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Mechanistic Studies of Photobase Generation from Ammonium Tetraorganyl Borate Salts[1]

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The photochemistry and photophysics of *N*,*N*,*N*-tributyl-*N*-acetonaphthone ammonium borate (**1**) and *N*,*N*,*N*-tributyl-*N*-acetobenzo[*b*]furan ammonium borate (**2**) have been investigated by steady-state spectroscopy, laser flash photolysis, and product analysis. Reaction of excited precursors leads to formation of tertiary amines by carbon−nitrogen bond cleavage. Laser flash photolysis and product analysis confirm homolytic carbon−nitrogen bond scission and the formation of respective acetyl radicals which, in acetonitrile, dimerize to form coupled products. In all cases, photodissociation occurs with such a short lifetime that it could not be measured by nanosecond flash photolysis. The quantum yield of disappearance was found to be higher for salts of the triphenylbutyl borate anion than for those of the tetraphenyl borate anion. A proposed mechanism involves electron transfer from borate to the excited acceptors as the primary photochemical step. The rate constants for excited-state quenching correlate with the free energy for electron transfer, as estimated from the excited-state energies and the reduction potentials of the acceptors.

Introduction

The generation of base in certain polymer films modifies the properties of the films, causing a difference in solubility between exposed and unexposed areas. Such films can be developed to yield either a positive or negative images.[2,3] A wide variety of base-generating precursors including cobalt−amine complexes, sulfonamides, and carbamate derivatives have previously been explored.[4−7] As a part of an effort[8] to design new precursors for tertiary amines, we have recently developed a system (Chart 1) that releases tertiary amines via a reductive photoinduced electron-transfer process. The system is designed so that the light absorption step by the acceptor chromophore is decoupled from the step that releases the amine. Therefore, chromophores with a wide range of absorption characteristics can be used without a change in the photocleavage. Moreover, to avoid back electron transfer (BET), our system has been designed to be self-dissociative,[9] decomposing rapidly before BET can take place.

Chart 1

1 **2**

a. X = Ph_3BBu
b. X = Ph_4B
c. X = BF_4

Borate salts **1a,b** and **2a,b** are potential photoinitiators for radical polymerization[10] as well as being precursors for photogeneration of tertiary amines, and both suggest potential π,π^* lowest lying excited states. In this paper, we attempt to establish a mechanism for the photogeneration of tertiary amines by direct observation of the reaction intermediates by a combination of steady-state spectroscopy, nanosecond flash photolysis, and product analysis. Chromophores **1** and **2** were used to study the rate constants of electron transfer and bond cleavage. The nonoxidizable tetrafluoroborates **1c** and **2c** were used as model compounds.

Experimental Section

Materials. Syntheses of **1a**−**c**, **2a**−**c**, and 2-bromomethylacetobenzo[*b*]furan have been described previously.[11] Unless mentioned, all other compounds were obtained from Aldrich. Acetonaphthone and 2-bromomethylacetonaphthone were re-

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crystallized from absolute ethanol prior to use. Spectroscopic grade solvents were purchased from Aldrich and used as received.

General Techniques. Absorption spectra were recorded using a Hewlett-Packard 8452A diode-array UV−vis spectrophotometer. Fluorescence and phosphorescence spectra were measured using a SPEX Fluorolog 2 spectrophotometer. Phosphorescence experiments were performed at 77 K in EPA (ether:isopentane:ethanol = 5:5:2) under argon with excitation at 355 nm. The source was a 3.0 ms Xe lamp pulse passed through the monochromator. The quantum yields of fluorescence and phosphorescence were determined relative to 9,10-diphenylanthracene[12] and benzophenone,[13] respectively. GC/MS was performed on a Hewlett-Packard 5988 mass spectrometer coupled to an HP 5880A GC, interfaced to an HP 2623A data processor. All electrochemical experiments were conducted on a BAS-100 potentiostat with a BAS PA-1 preamplifier. $Ag/AgNO_3$ with 0.1 M tetrabutylammonium perchlorate in acetonitrile was used as the reference electrode. The working electrode and counter electrode were platinum and a platinum wire, respectively. The scan rate was adjusted to 200 mV/s in all experiments.

Laser Flash Photolysis. The nanosecond laser flash photolysis experiments employed a kinetic spectrophotometric detection system that has been previously described.[14] The excitation source was the third harmonic from a Q-switched Nd:YAG laser (355 nm, 60 mJ/pulse, 8 ns pulse). However, a small fraction of pulse energy was used in order to eliminate unnecessary processes. Solutions were prepared at concentrations such that the absorbance was approximately 0.3−0.5 at the excitation wavelength and put into a 1.0 × 1.0 × 3.5 cm quartz cell with bleach at room temperature. After 20 min of argon bubbling, transient experiments were performed while the cell was continuously purged with argon gas. Quenching rate constants were measured using argon-saturated solutions which were prepared at each quencher concentration.

Quantum Yield for Disappearance by Steady-State Irradiation. solutions (3 mL) of **1a,b** and **2a,b** in acetonitrile in a quartz cell (1.0 × 1.0 × 3.5 cm) were deoxygenated by purging with oxygen-free argon for 10 min, sealed, and irradiated with a 200 W mercury lamp using a 360 ± 50 nm band glass filter. Acridine dimerization in air-saturated methanol (3×10^{-4} M, $\Phi_d = 0.032$, $\lambda_{ex} = 366$ nm) was used as an actinometer.[15] The bleaching of the samples and the chemical actinometer was monitored by UV−vis absorption spectroscopy. According to the Beer−Lambert law, the change in concentration of a solute versus irradiation time in the case of monochromatic light is expressed by the following equation:

$$-\mathrm{d}c/\mathrm{d}t = 10^3 \Phi_d I_0 / d[1 - \exp(-2.303A)] \qquad (1)$$

where I_0, d, Φ_d, and A denote the intensity of excitation light, path length of cell, quantum yield of the reaction, and absorbance at the excitation wavelength. The above equation can be integrated to the following:

$$\ln[\exp(2.303A) - 1] = -2.303 \times 10^3 \Phi_d e I_0 t + \ln[\exp(2.303A_0) - 1] \qquad (2)$$

Φ_d and I_0 can be calculated from the slope of the plot of ln[exp(2.303A) − 1] against irradiation time, t.

General Procedure for Photolysis. Preparative-scale photolysis was carried out in a Rayonet photochemical reactor fitted with filter-coated mercury lamps (300−400 nm) with output maximum at 350 nm. Samples for irradiation were placed in a ca. 15-mm internal diameter Pyrex tube immersed in a water-cooled bath during the course of reaction. The mixture of photoproducts was subjected to careful silica gel chromatography with hexanes−ethyl acetate (8:1) as eluent. All photoproducts were isolated and fully characterized by a combination of NMR, GC/MS, and elemental analysis.

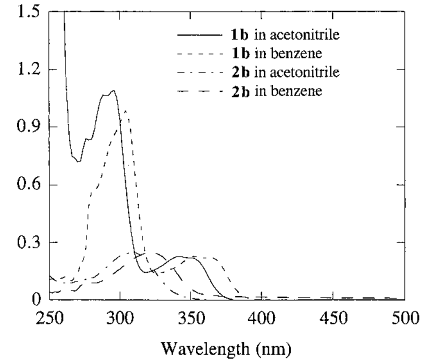

Figure 1. Absorption spectra of **1b** and **2b** in benzene and acetonitrile.

Table 1. Phosphorescence Data of 1c and 2c in EPA

borates	λ_{max} (nm)	E_T (kcal/mol)	τ_p (s)	Φ_p
1c	488, 525	58.6	1.04	5.5×10^{-4}
2c	491, 525	58.2	0.060	4.0×10^{-3}

Results

Steady-State Spectroscopy. The absorption spectra of **1b** and **2b** in acetonitrile and benzene are shown in Figure 1. The spectrum of **1b** has two clear peaks at 296 and 342 nm (log ϵ = 3.35) with different molar absorption coefficients. The spectrum of **2b** has one broad peak at 308 nm (log ϵ = 4.36) in acetonitrile and at 322 nm (log ϵ = 4.35) in benzene. In all cases, the spectra are red shifted in benzene with no significant change of shape. The spectra are found to be independent of the structure of the anions.

To determine the excited-state responsible for the proposed electron transfer, complexes **1c** and **2c**, with no oxidizable anions present, were studied. Both **1c** and **2c** fluoresce in acetonitrile and benzene upon excitation at 355 nm, although the quantum yield for fluorescence in benzene is found to be higher than it is in acetonitrile. No fluorescence quenching was observed for either chromophore in acetonitrile when tetrabutylammonium tetraphenylborate ($[Ph_4B^-][Bu_4N^+]$) was added. The phosphorescence spectra and lifetimes of **1c** and **2c** in EPA at 77 K (λ_{ex} = 355 nm) gave the lowest triplet energies (E_T) listed in Table 1. Quantum yields for triplet formation (Φ_T) were calculated by the following equation

$$\Phi_T = \Phi_p\{[k_T + (1/\tau_p)]/(1/\tau_p)\} \qquad (3)$$

where Φ_p, k_T, and τ_p denote the quantum yield of phosphorescence, the rate constant for deactivation of the triplet ($k_T = 1.43 \times 10^3$ s^{-1} for **1c** and $k_T = 2.10 \times 10^3$ s^{-1} for **2c** in EPA at 77 K), and the lifetime of phosphorescence, respectively. The Φ_T values of **1c** and **2c** were calculated to be 0.82 and 0.54, respectively.

Product Studies. The photocleavage of **1a,b** and **2a,b** was efficient in acetonitrile (Rayonet reactor λ = 350 nm), and irradiation times of less than 30 min were required to obtain 100% conversion. Conversion was determined by NMR by observing the disappearance of the methylene peaks around 4.50 ppm and the appear-

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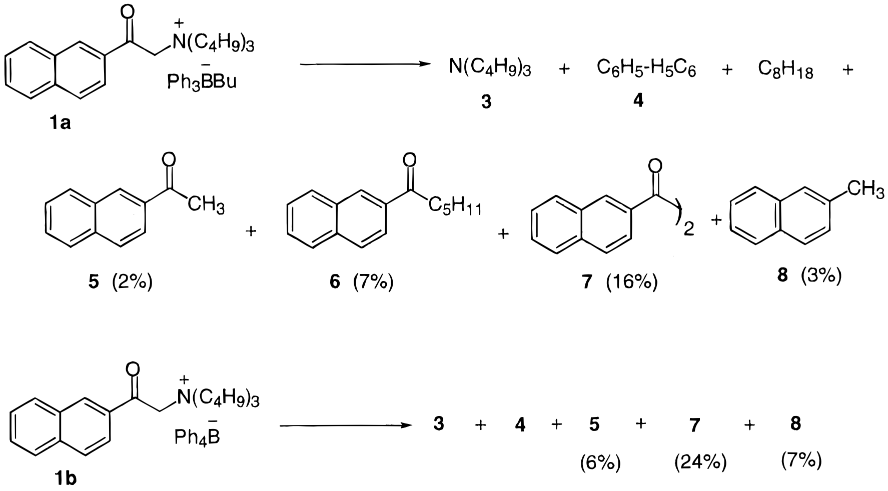
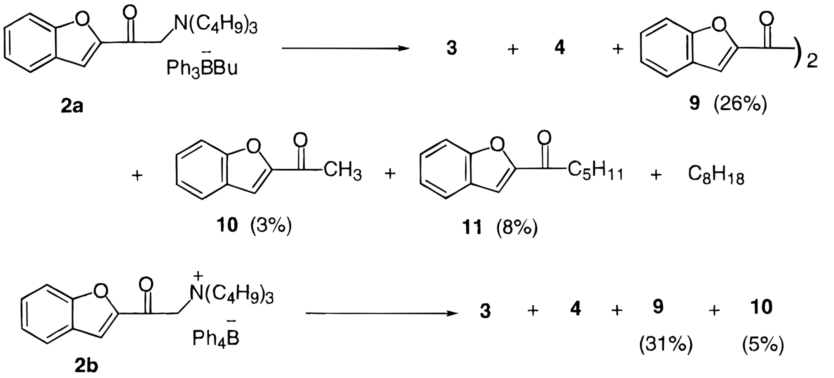
Scheme 1. Photolysis Products of 1a,b in Acetonitrile on Excitation at 350 nm



Scheme 2. Photolysis Products of 2a,b in Acetonitrile on Excitation at 350 nm



ance of a new peak at 2.45 ppm due to the formation of tributylamine. This clearly revealed that irradiation led to the cleavage of the carbon−nitrogen bond. Compounds **1**−**2c** undergo no reaction under similar experimental conditions, indicating that an oxidizable gegenion is required for photocleavage. Photolyses of **1a,b** in acetonitrile give a complex reaction mixture accompanied by the formation of tertiary amine in quantitative yield (Scheme 1). At low conversion (10%), the reaction shows the same product distribution, suggesting that no secondary photolysis occurs after the photocleavage process.

2a,b were converted to a complex reaction mixture in acetonitrile (Scheme 2). Tertiary amine formation was found to be quantitative and there was an absence of secondary photoproducts. Products were identified by comparison of GC retention times with authentic samples and by GC/MS analysis.

When photolysis reactions were performed on a preparative scale, the yields of the isolated products represent only the lower limits. Identification of products **5**−**7** (Scheme 1) and **9**−**11** (Scheme 2) clearly proves that radicals **12** and **14** are the common intermediates, respectively. The tertiary amines and biphenyl were formed in quantitative yield.

Laser Flash Photolysis. Photolysis of **1b** (355 nm excitation) in argon-saturated acetonitrile gives a transient species with an absorption maximum near 440 nm after 12 μs laser pulse (Figure 2). This transient decays in an exponential manner and is quenched by the addition of oxygen. As the transient decays, a second transient species with an absorption maximum around 400 nm appears concurrently. This 400 nm band has contributions from two species, one decays following first-order kinetics and the other decays by a bimolecular process ($k/\epsilon = 1.04 \times 10^6$ s^{-1} cm). The transient absorption spectra measured from **1a** (355 nm excitation) in deaerated acetonitrile (not shown) closely resemble those of **1b** under similar conditions. It appears likely that the same reactive intermediates are formed in both cases.

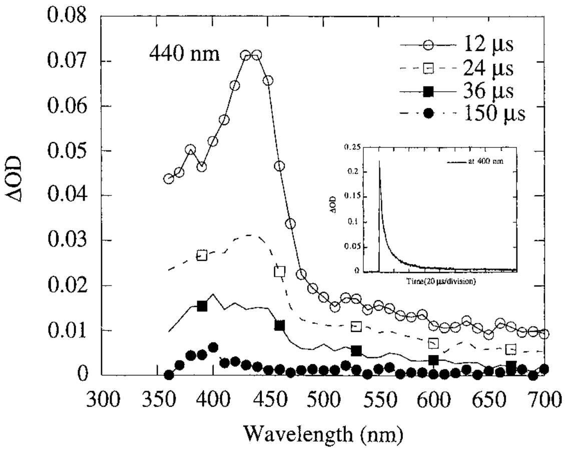


Figure 2. Time-resolved transient absorption spectra of **1b** in acetonitrile.

In an attempt to identify the reactive intermediates above, we studied compound **1c**, which contains the nonoxidizable anion, tetrafluoroborate. Steady-state

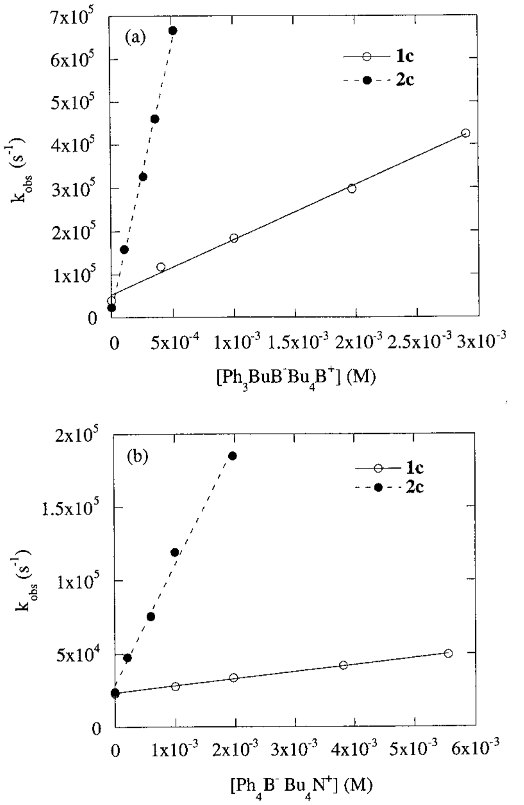


Figure 3. Stern–Volmer plots of **1c** and **2c** with tetrabutylammonium triphenylbutylborate (a) and with tetrabutylammonium tetraphenylborate (b) in acetonitrile.

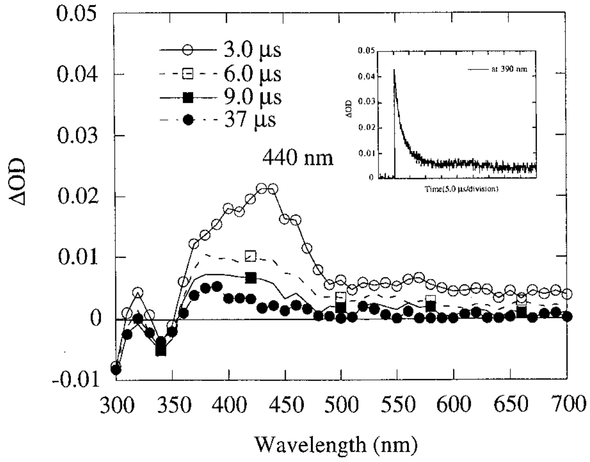


Figure 4. Time-resolved transient absorption spectra of 2-bromomethylacetonaphthone in acetonitrile.

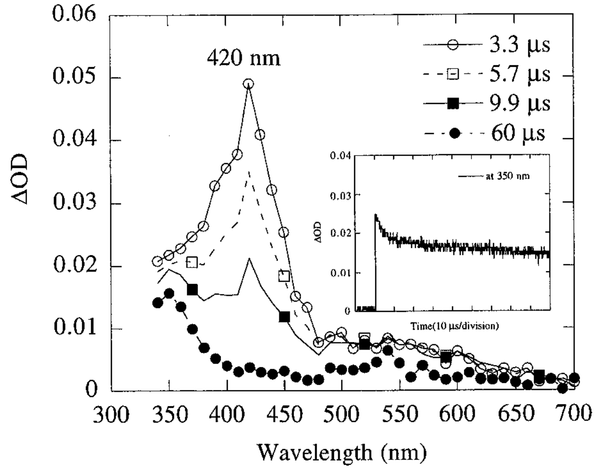
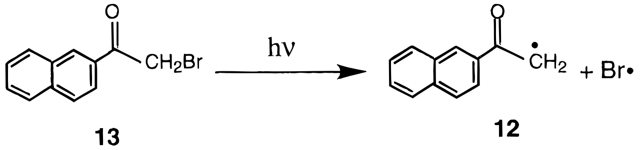


Figure 5. Time-resolved transient absorption spectra of **2b** in acetonitrile.

photolysis of **1c** in acetonitrile results in no reaction, while laser photolysis of **1c** in acetonitrile at 355 nm leads to a transient with absorption 430 nm that decays with a lifetime of 42.9 μs. This 430 nm absorption, which decays exponentially, has been assigned to the triplet state by comparison with an independently generated triplet transition from 2-acetonaphthone. Upon addition of [Ph_4B^-][Bu_4N^+] in acetonitrile, the decay of **1c** becomes more rapid due to quenching via intermolecular electron transfer ($k_q = 4.77 \times 10^6$ M^{-1} s^{-1}) (Figure 3). On the basis of these observations, we conclude that the 440 nm band of **1b** seen after the 12 μs laser pulse is due to the triplet state. The weak absorption generated around 400 nm after the 150 μs laser pulse is due to acetonaphthyl radical **12** that forms as the result of carbon–nitrogen bond scission.

To confirm this assignment, we flashed (355 nm) an argon saturated acetonitrile solution of 2-bromomethylacetonaphthone **13**, in an attempt to generate **12** independently. A transient (λ = 440 nm) was observed after 3.0 μs pulse.



This decayed with a lifetime of ca. 2.3 μs and was assigned to the triplet state of **13**. However, while this absorption decayed as expected, a weak broad absorption around 390 nm appeared after 37 μs (Figure 4). The decay behavior of this transient suggests two components, one of which is best fitted by second-order kinetics ($k/\epsilon = 2.62 \times 10^6$ s^{-1} cm). The behavior and the location of the absorption maximum near 400 nm are consistent with the transient obtained from **1b** after 150 μs. We therefore identify this transient as radical **12**.

Laser flash photolysis of **2c** in argon-purged acetonitrile (λ_{ex} = 355 nm, fwhm = 8 ns) gave an absorption transient at 420 nm, which was formed within the laser pulse (12 μs). This decayed as a single exponential with a lifetime of 44.0 μs. Introduction of oxygen resulted in a faster decay of this transient. This observed band can be confidently assigned to the triplet state of **2c**. When [Ph_4B^-][Bu_4N^+] was added to an acetonitrile solution of **2c**, triplet decay was more rapid, owing triplet quenching ($k_q = 8.14 \times 10^7$ M^{-1} s^{-1}).

An identical transient formed from **2a,b** is also observed at 420 nm immediately after the laser pulse in acetonitrile. As with **1b**, both **2a** and **2b** show a relatively weak, long-lived band at 350 nm 60 μs after the laser pulse (Figure 5; **2a** is not shown in the figure). Again, this consists of two components, one of which decays by second-order kinetics ($k/\epsilon = 1.60 \times 10^5$ s^{-1} cm). These results, therefore, provide strong evidence that the radical 2-acetylbenzo[*b*]furanyl is produced from triplet state quenching. This is further supported from laser flash photolysis data using 2-bromomethy-

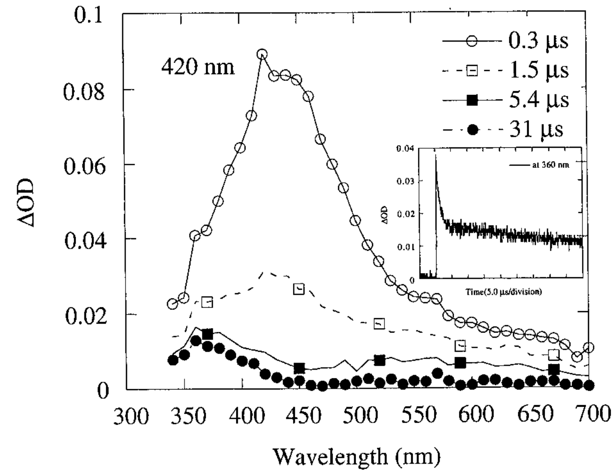


Figure 6. Time-resolved transient absorption spectra of 2-bromomethylacetobenzo[*b*]furan in acetonitrile.

Table 2. Free Energy Changes ($\Delta G°$) for Electron Transfer, Quenching Rate Constants (k_q), and Quantum Yields for Disappearance (Φ_d) of 1a,b and 2a,b

borates	$\Delta G°$ (eV)[a]	k_q (M^{-1} s^{-1})[b]	Φ_d[c]	Φ_d[d]
1a	−0.57	1.28×10^8	0.75[e]	0.50[g]
1b	−0.37	4.77×10^6	0.24[e]	0.33[g]
2a	−0.51	1.23×10^9	0.54[f]	0.67[h]
2b	−0.31	8.14×10^7	0.53[f]	0.50[h]

[a] Triplet state energy values for **1** and **2** are 2.54 and 2.53 eV, respectively. [b] Quenching data are for **1c** and **2c** with the two ammonium borates. [c] Triplet state quenching experiments. [d] Steady-state experiments. [e] [Borates] = 2×10^{-3} M, $\Phi_T = 0.82$. [f] [Borates] = 2×10^{-2} M, $\Phi_T = 0.54$. [g] 2×10^{-3} M in acetonitrile. [h] 2×10^{-2} M in acetonitrile.

lacetobenzo[*b*]furan. An analogous absorption around 350 nm is observed and is fit well to a second-order decay ($k/\epsilon = 5.7 \times 10^5$ s^{-1} cm) due to formation of 2-acetylbenzo[*b*]furanyl radical by carbon−bromine bond cleavage (Figure 6). In the case of **2b**, a very weak band around 550 nm appeared with the radical absorption at 350 nm. A confident assignment of this 550 nm absorption could not be made.

Thermodynamics for Electron Transfer. Reduction potentials for **1c** and **2c** in acetonitrile with tetrabutylammonium perchlorate were measured by cyclic voltammetry and found to be −1.27 and −1.32 eV, respectively. An irreversible one-electron reduction wave was observed, probably due to a fragmentation reaction. The oxidation potentials of $[Ph_4B^-][Bu_4N^+]$ and $[Ph_3BuB^-][Bu_4N^+]$ are known to be 0.90 and 0.70 V, respectively.[16] Free energy changes for electron transfer ($\Delta G°$) were calculated using the Weller equation[17] without taking into account the Coulombic term.[18] In all cases, the proposed electron transfer step is energetically favorable (Table 2). The rate constants for triplet quenching (k_q) of **1c** and **2c** by borate anions were determined by monitoring the triplet decay rate constant as a function of quencher (borate anion) concentration. The rate constants are listed in Table 2.

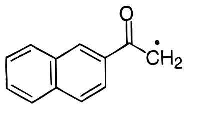
Quantum Yields. Since the quantum yield for disappearance (Φ_d) of the borates should be identical with the quantum yield of radical anion formation after electron transfer, the quantum yield of the photodissociation can be quantified from quenching experiments and steady-state experiments using a suitable actinometer. We employed acridine dimerization as the actinometer ($\Phi_d = 0.032$, $\lambda_{ex} = 366$ nm).[15] We also calculated Φ_d from quenching data using eq 4 to verify whether the values obtained by the two different methods are consistent.

$$\Phi_d = \Phi_T\{k_q[\text{borate}]/(k_T + k_q[\text{borate}])\} \qquad (4)$$

Φ_T is the quantum yield for triplet formation and k_T is the rate constant for deactivation of the triplet. The Φ_d values are summarized in Table 2.

Discussion

Quenching experiments suggest that the proposed electron transfer occurs from borate anions to the excited triplet states of the acceptors. All of the photoreactions are initiated by excitation of the electron acceptors in acetonitrile, since none of the borates absorb beyond 300 nm. As a result, C−N bond cleavage occurs, and radicals **12** and **14** are formed. Confirmation of the formation of these radicals was achieved by direct observation during laser flash photolysis. The decay behavior of each is bimolecular, suggesting the formation of radical-derived dimeric products. Additional support for formation of radicals comes from the isolated photolysis products. Since trends in the formation of the photoproducts and the excited-state chemistry are identical for both **1** and **2**, a common pathway for the formation of tertiary amines is suggested.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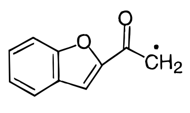
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A plausible mechanism for the formation of tertiary amines from **1a** or **1b** is given in Scheme 3. Electron transfer from the borate to the excited triplet state of chromophore ($^3T^*$) gives the radical anion of the chromophore **15** and the boranyl radical **X**, both of which dissociate rapidly. The carbon-centered radical anion **15** rearranges, then the carbon−nitrogen bond rapidly fragments to generate more stable radical anion **16**. The driving force for this is the formation of a stabilized anion **16** from a highly energetic radical anion **15**. This type of homolytic carbon−nitrogen bond scission is not unlikely, because of the small electronegativity difference between the carbon and nitrogen atom.[19] In fact, similar carbon−nitrogen cleavage reactions followed by elimination of tertiary amines have been previously reported.[8,20] Heterolytic carbon−nitrogen bond cleavage is ruled out, since it does not lead to formation of **12**. The whole process is rapid, and intermediates **15** and **16** are not observed with the detection system used in

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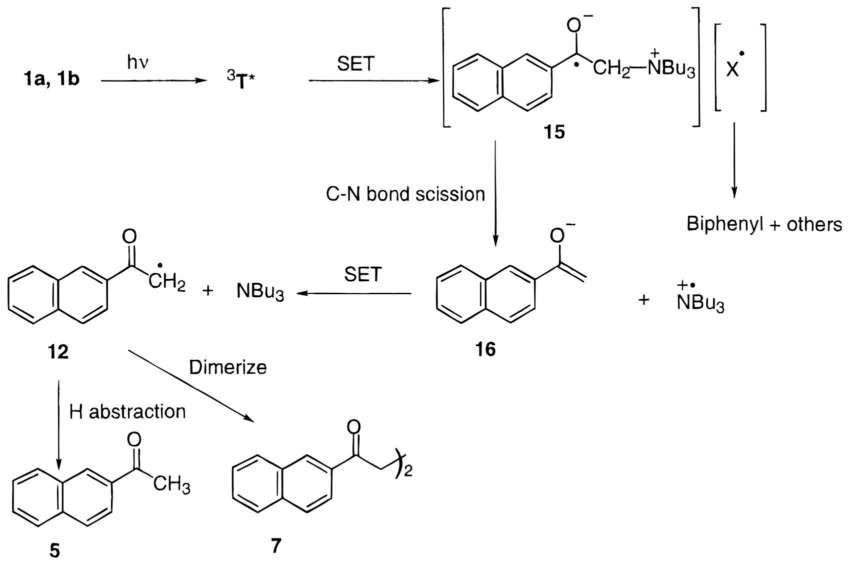
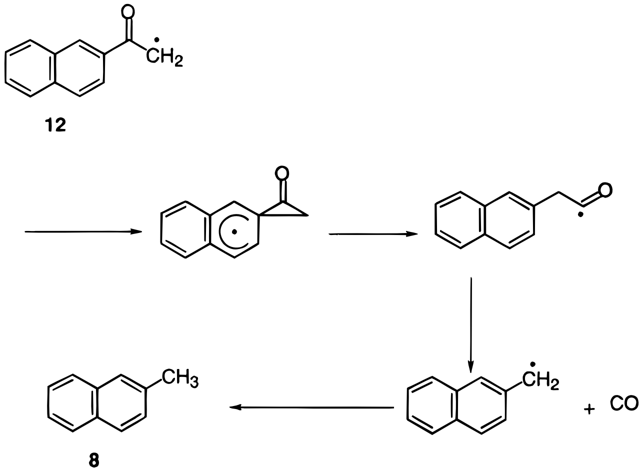
Scheme 3. Mechanism for Amine Formation in Acetonitrile



Scheme 4. Rearrangement Mechanism of Radical 12 in Acetonitrile



this study. Products **5** and **7** are the result of hydrogen abstraction from the solvent acetonitrile[21] and self-coupling of **12**, respectively.

An interesting observation is the rearrangement of radical **12** and the formation of **8** as a minor product, according to the mechanism shown in Scheme 4. The similar "neophyl-like" rearrangement followed by α-scission was also observed in the case of a benzoylalkyl radical.[22] However, this rearrangement was not observed in the case of radical **14**. A possible explanation for this behavior is the presence of the nearby oxygen atom with vacant orbitals. The increase in spin–orbit coupling,[23] due to the substitution of a skeletal atom of the system by oxygen, decreases the stabilization energy of **14**, and dimerization occurs without the "neophyl-like" rearrangement. In all cases, the formation of biphenyl is significant. This is thought to be formed from the two phenyl groups bound to boron via a rearrangement reaction.[23]

In general, the borate salts exist as solvent-separated ion pairs in polar solvents.[25] However, spectroscopic observation in acetonitrile reveals that borates **1**–**2** have more significant interaction between the ions than is expected for a solvent-separated ion pair.[26] As expected, quenching rate constants (Table 2) are high (close to the diffusional limit) and correlate with the oxidation potentials of the borates, the reduction potentials of the acceptors, and the triplet energy of the acceptors. The observed correlation between the quenching rate constants and $\Delta G°$ supports the conclusion that the quenching process is an electron transfer from the borates to the excited acceptors.

The radical pair **15,** which is the result of electron transfer, can disappear either by back electron transfer to the reactants or by rapid fragmentation of the carbon–nitrogen bond to tertiary amines. Therefore, the quantum efficiencies would be determined by the competition of back electron transfer and fragmentation reactions. Radical pair **15** was not observable within our experimental conditions due to its subpicosecond lifetimes.[26] The lifetimes of the tetraphenyl boranyl and triphenylbutyl boranyl radicals are known to be 45 ps and 250 fs, respectively.[27] Both oxidative and reductive cleavage take place in the present system in such a short period of time that back electron transfer cannot compete. Therefore, the efficiency of amine generation as a result of carbon–nitrogen bond scission is high. In this respect, steric effects likely play an important role due to the bulkiness of the tributyl group on nitrogen.[19a]

Since the experiments were conducted at different concentrations, it is difficult to compare the quantum yields of disappearance between **1** and **2**. However, high quantum yields for both systems indicate that the photodissociation occurs exclusively from the excited triplet states. The Φ_d obtained from the quenching

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experiments would be quite close to Φ_T , if the concentration of the donors is approximately 10^{-3} M. Actually, the Φ_T values of **1c** and **2c** agree with values of Φ_d calculated from the steady-state experiments. This result proves again that the reaction occurs via the triplet state. Due to identical triplet energy and lifetimes, both systems show almost the same photocleavage efficiency.

Conclusion

This work has shown the mechanistic details for the photogeneration of tertiary amines from tetraorganyl borates. Laser flash photolysis in acetonitrile leads to the formation of radicals, clearly indicating that the primary photochemical step in the photolysis is the homolytic cleavage of the carbon−nitrogen bond after electron transfer from the borate anion to acceptors. The quantum yields of the photodissociation are high, suggesting insignificant back electron transfer. From the high quantum yields, as well as the quenching rate constants, we conclude that the efficiency of photobase generation of all of the investigated borate complexes are high enough to be useful in photoimaging applications. Of particular interest is the case of epoxide cross-linking reactions, where tertiary amines act as photoinitiators and create photoimaging systems.[28] However, to determine the versatility of these systems in detail, it is necessary to determine the quantum yield of photodissociation in the actual polymer matrix; presently we are investigating such possibilities.

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