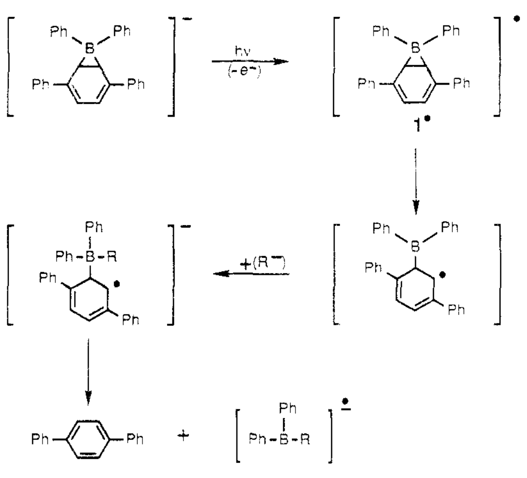
Scheme I



V. Photolysis of Borate 1: A Possible Mechanism for *p*-Terphenyl Formation. If photolysis of borate 1 does not lead to formation of diphenylborene, then some other mechanism must operate which leads to formation of *p*-terphenyl. Our experiments do not reveal the details of this mechanism. However, two important clues about its possible identity are the extraordinarily low oxidation potential of borate 1 and the observation that the borate is relatively stable to visible light irradiation except in the presence of compounds which can be reduced such as *trans*-stilbene and phenylacetylene. These facts suggest that the fragmentation of 1 by photolysis may be initiated by its loss of an electron. This possibility was examined by time-resolved absorption spectroscopy.

The radical anion of *trans*-stilbene has a well-characterized absorption band with a maximum at ca. 690 nm.[24] Irradiation of a THF solution of borate 1 containing *trans*-stilbene (2×10^{-2} M) with a frequency-doubled Nd-YAG laser (532 nm, 25 mJ, 20 ns) gives a weak transient absorption spectrum, recorded 100 ns after the laser pulse, consistent with the formation of the *trans*-stilbene radical anion. The stilbene radical anion spectrum is not detected from an identical irradiation of a solution that does not contain borate 1. On this basis we propose that photolysis of 1 under these conditions leads to electron transfer from the excited borate to stilbene. Similarly, irradiation of borate 1 with UV light could lead to photoejection of an electron and initiate a reaction sequence leading to *p*-terphenyl. The proposed mechanism is outlined in Scheme I.

UV irradiation of borate 1 leads to its direct loss of an electron from an upper excited state (1**) to solvent. Visible-light irradiation gives a lower energy excited state (1*) that cannot spontaneously lose an electron to solvent, but can transfer an electron to an acceptor such as *trans*-stilbene. Both of these electron-loss processes could give the boratanorcaradienyl radical (1•). Alkyl(triaryl)boranyl radicals are known to fragment rapidly to a borane and an alkyl radical.[25] This fragmentation of 1• results in the formation of a stabilized phenyl-substituted cyclohexadienyl radical. We have shown in related intermolecular examples that addition of a resonance-stabilized alkyl radical to a borane is a relatively slow process. This observation suggests that it is likely that the ring-opened radical lives long enough to undergo bimolecular reactions with reagents in solution. In Scheme I we suggest that an anionic species (R^-) combines with the ring-opened boron-containing radical and that fragmentation of the resulting radical anion gives *p*-terphenyl and a borane radical anion. Borane radical anions have been observed spectroscopically.[16] There are several possible choices for the anionic species R^-. Borate 1 itself could play this role. If so, the boron-containing product might be a dimeric borate anion radical, which could, in turn, serve as R^- leading ultimately to an oligomeric polyborate radical. This mechanism is highly speculative and is presented here only as one of several possibilities that could account for formation of *p*-terphenyl from the photolysis of 1 without simultaneous formation of diphenylborene.

Conclusions

In the effort to detect and characterize diphenylborene, we have examined the irradiation of boratanorcaradiene 1 with UV and visible light and reexamined the photolysis of tetraphenylborate. Photolysis of 1 with UV light gives *p*-terphenyl. If this reaction simultaneously generates diphenylborene, then the borene does not react with phenyl-substituted alkenes to give boratiranes, nor does it react with hydrogen atom donors or with proton donors to give the products expected, nor does it undergo ring expansion to a dehydroborepinate. Mindful of the limitations of "negative" experiments, we conclude that the photolysis of borate 1 does not generate diphenylborene. Instead, we propose an electron-transfer (photoionization) mechanism to give *p*-terphenyl in these reactions.

Our reexamination of the photolysis of tetraphenylborate reveals that each of the experiments claimed to show the detection and characterization of diphenylborene from this reaction is ambiguous. On this basis we conclude that there is no compelling evidence that diphenylborene is formed in the photolysis of tetraphenylborate or its irradiation products.

Experimental Section

General. THF and DME were dried by standard methods and distilled under a N_2 atmosphere immediately before use. Deuteriated acetic acid was purchased from Aldrich Chemical Co.; freshly opened vials were used for each experiment. Borate 1 as its tetramethylammonium salt was prepared by irradiation (254 nm) of tetramethylammonium biphenylyltriphenylborate, as previously described.[4] The borate was recrystallized from acetonitrile and then from THF; it contains no detectable impurities. Borate 1 as its potassium salt was purified by recrystallization three time from acetonitrile; it contains ca. 10% of potassium biphenylyltriphenylborate. Tetraphenylboratirene was prepared as previously described.[5] Sodium tetraphenylborate (Mallinckrodt) was purified by recrystallization from DME and diethyl ether. *trans*-Stilbene was recrystallized from ethanol, and styrene was distilled under vacuum before use as was the tri-*n*-butylstannane. The phenylacetylene was distilled just before use as was the *tert*-butyl bromide and benzyl chloride.

Spectroscopy. ^{1}H NMR spectra were recorded with a Varian XL 200 or General Electric QE-300 spectrometer in deuteriated solvents (acetonitrile, THF, or chloroform). No TMS was included to the solutions; chemical shifts were referenced to the residual proton resonances of the solvents. ^{11}B NMR spectra were recorded with a General Electric GN-300 NB spectrometer in 5- or 10-mm glass or quartz sample tubes. Solvents for the ^{11}B NMR spectra were acetonitrile or THF (or their deuteriated analogues). Chemical shifts were referenced to external $BF_3 \cdot O(Et)_2$ (δ 0.00) or sodium tetraphenylborate.

Mass spectroscopy by direct-probe techniques was performed on a Varian CH-5 spectrometer. Samples were introduced at room temperature and then heated to generate a measurable ion current. Gas chromatography/mass spectroscopy (GC/MS) was performed on a Hewlett-Packard 5890A chromatograph equipped with a 12

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m × 0.2 mm OV-1 capillary column coupled with a Hewlett-Packard 5970 quadrupole mass selective detector.

Laser spectroscopy was performed by excitation with a Q-switched Nd-YAG laser doubled to 532 (20-ns pulse width, ca. 25 mJ per pulse). Spectra were recorded with a Tektronix R7912 transient recorder 100 ns after the excitation pulse. The sample of borate 1 was prepared in THF in a stopcock-equipped quartz cell. The optical density at the laser wavelength was 2.1, and the *trans*-stilbene concentration was 0.1 M.

ESR spectroscopy was performed on solutions of borate 1 prepared in 2-methyltetrahydrofuran in a quartz EPR tube. The sample was degassed by the freeze–pump–thaw method and then sealed under vacuum. Spectra were recorded during and after irradiation at 77 and 8 K with UV light (unfiltered medium-pressure Hg lamp). The microwave power of the Bruker ESP-300 spectrometer was kept below 10 mW in an attempt to avoid saturation of the signal in the low-temperature samples. No evidence for the formation of triplet species was apparent from inspection of these spectra. In a control experiment, it was shown that the spectrum of diphenylcarbene was easily observed under these conditions. Finally, it was noted that the red color of borate 1 appeared to be bleached much more slowly by irradiation in the frozen solution than by a similar irradiation of a fluid solution at room temperature.

Photolysis of Borate 1. A solution of 1 (both the tetramethylammonium and potassium salts were used in separate experiments; they gave identical results) in THF (5×10^{-4} to 1×10^{-2} M, 1–5 mL; CD_3CN was used as the solvent for experiments that were analyzed directly by ^1H NMR spectroscopy) was prepared and degassed by three freeze–pump–thaw cycles and then sealed in a glass ampule (often an NMR tube). The sample (for UV irradiation) was placed in a Rayonet photoreactor equipped with 350-nm lamps, and the course of the reaction was monitored by means of ^1H and ^{11}B NMR spectroscopy. Usually, the reaction was stopped when the visible red color of 1 was bleached and the ^{11}B NMR signal for the starting material could not be detected. The ^1H NMR spectrum of the reaction solution showed the presence of *p*-terphenyl (δ 7.75, 7.70, 7.40, 7.30) before the ampule was opened. The identity and yield (85–95%) of this product was confirmed by GC (the yields were determined by comparison with tetradecane as an internal standard) and by GC/MS (the fragmentation pattern is identical with authentic *p*-terphenyl).

Irradiation in the visible spectral region was performed similarly except that a sodium vapor lamp equipped with a UV-cutoff filter was used (primary emission at 500 nm). No bleaching was detectable, and no consumption of 1 was measurable by ^{11}B NMR spectroscopy even after 24 h of irradiation.

Photolysis of Borate 1 in the Presence of *trans*-Stilbene. A 3.3×10^{-3} M degassed, sealed solution of 1 as its tetramethylammonium salt in THF (1–5 mL; CD_3CN was used as the solvent in experiments analyzed directly by ^1H NMR spectroscopy) containing *trans*-stilbene (2.0×10^{-2} to 0.2 M) was irradiated at 350 nm (the borate is the primary light absorber in this experiment, but because the Rayonet 350-nm lamps tail to ca. 300 nm, a small amount of light is adsorbed by the stilbene). The red color of the starting borate disappeared after ca. 35 min of irradiation. Analysis of the ^1H NMR spectrum of the sealed reaction mixture showed resonances characteristic of *p*-terphenyl. Analysis of the sealed reaction mixture by ^{11}B NMR spectroscopy showed no resonance at δ −9.6 (THF) characteristic[15] of boratirane 3. Comparison with an authentic ^{11}B NMR spectrum of 3 shows a limit of detectability of 3% in the photolysis experiment. Analysis of the photolysis solution by GC/MS showed *p*-terphenyl, *cis*-stilbene (presumably formed from light absorbed directly by *trans*-stilbene, see below), and bibenzyl (40–45% of the amount of *p*-terphenyl formed).

Irradiation of an identical solution of borate 1 and stilbene in THF with 500-nm light results in the complete consumption of the borate in ca. 3 h. Analysis of the reaction mixture shows that no boratirane 3 is formed, only trace amounts of *cis*-stilbene are present, and the yield of bibenzyl is 33%.

Photolysis of Borate 1 in the Presence of Styrene. A 5×10^{-3} M degassed, sealed solution of 1 as its tetramethylammonium salt in THF (5 mL) containing styrene (5×10^{-2} M) was irradiated at 350 nm. After the red color of the starting borate disappeared; analysis of the sealed reaction mixture by ^{11}B NMR spectroscopy showed no resonance near δ −9.6 that would be characteristic of a boratirane.

Photolysis of Borate 1 in the Presence of Tri-*n*-butylstannane. A 5×10^{-3} M degassed, sealed solution of 1 as its potassium salt in THF (5 mL, with ca. 10% CD_3CN for an internal lock signal) containing tri-*n*-butylstannane (5×10^{-2} M) was irradiated at 350 nm. After the red color of the starting borate disappeared; analysis of the sealed reaction mixture by ^{11}B NMR spectroscopy showed no resonances that would be characteristic of a borohydride.

Photolysis of Borate 1 in the Presence of Phenylacetylene. A degassed, sealed solution of 1 (3×10^{-3} to 2×10^{-2} M) as its tetramethylammonium or potassium salt in THF (5 mL) containing phenylacetylene (3×10^{-3} to 2×10^{-2} M) was irradiated at 350 nm. After 6 h of irradiation the ^{11}B NMR spectrum showed complete consumption of borate 1, and the red color of the starting borate was replaced by a dark brown solution. Analysis of the sealed reaction mixture by ^{11}B NMR spectroscopy showed no resonances characteristic of a borohydride.

Photolysis of Borate 1 in the Presence of Methyl Bromide. A degassed, sealed solution of 1 (5×10^{-2} M) as its potassium salt in THF (0.7 mL) containing methyl bromide (3×10^{-2} M, added in 0.3 mL of diethyl ether) was irradiated at 350 nm. The characteristic red color of borate 1 was bleached after ca. 90 min of irradiation. In the absence of light, there was no reaction of borate 1 under these conditions after 6 h. Analysis of this reaction by ^1H NMR spectroscopy showed complete reaction of borate 1, unreacted methyl bromide, *p*-terphenyl, and some 2′-methyl-*p*-terphenyl, but no methyl resonances in the range from δ 1.8 to 3.8 that would be indicative of the formation of borepin 5 were detectable.

Photolysis of Borate 1 in the Presence of *tert*-Butyl Bromide. A degassed, sealed solution of 1 (5×10^{-3} M) as its potassium salt in THF (1 mL) containing *tert*-butyl bromide (3×10^{-2} M) was irradiated at 350 nm. The characteristic red color of borate 1 was bleached after ca. 30 min of irradiation. In the absence of light, there was no reaction of borate 1 under these conditions. Analysis of this reaction by GC/MS and, after removal of the solvent in an Vacuum Atmospherics drybox, by direct-probe mass spectroscopy showed *p*-terphenyl and trace amounts of biphenyl, but no compounds having molecular ion with *m*/*e* 166 that would be indicative of the presence of borepin 6.

Photolysis of Borate 1 Followed by the Addition of Benzenesulfonic Acid. A degassed, sealed solution of 1 (1×10^{-3} M) as its potassium salt in THF (1 mL) in one chamber of a two-chambered apparatus was cooled to −40 °C and irradiated at 350 nm. The characteristic red color of borate 1 was bleached after ca. 3 h of irradiation. The contents of the second chamber, benzenesulfonic acid (10 equiv based on the starting borate dissolved in 0.1 mL of acetonitrile) was added to the reaction mixture without warming when the irradiation was complete. Analysis of the reaction by GC/MS and, after removal of the solvent in an Vacuum Atmospherics drybox, by direct probe mass spectroscopy showed p-terphenyl and trace amounts of biphenyl, but no compounds having molecular ion with *m*/*e* 166 that would be indicative of the presence of borepin 6.

Attempt To Detect Tetraphenylboratirene by the Addition of Diphenylacetylene to Irradiated Solutions of Sodium Tetraphenylborate. A DME solution of sodium tetraphenylborate (0.036 M, 4 mL) in a quartz 10-mm NMR tube was purged with N_2 for 4 h and then sealed with a rubber septum. The ^{11}B NMR spectrum of this sample is shown in Figure 1A. The tube was placed in a Rayonet photoreactor equipped with 254-nm lamps and irradiated for 2 h. The ^{11}B NMR spectrum of this sample is shown in Figure 1B. Nearly all of the tetraphenylborate (δ −6.7) has been consumed, and the spectrum of triphenylboratanorcaradiene (δ −27) is apparent. Continued irradiation for 5 h results in nearly complete consumption of the triphenylboratanorcaradiene with formation of many unidentified boron-containing products. The sample was opened in a Vacuum Atmospherics drybox, 50 mg (0.28 mmol) of diphenylacetylene was added, the tube was resealed, and the ^{11}B NMR spectrum was recorded (Figure 1C). The NMR tube was returned to the Vacuum Atmospherics drybox, and 1.2 mg (2.9×10^{-3} mmol) of tetramethylammonium tetraphenylboratirene (2) was added to the sample. The ^{11}B NMR spectrum of this mixture is shown in Figure 1D. The resonance at δ −16.1 is due to the boratirene.

Analysis of Hydrogen Formed from Addition of Acetic Acid to Irradiated Solutions of Tetraphenylborate. A sealed, degassed solution of sodium tetraphenylborate in DME (1.0 g in 80 mL of solvent) was irradiated (254 nm) in a Rayonet photoreactor for 24 h. After irradiation, the sample was opened in a Vacuum Atmospheric drybox, and then acetic acid (HOAc, 200 μL) or DOAC (98% atom D) was added to the solution. The evolved hydrogen gas was collected in a standard volumetric burette in 10% yield based on complete consumption of tetraphenylborate and the assumption that each mole of tetraphenylborate will give 1 mol of hydrogen gas. The hydrogen gas formed from the addition of deuteriated acetic acid was transferred immediately by vacuum and then analyzed through the gas inlet probe of a Varian CH-5 mass spectrometer. The ratio of H_2:HD:D_2 in the sample was calculated by comparison of the areas of the peaks with m/e 2, 3, and 4, respectively. In an independent experiment, the mass spectrometer and analytical method were calibrated with an authentic mixture of H_2 and D_2. The instrument response is 1:1 within experimental error.

Reaction of Borate 1 with Benzyl Chloride in the Presence of Pyridine. A DME solution of borate **1** as its potassium salt (15 mg, 1 mL) was prepared in a Vacuum Atmospherics drybox. A 2.5-mg (0.032-mmol) portion of pyridine was added to the solution. There was no consumption of the borate after 24 h. A 27.5-mg (0.22-mmol) portion of benzyl chloride was added to the pyridine-containing solution of borate 1. The red color of borate 1 was completely bleached 6 h after the addition of the benzyl chloride.

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[2+2] Photocycloaddition Reaction of Aryl-1,3-butadiynes with Some Olefins

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1-Aryl-1,3-butadiynes **1–6** were photolyzed in 2,3-dimethyl-2-butene (DMB) to obtain [2+2] type photocycloadducts **7–12**, except for **5** which yields two primary photoadducts (**11**, **13**) and a secondary photoadduct (**14**). Azulene quenching, fluorescence, and exciplex emission studies suggest the reaction to proceed from both singlet and triplet excited states in compounds **1–4** while only the triplet excited state is reactive in compounds **5** and **6**.

Introduction

The [2+2] photocycloaddition reaction of olefins has been extensively studied, but only a few examples have been reported for alkynes.[1-3] In most cases cyclobutene rings are formed, but bicyclopropyl photoadducts as minor products were also observed.[3] When two alkene units are incorporated into a rigid molecule such as cyclohexa-1,4-diene, the major photoproduct was the bicyclopropyl adduct.[4,5]

Photochemistry of conjugated polyynes attracted some interest recently because of the phototoxicity of the compounds to various organisms. In particular, 1-phenyl-1,3,5-heptatriyne (PHT) has been studied extensively because of the strong phototoxicity to variety of substrates in aerobic or anaerobic conditions.[6-11] There are, however, only a few reports on the photochemistry of conjugated polyynes. We reported previously the photocycloaddition reaction of 1,6-diphenyl-1,3,5-hexatriyne (DPH) and PHT with 2,3-dimethyl-2-butene (DMB).[12-14] Little is known, however, of the photocycloaddition reaction of the conjugated aryl-1,3-butadiyne system, and the photocycloaddition reaction of the compounds with olefins was, therefore, investigated to give insight into the influence of C1 and C4 substituents on the photochemistry of aryl-1,3-butadiynes.

Results and Discussion

Photoreaction of 1–6 with DMB. Irradiation of 1-(1-naphthyl)-1,3-butadiyne (**1**), 1-(1-naphthyl)-4-phenyl-1,3-butadiyne (**2**), 1-(1-naphthyl)-5,5-dimethyl-1,3-hexadiyne (**3**), and 1-(1-naphthyl)-1,3-pentadiyne (**4**) in deaerated DMB solution with 350-nm UV light gave 1:1

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