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Phototransposition Reactions of Arylboronate Esters in Acetonitrile and 2,2,2-Trifluoroethanol

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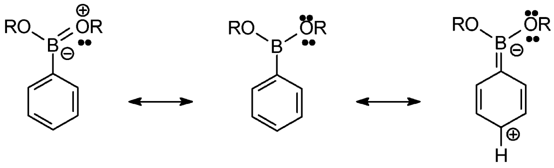
The phototransposition (para, meta, ortho) reactions of the arylboronate esters 4-, 3-, and 2-(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolanyl)toluenes (**1**, **2**, and **3**, respectively) in both acetonitrile and 2,2,2-trifluoroethanol (TFE) using 254 nm irradiation have been examined. The irradiations resulted in steady-state compositions of para (5%), meta (19%), and ortho (76%) isomers in acetonitrile starting from the ortho isomer and para (12%), meta (54%), and ortho (35%) isomers in TFE starting from the para isomer. Analysis of the ^{13}C NMR spectrum of the product mixture obtained from the photochemistry of the para isomer selectively deuterated at C3 and C5 (**1d$_2$**) revealed that the boron-substituted carbon is the active one in the phototransposition reactions in both acetonitrile and TFE. Similar results were observed for irradiations of **1** in cyclohexane. Fluorescence spectra, singlet-state lifetimes, and Stern−Volmer quenching of fluorescence with 2,3-dimethyl-1,3-butadiene indicated that the excited singlet states of these three isomers were spectroscopic minima and that the excited singlet state was the reactive one for **3** in acetonitrile.

Introduction

Arylborane compounds have attracted considerable synthetic interest because of their use in the Pd-catalyzed Suzuki coupling reaction with aryl halides to form biaryl derivatives in good yield.[1] In contrast, the physical organic chemistry of arylboranes, in particular the effect of borane as a substituent, has received little attention. In fact, the question of whether borane substituents are electron-withdrawing or -donating is not yet answered and has attracted only minimal interest.

Boron is less electronegative than carbon, and therefore, the $-BH_2$ group should be inductively electron-donating (a σ donor). In contrast, it is isolobal with $-CH_2^+$ and, therefore, should have a strong electron-withdrawing resonance effect in $ArBH_2$ compounds (a π acceptor).[2] Unfortunately, these hydrogen-substituted arylboranes are often unstable. Stabilization of the borane by alkoxy (arylboronate esters) or hydroxy (arylboronic acids) groups, as in **A**, makes them easy to handle but, of course, completely changes their nature as a substituent because of the importance of resonance structures **B**, competing with those like **C**. In fact, gas-phase photoelectron spectra and CNDO/2 modeling of the ionization potential for **A** ($R = CH_3$) indicate that the dialkoxyborane is overall electron donating by its inductive effect, reflecting the importance of structure **B**.[3]



B **A** **C**

Hammett σ values for the $-B(OH)_2$ substitutent, as determined by the pK_a of the corresponding substituted benzoic acid in water,[4] are $\sigma_p = 0.12$ and $\sigma_m = -0.01$ indicating that the substituent is mildly electron-withdrawing from the para position. Values of $\sigma_p = 0.04$ and $\sigma_m = 0.01$, estimated by calculations on the basis of ^{19}F NMR chemical shifts of substituted fluorobenzenes,[5] also indicate no significant electron-withdrawing or donating effect. Another issue is the expected Lewis acid/base interactions possible with the borane substituent in complexing solvents such as alcohols and ethers. For instance, the dipole moment of phenyl difluoroborane ($PhBF_2$) increases from 1.90 D in benzene to 3.63 D in dioxane[6] as a consequence of the high polarity in the complex ($PhBF_2^-{-}^+OR_2$) formed.

We have previously reported on the phototransposition reactions (ortho, meta, para) in acetonitrile, eq 1 (shown for the three toluonitriles)[7] and the photoaddition reactions in 2,2,2-trifluoroethanol (TFE), eq 2 (shown for

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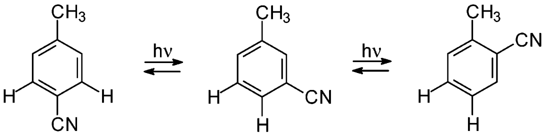
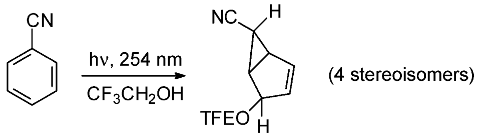
TABLE 1. Photophysical Properies of Arylboranes 1−3

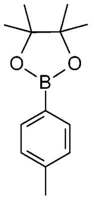
	sol	λ(max) (nm)	ϵ (M^{-1} cm^{-1})	λ(max) (nm)	ϵ (M^{-1} cm^{-1})	E (S_1)[a] (kJ/mol)	Φ_f[b]	τ[c] (ns)	$k_f/10^7$ (s^{-1})	$k_f/10^{7d}$ (s^{-1})
1	C_6H_{12}	227	17 500	265	337	427	0.17	16.8	1.0	
1	An	227	15 300	265	378	430	0.10	13.5[e]	0.70	0.63
1	TFE	227	14 200	279	407	430	0.036	4.0	0.88	
2	An	227	14 300	273	816	422	0.14	9.4	1.5	1.4
2	TFE	223	9620	284	784	422	0.082	5.2	1.6	
3	An	224	9500	274	820	418	0.16	8.2	2.0	1.4
3	TFE	221	7780	285	769	418	0.056	2.9	1.9	

[a] Obtained from the overlap of the normalized excitation and fluorescence spectra. [b] Relative to a value of 0.24 for anisole; estimated error ±10%. [c] From nanosecond single-photon counting, error ±2%. [d] Calculated from eq 3. [e] A value of 13.8 ns was obtained in methanol.





benzonitrile),[8] of a range of substituted benzenes. The topic has been recently reviewed.[9] A survey of substituted benzenes[10] indicated that electron-withdrawing groups (CN, CF_3, F) make these reactions more efficient. In view of our interest in these reactions, we now report the photochemistry and photophysics of the arylboronate esters **1**, **2**, and **3** in acetonitrile and TFE. These known 4-, 3-, and 2-(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolanyl)toluenes were chosen both because of their ease of synthesis and because of their stability, which allows for their purification by distillation and the use of GC for the analysis of reaction mixtures. Isomers **1**, **2**, and **3** were obtained in good yields, 93, 89, and 91%, respectively, according to the method of Masuda et al.[11] from the corresponding iodotoluene and pinacol borane. In our hands, only low yields were obtained using aryl bromides.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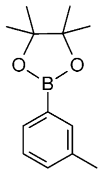
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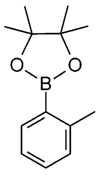
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Results and Discussion

Photophysical Properties of 1−3. The UV spectrum of $C_6H_5B(OR)_2$, R = 1-butyl, in the gas phase, has the typical longer wavelength ^1L_b (λ_{max} = 267 nm, ϵ = 331 M^{-1} cm^{-1}) and shorter wavelength ^1L_a (λ_{max} = 220 nm, ϵ = 10 200 M^{-1} cm^{-1}) bands expected from a substituted benzene derivative. These values differ only slightly from those of toluene (λ_{max} = 261 nm, ϵ = 238 M^{-1} cm^{-1} and λ_{max} = 210 nm, ϵ = 8870 M^{-1} cm^{-1})[12] indicating no significant strong interaction of the borane with the aromatic ring. The corresponding spectral data, given in Table 1 for **1**−**3** in both acetonitrile and TFE, have similar absorption bands. An interesting feature of these spectra is that, in both solvents and relative to the other two isomers, the para isomer (**1**) has the ^1L_b band with a λ_{max} at shorter wavelength by ~10 nm and a lower ϵ value by a factor of ~0.5. The same effect was noticed previously for the methylbenzonitriles with λ_{max} = 268 nm (ϵ = 700 M^{-1} cm^{-1}), λ_{max} = 276 nm (ϵ = 1910 M^{-1} cm^{-1}), and λ_{max} = 276 nm (ϵ = 1360 M^{-1} cm^{-1}) values for the para, meta, and ortho isomers, respectively. The higher ϵ values for the nitrile-substituted aromatics reflect the stronger π-acceptor interaction relative to the dialkoxyboranyl substitutent.

The fluorescence and excitation spectra for all three isomers in both solvents have the expected mirror image relationship for simple substituted benzenes with a well defined 0,0 band overlap and a small Stokes shift (~15 nm separation between the emission and excitation λ_{max} values). Again, the para isomer has a shorter wavelength 0,0 band resulting in a somewhat higher excited-state energy for S_1. Fluorescence quantum yields (measured relative to anisole, $\Phi_f = 0.24$[13]) and excited singlet state lifetimes are also reported in Table 1. The values of $k_f = \Phi_f\tau$ indicate that the radiative transition from S_1 to S_0 is slower for the para isomer in agreement with the lower ϵ value.

The theoretical relationship between the radiative lifetime ($\Phi_f = 1/k_f$) and the absorbance spectrum is given in eq 3,[14,15] where n is the refractive index of the solvent, ν_f is the expectation value for the frequency of the fluorescence spectrum, and the final term is the integrated absorbance spectrum. The constant gives k_f in units of s^{-1} if the frequency values are expressed in wavenumbers (cm^{-1}) and molar absorptivity ϵ is in the usual units (M^{-1} cm^{-1}). This equation is derived on the basis of the oscillator strength model and on the assumption that the first excited singlet state (S_1) and the ground state (S_0) have similar geometries. It has been used successfully in the past for simple aromatic compounds such as benzene, toluene, and *o*-xylene[16] and, in our laboratory, for a series of ten substituted aryl allyl

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ethers.[17] The calculated values of k_f for **1**−**3** in acetonitrile are given in Table 1. The agreement between the experimental and calculated values is excellent.

$$k_f = (2.88 \times 10^{-9}) n^2 \langle \bar{\nu}_f^{\,-3} \rangle \int \epsilon \ln \bar{\nu} \qquad (3)$$

The lower quantum yields of fluorescence and shorter singlet lifetimes for all three isomers in TFE relative to in acetonitrile indicate a pathway for deactivation of S_1 in TFE that is more efficient than that in acetonitrile. The absorption spectra have a shift in λ_{max} of about 10 nm to longer wavelength in TFE relative to acetonitrile as a result of changes in the relative intensity of vibrational modes. The 0,0 band, as indicated by the $E(S_1)$ values, are the same in the two solvents. Therefore, this effect occurs in the excited state and does not reflect a ground-state interaction between the boronate esters and TFE. This observation is in contrast to that for *p*-tolunitrile which has a quantum yield of fluorescence that is higher in TFE (0.20) than that in acetonitrile (0.16).

Stern−Volmer plots for the quenching of the fluorescence quantum yields of the meta and ortho boronates, **2** and **3**, by 2,3-dimethyl-1,3-butadiene in acetonitrile were linear (Figures S1 and S2 for **2** and **3**, respectively, Supporting Information), giving $k_q\tau$ values of 67.4 and 44.2 M^{-1}, respectively. Data could not be obtained for the para isomer **1** because the shorter wavelength λ_{max} and lower ϵ value resulted in competitive absorption by the diene. The k_q values obtained for **2** and **3** of 7.7 and 5.4 $\times$ 10^9 M^{-1} s^{-1}, respectively, are slightly less than the diffusional rate constant in acetonitrile of 1.3 $\times$ 10^{10} M^{-1} s^{-1}.[18] The quenching of the excited singlet state of substituted aromatics by alkylated dienes involves some electron-transfer character.[19] The higher values for the quenching of *p*-, *m*-, and *o*-methylbenzonitrile (2.0, 1.5 and 2.0 $\times$ 10^{10} M^{-1} s^{-1}, respectively)[7] indicate that, as expected, the nitrile group is a better electron-acceptor than the boronate ester.

Photochemical Interconversion of 1−3 in Acetonitrile. Plots for the phototransposition (254 nm Rayonet lamps, 25 °C) of **1**−**3** are given in Figures S3, S4 and 1, respectively (Figures S3 and S4, Supporting Information; Figure 1, shown here). The reactions were monitored by GC/FID but not quantified because conditions were not found that separated the ortho from the para isomer. The percentage composition was therefore determined from peak heights in the ^{1}H NMR spectra using the signals at δ 2.37, 2.35, and 2.53 ppm for the methyl groups for the isomers **1**, **2**, and **3**, respectively. Because the methyl groups in the para and meta isomers have such similar chemical shifts, determining their ratios reliably at very low conversions was not possible. The data shown in Figures 1, S3, and S4 are normalized to 100% for the sum of the three isomers but the mass balance (by GC/FID) at the end of each run is still very good: para, 82%; meta, 87%; and ortho, 75%. All three isomers are seen to be approaching a steady-state composition by photochemical equilibration.

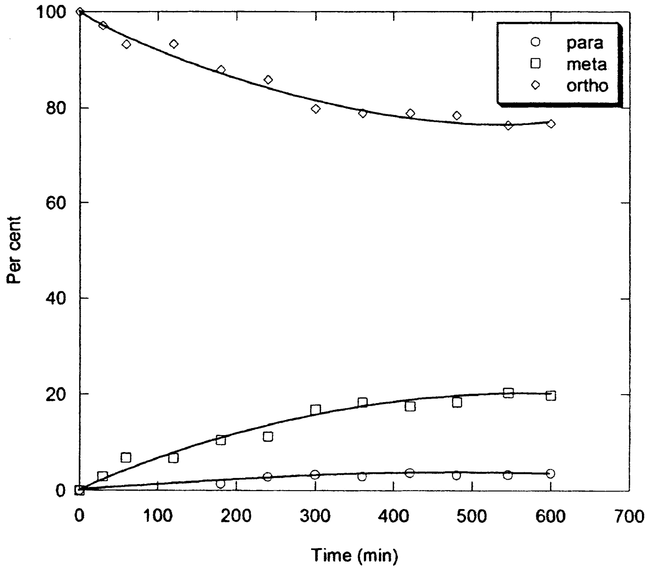

FIGURE 1. Plots for the phototransposition reaction of the ortho isomer **3** in acetonitrile (**1**, ○; **2**, □; **3**, ◇).

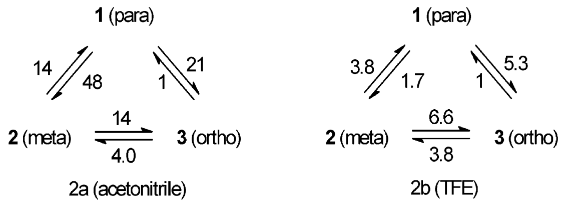

FIGURE 2. Relative efficiencies for phototransposition of **1**−**3** in acetonitrile (**2a**) and TFE (**2b**).

The percentage composition at photoequilibration can be calculated using the relative efficiency of each of the conversions possible as shown in Figure 2a. These values are estimated from three factors: 1, the relative reactivity of each isomer as estimated from its percent conversion after 100 minutes (para, 48%; meta, 17%; and ortho, 4%); 2, the isomer ratio for each isomer extrapolated to as low a conversion as possible (meta/ortho = 2.3 from para, ortho/para = 1.0 from meta and meta/para = 4.0 from ortho); 3, the molar absorptivity (ϵ) for each isomer at 254 nm (para (275 M^{-1} cm^{-1}), meta (323 M^{-1} cm^{-1}) and ortho (240 M^{-1} cm^{-1})). The least efficient process (ortho to para) is then assigned a value of 1. Values of the isomer composition at complete photoequilibration can then be calculated using the steady-state approximation giving **1** (5%), **2** (19%), and **3** (76%). The plots indicate that the ortho isomer (Figure 1) has reached the steady-state composition after 500 min but that the other two isomers have not.

The multiplicity of the reactive excited state was determined only for the meta isomer (**2**). Photolysis in the absence or the presence (1.0 $\times$ 10^{-3} M) of 2,3-dimethyl-1,3-butadiene gave essentially the same conversion (16% versus 14%) after 180 min of irradiation in acetonitrile. At this concentration of the diene (Stern−Volmer plot, Figure S1, Supporting Information), the excited singlet state of **2** is only slightly quenched (I_0/I = 1.08). Making the reasonable assumption that the triplet excited state is considerably longer lived than the singlet

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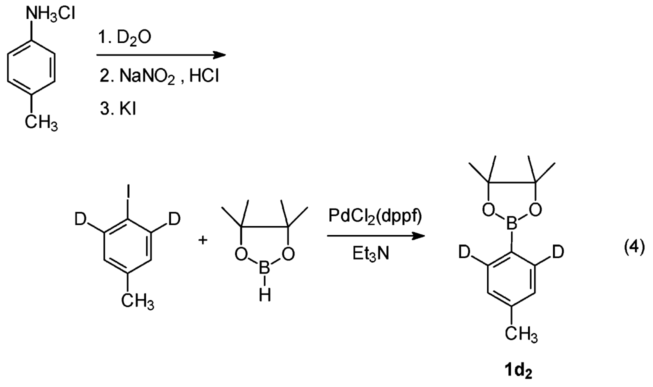
state and would therefore be quenched, the likely conclusion is that the singlet excited state is the reactive one.

Photochemistry of 3,5-Dideuterio-4-(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolanyl)toluene, 1d$_2$, in Acetonitrile. This compound was prepared as shown in eq 4, analogous to our previously reported synthesis of the corresponding 2,6-dideuterio-4-methylbenzonitrile. It has all of the chemically distinct aromatic carbons labeled so that their fate can be tracked in the phototransposition reaction. Because of the enhanced signal dispersion, identification of the ^{13}C NMR signals of those carbons which have H (or D) attached is the most reliable method for following the phototransposition, as the deuterium-substituted carbons have very weak signals compared to those that are proton-substituted (less than 1%, and split into a triplet). As shown in eqs 5 and 6, quite different substitution patterns are obtained for the photogenerated meta (**2d$_2$**) and ortho (**3d$_2$**) isomers if the borane-substituted carbon is the active one in the phototransposition (eq 5) as compared to the case where the methyl-substituted carbon is the active one (eq 6, meta (**2d$_2$′**) and ortho (**3d$_2$′**)). Competition between these two pathways (or other mechanistic possibilities) would result in complex mixtures of deuterated isomers.



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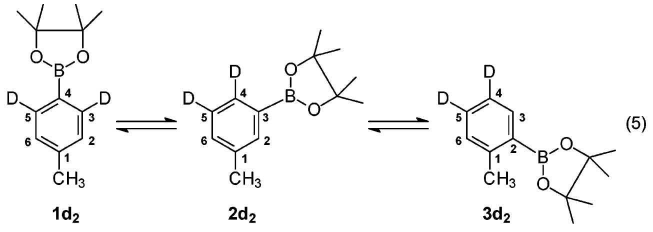

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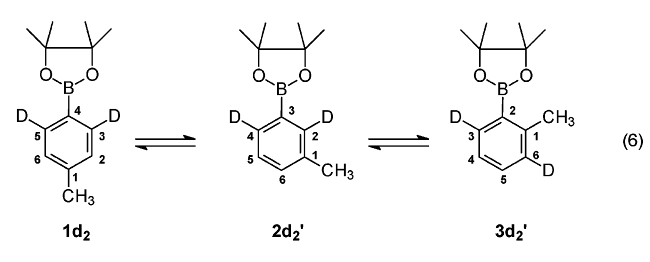

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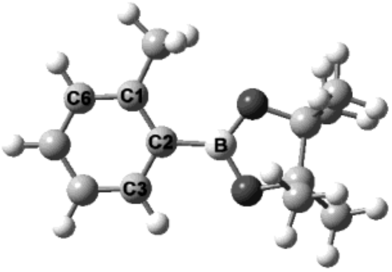
This approach requires assignment of the nonquaternary aromatic carbons in all three isomers. The effect of the $-B(OCH_3)_2$ substituent on the ^{13}C NMR chemical shifts of aromatic carbons has been determined (relative to benzene, 128.5 ppm): para (+1.3 ppm), meta (−0.6 ppm), and ortho (+5.1 ppm).[20] By analogy, these values allow assignment of the chemical shift effect of the 4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl substituent from the reported ^{13}C NMR spectrum of (4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)benzene: para (+2.7 ppm), meta (−0.8 ppm), and ortho (+6.2 ppm).[21] Using these values and the standard literature values[22] for the effect of a methyl substituent in monosubstituted benzene derivatives (para (−2.9 ppm), meta (−0.1 ppm), and ortho (0.7 ppm)) gives calculated chemical shifts for **1**−**3**. These values, along with the experimental ones, are given in Table 2. The agreement is seen to be excellent (differences < 0.7 ppm), except for the values for C3 and C6 in the ortho isomer **3** (differences = 1.6 and 1.7 ppm, respectively). These assignments were fully supported by a combination of COSY, HSQC, and HMBC NMR spectra on the pure isomers.

TABLE 2. Observed[a] and Calculated[b] (in Parentheses) Chemical Shifts (ppm) for the Hydrogen-Substituted Carbons of the Aryl Rings of the Boronate Esters 1−3 (See Eq 5 or 6 for Numbering of the Carbons)

compd	C$_2$	C$_3$	C$_4$	C$_5$	C$_6$
1 (para)	128.9	135.1		135.1	128.9
	(128.4)	(134.6)		(134.6)	(128.4)
2 (meta)	135.7		132.1	128.0	132.4
	(135.4)		(131.8)	(127.6)	(131.9)
3 (ortho)		136.2	125.0	131.1	130.1
		(134.6)	(124.8)	(131.1)	(128.4)

[a] Observed chemical shifts relative to the central line in CDCl$_3$ assigned a value of 77.4 ppm. [b] Calculated chemical shifts (see text).

The larger discrepancy for carbons C3 and C6 in the ortho isomer **3** can be explained from the results of Gaussian 98 calculations (RB3LYP 6-31G (d)) for minimized geometries. The ortho relationship of the methyl and boronate groups in **3** distort the geometry. The B−C2−C1 angle is larger (124.5°) and the B−C2−C3 angle smaller (117.0°) (as shown in **4**, the minimized geometry for **3**) than the corresponding angles in the para isomer (both 121.2°). Similarly, the $H_3C-C1-C2$ angle is larger (122.2°) and the $H_3C-C1-C6$ angle smaller (118.9°) than those in the para isomer (120.9°). These geometric distortions, due to steric interactions in the ortho isomer, presumably alter the effect that the substituents will have on ^{13}C NMR chemical shifts. This effect also makes the ortho isomer the least stable (by



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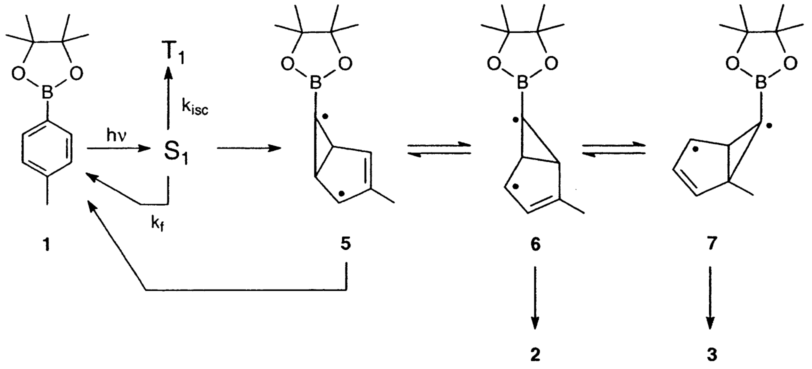
SCHEME 1. Proposed Mechanism for the Phototransposition Reaction of the *p*-Boronate Ester 1 in Acetonitrile



the same calculations) of the three isomers: para (arbitrarily = 0.0 kcal/mol), meta (+ 0.26 kcal/mol), and ortho (+1.7 kcal/mol). Clearly, the photochemical equilibrations in acetonitrile which result in the ortho isomer (54%) being the major and the para isomer (12%) the minor component are not controlled, as expected for a photochemical reaction, by the thermodynamic stability of the three.

In agreement with these ^{13}C NMR spectral assignments, the deuterated para isomer **1d$_2$** had a strong signal at 128.9 ppm and a very weak signal (less than 1%) barely visible in the noise at 135.1 ppm. Photolysis of this compound (91 mg in 100 mL of acetonitrile, Rayonet reactor, 254 nm lamps, 180 min) gave a mixture of **1d$_2$**, **2d$_2$**, and **3d$_2$**. The ^{13}C NMR spectrum of this mixture was consistent with the phototransposition as described by eq 5, a result demonstrating that the borane-substituted carbon is the dominant one in the mechanism of rearrangement. Strong signals were observed for the meta isomer (**2d$_2$**) for C6 (132.4 ppm) and C2 (135.7 ppm) indicating proton substitution, and weaker signals for C4 (132.1 ppm) and C5 (128.0 ppm) indicating deuterium substitution. The weaker signals were approximately 10% of the intensity of the stronger ones indicating that they are from hydrogen-substituted carbons as a result of the minor intervention by the pathway shown by eq 6. A corresponding analysis for deuterium distribution in the ortho isomer **3d$_2$** formed in this experiment provided further evidence for the dominance of the pathway in eq 5. The fact that the methyl-substituted carbon undergoes phototransposition in competition with the boron-substituted one is reasonable in view of the well-known phototransposition reactions of methyl-substituted benzenes.[23]

On the basis of these results, the mechanism proposed for the major pathway for the phototransposition reaction in acetonitrile is outlined in Scheme 1. Excitation gives the reactive excited-state S$_1$ (the fluorescence quenching studies suggest T$_1$ is unreactive). The fluorescence data for S$_1$ indicate that it is a minimum on the excited-state surface with very little change in geometry from S$_0$. Therefore, a barrier separates S$_1$ from **5**, a bicyclo[3.1.0]-hexenyl biradical which is boron-substituted at C6 (as indicated by the results for **1d$_2$**), presumably now on the ground-state surface. Migration of C6 around the periphery of the other five carbons gives **6** and **7**, precursors for the meta **2** and ortho **3** isomers, respectively. Return of **5** to **1** may be quite efficient and provide an internal conversion process which will reduce the quantum yield of reaction considerably. Irradiation of either of the other isomers puts them on the surface connecting **5**, **6** and **7** but the efficiency for each will be different. This mechanism is the same as that proposed for the toluonitriles and other substituted benzenes.

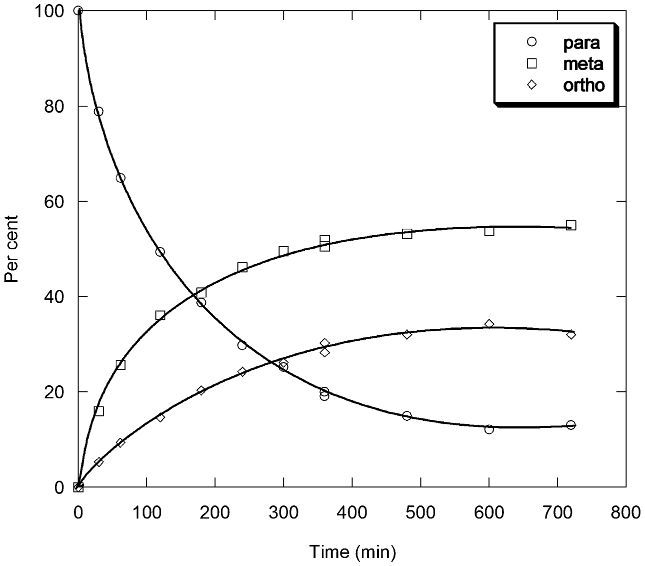


FIGURE 3. Plots for the phototransposition reaction of the para isomer **1** in TFE (**1**, ○; **2**, □; **3**, ◇).

Photochemistry of the Boronate Esters 1–3 and 1d$_2$ in TFE. The phototransposition reactions of the boronate esters **1**–**3** were also observed to be quite efficient in TFE as shown in Figures 3, S5, and S6 (Figure 3 shown here; Figures S5 and S6, Supporting Information). Again, the percent composition values are normalized to 100% for the sum of the three isomers. As described above for the results in acetonitrile, the relative efficiency for each conversion can be estimated from the rates of disappearance of each isomer, the ratio of products formed at low conversion from each isomer, and the molar absorptivities (ϵ) at 254 nm. These values are shown in Figure 2b with the least efficient process (ortho to para) again assigned a value of one. Using these efficiencies and applying the steady-state approximation, values for the isomer composition at the photostationary state can be calculated giving **1** (8%), **2** (57%), and **3**

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[23] Reference 9 and references therein.

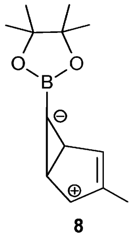
(35%). The observed values (**1** (12%), **2** (54%), and **3** (34%)) for the para isomer (Figure 3), the most reactive one, are in good agreement with this prediction. The other two isomers were still approaching these steady-state values when the irradiations were stopped.

The mass balance for the photoequilibrations in TFE was not nearly as high as that for the reaction in acetonitrile. For instance, at 68% conversion of the meta isomer **2**, the material balance for **1**−**3** was only 56%. From GC traces, most of the remaining material balance could be accounted for by two major peaks (and several minor ones) at longer retention times. The same GC peaks were observed for all three starting isomers. By GC/MS, these peaks correspond to structures resulting from addition of TFE to the arylboranes. As yet, we have been unable to isolate and characterize these photoproducts. By analogy with the reactions of benzonitrile, eq 2, they are possibly bicyclo[3.1.0]hex-2-ene derivatives. A major difference between the benzonitriles and the arylboronate esters is that for the former only photoaddition and no phototransposition was observed in TFE, whereas for the latter the two processes seem to be competitive.

To confirm that the boron-substituted carbon was the active one, **1d$_2$** was also irradiated in TFE. The ^{13}C NMR spectrum for the mixture obtained from the TFE irradiation was not as clean in the aromatic region as that obtained from the photolysis in acetonitrile, presumably because of the formation of the photoaddition products described above. However, the conclusion was the same: the dominant process for rearrangement is that shown in eq 5, with a minor intervention (approximately 10%) of other processes (as in eq 6) involving the methyl-substituted carbon.

As shown in Table 1, the fluorescence quantum yield is lower and the excited singlet state lifetime is shorter for all three isomers in TFE as compared to acetonitrile. These observations suggest that TFE provides a pathway for deactivation of the excited state that does not occur in acetonitrile. Considering that this could be a consequence of the acidity of TFE, the fluorescence of **1** in TFE-OD was also examined. The fluorescence quantum yield was slightly higher (0.042 vs 0.036) and the singlet lifetime slightly longer (4.3 vs 4.0 ns) in TFE-OD vs TFE-OH. This indicates that the excited state is quenched slightly less in TFE-OD, but the ratio is certainly not large enough to be a primary isotope effect. Therefore, proton transfer is not responsible for the enhanced reactivity of S$_1$ of **1** in TFE.

Photochemistry of the Boronate Ester 1 and 1d$_2$ in Cyclohexane. The previous results for benzonitrile derivatives in TFE, which result in protonation at the nitrile-substituted carbon (eq 2), indicate that the reactive intermediates **5**−**7** have some zwitterionic character (as shown in **8**). To assess the importance of the polarity of these intermediates, the photochemistry of **1** and **1d$_2$** was also examined in cyclohexane. Phototransposition still occurred although less efficiently than in the other solvents (48% conversion after 355 min in cyclohexane compared to 80% in TFE). Moreover, the results for **1d$_2$** revealed a high selectivity for reaction according to the pathway in eq 5 indicating that again the boron-substituted carbon is the active one. Only very small changes in absorbance spectra were observed on changing the solvent from cyclohexane to acetonitrile to TFE (Table 1). In contrast, the fluorescence quantum yields (0.17, 0.10, 0.036) and excited singlet state lifetimes (16.8, 13.5, 4.0 ns) decrease significantly through the same sequence of solvents.



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Photolysis of the para isomer **1** in methanol also demonstrated that the phototransposition reaction still occurs but again somewhat less efficiently (57% conversion after 355 min in methanol compared to 80% in TFE). No photoaddition products were detected in methanol as expected on the basis of the observation that higher acidities are required to generate photoaddition products for the other substituted benzenes.[8,24] The excited singlet state lifetime (13.8 ns, Table 1) for **1** in methanol is essentially the same as in acetonitrile. The likely cause of these solvent effects is that the reactive intermediates **5**−**7** can have a range of polarities from purely diradical with no charge separation to having considerable zwitterionic character (as shown in **8**). In fact the efficiencies of reaction and the changes in the fluorescence values follow solvent polarity scales. For instance, Y_{OTS} values (in brackets) for S$_N$1 reactivity increase in the order cyclohexane (no Y value available) $\ll$ acetonitrile (−3.21) < methanol (−0.92) < TFE (1.77),[25] as do E_T values (30.9, 45.6, 55.4, 59.8).[26] This order is not that expected if reactivity depended on the solvent forming a Lewis acid/base adduct with the boronate group. That order, which should follow nucleophilicity, would be cyclohexane $\ll$ TFE < acetonitrile < methanol.[27]

Conclusions

The phototranspositions observed for the arylboronate esters indicate that they have reactivity typical of other substituted benzenes. The proposed rate-determining step is reaction from the excited singlet state, S$_1$, of the substrate leading to the formation of bicyclo[3.1.0]hexenyl intermediates that can be formed in solvents of very low (cyclohexane) or high (TFE) ionizing ability. The borane-substituted carbon is the active one over this range of solvents. This suggests that, at least in the excited state and by analogy to the arylnitriles, the boronate group is electron withdrawing. In TFE, phototransposition reactions were also observed but preliminary evidence was obtained as well for the photoaddition products of TFE. We have also begun a study of the cycloaddition of alkenes to these arylboronates and have GC/MS evidence that adducts are formed. In the past, both inter- and

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intramolecular alkene and diene photocycloadditions to substituted benzenes have proven to be valuable for the synthesis of complex polycyclic systems.[28] We hope to report on these other new photoreactions soon.

Experimental Section

General Procedures. All reported ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ (^{1}H, 250 MHz, referenced to internal TMS at 0.0 ppm, ^{13}C, 125 MHz, referenced to the central line of $CDCl_3$, at 77.4 ppm). GC/MS analyses were performed using a Supelco 30 m × 0.25 mm MDN-5S 5% phenyl methylsiloxane, film thickness 0.50 μm, temperature programmed: 100 °C, 1 min; 10 °C/min to 210 °C; 240 °C, 3 min. GC/FID analyses were done in a similar way except on a Supelco DB200 column.

Preparation of the Tolueneboronate Esters 1−3. According to the published procedure, but with extended reaction times of 2 days at 80 °C, the 2-, 3-, and 4-(4′4′,5′5′-tetramethyl-1′,3′,2′-dioxaborolanyl)toluenes were prepared on a 10 mmol scale in yields of 89−93% from the corresponding iodotoluene and pinacol borane catalyzed by $PdCl_2(pddf)_2$. A modification to the workup procedure was made in that the crude reaction mixture was simply filtered through a plug of Celite and then purified by bulb-to-bulb distillation with the required products obtained at 120 °C (0.5 Torr). ^{1}H and ^{13}C NMR spectra and MS were in agreement with those previously reported for the para (**1**) and ortho (**3**) isomers as was the ^{1}H NMR spectrum for the meta (**2**).[29]

3,5-Dideuterio-4-(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolanyl)toluene (1d$_2$). 3,5-Dideuteriotoluidine deuteriochloride was prepared by exchange of protons ortho to the ammonium group in *p*-toluidine hydrochloride by repeated reflux in D_2O. Diazotization followed by treatment with potassium iodide[30] gave 3,5-dideuterio-4-iodotoluene with less than 2% protons at C3 and C5. Suzuki coupling with pinacol borane, as described above, gave the title product: ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 12H), 2.36 (s, 3H), 7.19 (bs, 2H); ^{13}C NMR ($CDCl_3$) δ 22.0 ($ArCH_3$), 25.2 (4′,4′,5′,5′-tetramethyl), 83.9 (C4′,C5′), 128.9 (C2, C6), 141.7 (C1) in agreement with the literature spectrum except with a very weak the signal for C3 and C5 (see Table 2 and discussion in text); GC/MS *m*/*z* 220 ($M^+ + 1$, $^{12}C_{13}{}^{11}BD_2H_{19}O_2$, 23), 219 ($M^+$, $^{12}C_{13}{}^{10}BD_2H_{19}O_2$, 8.70), 205 (37), 134 (63), 121 (100), 120 (73), 119 (32), 93 (19), 85 (18). The MS fragmentation is also in agreement with that previously reported although all signals, except the one at *m*/*z* 85, are higher by 2 units because of deuterium substitution.

Irradiation of Boronate Esters. A solution of ~25 mg of the ester in 25 mL of acetonitrile or TFE was purged of oxygen with nitrogen and then irradiated in a Rayonet reactor with 254 nm lamps. The temperature was controlled at 25 °C with water in a circulating immersion tube. The progress of the reaction was monitored by GC/FID although the ortho isomer **3** was not resolved from the para **1**. The solvent was then removed from each sample by rotary evaporation with a water aspirator and the residue taken up in $CDCl_3$ for ^{1}H NMR spectral analysis. The isomer composition was obtained from the signal heights for the methyl group in the mixture for **1**, **2**, and **3** at δ 2.37, 2.35, and 2.53, respectively.

Absorbance Measurements. Absorbance spectra were recorded at 25 °C at 1 nm resolution. The integrated spectra needed for eq 3 were obtained by summing the 1 nm incremental areas (the absorbance values converted to ϵ by dividing by the molar concentration) over the complete absorption band.

Fluorescence Measurements. All samples were degassed by three freeze−pump−thaw cycles and then thermostated at 25 °C. Fluorescence quantum yields were determined using solutions of matched absorbance by comparison with the known fluorescence quantum yield of 0.24 for anisole. The expectation values necessary for eq 3 were obtained by summing the 1 nm incremental areas over the complete emission band. Singlet lifetimes were measured by monitoring fluorescence decay using a PRA time-correlated single-photon-counting apparatus with a hydrogen flash lamp of pulse width about 1.8 ns.

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Supporting Information Available: Figures S1−S6. This material is available free of charge via the Internet at http://pubs.acs.org.

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