Synthesis of Tetraorganylborate Salts: Photogeneration of Tertiary Amines

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Received May 22, 2001. Revised Manuscript Received July 3, 2001

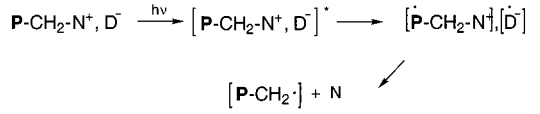
We report the synthesis of a series of new ammonium tetraorganylborates strategically designed to, upon photolysis, generate tertiary amines. Experiments in acetonitrile show amine formation in reasonably high quantum yield that depends on the photoreactive acceptor, the borate, and the substituents on the nitrogen atom. The reactive triplet state is reduced by the borate, and this is followed by rapid homolysis of the carbon−nitrogen bond.

Introduction

Photochemical genesis of organic bases is potentially important in thin-film imaging.[1,2] Most known photobase generators yield primary and secondary amines, though tertiary amines are often better catalysts.[3−5] We have shown that chromophore ammonium salts in which the partner ion is a tetraorganylborate produce two free radicals, a borane and an amine, when irradiated.[6] These systems have been shown to initiate both acrylate polymerization[6] and the polymerization of epoxides[4d] in prior studies.

The molecular design of the current system masks a tertiary amine with a photolabile electron acceptor complexed as a quaternary ammonium salt with a tetraorganylborate anion. Chromophore **P**, designed to be both a good electron acceptor and a light absorber, is attached to the tertiary amine through a spacer methylene group (Scheme 1). The neutral amine nitrogen, complexed as a quaternary nitrogen, binds the donor **D** (triphenylbutyl- or tetraphenylborate). After the absorption of light, electron transfer from the donor to the excited state of the chromophore creates an unstable radical cation/radical anion pair. These highly

Scheme 1. Strategy for Photogeneration of Tertiary Amines



energetic intermediates decompose immediately to a pair of radicals, triarylborane and amine. This is one of the few reactions of which we are aware where one photochemical event induces the formation of two radicals, a Lewis acid and a Lewis base. The strategy allows substantial flexibility in molecular design. One can manipulate the light absorption at will depending on the structure of the chromophore while managing a uniform reaction for formation of the tertiary amine. Substituents that improve sensitivity can be introduced without changing the product-forming steps provided the electron-transfer processes are unaffected. Generally photoinduced electron-transfer reactions (PET) are complicated by back-electron-transfer reactions that decrease their overall efficiency. Our strategy was to select chromophores inclined to produce long-lived excited states upon absorption that could rapidly dissociate after electron transfer.[7] The rate of the bond cleavage step is a major factor in the effectiveness of the overall process.

The present work provides evidence that these processes do, indeed, occur and with good efficiency. Moreover, amine release rates tend to be highly sensitive functions of the structure of the chromophore, the electron donors, and the substituents on the nitrogen atom of the ammonium salt.

Results and Discussion

The syntheses of the tetraorganylborate salts to serve as photoprecursors to tertiary amines are shown in Scheme 2.

The precursors incorporated three chromophores with differing reduction potentials and two borate anions as donors. A tertiary amine was allowed to react with

† Contribution No. 448 from the Center for Photochemical Sciences.

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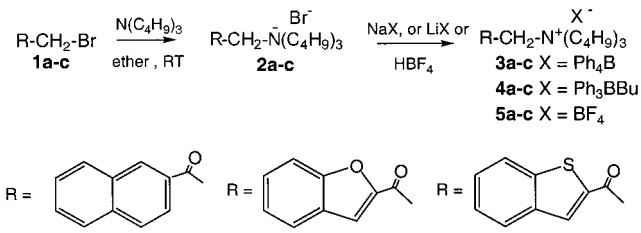
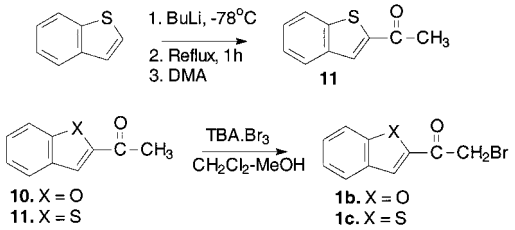
10.1021/cm0105054 CCC: $20.00
Published on Web 09/27/2001

Scheme 2. Synthesis of Tertiary Amine Generating Precursors



Scheme 3. Synthesis of Bromoacetyl Compounds



α-bromoacetyl compounds **1a**−**c** in ether at room temperature to afford ammonium bromides **2a**−**c** in good yield and high purity. Each bromide precipitated from the reaction mixture at room temperature. Strictly anhydrous reaction conditions are critical however since even small amounts of water reduced the yield of product significantly. Borate salts **3a**−**c** and **4a**−**c** were obtained by reaction in water with sodium tetraphenylborate and lithium triphenylbutylborate,[8] respectively. Using a similar strategy, tetrafluoroborate was incorporated as **5a**−**c** by reaction with HBF_4. The latter compounds were used in control experiments since no electron transfer was to be expected.

Compounds **1b** and **1c** were made from bromoacetyl derivatives **10** and **11**, Scheme 3. To circumvent the troubles with this reaction previously reported,[9] we employed solid tetrabutylammonium tribromide ($TBABr_3$).[10]

Reaction of **10** and **11** with equimolar $TBABr_3$ in dichloromethane/methanol gave good yields of **1b,c**. The reaction mixture changes from its initial dark red to colorless upon completion of the reaction. Removal of trace amounts of dibromoacetyl derivatives could be easily effected by recrystallization. Lithiation of benzo[*b*]thiophene with butyllithium followed by treatment with *N*,*N*-dimethylyacetamide (DMA) allowed isolation of 2-acetylbenzo[*b*]thiophene (**11**) in 73% yield. In our hands the formation of the lithium reagent required forcing conditions; nearly complete formation of the lithium salt was achieved by refluxing a solution of benzo[*b*]thiophene and butyllithium in ether for 1 h.

The steady-state UV−vis spectra for each of the borate salts, Figure 1, show nearly identical transitions above 300 nm. Substantial tail absorptions up to nearly 350 nm are always observed. Only the structure of the chromophore influences the spectra. Neither substituents on the nitrogen atom nor the structure of the counterion have much influence on either the extinction coefficient or the wavelength of maximum absorption of the aroyl chromophore.

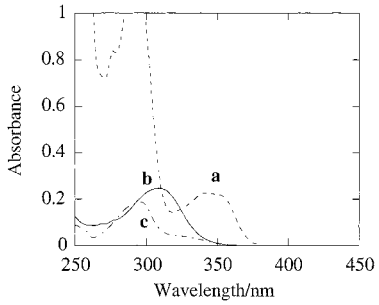


Figure 1. Absorption spectra of **3a** (a), **3b** (b), and **3c** (c) in acetonitrile.

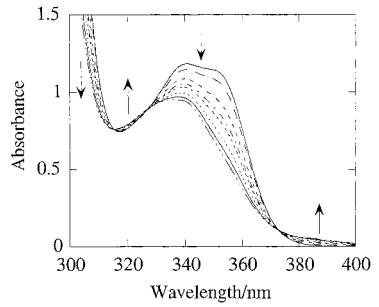


Figure 2. Irradiation of **3a** in acetonitrile (0.5 M) as a function of time.

Photolysis of control compounds **5a**−**c** in acetonitrile (350 nm) for 1 h produced no observable changes (^1H NMR), and no products could be detected by HPLC. Irradiation of **5a**−**c** in the presence of a polymerizable monomer (methyl methacrylate) also produced no polymer. In contrast, the absorption spectrum of **3a** (5×10^{-4} M in acetonitrile) upon irradiation at 365 nm (band-pass filter) changes dramatically in just 10 min (Figure 2).

Three isobestic points (317, 330, and 373 nm) were observed, indicating that the photoreaction proceeds cleanly without side reactions.

Irradiation of an acetonitrile-d_3 solution of borate salts at 305 nm for 30 min resulted in amine (^1H NMR). In most cases the formation of amine proceeds efficiently and quantitatively. Conversion was monitored from the disappearance of the methylene peak (δ 4.70 ppm), and the appearance of a new peak was attributed to the corresponding amine (δ 3.40 ppm).

Since the photodissociation proceeds cleanly, and amine is formed as the sole product, we assume that the quantum yield of the photodisappearance of starting material and the photoappearance of amine are the same. These quantum yields strongly depend on the structure of the borate salt, Table 1.

The quantum yield of dissociation and amine formation is always higher for compounds with the triphenylbutylborate anion than for those with the tetraphenylborate anion. The effect of changing the ammonium ions was parallel in each instance. Compounds containing the benzo[*b*]thiophene chromophore resulted in higher quantum yields than did those with benzo[*b*]furan or naphthalene, likely due to the difference in the reduction potentials. The presence of bulky substitutents on nitrogen increases the efficiency of the decomposition

(8) The lithium salt of triphenylbutylborate was prepared by treating 1.6 M butyllithium in hexanes with triphenylboron in benzene at 10 °C.

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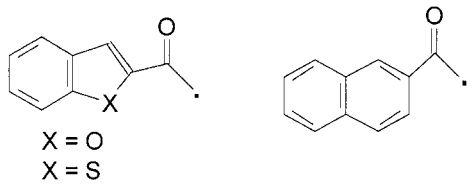
Table 1. Quantum Yields of Photodissociation in Acetonitrile

precursor	$\Delta G°$ (eV)[a]	ϕ_d	precursor	$\Delta G°$ (eV)[a]	ϕ_d
3a	−0.37	0.33	**3c**	−0.28	0.56
4a	−0.57	0.50	**4c**	−0.48	0.79
3b	−0.31	0.50	**8a**		0.21
4b	−0.51	0.67	**9a**		0.26

[a] $\Delta G°$ was calculated using the equation[11] $\Delta G° = E_{ox} - E_{red} - E_{0-0}$. E_{ox} is the oxidation potential for the donors, E_{red} is the reduction potential for **5a**−**c**, and E_{0-0} is the triplet state energy.

Chart 1



reaction by promoting carbon−nitrogen cleavage due to the release of B-strain (compare **3a** with **8a** or **8b**).[12] In this respect, bulky substituents on nitrogen may also provide effective hyperconjugative interaction of the carbon−nitrogen bond with the extended π-system of the acceptor, thus making for effective dissociation.[13] In principle, the efficiency of amine formation can be controlled by the electron-transfer rate from borate to acceptor in that dissociation proceeds rapidly after that.

High quantum yields of amine formation are characteristic features of each of the borate salts, except for the precursors containing tetrafluoroborate anion, indicating electron transfer from the borate anion to the chromophore is necessary for carbon−nitrogen bond cleavage. Electron-transfer reactions between the chromophore-containing compounds in their triplet states and triphenylbutyl- or tetraphenylborate are, indeed, observed with different rate constants.[14] The quantum yields in the singlet-state reactions are low because of a short life caused by other deactivation processes.[15] The oxidation potentials of triphenylbutyl- and tetraphenylborate have been found to be 0.70 V vs SCE and 0.90 V vs SCE, respectively.[16] Therefore, borate precursors containing triphenylbutyl anion generate amine with high efficiency.

Detailed product analysis[14] indicates a mechanism that is more or less similar operates in each case. Each reaction produces the respective acyl free radical, Chart 1. [14,17] Homolytic dissociation of the carbon−nitrogen bond is likely because of the relative similarity of the electronegativities of nitrogen and carbon. Heterolytic cleavage is ruled out since this would not lead to the observed products.

Conclusion

We have presented a new sequence of reactions leading to tertiary amine generation that involve photoinduced electron transfer reactions from the triplet excited state. The reactions proceed cleanly, and involve a number of chromophore acceptors. There are no secondary reactions. The systems are dissociative, hence back electron transfer is precluded. The pathway for photogenerating the tertiary amines is not only pertinent to the synthetic focus of the work but also of interest for producing images in polymer films. Regardless of mechanism, it is clear that the release of tertiary amines can be used to catalyze epoxy cross-linking.[18] We do not know, at this moment, what role conformational effects play in the photogeneration of amine. However, continuing work will develop new strategies to increase the efficiency.

Experimental Section

General Procedures. Melting point determinations were made using a Thomas capillary melting point apparatus; all temperatures are uncorrected. Elemental analysis was performed by Atlantic Microlab, Inc., Georgia. ^{1}H NMR and ^{13}C NMR spectra were taken on Gemini GEM-200 (200 MHz) and Gemini GEM-200 (50 MHz) spectrometers, respectively. The chemical shifts are reported in δ units, unless otherwise mentioned. Photolysis experiments were carried out in a Rayonet photochemical reactor fitted with mercury lamps (300−400 nm). UV−vis spectra were recorded on a Hewlett-Packard 8452 diode array spectrophotometer. Unless otherwise indicated, all reagents and solvents were obtained from Aldrich Chemical Co. and used as received.

Quantum Yield Determination. In each experiment, 3.0 mL of a sample solution in acetonitrile in a quartz cell (1.0 × 1.0 × 3.5 cm) was deoxygenated by purging with oxygen-free argon for 10 min, the quartz cell was sealed, and the sample was irradiated with a 20 W mercury lamp at 350 nm using a 350 ± 50 nm band glass filter. Acridine dimerization in air-saturated methanol (3.0×10^{-4} M, $\phi_f = 0.032$, $\lambda_{ex} = 350$ nm) was used as the actinometer.[19] The extent of photodissociation of the sample was monitored by steady-state UV−vis absorption spectroscopy. Quantum yields were determined from the initial 10% conversions. According to the Beer−Lambert law, the change of concentration vs irradiation time is expressed as follows:

$$-dc/dt = (10^3 \phi_d I_0/d)[1 - \exp(-2.303A)]$$

where I_0, d, ϕ_d, and A denote the intensity of the excitation light, path length of the cell, quantum yield of the reaction, and absorbance wavelength, respectively. The above equation can be rewritten as

$$\ln[\exp(2.303A) - 1] = -2.303 \times 10^3 \phi_d \epsilon I_0 t + \ln[\exp(2.303A_0) - 1]$$

ϕ_d and I_0 can be calculated from the plot of $\ln[\exp(2.303A_0) - 1]$ vs irradiation time. The quantum yields reported are the average of three measurements.

General Procedure for the Synthesis of Ammonium Bromide Salts. Tertiary amine was added in excess to a solution of the respective bromoacetyl compound in anhydrous diethyl ether. The reaction was stirred at room temperature overnight. A thick white precipitate formed. This was filtered and washed with ether. Recrystallization from the appropriate solvent afforded white crystals (70−75% yield).

***N*-(2-Acetylnaphthone)-*N*,*N*,*N*-tributylammonium Bromide (2a).** Mp: 138−139 °C (acetone). ^{1}H NMR (CD_3CN, δ): 9.15 (s, 1H), 8.20 (d, J = 8.0 Hz, 1H), 8.02 (m, 3H), 7.67 (m, 2H), 5.38 (s, 2H), 3.66 (t, J = 8.6 Hz, 6H), 1.75 (m, 6H), 1.35 (m, 6H), 0.95 (t, J = 7.4 Hz, 9H). ^{13}C NMR (CD_3CN, δ): 192.49,

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137.64, 133.78, 132.80, 132.23, 131.09, 130.67, 130.0, 128.89, 128.36, 123.99, 61.98, 61.41, 25.29, 20.70, 13.95. Anal. Calcd for $C_{24}H_{36}BrNO$: C, 66.39; H, 8.29; Br, 18.41; N, 3.22. Found: C, 66.52; H, 8.31; Br, 18.46; N, 3.21.

***N*-(2-Acetylbenzo[*b*]furan)-*N*,*N*,*N*-tributylammonium Bromide (2b).** Mp: 157−58 °C (ethyl acetate−acetone). ^{1}H NMR (CD_3CN, δ): 8.42 (s, 1H), 7.86 (d, J = 7.4 Hz, 1H), 7.65 (m, 2H), 7.41 (m, 1H), 5.17 (s, 2H), 3.63 (m, 6H), 1.75 (m, 6H), 1.37 (m, 6H), 0.95 (m, 9H). ^{13}C NMR (CD_3OD, δ): 182.37, 157.38, 151.10, 130.85, 127.99, 125.63, 125.19, 117.77, 113.31, 61.63, 61.01, 25.27, 20.65, 13.95. Anal. Calcd for $C_{22}H_{34}BrNO_2$: C, 62.30; H, 8.02; Br, 18.84; N, 3.30. Found: C, 62.43; H, 8.07; Br, 18.89; N, 3.28.

***N*-(2-Acetylbenzo[*b*]thiophene)-*N*,*N*,*N*-tributylammonium Bromide (2c).** Mp: 165−66 °C (ethyl acetate−ethanol). ^{1}H NMR (CD_3OD, δ): 8.52 (d, J = 3.6 Hz, 1H), 8.04 (q, J = 7.2 Hz, 2H), 7.55 (m, 2H), 4.90 (s, 2H), 3.67 (m, 6H), 1.77 (m, 6H), 1.45 (m, 6H), 1.00 (t, J = 7.4 Hz, 9H). ^{13}C NMR (CD_3OD, δ): 186.92, 142.27, 140.82, 140.16, 133.96, 129.89, 127.96, 126.70, 123.97, 61.79, 61.48, 25.27, 20.69, 13.93. Anal. Calcd for $C_{22}H_{34}BrNOS$: C, 60.03; H, 7.72; Br, 18.16; S, 7.27. Found: C, 59.93; H, 7.76; Br, 18.19; S, 7.25.

***N*-(2-Acetylnaphthone)-*N*,*N*,*N*-triethylammonium Bromide (6a).** Mp: 203−204 °C (acetone). ^{1}H NMR (CD_3OD, δ): 8.88 (s, 1H), 8.15 (d, J = 8.0 Hz, 1H), 8.05 (dd, J = 2.4 Hz, 8.0 Hz, 1H), 8.01 (s, 1H), 7.96 (t, J = 6.6 Hz, 1H), 7.65 (m, 2H), 4.85 (s, 2H), 3.81 (m, 6H), 1.38 (t, J = 7.40 Hz, 9H). ^{13}C NMR (CD_3OD, δ): 192.32, 137.63, 133.77, 132.80, 132.19, 131.08, 130.67, 129.96, 128.91, 128.37, 124.01, 60.44, 55.77, 8.29. Anal. Calcd for $C_{18}H_{24}BrNO$: C, 61.75; H, 6.86; Br, 22.83. Found: C, 61.55; H, 6.74; Br, 22.97.

***N*-(2-Acetylnaphthone)imidazole Bromide (7a).** Mp: 163−164 °C. ^{1}H NMR (CD_3OD, δ): 8.61 (m, 1H), 8.26 (s, 1H), 7.93 (m, 4H), 7.54 (m, 2H), 7.27 (d, J = 10.6 Hz, 2H), 4.92 (s, 2H). Anal. Calcd for $C_{15}H_{13}BrN_2O$: C, 56.82; H, 4.10; Br, 25.20; N, 8.83. Found: C, 56.43; H, 4.09; Br, 25.36; N, 8.74.

General Procedure for the Synthesis of Tetraphenylborate Salts. To a solution of the respective ammonium bromide in water was added, with stirring, an equimolar amount of aqueous sodium tetraphenylborate. A thick white precipitate formed immediately. After 30 min of stirring the precipitate was filtered and washed with water. After recrystallization, white needles of tetraphenylborate salts (72−84%) were obtained.

***N*-(2-Acetylnaphthone)-*N*,*N*,*N*-tributylammonium Tetraphenylborate (3a).** Mp: 147−148 °C (ethanol−acetone). ^{1}H NMR (CD_3CN, δ): 8.63 (s, 1H), 8.02 (m, 4H), 7.02 (m, 2H), 7.28 (m, 8H, ortho to B), 6.99 (t, J = 7.6 Hz, 8H, meta to B), 6.85 (m, 4H, para to B), 3.58 (m, 6H), 1.68 (m, 6H), 1.3 (m, 6H), 0.95 (m, 9H). Anal. Calcd for $C_{48}H_{56}BNO$: C, 85.62; H, 8.32; N, 2.08. Found: C, 85.43; H, 8.38; N, 2.07.

***N*-(2-Acetylbenzo[*b*]furan)-*N*,*N*,*N*-tributylammonium Tetraphenylborate (3b).** Mp: 173−174 °C (ethyl acetate). ^{1}H NMR (CD_3CN, δ): 7.83 (m, 2H), 7.62 (m, 2H), 7.19 (m, 5H), 7.25 (m, 8H, ortho to B), 6.99 (m, 8H, meta to B), 6.83 (m, 4H, para to B), 4.65 (s, 2H), 3.46 (m, 6H), 1.65 (m, 6H), 1.30 (m, 6H), 0.95 (m, 9H). Anal. Calcd for $C_{46}H_{54}BNO_2$: C, 83.29; H, 8.14; N, 2.11. Found: C, 83.42; H, 8.16; N, 2.10.

***N*-(2-Acetylbenzo[*b*]thiophene)-*N*,*N*,*N*-tributylammonium Tetraphenylborate (3c).** Mp: 171−172 °C (ethyl acetate). ^{1}H NMR (CD_3CN, δ): 8.25 (s, 1H), 8.0(t, J = 8.2 Hz, 2H), 7.56 (m, 2H), 7.26 (m, 8H, ortho to B), 6.99 (t, J = 7.4 Hz, 8H, meta to B), 6.85 (m, 4H, para to B), 4.80 (s, 2H), 3.51 (m, 6H), 1.70 (m, 6H), 1.38 (m, 6H), 0.96 (t, J = 6.8 Hz, 9H). Anal. Calcd for $C_{46}H_{54}BNOS$: C, 81.33; H, 7.95; S, 4.71. Found: C, 81.25; H, 8.07; S, 4.63.

***N*-(2-Acetylnaphthone)-*N*,*N*,*N*-triethylammonium Tetraphenylborate (8a).** Mp: 186−87 °C (ethanol). ^{1}H NMR (CD_3CN, δ): 8.65 (s, 1H), 8.09 (d, J = 7.6 Hz, 1H), 8.0 (m, 3H), 7.71 (m, 2H), 7.26 (m, 8H, ortho to B), 6.99 (t, J = 7.40 Hz, 8H, meta to B), 6.84 (t, J = 7.4 Hz, 4H, para to B), 4.87 (s, 2H), 3.62 (m, 4H), 1.28 (t, J = 7.4 Hz, 6H). ^{13}C NMR (CD_3CN, δ): 190.07, 164.43, 163.78, 163.13, 162.47, 135.04, 130.51, 129.43, 128.56, 127.56, 127.29, 125.30, 122.58, 121.46, 117.00, 58.47, 54.23, 6.86. Anal. Calcd for $C_{42}H_{44}BNO$: C, 85.61; H, 7.47. Found: C, 85.42, H, 7.43.

***N*-(2-Acetylnaphthone)imidazole Tetraphenylborate (9a).** ^{1}H NMR (CD_3CN, δ): 7.97 (m, 1H), 7.35 (m, 5H), 7.01-(m, 4H), 6.55 (m, 8H, ortho to B), 6.32 (t, J = 7.4 Hz, 8H, meta to B), 6.16 (t, J = 7.4 Hz, 4H, para to B), 5.09 (s, 2H). Anal. Calcd for $C_{39}H_{33}BN_2O$: C, 84.21; H, 5.93; N, 5.03. Found: C, 83.96; H, 5.88; N, 5.10.

General Procedure for the Synthesis of Triphenylbutylborate Salts 4a−c. An aqueous solution of lithium triphenylbutylborate[8] was added slowly, with stirring, to an aqueous solution of the respective ammonium bromide salt. An amount of lithium triphenylbutylborate slightly in stoichiometric excess was used to ensure complete conversion. A white solid gradually precipitated, and the resulting mixture was stirred for an additional 30 min. The solid was filtered, washed with water, and then air-dried overnight. After recrystallization, the salt was obtained as white crystals (55−68% yield).

***N*-(2-Acetylnaphthone)-*N*,*N*,*N*-tributylammonium Triphenylbutylborate (4a).** Mp: 130−131 °C (ethanol−acetone). ^{1}H NMR (CD_3CN, δ): 8.63 (s, 1H), 8.02 (m, 4H), 7.70 (m, 2H), 7.28 (m, ortho to B, 6H), 6.96 (m, meta to B, 6H), 6.83 (m, para to B, 3H), 4.89 (s, 2H), 3.56 (m, 6H), 1.70 (m, 6H), 1.38 (m, 8H), 0.95 (m, 13H), 0.75 (t, J = 7.4 Hz, 3H). Anal. Calcd for $C_{46}H_{60}BNO$: C, 84.57; H, 9.18; N, 2.14. Found: C, 84.65; H, 9.19; N, 2.15.

***N*-(2-Acetylbenzo[b]furan)-*N*,*N*,*N*-tributylammonium Triphenylbutylborate (4b).** Mp: 121−122 °C (ethanol). ^{1}H NMR (CD_3CN, δ): 7.89 (m, 1H), 7.84 (d, J = 3.0 Hz, 1H), 7.66 (m, 2H), 7.43 (m, 1H), 7.27 (br s, 6H, ortho to B), 6.96 (m, 6H, meta to B), 6.83 (m, 3H, para to B), 4.67 (s, 2H), 3.49 (m, 6H), 1.64 (m, 8H), 1.32 (m, 8H), 0.95 (m, 11H), 0.78 (t, J = 7.4 Hz, 3H). Anal. Calcd for $C_{44}H_{58}BNO_2$: C, 82.15; H, 9.02; N, 2.18. Found: C, 82.29; H, 9.08; N, 2.20.

***N*-(2-Acetylbenzo[*b*]thiophene)-*N*,*N*,*N*-tributylammonium Triphenylbutylborate (4c).** Mp: 117−118 °C (ethyl acetate−hexane). ^{1}H NMR (CD_3CN, δ): 8.25 (s, 1H), 8.03 (t, J = 7.8 Hz, 2H), 7.57 (m, 2H), 7.27 (br s, 6H, ortho to B), 6.98 (m, 6H, meta to B), 6.79 (t, J = 7.0 Hz, 3H, para to B), 4.79 (s, 2H), 3.53 (m, 6H), 1.95 (m, 2H), 1.68 (m, 6H), 1.34 (m, 10H), 0.95 (m, 9H), 0.78 (t, J = 7.2 Hz, 3H). Anal. Calcd for $C_{44}H_{58}BNOS$: C, 80.16; H, 8.80; S, 4.85. Found: C, 80.38; H, 8.78; S, 4.86.

General Procedure for the Synthesis of Tetrafluoroborate Salts 5a−c. The respective ammonium bromide salt was dissolved in a minimum amount of water, and insoluble materials (if any) were filtered. Aqueous fluoroboric acid (48% by weight) was added dropwise in excess at room temperature with vigorous stirring. A white precipitate formed immediately. The mixture was diluted with water and stirred for an additional 30 min. The white product was filtered and washed with water (70−78% yield). No effort was taken for further purification.

***N*-(2-Acetylnaphthone)-*N*,*N*,*N*-tributylammonium Tetrafluoroborate (5a).** Mp: 98−99 °C. ^{1}H NMR (CD_3CN, δ): 8.70 (s, 1H), 8.03 (m, 4H), 7.71 (m, 2H), 4.95 (s, 2H), 3.58 (m, 6H), 1.71 (m, 6H), 1.39 (m, 6H), 0.96 (t, J = 7.4 Hz, 9H). Anal. Calcd for $C_{24}H_{36}BF_4NO$: C, 65.35; H, 8.16; Br, 0.0. Found: C, 65.41; H, 8.17; Br, 0.0.

***N*-(2-Acetylbenzo[*b*]furan)-*N*,*N*,*N*-tributylammonium Tetrafluoroborate (5b).** Mp: 115−116 °C. ^{1}H NMR (CD_3CN, δ): 7.90 (m, 2H), 7.66 (m, 2H), 7.23 (m, 1H), 4.74 (s, 2H), 3.52 (m, 6H), 1.70 (m, 6H), 1.35 (m, 6H), 0.97 (m, 9H). Anal. Calcd for $C_{22}H_{34}BF_4NO_2$: C, 61.30; H, 7.89; Br, 0.0. Found: C, 61.33; H, 7.85; Br, 0.0.

***N*-(2-Acetylbenzo[*b*]thiophene)-*N*,*N*,*N*-tributylammonium Tetrafluoroborate (5c).** Mp: 131−1320 °C. ^{1}H NMR (CD_3CN, δ): 8.43 (d, J = 3.6 Hz, 1H), 8.01 (m, 2H), 7.52 (m, 2H), 4.87 (s, 2H), 3.62 (m, 6H), 1.72 (m, 6H), 1.43 (m, 6H), 0.97 (t, J = 7.4 Hz, 9H). Anal. Calcd for $C_{22}H_{34}BF_4NOS$: C, 59.11; H, 7.61; Br, 0.0. Found: C, 59.00; H, 7.66; Br, 0.0.

2-Acetylbenzo[*b*]thiophene (11). A solution of *n*-butyllithium (29.0 mL, 46.0 mmol, 1.6 M in hexane) was slowly added to benzo[*b*]thiophene (5.15 g, 38.38 mmol) in anhydrous

ether (60 mL) under nitrogen at −78 °C. The solution was warmed to room temperature and then refluxed for 1 h. A white precipitate formed. The reaction mixture was again cooled to 0 °C, and *N*,*N*-dimethylacetamide (4 mL, 43.0 mmol) was added dropwise. The resulting thick precipitate was stirred at 0 °C for 30 min and warmed to room temperature for 10 min. The reaction was then stirred for 3 h. A 15% aqueous ammonium chloride solution (50 mL) was added, the organic layer was separated, and the aqueous layer was extracted with ether (2 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, and filtered. The solvent was evaporated in vacuo, and the residue was recrystallized from methanol−water (1:1). The product was obtained as crystals (4.49 g, 73%). Mp: 83−84 °C. ^{1}H NMR ($CDCl_3$, δ): 7.95 (s, 1H), 7.88 (m, 2H), 7.45 (m, 2H), 2.67 (s, 3H). ^{13}C NMR ($CDCl_3$, δ): 194.32, 145.92, 144.57, 141.13, 131.81, 129.49, 127.97, 127.03, 124.97, 28.80. MS: *m*/*z* 176 (M^+), 161 (100), 133, 89, 63, 43.

2-(Bromoacetyl)benzo[*b*]thiophene (1c). To a solution of 2-acetylbenzo[*b*]thiophene (3.43 g, 19.46 mmol) in a dichloromethane (50 mL)−methanol (20 mL) mixture was added tetrabutylammonium tribromide (9.60 g, 19.92 mmol) at room temperature. The reaction mixture was refluxed for 1 h, during which decoloration of the initial dark red color occurred. The solvent was evaporated in vacuo, water (100 mL) was added, and the mixture was extracted with ether (2 × 50 mL). The combined ether layers were dried over magnesium sulfate. Evaporation of the solvent afforded a solid residue, which was recrystallized from ethanol−water (1:2). Compound **1c** was obtained as colorless needles (3.52 g, 71%). Mp: 107−108 ° C. ^{1}H NMR ($CDCl_3$, δ): 8.07 (s, 1H), 7.91 (t, J = 7.4 Hz, 2H), 7.48 (m, 2H), 4.46 (s, 2H). ^{13}C NMR ($CDCl_3$, δ): 187.97 (C═O), 144.95, 142.13, 140.86, 132.92, 130.10, 128.32, 127.36, 125.00, 32.42.

2-(Bromoacetyl)benzo[*b*]furan (1b). This compound was synthesized as above, stirring at room temperature for 20 h. After recrystallization from ethanol−water (1:2), white crystals were obtained (76% yield). Mp: 86−87 °C. ^{1}H NMR ($CDCl_3$, δ): 7.76−7.48 (m, 4H), 7.34 (m, 1H), 4.46 (s, 2H). ^{13}C NMR ($CDCl_3$, δ): 182.14, 155.70, 149.93, 128.86, 126.40, 124.15, 123.44, 114.76, 112.41, 30.23. MS: *m*/*z* 240 (M^+), 145 (100), 131, 89, 63.

Acknowledgment. We gratefully acknowledge financial support from the National Science Foundation (Grant NSF 9526755) and the Office of Naval Research (Grant N00014-97-1-0834).

CM0105054