and saturated with DMF and then treated twice with 20% piperidine in DMF (1 min, 7 min) at room temperature. After removal of excess reagent the peptidyl-resin was washed liberally with DMF and treated with 1 (0.405 g, 2.76 mmol) and DIEA (0.545 mL, 3.13 mmol) diluted to 1.5 mL with DMF, and the reaction was allowed to proceed at 47-8 °C for 135 min after which the Kaiser ninhydrin test[14] of a resin sample was negative. The resulting peptidyl-resin was washed four times each with DMF then CH_2Cl_2, and the Boc group cleaved with TFA/CH_2Cl_2 (1:1) for 15 min at room temperature. After removal of excess reagent the peptidyl-resin was washed successively with CH_2Cl_2, MeOH, and ether and dried in vacuo to yield 0.215 g of peptidyl-resin. The entire sample was treated at 0 °C with 10 mL of HF containing 0.5 mL of anisole, and the mixture was stirred for 1 h. After evaporation of HF, the resin was washed four times with ether and the crude product extracted with 10 mL of 5% aqueous acetic acid. Lyophilization of the extract furnished 83 mg of white powder (88% overall yield based on starting resin substitution and assuming isolation of the diacetate salt). HPLC data for the crude product is given in Figure 4. The crude product was purified by preparative HPLC as described in the General Experimental Section to yield 45 mg (43%, as the bis-TFA salt) of homogeneous product: MS/FAB 821 $(M + H)^+$, calcd (as free peptide) 820 (M); amino acid analysis, Asp 0.91 (1), Pro 1.16 (1), Gly 0.99 (1), Leu 1.05 (1), His 0.87 (1), Lys 0.97 (1), Arg 1.04 (1).

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Supplementary Material Available: ^1H NMR spectra of guanidine products **5**–**10** (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Photochemistry of 4-Substituted (Phenylethynyl)triphenylborate Salts: Analysis of the Visible-Region Electronic Absorption Spectra of Tetraarylboratirene Anions

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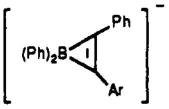
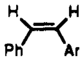
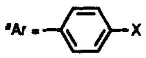
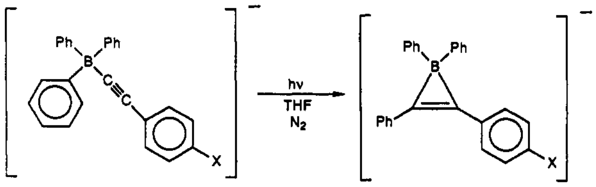
Introduction

Interest in the chemistry of boron-containing substances has recently been boosted[1] by the discovery that highly reactive compounds containing a boron atom in a three-membered ring can be isolated and fully characterized.[2,3] One of the unusual features of these compounds is their relatively intense color. The boratanorcaradiene anions are deep red, and the boratirene anions are yellow.[3] For comparison, the hydrocarbon analogues of these compounds, norcaradienes and cyclopropenes, respectively, are colorless with strong absorptions only in the deep UV spectral region.[4] We have attributed the unusual absorption of the three-membered boron-containing anions to an electronic effect.[3,5] Others have suggested that the color is due to a small amount of ring-opened carbanion present in equilibrium with the ring-closed structure that is characterized by NMR spectroscopy and by X-ray crystallography.[6] We report herein the results of investigations designed to help resolve this issue. Irradiation of 4-substituted (phenylethynyl)triphenylborate anions (**1**, **2**, or **3**) gives substituted boratirenes **4**, **5**, **6**, respectively, as is shown in eq 1. The substituents were chosen so that they might alter the amount of ring-opened anion present in equilibrium but, by analogy with other chromophores, should affect only slightly the absorption spectrum of the ring-closed borate anion.[7]

Table I. Absorption Spectra in Acetonitrile Solvent

compd[a]	λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1}) H	OMe	F
$[(Ph)_3BC{\equiv}CAr]^-$	259 (19 300) 266 (19 200)	260 (28 000) 269 (28 000)	255–260 (19 000)
	274 (16 000) 325 (11 500) 400 (2000)	260 (20 300) 340 (6000) 400 (1900)	270 (20 000) 330 (7000) 390 (1300)
	276 (10 900)	285 (14 400)	274 (11 000)





(1)

1, X = H
2, X = F
3, X = OCH_3

4, X = H
5, X = F
6, X = OCH_3

Results

The synthesis of borate **1** has already been reported,[3] borates **2** and **3** were prepared by an analogous procedure starting from (4-fluorophenyl)acetylene and (4-methoxyphenyl)acetylene. As potassium salts, borates **2** and **3** show single peaks in their ^{11}B NMR spectra at δ −12.6 and −12.7, respectively. Significantly, the UV spectra of borates **1**, **2**, and **3** are very similar both in band position and intensity. These data are summarized in Table I.

The irradiation of the potassium salt of borate **2** in THF solution at 254 nm was followed by ^{11}B NMR spectroscopy. As the reaction proceeds, the resonance due to starting material decreases and a new peak at δ −16.3 appears. A

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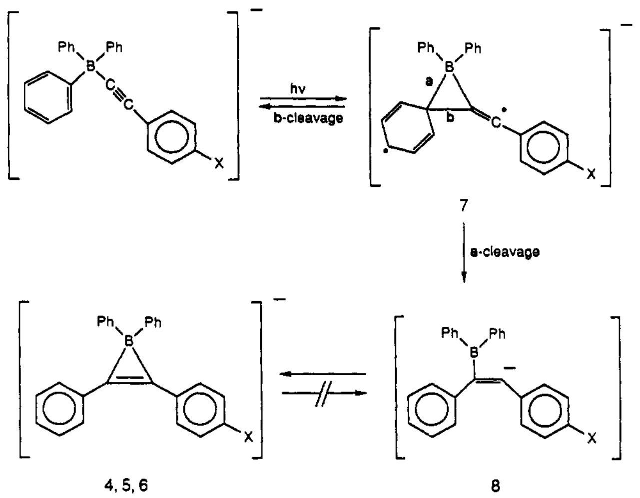
0022-3263/92/1957-2502$03.00/0

Scheme I



similar result is obtained when borate **3** is irradiated except that in this case the reaction is much slower and the product resonance is observed at δ −16.8. When the irradiation of borates **2** or **3** is carried out in the presence of CH_3OD, the product peak in the ^{11}B NMR spectrum is not observed and a mixture of cis-4-substituted (1,2-dideuterio)stilbenes is obtained along with the trans isomers presumably formed by photoisomerization. These findings indicate formation of the boratirenes **5** and **6** from irradiation of borates **2** and **3**.

The tetramethylammonium salts of boratirenes **5** and **6** were isolated from the reaction mixture by precipitation with hexane. This procedure gives air- and water-sensitive yellow solids that show single ^{11}B NMR absorptions at δ −16.5 and −16.9 in acetonitrile and ^{1}H NMR spectra consistent with boratirene structures. When CH_3CO_2D is added to THF solutions of these solids, their color is bleached immediately and the cis-4-substituted (1,2-dideuterio)stilbenes are the major products. However, we are unable to obtain completely satisfactory elemental analyses for **5** or **6** (see Experimental Section).

The UV–vis absorption spectra of boratirenes **4**, **5**, **6** are very similar. The data are summarized in Table I. Each boratirene shows three bands: a strong UV absorption at ca. 270 nm and weaker shoulders at ca. 330 nm and at ca. 400 nm. It is the latter absorption that gives the boratirenes their characteristic yellow color.

Discussion

The photochemistry of borates **2** and **3** is analogous to that reported previously for **1**. Electronic excitation of the arylacetylene chromophore initiates a di-π-borate rearrangement that gives the substituted boratirenes in good yield. Interestingly, the relative quantum yield for rearrangement of the methoxy-substituted borate is ca. 5 times less than for the parent compound and for the fluorine-substituted example. It is difficult to reach firm conclusions on the basis of quantum yield data. Nevertheless, this observation seems to support the reaction mechanism shown in Scheme I.

The first chemical step in the proposed mechanism, after excitation, is formation of a bond between a boron-bound carbon of a phenyl group and the boron-bound carbon of the acetylene group to form intermediate biradical anion **7**. Intermediate **7** may follow two different reaction paths. Cleavage of the bond labeled b regenerates the starting borate. Cleavage of the bond labeled a forms anion **8**. We suggest that ring-closure of anion **8** generates the observed boratirenes. The effect of the substituent on the relative quantum efficiencies of this reaction might be due to the partitioning of biradiacal anion **7**. Anion **8** is drawn in Scheme I as the resonance structure that emphasizes localization of negative charge on the α-carbon atom of the substituted benzene group. An electron-donating substituent, such as the methoxy, will destabilize this structure. It is reasonable to suggest that an increase in the energy for **8** will lead to a relative decrease in a-bond cleavage and a concomitant decrease in quantum efficiency.

Similar reasoning permits examination of the hypothesis that the color of boratirenes is due to a small amount of anion **8** in equilibrium with the ring-closed structures **4**, **5**, and **6**. If this were true, it is reasonable to expect that there would be significantly less **8** in the mixture for the 4-methoxy-substituted compound than for the 4-fluorine-substituted example. With the assumption that the carbanions will have similar extinction coefficients, this hypothesis leads to prediction of a significantly less intense visible absorption for **6** than for **4** or **5**. The experiments rule this out. In fact there is a slight increase in the intensity of the visible absorption band for **6** which is consistent with the observed substituent effects seen in substituted *cis*-stilbenes (see Table I).

In summary, two lines of evidence have been developed to support the proposal that the color of boratirenes is due to low-energy electronic transition of the ring-closed structure and not the result of a small amount of ring-opened anion. In previous work[3] we showed that the intensity of the visible absorption band of **4** is essentially independent of temperature from 23 to −196 °C. This observation is inconsistent with the possibility that the color is due to a small amount of a strongly absorbing structure present in equilibrium with the borate detected by NMR spectroscopy. In the present work we show that substituent effects on the visible absorption are consistent with its assignment to the ring-closed structure.

Experimental Section

General. All glassware was oven dried overnight and cooled in a N_2 atmosphere. THF was distilled from sodium/benzophenone. Acetonitrile was distilled from calcium hydride under N_2. Hexane was stored over 3-Å molecular sieves. ^{1}H and ^{13}C NMR spectra were obtained on Varian XL-200 or General Electric QE-300 spectrometers in acetonitrile-d_3, acetone-d_6, or tetrahydrofuran-d_8 solvent. ^{11}B NMR spectra were obtained on a General Electric QE-300NB spectrometer. Mass spectral data were obtained on a GC/MS on a Hewlett-Packard 5970 mass selective detector (EI, 70 ev) in line with a Hewlett-Packard 5890 GC. Gas chromatography was performed on a Hewlett-Packard 5890 gas chromatograph equipped with 100% methylsiloxane column. UV–vis spectra were determined on a Perkin-Elmer 552 spectrometer. Elemental analyses were performed by the University of Illinois Microanalytical Laboratory.

(4-Fluorophenyl)acetylene. A mixture of 4-fluoroacetophenone (13.3 g, 96 mmol) and phosphorous pentachloride (21.4 g, 102 mmol) was heated to 70 °C. The phosphorous oxychloride was removed and the residue was distilled under reduced pressure yielding 16 g of a mixture of 1-chloro-1-(4′-fluorophenyl)ethene and 1,1-dichloro-1-(4′-fluorophenyl)ethane: bp 102–107 °C (18 mmHg). An ethanol solution containing KOH (25 g) of these chlorides was heated at reflux for 3 h, and the resulting solution was poured into ice–water. The oil that separated was extracted with ether. The ether extracts were combined and dried over potassium carbonate. The ether was removed, and the residue was distilled under reduced pressure to give pure (4-fluorophenyl)acetylene:[8] ^{1}H NMR ($CDCl_3$) δ 3.05 (s, 1 H), 7.01 (t, 2 H), 7.45 (dd, 2 H).

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(4-Methoxyphenyl)acetylene. Potassium hydroxide (2.75 g, 49 mmol) was placed in a 25-mL three-neck round-bottom flask fitted for distillation. The system was maintained under ca. 30 mmHg pressure throughout the procedure. The flask was heated slowly until the KOH melted (170–175 °C). β-Bromo-4-methoxystyrene (2.12 g, 10 mmol) was added slowly to molten KOH. While the β-bromo-4-methoxystyrene was being added, the temperature of the oil bath was kept below 185 °C to avoid distillation of starting material. The distillate was separated, and the organic layer was dried with KOH and distilled under reduced pressure. The main fraction boiled at 85 °C (11 mmHg):[9] ^{1}H NMR (CD_3Cl) δ 3.01 (s, 1 H), 3.81 (s, 3 H), 6.85 (d, 2 H), 7.44 (d, 2 H). Anal. Calcd for C_9H_8O: C, 81.79; H, 6.10. Found: C, 81.50; H, 6.22.

Potassium [(4-Fluorophenyl)ethynyl]triphenylborate. A THF solution of (4-fluorophenyl)acetylene (10 mmol, 1.2 g) was placed in a 100-mL round-bottom flask equipped with a low-temperature thermometer and a N_2 inlet. A hexane solution of nBuLi (1.6 M, 10 mmol) was added slowly to the reaction mixture at −78 °C. This mixture was stirred for 1 h, and then a THF solution of triphenylborane (2.42 g, 10 mmol) was added. The reaction solution was warmed to room temperature, the solvent was evaporated, and the residue was dissolved in water. After extraction with hexane, the solution was filtered and an aqueous solution of KCl (ca. 1 g) was added. The white solid that formed was removed by filtration, washed with water, and then dried under high vacuum: ^{1}H NMR ($(CD_3)_2CO$) δ 6.83 (t, 2 H), 6.98 (t, 9 H), 7.37 (dd, 2 H), 7.52 (bd, 6 H); ^{11}B NMR (THF) δ −12.6; UV-vis λ_{max} (CH_3CN) 258 nm (ϵ = 22 000 M^{-1} cm^{-1}). Anal. Calcd for $C_{26}H_{19}BFK$: C, 78.00; H, 4.78; B, 2.70; F, 4.75; K, 9.77. Found: C, 77.78; H, 4.81; B, 2.92; F, 4.63; K, 9.53.

Tetramethylammonium [(4-Fluorophenyl)ethynyl]triphenylborate. The same procedure was followed as in the preparation of the potassium salt of this borate except that tetramethylammonium bromide was added to the filtered aqueous solution: ^{1}H NMR (CD_3CN) δ 2.90 (s, 12 H), 6.91–7.08 (m, 11 H), 7.35–7.42 (m, 8 H); ^{11}B NMR (CH_3CN) δ −12.2; UV-vis λ_{max} (CH_3CN) 255–260 nm (ϵ = 19 000 M^{-1} cm^{-1}). Anal. Calcd for $C_{30}H_{31}NBF$: C, 82.76; H, 7.18; N, 3.22; B, 2.48; F, 4.36. Found: C, 82.62; H, 7.29; N, 3.26; B, 2.59; F, 4.23.

Potassium [(4-Methoxyphenyl)ethynyl]triphenylborate. The procedure described for [(4-fluorophenyl)ethynyl]triphenylborate was followed with (4-methoxyphenyl)acetylene: ^{1}H NMR ($(CD_3)_2CO$) δ 3.74 (s, 3 H), 6.80 (m, 5 H), 6.96 (t, 6 H), 7.29 (d, 2 H), 7.52 (bd, 6 H); ^{11}B NMR (THF) δ −12.7; UV-vis λ_{max} (CH_3CN) 260 nm (ϵ = 24 100 M^{-1} cm^{-1}), 270 (24 200). Anal. Calcd for $C_{27}H_{22}OBF$: C, 78.64; H, 5.38; B, 2.62; K, 9.48. Found: C, 78.62; H, 5.42; B, 2.78; K, 9.32.

Tetramethylammonium [(4-methoxyphenyl)ethynyl]triphenylborate: ^{1}H NMR ($(CD_3)_2CO$) δ 3.13 (s, 12 H), 3.74 (s, 3 H), 6.77–6.81 (m, 5 H), 6.96 (t, 6 H), 7.28 (d, 2 H), 7.51 (bd, 6 H); ^{11}B NMR (CH_3CN) δ −12.2; UV-vis λ_{max} (CH_3CN) 260 nm (ϵ = 28 000 M^{-1} cm^{-1}), 269 (28 000). Anal. Calcd for $C_{31}H_{34}BNO$: C, 83.22; H, 7.66; N, 3.58; B, 2.42. Found: C, 82.86; H, 7.68; N, 3.68; B, 2.59.

Photolysis of Potassium [(4-Fluorophenyl)ethynyl]triphenylborate. A N_2-purged THF solution of the borate (0.08 M) was irradiated at 254 nm in the presence of undecane as an internal standard. The solution turned dark red. When the photolysis solution was monitored by ^{11}B NMR spectroscopy, the resonance of starting borate at δ −12.6 disappeared and was replaced by a peak at δ −16.3. Acetic acid was added to the reaction mixture when the NMR spectrum showed complete consumption of the starting borate. The red color disappeared, and analysis by GC showed that a mixture of *cis*- and *trans*-4-fluorostilbene (42% and 17%, respectively) had been formed. When this photolysis was carried out in the presence of CH_3OD, the reaction solution did not turn red and analysis by GC/MS showed the formation of dideuterated 4-fluorostilbene.

Tetramethylammonium 1,1,3-Triphenyl-2-(4′-fluorophenyl)boratirene (5). A THF solution of borate 2 (0.01 M, 150 mL) in a quartz round-bottom flask was degassed, sealed, and irradiated at 254 nm. When the reaction was complete, the solution was opened in a drybox and diluted with 200 mL of hexane. The yellow solid that formed was isolated by filtration (crude isolated yield = 35%): ^{1}H NMR (CD_3CN) δ 2.96 (s, 12 H), 6.8–7.1 (m, 10 H), 7.23 (t, 1 H), 7.4–7.5 (m, 8 H); ^{11}B (CH_3CN) δ −16.5; UV-vis λ_{max} (CH_3CN) 270 (ϵ = 20 000 M^{-1} cm^{-1}), 330 (7000), 390 (1300). The absorption at 390 nm was bleached when the boratirene solution is exposed to air. Anal. Calcd for $C_{30}H_{31}NBF$: C, 82.76; H, 7.18; N, 3.22; B, 2.48; F, 4.36. Found: C, 81.20; H, 7.23; N, 3.25; B, 2.77; F, 4.10. We commonly observe insufficient carbon in boron-containing compounds, perhaps due to formation of boron carbide. The ^{1}H NMR spectrum of this compound is included in the supplementary material.

Photolysis of Potassium [(4-Methoxyphenyl)ethynyl]triphenylborate. A N_2-saturated THF solution of borate 3 (0.08 M) containing undecane as an internal standard was irradiated at 254 nm. The progress of the reaction was monitored by ^{11}B NMR spectroscopy. During the irradiation, the solution became dark red and the resonance of starting borate at δ −12.7 was replaced by one at δ −16.8. Acetic acid was added to the reaction mixture when borate 3 was completely consumed. Analysis of this solution by GC showed *cis*- and *trans*-4-methoxystilbene (27% and 14%, respectively). When the photolysis was performed in the presence of CH_3OD, dideuterated 4-methoxystilbenes were obtained.

Tetramethylammonium 1,1,3-Triphenyl-2-(4′-methoxyphenyl)boratirene (6). A THF solution of borate 3 (0.0075 M) was degassed and sealed in a quartz round-bottom flask. This solution was irradiated at 254 nm and, when reaction was complete, diluted with hexane in a drybox. A yellow solid precipitated when this solution was stored in a freezer overnight: ^{1}H NMR (CD_3CN) δ 2.76 (s, 12 H), 3.77 (s, 3 H), 6.8–7.2 (m, 10 H), 7.2–7.6 (m, 9 H); ^{11}B NMR (CH_3CN) δ −16.9; UV-vis λ_{max} (CH_3CN) 260 nm (ϵ = 20 300 M^{-1} cm^{-1}), 340 (6000), 400 (1900). When an acetonitrile solution of this solid is exposed to air or water, the absorption at 400 nm is bleached. Despite repeated attempts, we were unable to obtain a satisfactory elemental analysis of this compound. This is a consequence of its high reactivity toward oxygen when the last traces of solvent are removed. The ^{1}H NMR spectrum of this compound is included in the supplementary material.

Acknowledgment. We thank the National Science Foundation for their generous support of this research.

Supplementary Material Available: ^{1}H NMR spectra of compounds 5 and 6 (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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Syntheses of Dipentafulvenes: Bichromophoric Effects Correlated with Structure

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Introduction

The polarity of the carbon–carbon double bond exocyclic to pentafulvenes is a major contributor to the overall dipole moment in monofulvenes. For example, 6,6-dimethylfulvene, 1, has a dipole moment of 0.44 D.[1] The exocyclic bond polarizability of pentafulvenes results in ketone-like reactivity. Alkyl- and aryllithium reagents add to the exocyclic carbon–carbon double bond,[2,3] and strong bases

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