Arrhenius plot[28] gives an activation energy of 3.9 kcal/mol for the cleavage.

The subtle mechanistic differences between electron-transfer photofragmentation of aminoalcohols and diamines are underlined by comparing the reactivity of **1** and **2** under various conditions. The independence of reactivity on acceptor anion radical basicity is manifested by a pronounced sensitivity of the relative reactivity to acceptor. Thus, **1** is far more reactive than **2** with cyanoaromatics whose anion radicals are relatively poor bases (Table I) and correspondingly less reactive than **2** with quinones such as TI or L where the oxygen-localized radical anion should be quite basic. The relative reactivity **1**/**2** with the same acceptor (TI, Table I) also shows a strong increase with solvent polarity resulting in an order reversal in the case of CH_3CN. The increase in reactivity reflects a nearly constant reaction efficiency of **1**/TI for the three solvents, contrasted to a sharp decrease in reactivity for **2**/TI as solvent polarity increases; due to the requirements for direct involvement of the anion radical in the fragmentation of the aminoalcohol.

We expect photooxidative fragmentation of 1,2-diamines to be a general process; the reactions of disecondary, diprimary, or mixed amines should be particularly interesting. These compounds should have the possibility of both deprotonation-assisted and unassisted fragmentation reactions within the geminate radical ion pair. This should result in an increase of the relative reactivity of the diamine with acceptors with basic radical anions and in nonpolar media but still permit reactivity to persist when aminoalcohols are unreactive. In summary, these studies demonstrate that chemically clean oxidative photofragmentation of 1,2-diamines can occur by a mechanism similar to the cleavage of aminoalcohols but in a process which may be much more versatile.

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[28] Temperatures studied (−62, −42, −23, 0, +27, and +56 °C). Correlation coefficient for plot = 0.992.

1,1,2,3-Tetraphenylboratirene: First Isolation and Characterization of a Boratirene

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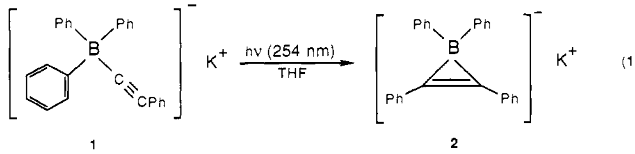
We report herein the preparation and characterization of the first example of a new class of highly strained boron-containing compounds. Irradiation (254 nm) of potassium triphenyl(phenylethynyl)borate (**1**) in THF solution gives 1,1,2,3-tetraphenylboratirene (**2**) as the predominant product, eq 1. Potassium tetraphenylboratirene is a stable, air- and water-sensitive, bright yellow crystalline solid.



1 2

Replacement of carbon by a tetravalent, anionic borate group forms a new family of compounds having the same bonding pattern and number of electrons as the hydrocarbon but differing in the number of nuclear protons. The effect of this atomic mutation on chemical and physical properties has been the object of long-standing and increasing theoretical[1] and experimental[2] interest. For example, we recently reported that tetraphenylboratirane,[3] a cyclopropane analogue, has an exceedingly low oxidation potential (−0.8 V, irreversible vs $Ag/AgNO_3$) when compared with the hydrocarbon. Similarly, we discovered that tetraphenylboratanorcaradiene[4] is an intensely colored, red compound in contradistinction to its colorless hydrocarbon analogue. On the basis of ab initio molecular orbital calculations, these changes were attributed to an increase in occupied-orbital energies due to the net reduction of nuclear charge that occurs when borate replaces carbon. The synthesis and examination of the chemical and physical properties of boratirene **2** provide additional insight into this effect.

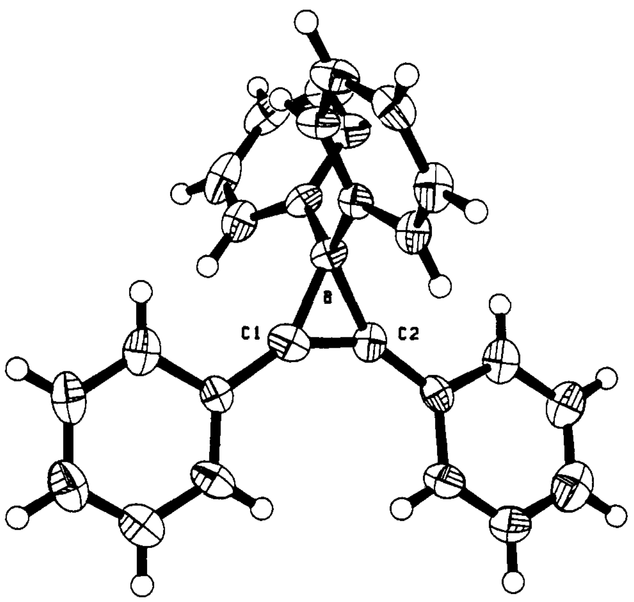


Figure 1. X-ray crystal structure for boratirene **2**. The potassium counter ion and a coordinated THF are not shown.

On the basis of our experience with the irradiation of $[(\mathrm{Ph})_4\mathrm{B}]^-$,[5] $[(\mathrm{Ph})_3(\mathrm{PhPh})\mathrm{B}]^-$,[4] and $[(\mathrm{Ph})_3(\mathrm{PhCH{=}CH})\mathrm{B}]^-$[3] and Eisch's[6] report that photolysis of $[(\mathrm{Ph})_3(\mathrm{PhC{\equiv}C})\mathrm{B}]^-$ followed by acid hydrolysis gives a 6:1 mixture of *cis*-stilbene and biphenyl, we supposed that irradiation of borate **1** would initiate a di-π-borate rearrangement[7] and give boratirene **2**. Borate **1** is conveniently prepared from triphenylborane and lithium phenylacetylide. Its potassium salt is an air-stable, white crystalline solid that shows

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[1] (a) Dewar, M. J. S. *Prog. Boron. Chem.* **1964**, *1*, 235. (b) Krogh-Jespersen, K.; Schleyer, P. v. R.; Pople, J. A.; Cremer, D. *J. Am. Chem. Soc.* **1978**, *100*, 4301. (c) Krogh-Jespersen, K.; Cremer, D.; Dill, J. D.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 2589. (d) Disch, R. L.; Sabio, M. L.; Schulman, J. M. *Tetrahedron Lett.* **1983**, *24*, 1863. (e) Frenking, G.; Schaefer III, H. F. *Chem. Phys. Lett.* **1984**, *109*, 521. (f) Pople, J. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1986**, *129*, 279. (g) Drewello, T.; Kock, W.; Lebrilla, C. B.; Stahl, D.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 2922. (h) Sheldon, J. C.; Currie, G. J.; Bowie, J. H. *J. Am. Chem. Soc.* **1988**, *110*, 8266.

[2] (a) Letsinger, R. L.; Skoog, I. H. *J. Am. Chem. Soc.* **1955**, *77*, 5176. (b) van Tamelen, E. E.; Brieger, Gl.; Untch, K. G. *Tetrahedron Lett.* **1960**, 14. (c) Jutzi, P. *J. Organomet. Chem.* **1969**, *19*, P1. (d) Grisdale, P. J.; Williams, J. L. R. *J. Organomet. Chem.* **1970**, *22*, C19. (e) Eisch, J. J.; Galle, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 4436. (f) Sobieralski, T. J.; Hancock, K. G. *J. Am. Chem. Soc.* **1982**, *104*, 7533. (g) Sobieralski, T. J.; Hancock, K. G. *J. Am. Chem. Soc.* **1982**, *104*, 7542. (h) Lee, D. Y.; Martin, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 5745. (i) Eisch, J. J.; Galle, J. E.; Kozima, S. *J. Am. Chem. Soc.* **1986**, *108*, 379. (j) Nakadaira, Y.; Sato, R.; Sakurai, H. *Chem. Lett.* **1987**, 1451. (k) Ashe III, A. J.; Drone, F. J. *J. Am. Chem. Soc.* **1987**, *109*, 1879.

[3] Kropp, M.; Bhamidapaty, K.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 6252.

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

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

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

[7] Named by analogy to the well-known di-π-methane rearrangement. Zimmerman, H. E. *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 131.

0002-7863/89/1511-2316$01.50/0

an ^{11}B NMR absorption band at δ −12 (CD_3CN, $BF_3{\cdot}OEt_2$ = 0.00). The UV absorption spectrum of **1** has a maximum at 259 nm (ϵ = 19 000 M^{-1} cm^{-1}) in acetonitrile solution.

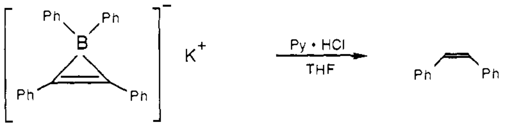
Irradiation of borate **1** (0.08 M) in a THF solution under a N_2 atmosphere causes the initially colorless solution to become deeply orange. ^{11}B NMR spectral analysis of the solution after irradiation shows that the peak for **1** at δ −12 has been replaced by two new absorptions at δ −16 and −38 in a ratio of approximately 5:1. The major product may be isolated from the crude photolysis mixture by dilution with hexane and filtration of the yellow-orange precipitate.[8] Recrystallization of the crude solid from a mixture of hexane and THF gives analytically pure, crystalline material.

The isolated product is isomeric with the starting material[9] and shows a single peak at δ −16 in its ^{11}B NMR spectrum. The ^{1}H NMR spectrum[10a] of this borate product has six multiplets in the aromatic region; four correspond to four hydrogens each, and two account for two hydrogens each. There are nine resonances in the ^{13}C NMR spectrum[10b] of the borate; two of these (δ 161.1 and 149.5) are coupled to boron. These NMR spectral data are consistent with a structure having C_{2v} symmetry that contains two pairs of unique phenyl groups.

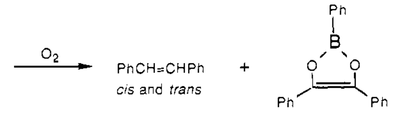
The structure of the isolated borate was confirmed to be boratirene **2** by X-ray crystallography, Figure 1.[11] The borate-containing, three-membered ring has a C–B–C angle of 50.6° (3) and the two C–C–B angles are 65.4 (4) and 64.0° (4). The ring carbon–boron bond distances are 1.578 (8) and 1.597 (8) Å, and the carbon–carbon bond distance is 1.357 (7) Å. The carbon–carbon bond distance of **2** falls within the range of bond lengths found for phenyl-substituted cyclopropenes.[12]

The UV absorption spectrum of boratirene **2** in CH_3CN solution shows a maximum at 269 nm (ϵ = 21 000 M^{-1} cm^{-1}) and two shoulders[13] at 350 nm (ϵ = 4500 M^{-1} cm^{-1}) and 450 nm (ϵ = 600 M^{-1} cm^{-1}). The absorptions at 350 and 450 nm disappear when the solution is opened to the air. Cyclic voltammetric oxidation of **2** in acetonitrile solution shows a single, irreversible wave at −0.6 V vs $Ag/AgNO_3$. These findings highlight the effect of changing a carbon atom to a borate group.

We have begun the investigation of the chemical properties of boratirenes. Addition of pyridine hydrochloride to a THF solution of boratirene **2** gives *cis*-stilbene in nearly quantitative yield, eq 2. Saturation of a boratirene solution with oxygen and analysis by means of gas chromatography reveals formation of *cis*- and *trans*-stilbene, benzil, deoxybenzoin, and 2,4,5-triphenyl-1,3,2-dioxaborole, eq 3. The benzil and deoxybenzoin presumably arise from secondary oxidation of the first-formed borole.[14]



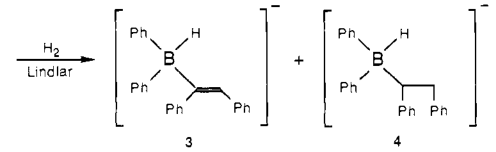
(2)



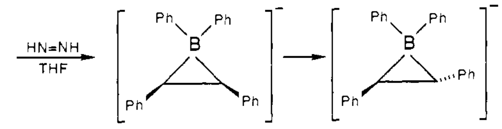
(3)

Reduction of boratirene **2** with Lindlar's catalyst under H_2 gives two borohydrides. The major reduction product was isolated by precipitation with hexane and determined to be diphenyl-(*Z*-1,2-diphenylethenyl)borohydride (**3**), eq 3, on the basis of its ^{1}H NMR spectrum and the acid-catalyzed hydrolysis of the reduction reaction mixture to *cis*-stilbene and bibenzyl in a ratio of 10:1. The minor product (**4**) presumably arises from reduction of **3**.

Reduction of boratirene **2** with diimide[15] in refluxing THF solution gives a different result. Under these conditions, the exclusive reduction product is *trans*-1,1,2,3-tetraphenylboratirane, eq 5, whose structure was verified by comparison with an authentic sample.[3] We suppose that the *trans*-boratirane must arise by isomerization of the initially formed cis-disubstituted compound, although our efforts to observe this isomer have been unsuccessful so far.



(4)



(5)

To expand our understanding of the perturbation caused by conversion of a cyclopropene to a boratirene, we carried out ab initio molecular orbital calculations using a 3-21G basis set[16] on the parent structures $(C_2H_4B)^-$ and C_3H_4. These results show that the bonding molecular orbitals of the boratirene are uniformly much higher in energy than the corresponding orbitals of cyclopropene. This finding is consistent with the observed low oxidation potential, high reactivity, and the visible color of **2**. From these results, it seems likely that the low-energy optical absorptions of the ring-strained borates is due to photoionization from the high-lying HOMO. We are continuing to study the di-π-borate rearrangement and the novel compounds it generates.

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Supplementary Material Available: Listings of atomic positions and thermal parameters and bond distances and angles for **2** (4 pages); listing of observed and calculated structures factors for boratirene **2** (9 pages). Ordering information is given on any current masthead page.

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(8) The minor photoproduct (^{11}B NMR δ −38) is assigned to the boratanorcaradiene formed from di-π-borate rearrangement between two phenyl groups of **1** by analogy to the chemistry of tetraphenylborate and triphenylbiphenylborate.[4,5] ^{1}H NMR signals for the expected boratanorcaradiene are seen at δ 5.65, 5.96, and 6.04 in the crude photolysis solution.

(9) Anal. Calcd for $C_{30}H_{32}BN$: C, 86.33; H, 7.73; N, 3.36. Found (1): C, 86.50; H, 7.62; N, 3.41. Found (2): C, 85.80; H, 7.78; N, 3.41.

(10) (a) ^{1}H NMR (**2**, tetraphenylarsonium salt, 300 MHz): δ 6.28 (m, 2 H), 6.93 (m, 2 H), 6.96 (t, 4 H), 7.22 (t, 4 H), 7.41 (br d, 4 H), 7.47 (d, 4 H), 7.64–7.87 (m, 20 H, Ph_4As^+). (b) ^{13}C NMR (**2**, potassium salt, 75 MHz) δ 122.0, 123.65, 126.08, 127.7, 128.31, 134.35, 141.79, 149.56, 161.06.

(11) Crystal data for $[K]\,[C_{26}H_{20}B]{\cdot}[C_4H_8O]$: monoclinic, space group $P2_1/c$, a = 14.548 (6) Å, b = 11.193 (6) Å, c = 15.509 (7) Å, β = 99.83 (3)°, V = 2488 (3) Å^3, and Z = 4. Diffraction data: Enraf Nonius CAD4 automated k-axis diffractometer, Mo radiation ($\lambda(K\alpha)$ = 0.71073 Å), range 2.0 < 2 < 46.0 ($\pm h+k-l$), 3888 reflections (3448 unique, R_i = 0.034, 2052 observed). $I > 2.58\sigma(I)$; corrected for anomalous dispersion, absorption, Lorentz, and polarization effects but not corrected for crystal decay (none observed). Solution: direct methods (SHELXS-86). Refinement: hydrogen atoms were included as idealized fixed contributors and remaining atoms independently refined (SHELX). Final: difference Fourier map (range +0.47 > e/A^3 > 0.25); final variance between observed and calculated structure factors showed a slight dependence on sin (θ); agreement factors, R = 0.061, R_w = 0.076, and E = 1.74.

(12) (a) Domnin, I. N.; Kopf, J.; Keyaniyan, S.; De Meijere, A. *Tetrahedron* **1985**, *41*, 5377. (b) Ammon, H. L.; Sherrer, C.; Agranat, I. *Chem. Scr.* **1978**, *11*, 39. (c) Starova, G. L.; Domnin, I. N.; Markin, V. N. *Vest. Leningr. U., Fiz. Khim.* **1984**, 58.

(13) The boratirene decomposes slowly in acetonitrile, but the decomposition product shows no absorptions above 300 nm.

(14) Letsinger, R. L.; Hamilton, S. B. *J. Org. Chem.* **1960**, *25*, 592.

(15) Corey, E. J.; Mock, W. L. *J. Am. Chem. Soc.* **1962**, *84*, 685.

(16) The calculations were performed at the National Center for Supercomputing Applications at the University of Illinois. GAUSSIAN: Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Topiol, S.; Pople, J. A. Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 1984.