PERKIN 2

Tetraorganylborate salts as convenient precursors for photogeneration of tertiary amines

Ananda M. Sarker, Adrian Lungu, Alexander Mejiritski, Yuji Kaneko and Douglas C. Neckers *

Center for Photochemical Sciences,[1] Bowling Green State University, Bowling Green, OH 43403, USA

Received (in Gainesville, FL) 16th January 1998, Accepted 5th July 1998

Photoreactions of *p*-(benzoyl)benzyl trisubstituted ammonium tetraorganylborate salts for the generation of tertiary amines in solution and rigid matrices are described. Structural modification of the complexes allows study of the influence of steric and electronic effects on the photogeneration of amines. Flash photolysis, cyclic voltammetry and product analysis indicate that single electron transfer from borate to excited benzophenone is followed by homolytic C–N bond cleavage. Photoliberation of the tertiary amine is controlled by the rate of the electron transfer reaction.

Introduction

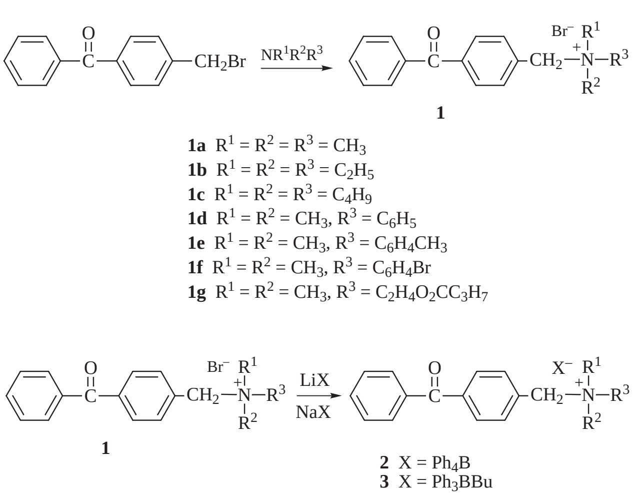
Compounds that act as sources of organic bases when irradiated have recently found applications specifically in thin film imaging.[2–4] Said photobase generators are expected to be promising as crosslinkers for epoxides, complementing the better known commercial photoacid catalysts. Examples,[5] including photoreactive carbamates,[6] are limited in that they only form primary and secondary amines. Though photoformation of tertiary amines is relatively new,[7] they are often better catalysts,[8] particularly in acyl transfer reactions where the less substituted amines generally give amides.[9]

Recent work from our laboratories and others[10–12] reports the use of single electron transfer from borate anions in various applications in both solutions and solids. We have used such reactions in the design of photoreactive complexes which serve as precursors for tertiary amines.[13] Our approach masks the desired amines with a photolabile electron acceptor such as a benzophenone complexed as a quaternary ammonium salt with a borate anion. Since *p*-(benzoyl)benzyl ammonium borates decompose when irradiated with UV light, liberating free amines by benzophenone triplet state oxidation of the borates followed by rapid C–N bond cleavage, in this work we probe factors affecting the quantum efficiency of bond cleavage. In addition to varying the anion, we have also considered various ammonium complexes. In particular we investigate steric and electronic factors on nitrogen as affecting amine formation. We also demonstrate the use of tertiary amine formation in a thin film modifying system involving epoxy polymer.

In this paper we report studies emphasizing the factors affecting the quantum efficiency of bond cleavage. Parameters to be examined are the variation of anions and substituents on nitrogen and their effect, in terms of electronic and steric factors, on amine formation. In addition, we demonstrate the use of amine formation in an imaging system involving epoxy polymer.

Results and discussion

The treatment of amines (excess) with 4-(bromomethyl)benzophenone generates a series of *p*-(benzoyl)benzylammonium bromides **1** (Scheme 1), that are easy to isolate. Since primary and secondary amines are not sufficiently nucleophilic to react with 4-(bromomethyl)benzophenone, our synthetic strategy has been limited to tertiary amines. All the quaternary ammonium bromides are solid and purified by crystallization save for **1f** which, due to its extreme hygroscopic nature, was used in the next step without further purification. Organylborate derivatives **2**–**3** are obtained upon treatment of bromides with lithium or sodium borate salts in water. All the borates are crystalline and easily separated from the reaction as chromatographically pure solid precipitates with appropriate solvents.



1

1a $R^1 = R^2 = R^3 = CH_3$
1b $R^1 = R^2 = R^3 = C_2H_5$
1c $R^1 = R^2 = R^3 = C_4H_9$
1d $R^1 = R^2 = CH_3$, $R^3 = C_6H_5$
1e $R^1 = R^2 = CH_3$, $R^3 = C_6H_4CH_3$
1f $R^1 = R^2 = CH_3$, $R^3 = C_6H_4Br$
1g $R^1 = R^2 = CH_3$, $R^3 = C_2H_4O_2CC_3H_7$

1

2 $X = Ph_4B$
3 $X = Ph_3BBu$

Scheme 1

In order to investigate the effect of both steric and electronic factors on the photocleavage of the C–N bond in the precursors, several structural variations were carried out. For example, variation in the structure of the amine may confer considerable steric demands on the C–N bond cleavage step, while its electronic nature may play a role in subsequent stabilization.

Photochemistry

The UV–VIS spectra of all borate complexes are nearly identical and similar to that of benzophenone with n–π* transitions centered at 334–340 nm. There is a substantial tail beyond this absorption that allows photolysis with Pyrex-filtered light. The extinction coefficients of the n–π* transitions are nearly identical for all of the compounds (ε ~200 l mol^{-1} cm^{-1}). Neither substituents on the nitrogen atom nor the counter-anions influence the UV spectra significantly in terms of absorption wavelength or extinction coefficient so exposure to

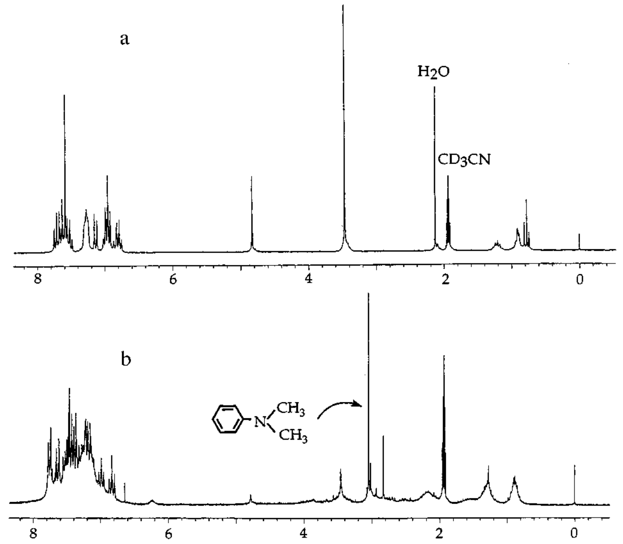


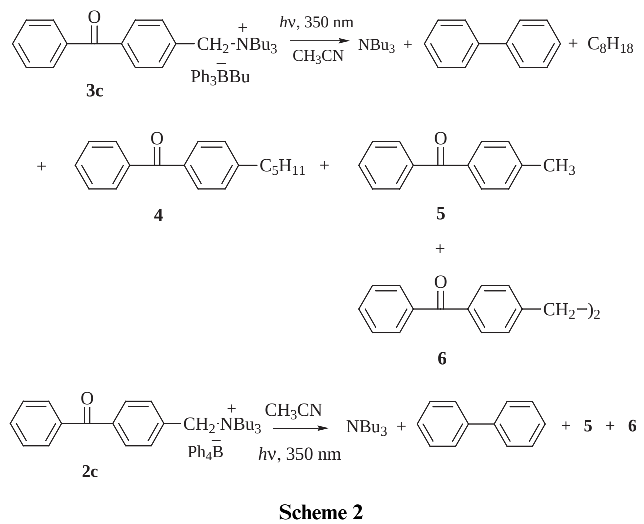
Fig. 1 ^{1}H NMR of **3d** in deuterated acetonitrile (a) before photolysis and (b) after 60 min photolysis.

irradiation within this absorption region is expected to promote the benzophenone moiety to its excited triplet state.

Irradiation of an acetonitrile-d$_3$ solution of borate salt **3d** at 350 nm resulted in *N*,*N*-dimethylaniline in high yield in 60 min as indicated by ^{1}H NMR spectroscopy (Fig. 1). Conversion to amine was measured by monitoring the disappearance of reactant *p*-benzoylbenzyl methylene peaks at 4.80 ppm and the appearance of the new peak at 3.04 ppm due to amine formation. For each of the borates, the integrated area of the *p*-benzoylbenzyl methylene peak decreased, while the integrated area of the expected *N*-methylene/methyl amine peaks increased as the exposure time in a Rayonet photochemical reactor increased. Photodecomposition of the individual borate derivatives in acetonitrile and in hydrogen donating solvents (methanol, *etc.*) yield tertiary amines in different time frames. In contrast, irradiation of compound **1c**, with the more difficult to oxidize bromide anion[14] present, leads to no significant consumption of the starting material under the same experimental conditions. This indicates that efficient electron transfer from the borate anion to the benzophenone excited state is the primary reaction responsible for cleavage of the C–N bond.

Photoproduct analysis

Photolysis of compounds **2c** and **3c** in acetonitrile at λ >300 nm using a high pressure mercury arc lamp generated products identified (Scheme 2) by HPLC, GC and GC-MS in comparison with authentic samples and characterized, after chromatography, by melting point, NMR, MS and elemental analysis. The main photolysis products identified are shown in Scheme 2. Identification of products **4**, **5** and **6** clearly proves that *p*-benzoylbenzyl radical is the common intermediate for these products. The common minor product **5** is formed in both cases *via* hydrogen abstraction from solvent. The presence of dimerized product **6** and minor crossover product **4** suggests that the radicals recombine outside the solvent cage.



Scheme 2

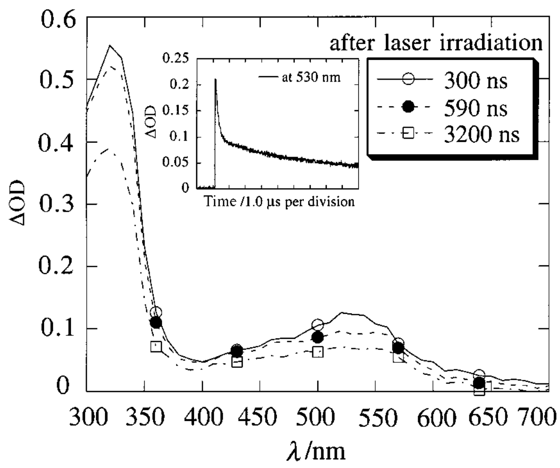


Fig. 2 Time-resolved transient absorption spectra of **2c** in acetonitrile (1 × 10^{-3} M).

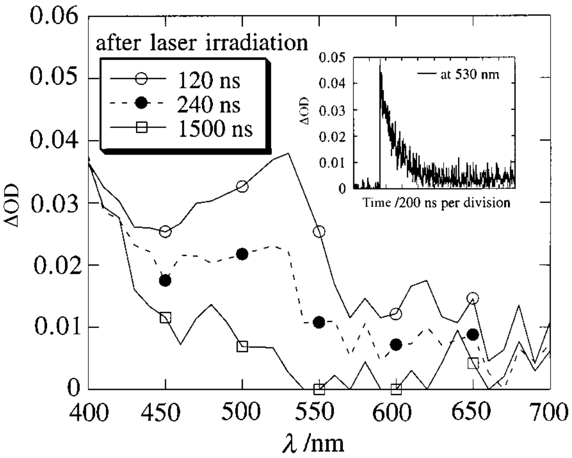


Fig. 3 Time-resolved transient absorption spectra of 4-(bromomethyl)benzophenone in acetonitrile (1 × 10^{-3} M).

Time-resolved spectroscopy

Fig. 2 shows the transient spectrum obtained upon laser flash photolysis (355 nm, 7 ns, 70 mJ) of **2c** in argon purged acetonitrile (1.0 × 10^{-3} M). The absorption maxima are at 335 and 530 nm, and both are quenched by oxygen but at different rates. The time course of the signal at 530 nm (inset, Fig. 2) indicates two components. The faster component decays following a first order kinetic law, while the slower component is best fitted with second order kinetics ($k/\varepsilon = 1.17 \times 10^6$ cm s^{-1}). Under the same conditions, a solution of **7c**, for which no electron transfer is expected, displays triplet–triplet absorption with maxima at 320 and 550 nm[15] ($\tau = 13.2$ ms). The decay curves for **7c** around 530 nm evolve from one component in the absence of Ph$_4$B to two components when Ph$_4$B anion is added. Therefore, we assign the decays at 530 nm to the absorption of *p*-benzoylbenzyl radical and to triplet decay. Assignment of the decay at 530 nm to the radical is further confirmed by comparing the spectra generated from 4-(bromomethyl)benzophenone under the same conditions (Fig. 3). A transient is observed

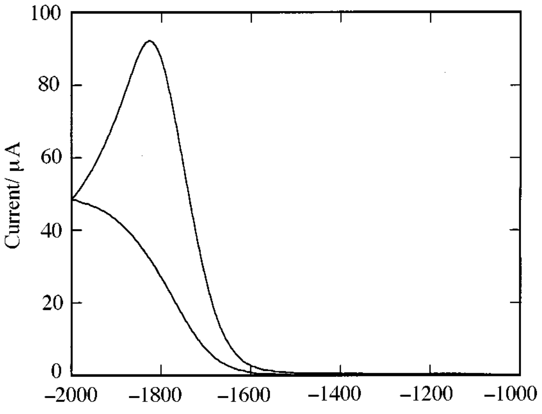


Fig. 4 Cyclic voltammogram of **1c** with tetrabutylammonium perchlorate in acetonitrile (1×10^{-2} M).

with a maximum at 530 nm and this decays with second order kinetics ($k/\varepsilon = 2.49 \times 10^8$ cm s^{-1}). The only possible radical product that might be observed in this case is *p*-benzoylbenzyl radical.

The shorter component (lifetime 200 ns) observed at 530 nm is assigned to the decay of **2c** triplet (when the concentration of **2c** is 1×10^{-3} mol l^{-1}). The 200 ns lifetime transient implies the triplet lifetime of benzophenone chromophore in a solution containing 1×10^{-3} M Ph_4B anion. The absorptions in the near UV are difficult to assign due to the complex nature of the decays in this region. We suspect that the triplet decay, *p*-benzoylbenzyl radical decay and the increase of products formation ought to be observed in the same time frame in the near UV region. We have therefore not assigned the decay in this region.

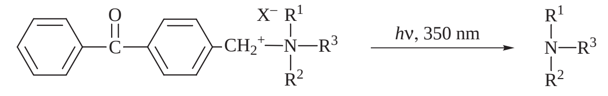
Cyclic voltammetry measurements

The electrochemical behavior of benzophenone as well as substituted benzophenones is known.[16] All exhibit reversible single electron reduction waves. In contrast, cyclic voltammetry measurements of compound **1c** in acetonitrile with tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte (sweep rate = 200 mV s^{-1}) reveal an irreversible single electron reduction wave with the peak potential at *ca.* −1.83 V *vs.* Ag/AgNO$_3$ and −1.49 V *vs.* SCE (Fig. 4). Similarly, the same irreversible wave was observed for other ammonium bromide derivatives. These irreversible reduction waves are scan rate independent, for which peak currents are proportional to the square root of scan rate. These findings are taken as evidence for an irreversible reaction, most likely rapid carbon–nitrogen bond cleavage, of benzophenone ammonium cation after one electron reduction.

Photoefficiency

The relative efficiency of tertiary amine generation was determined by monitoring the ^{1}H NMR signal near 4.80 ppm assigned to methylene groups attached to the quaternary nitrogen of the starting borates (Fig. 1) which disappears as the photocleavage reaction occurs. The integrated area of the signals from the aromatic protons (8–6.6 ppm) was chosen as the reference based on the assumption that there is no change in the total number of the aromatic protons. Parallel actinometric runs were compared to a benzophenone–benzhydrol solution.[17] In all cases, conversion was kept below 20% in order to avoid any related secondary photochemistry. A linear relationship was obtained between conversion and irradiation time for the 350 nm photolysis of borate **3c** (Fig. 5) demonstrating that no secondary photoreaction occurs up to 35–40% conversion. Although all experiments were carried out in the presence of oxygen, no significant difference was observed in the absence of oxygen. The relative quantum yield values are reported in Table 1 (no quantum yield measurements were performed for **7c**).

Table 1 Quantum yields of base formation for organylborate salts.[a]



1 X = Br
2 X = Ph_4B
3 X = Ph_3BBu

Sample[b]	R¹	R²	R³	Φ[c]
1c	Bu	Bu	Bu	0.06
2a	Me	Me	Me	0.38
2b	Et	Et	Et	0.52
2c	Bu	Bu	Bu	0.61
2e	Me	Me	$C_6H_4CH_3$	0.32
2f	Me	Me	C_6H_4Br	0.30
3c	Bu	Bu	Bu	0.98
3d	Me	Me	C_6H_5	0.71
3e	Me	Me	$C_6H_4CH_3$	0.40
3f	Me	Me	C_6H_4Br	0.38
3g	Me	Me	$C_2H_4O_2CC_3H_7$	0.41

[a] Benzophenone–benzhydrol reaction was employed as an actinometer. [b] 0.01 M solution in acetonitrile. [c] Reported yields are the average of two measurements.

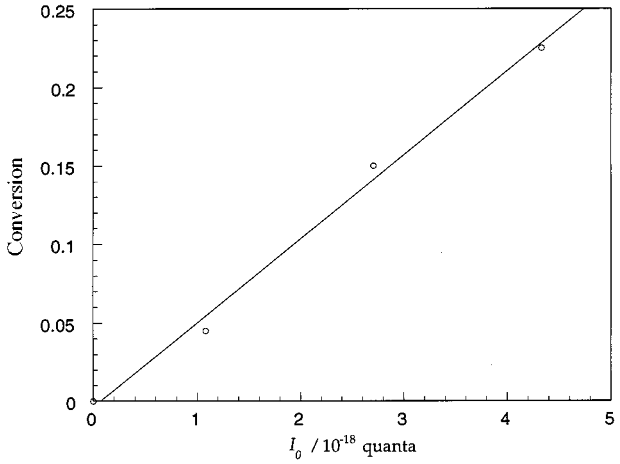


Fig. 5 Conversion *vs.* accumulated dose of 350 nm light for the photolysis of **3c**.

Steric, electronic and anionic effects

The relative quantum efficiencies (Table 1) suggest that the photosensitivity of the ammonium borate salts is affected by a combination of steric and electronic effects in the benzophenone ammonium cation, as well as by the structure of the electron donating anions. The electron donor capability of the anion and the electronic nature and steric bulk of substituents on nitrogen have an impact on the efficiency of the process. In principle, the efficiency of photolysis may be controlled by the electron transfer rate from the borate anion to the triplet state of the ketone.

As expected, the quantum efficiency of borate disappearance is higher for Ph_3BBu^n than for Ph_4B since the triphenyl-*n*-butylborate anion is more easily oxidized than is tetraphenylborate.[18] Previous work with cyanine tetraphenylborates had shown that back electron transfer competes with forward electron transfer,[19] while in triphenylbutylborate back electron transfer was prevented due to its dissociative nature.[10c] The lifetime of the tetraphenylboranyl radical (45 ps[20]) is long enough for back electron transfer to occur from the long-lived cyanine radical. On the other hand, triphenyl-*n*-butylboranyl radical

Table 2 Thermal properties of organylborate salts.

Salt	Melting point, T_m/°C	Decomposition point, T_d/°C[a]
2a	201–202	229
2b	226–227	238
2c	197–198	246
2e	188–189	218
3c	133–134	222
3d	150–152	198
3e	123–125	189
3g	110–111	212

[a] Decomposition temperature was taken as the temperature of 5% weight loss.

has a lifetime of 250 fs[20] and this is too short a time for back electron transfer to compete in any significant amount with dissociation. However, the amine formation observed as the end result of the photolysis of both **2c** and **3c** suggests that *p*-benzoylbenzylammonium cation dissociation (C–N bond cleavage) is so rapid that back electron transfer does not compete.[13]

The presence of bulky substituents on the quaternary nitrogen increases the efficiency of the process by promoting the C–N bond cleavage due to the release of B-strain energy (for example, **2c** in comparison with **2a**, **2b**).[21] Comparison of various aryl substituted quaternary salts gives no indication of significant electronic influences on the process. The electronic (donating or withdrawing) nature of the *para* substituents on the benzene ring on the amine side had virtually no influence on the relative quantum yields since these groups are far away from the reaction center (**3e** and **3f**). A similar behavior is observed in the case of the Ph_4B counter anion (**2e** and **2f**).

Thermal stability

Prolonged exposure of all borate complexes to air, light and moisture resulted in no detectable decomposition. TGA results (under nitrogen) are collected in Table 2. The stability limit T_d (decomposition temperature), which was taken as the temperature at which 5% weight loss of a sample occurred, varied from 212 to 246 °C, indicating that each had excellent thermal stability. No particular relationship was observed between the structure of the complexes and their thermal stability. However, complexes with tetraphenylborate anions formed more thermally stable complexes than did the corresponding triphenylborate analogs, probably due to the symmetrical structure of the tetraphenylborate which leads to an effective crystal packing.

Lithographic evaluation

As mentioned earlier, evaluating the relative yield of tertiary amine formation in the solid state is difficult because of the lack of suitable analytical methods. This is not the case if the borate complexes are part of a polymer as a pendant group.[22]

Since the tetraorganylborate salts formed amines upon photolysis, we tested them as curing agents for thermally driven amine catalyzed epoxy crosslinking.[23] Target complexes were incorporated in a solid matrix of a polymer having pendant epoxy groups, poly(glycidyl methacrylate). The borate salt was added to glycidyl polymer solution in a mixture of methyl ethyl ketone and *N*,*N*-dimethylformamide such that the molar ratio between the epoxide and borate moieties was 2 : 1. Spin coated films of uniform thickness were prepared and prebaked at 80 °C for 60 min which induced no curing. Films were then exposed imagewise to different doses of defocused UV irradiation filtered through a 360 nm filter (bandwidth ~40 nm). Regardless of exposure dose, the exposed areas remained completely soluble in acetonitrile. However after postbake (5 min) at 80 °C, immersion of the films in a bath of acetonitrile led to immediate dissolution of nonirradiated areas. Films were retained in the irradiated areas. Differential solubility in acetonitrile allowed formation of negative-tone photoimages of the mask and these were observed by atomic force microscopy (Fig. 6).

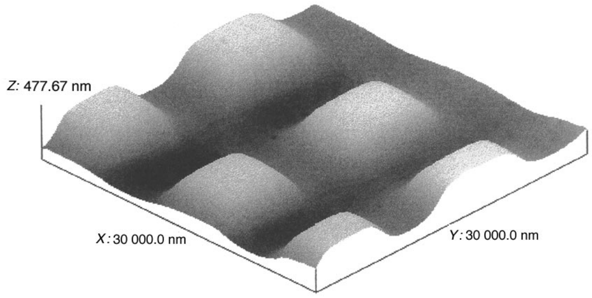


Fig. 6 Negative-tone photoimage obtained after the photolysis of **2c** in epoxide matrix, postbake and development in acetonitrile.

Exposure doses of less than 900 mJ cm^{-2} were sufficient to produce images with a retained film thickness reaching its maximum of ~0.3 μm for compound **2c**. Under similar exposure conditions, the required dose for **3c** was less than 400 mJ cm^{-2}. In the case of **1c**, on the other hand, a maximum film thickness could not be reached even for doses exceeding 4000 mJ cm^{-2}. The large differences in the sensitivity for these resist formulations paralleled the differences in quantum yields of amine generation measured in solution. The borate salt that undergoes the most efficient photodecomposition to tertiary amine affords the more sensitive resist.

Mechanism

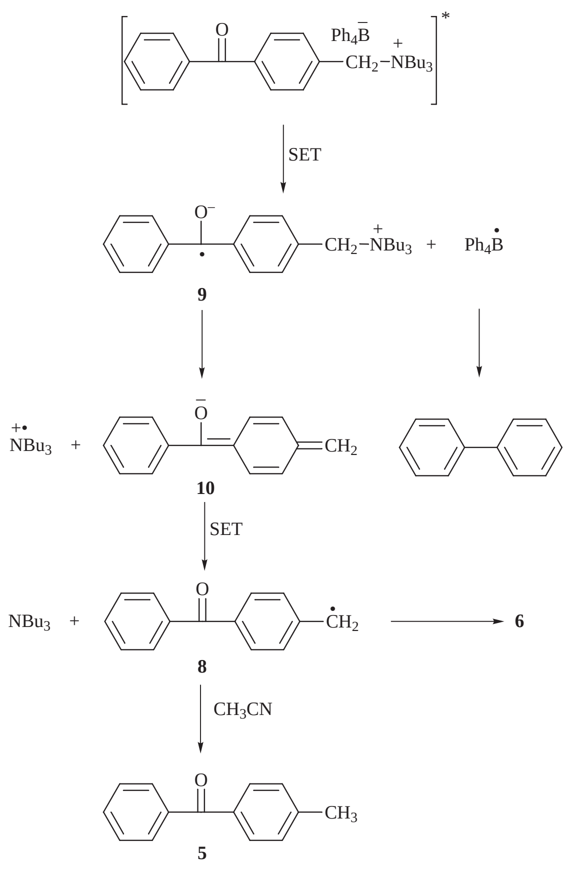
Triplet state quenching experiments[24] and the negative $\Delta G°$ value[25] associated with electron transfer from borate to the excited triplet state of benzophenone indicate photocleavage proceeds as in Scheme 3. Electron transfer from borate anion to the benzophenone-like triplet likely gives the radical anion and boranyl radical. We were unable to detect radical anion **9** under the experimental conditions due to the rapid cleavage of the carbon–nitrogen bond which occurs homolytically leading to the *p*-benzoylbenzyl radical **8**. As we have indicated above this was detected by laser flash photolysis. Further support for formation of radical **8** comes from isolated photolysis products (Scheme 2). Heterolytic C–N bond scission is ruled out because of the absence of products that can be attributed to ionic intermediates. For example, acetamide would be an expected product in acetonitrile. Furthermore, the formation of radical **8** is not explained if one assumes the C–N bond breaks heterolytically in **9**.

The high yields for the photofragmentation arise in part because the boranyl radical fragments rapidly following oxidation. However, back electron transfer is also precluded because the geminate radical pair is a triplet, and thus the back electron transfer is spin-forbidden.

Experimental

General

Unless otherwise indicated, all compounds were obtained from Aldrich. All deuterated solvents were used as received. Acetonitrile used for cyclic voltammetry and photolysis experiments was of HPLC grade (Aldrich) and distilled from CaH_2. 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. ^1H and ^{13}C NMR spectra were taken on a Gemini GEM-200 (200 and 50 MHz, respectively) spectrometer. Chemical shifts are given in ppm and *J* values in Hz. UV–VIS spectra were recorded on a Hewlett-Packard 8452 diode array spectrophotometer. GC-MS measurements were performed on a



Scheme 3

Hewlett-Packard 5988 mass spectrometer coupled to an HP 5880A GC instrument, interfaced to an HP 2623A data processor. GC measurements were carried out on a Hewlett-Packard 5890 gas chromatograph.

Nanosecond flash photolysis studies were performed using a kinetic spectrophotometric detection system. Excitation pulses (7 ns) of light were generated at 355 nm, the third harmonic of a Q-switched Nd:YAG laser. Typical excitation pulse amplitudes were a few millijoules per pulse. Transients produced were followed temporally and spectroscopically by a computer-controlled kinetic spectrophotometer.

Thermogravimetric analysis (TGA) was carried out on a DuPont TGA-951 instrument with a thermal analyzer 2100 system. TGA samples were heated at a rate of 20 °C min^{-1} in a purified nitrogen gas flow of 20 $\text{cm}^3\ \text{min}^{-1}$.

The reduction potentials were measured on a BAS-100 potentiostat equipped with a BAS PA-1 preamplifier in acetonitrile containing 0.1 M tetrabutylammonium perchlorate (TMAB) as the supporting electrolyte. A platinum working electrode, a Ag/Ag^+ non-aqueous reference electrode and a platinum wire as a counter electrode were employed in all experiments.

Quantum yield determinations

In this experiment, 1 ml of a 0.01 M solution of **2**–**3** in deuterated acetonitrile in a quartz cell (10 cm pathlength) was deoxygenated by purging with oxygen free nitrogen for 20 min, and then sealed. Irradiation was performed in a Rayonet reactor with filter coated Hg lamps (300–400 nm) at several time intervals. The maximum degree of photodecomposition achieved in deuterated acetonitrile was 20%. Parallel experiments were performed under the same conditions with the actinometer.[17] After irradiation was complete, the borate solution was transferred to an NMR tube and the spectrum acquired. Photodecomposition was measured by integrating the peak near 4.80 ppm due to methylene groups attached to the nitrogen atom (Fig. 1) with the absorption due to the aromatic protons used as the reference. Relative quantum yields of decomposition were calculated from the degree of conversion (decomposition) and the amount of absorbed radiation. We estimate an experimental error of 6%.

General procedure for synthesis of benzophenone ammonium bromide

To a solution of 4-(bromomethyl)benzophenone in chloroform–ether (1 : 1) a respective amine was slowly added in excess at room temperature with stirring. A white precipitate formed within 12 h (in some cases immediately). The precipitate was separated by filtration and dried. After recrystallization from suitable solvent, white crystals were obtained as product (70–80% yield).

***p*-(Benzoyl)benzyl-*N*,*N*,*N*-trimethylammonium bromide (1a).** Mp 220–222 °C (acetone). $\delta_H(\text{CD}_3\text{OD})$ 7.84 (m, 6H), 7.67 (d, *J* 7.0, 1H), 7.55 (t, *J* 7.0, 2H), 4.71 (s, 2H), 3.21 (s, 9H). $\delta_C(\text{CD}_3\text{OD}$, 50 MHz) 197.43, 140.75, 138.13, 134.25, 133.18, 131.42, 131.07, 129.67, 69.55, 53.42. (Calc. for $\text{C}_{17}\text{H}_{20}\text{BrNO}$: C, 61.11; H, 5.99; N, 4.19; Br, 23.92%. Found: C, 60.94; H, 5.92; N, 4.22; Br, 24.06).

***p*-(Benzoyl)benzyl-*N*,*N*,*N*-triethylammonium bromide (1b).** Mp 184–186 °C (acetone). $\delta_H(\text{CD}_3\text{OD})$ 7.83 (m, 6H), 7.67 (d, *J* 7.0, 1H), 7.56 (t, *J* 7.2, 2H), 4.63 (s, 2H) (q, *J* 7.4, 6H), 1.47 (t, *J* 7.4, 9H). $\delta_C(\text{CD}_3\text{OD}$, 50 MHz) 197.38, 140.66, 138.15, 134.25, 133.89, 132.93, 131.54, 131.09, 129.69, 60.77, 54.02, 8.22. (Calcd. for $\text{C}_{20}\text{H}_{26}\text{BrNO}$: C, 63.86; H, 6.91; N, 3.72; Br, 21.25%. Found: C, 63.92; H, 6.92; N, 3.68; Br, 21.33).

***p*-(Benzoyl)benzyl-*N*,*N*,*N*-tributylammonium bromide (1c).** Mp 160–161 °C (acetone). $\delta_H(\text{CD}_3\text{OD})$ 7.90 (m, 4H), 7.68 (m, 1H), 7.58 (m, 4H), 5.11 (s, 2H), 3.50 (m, 6H), 2.06 (m, 6H), 1.43 (m, 6H), 1.00 (t, *J* 7, 9H). $\delta_C(\text{CD}_3\text{OD}$, 50 MHz) 199.18, 142.61, 139.99, 136.11, 135.73, 134.91, 133.38, 132.91, 131.54, 64.40, 61.50, 27.02, 22.54, 15.86. (Calcd. for $\text{C}_{26}\text{H}_{38}\text{BrNO}$: C, 67.86; H, 8.26; Br, 17.37%. Found: C, 67.79; H, 8.28; Br, 17.43).

***p*-(Benzoyl)benzyl-*N*,*N*-dimethyl-*N*-phenylammonium bromide (1d).** Mp 132–133 °C (ethyl acetate–ethanol). $\delta_H(\text{CD}_3\text{CN})$ 7.67 (m, 12H), 7.26 (d, *J* 8.4, 2H), 5.17 (s, 2H), 3.66 (s, 6H). $\delta_C(\text{CD}_3\text{OD}$, 50 MHz) 197.33, 145.70, 140.71, 138.08, 134.22, 133.85, 133.05, 131.93, 131.56, 131.0, 130.96, 129.63, 122.66, 73.69, 54.19. (Calcd. for $\text{C}_{22}\text{H}_{22}\text{BrNO}$: C, 66.70; H, 5.55; N, 3.53%. Found: C, 66.90; H, 5.66; N, 3.49).

***p*-(Benzoyl)benzyl-*N*,*N*-dimethyl-*N*-tolylammonium bromide (1e).** Mp 112–114 °C (acetone). $\delta_H(\text{CD}_3\text{OD})$ 7.67 (m, 7H), 7.55 (d, *J* 7.4, 2H), 7.45 (d, *J* 8.4, 2H), 7.26 (d, *J* 8.4, 2H), 4.89 (s, 2H), 3.70 (s, 6H), 2.44 (s, 3H). $\delta_C(\text{CD}_3\text{OD}$, 50 MHz) 197.36, 143.28, 142.61, 140.61, 138.06, 134.20, 133.89, 133.20, 131.89, 130.20, 130.92, 129.63, 122.43, 73.55, 54.28, 20.85. (Calcd. for $\text{C}_{23}\text{H}_{24}\text{BrNO}$: C, 67.35; H, 5.85; N, 3.41; Br, 19.48%. Found: C, 67.38; H, 5.85; N, 3.39; Br, 19.56).

***p*-(Benzoyl)benzyl-*N*,*N*-dimethyl-*N*-(butanoyloxyethyl)-ammonium bromide (1g).** Mp 152–154 °C (ethyl acetate–ethanol). $\delta_H(\text{CD}_3\text{CN})$ 7.80 (m, 4H, aromatic protons *ortho* to C=O), 7.67 (m, 1H, aromatic proton *para* to C=O), 7.55 (m, 4H, aromatic protons *meta* to C=O), 4.98 (s, 2H, Ar–CH_2), 4.58 (s, 2H, O–CH_2), 3.88 (m, 2H, N–CH_2), 3.21 (s, 6H), 2.60 (m, 1H), 1.16 (d, 6H). (Calcd. for $\text{C}_{22}\text{H}_{28}\text{BrNO}_3$: C, 60.86; H, 6.45; N, 3.22%. Found: C, 60.62; H, 6.40; N, 3.16).

General procedure for synthesis of benzophenone ammonium borate

The ammonium bromide salt was dissolved in a minimum amount of water and insoluble materials, if present, filtered. An equivalent amount of the lithium salt of triphenyl-*n*-butylborate or sodium salt of tetraphenylborate in water was added dropwise at room temperature with stirring. Thick white precipitate formed immediately. This was diluted by adding water and separated by filtration. After recrystallization from organic solvents, borate complexes were obtained as white needles (68–75% yield).

***p*-(Benzoyl)benzyl-*N*,*N*,*N*-trimethylammonium tetraphenylborate (2a).** Mp 201–202 °C (ethanol–acetonitrile). δ_H(acetone) 7.83 (m, 4H), 7.68 (m, 1H), 7.58 (m, 4H), 7.27 (br s, 8H, *ortho* to B), 6.99 (t, *J* 7.0, 8H, *meta* to B), 6.83 (t, *J* 7.0, 4H, *para* to B), 4.37 (s, 2H), 2.94 (s, 9H). (Calcd. for $C_{41}H_{40}BNO$: C, 85.90; H, 6.98; N, 2.44%. Found: C, 86.00; H, 6.97; N, 2.49).

***p*-(Benzoyl)benzyl-*N*,*N*,*N*-triethylammonium tetraphenylborate (2b).** Mp 226–227 °C (ethanol–acetonitrile). δ_H(CD_3CN) 7.81 (m, 4H, *ortho* to carbonyl), 7.60 (m, 5H, *meta* and *para* to carbonyl), 7.26 (m, 8H, *ortho* to B), 6.99 (t, *J* 7, 8H, *meta* to B), 6.82 (t, *J* 7.0, 4H, *para* to B), 4.36 (s, 2H), 3.17 (q, *J* 7.2, 6H), 1.34 (t, *J* 7.4, 9H). (Calcd. for $C_{44}H_{46}BNO$: C, 85.90; H, 7.47; N, 2.29%. Found: C, 86.02; H, 7.46; N, 2.30).

***p*-(Benzoyl)benzyl-*N*,*N*,*N*-tributylammonium triphenyl-*n*-butylborate (3c).** Mp 133–134 °C (ethyl acetate–ethanol). δ_H(acetone) 7.92 (d, *J* 8.4, 2H), 7.80 (m, 4H), 7.68 (m, 1H), 7.59 (t, *J* 7.6, 2H), 7.35 (m, 6H, *ortho* to B), 6.89 (m, 6H, *meta* to B), 6.75 (t, *J* 7.4, 3H, *para* to B), 4.73 (s, 2H, N–CH_2–Ph), 3.36 (m, 6H, N–CH_2–CH_2), 1.95 (m, 8H, N–CH_2–CH_2, B–CH_2), 1.45 (m, 6H, N–C_2H_4–CH_2), 1.23 (m, 2H, BCH_2–CH_2), 1.02 (m, 11H, N–CH_3 and B–C_2H_4–CH_2), 0.7 (t, *J* 7.4, 3H, B–CH_3). δ_{11B}(DMSO): −29.41. (Calcd. for $C_{48}H_{62}BNO$: C, 84.87; H, 9.13; N, 2.06%. Found: C, 84.93; H, 9.21; N, 2.00).

***p*-(Benzoyl)benzyl-*N*,*N*,*N*-tributylammonium tetraphenylborate (2c).** Mp 197–198 °C (ethanol–acetone). δ_H(CD_3CN) 7.83 (m, 4H), 7.68 (m, 1H), 7.54 (m, 4H), 7.26 (m, 8H, *ortho* to B), 6.99 (t, *J* 7.4, 8H, *meta* to B), 6.83 (t, *J* 7.4, 4H, *para* to B), 4.39 (s, 2H), 3.05 (m, 6H), 1.75 (m, 6H), 1.37 (m, 6H), 0.99 (t, *J* 7.4, 9H). (Calcd. for $C_{50}H_{58}BNO$: C, 85.87; H, 8.29; N, 2.00%. Found: C, 85.87; H, 8.41; N, 2.08).

***p*-(Benzoyl)benzyl-*N*,*N*-dimethyl-*N*-phenylammonium triphenyl-*n*-butylborate (3d).** Mp 150–152 °C (ethyl acetate–ethanol). δ_H(CD_3CN) 7.60 (m, 12H), 7.27 (m, 6H), 7.14 (d, *J* 8.4, 2H), 6.96 (m, 6H), 6.80 (m, 3H), 4.83 (s, 2H), 3.47 (s, 6H), 1.21 (m, 2H), 0.91 (m, 4H), 0.78 (t, *J* 7.2, 3H). (Calcd. for $C_{44}H_{46}BNO$: C, 85.90; H, 7.47; N, 2.29%. Found: C, 85.97; H, 7.48; N, 2.31).

***p*-(Benzoyl)benzyl-*N*,*N*-dimethyl-*N*-tolylammonium triphenyl-*n*-butylborate (3e).** Mp 123–125 °C (ethanol). δ_H(acetone) 7.73 (m, 7H, benzophenone moiety), 7.56 (d, *J* 7.4, 2H, aromatic attached to N), 7.46 (d, *J* 7.4, 2H, aromatic attached to N), 7.35 (m, 8H, *ortho* to B and benzophenone moiety), 6.90 (t, *J* 7.2, 6H, *meta* to B), 6.78 (m, 3H, *para* to B), 5.16 (s, 2H), 3.73 (s, 6H), 2.42 (s, 3H), 1.26 (m, 2H, B–CH_2), 1.08 (m, 4H), 0.77 (t, *J* 7.5, 3H). (Calcd. for $C_{45}H_{48}BNO$: C, 85.89; H, 7.63; N, 2.22%. Found: C, 86.15; H, 7.60; N, 2.21).

***p*-(Benzoyl)benzyl-*N*,*N*-dimethyl-*N*-tolylammonium tetraphenylborate (2e).** Mp 188–189 °C (ethanol). δ_H(acetone) 7.77–7.62 (m, 7H, benzophenone moiety), 7.57 (d, 7.4, 2H, aromatic attached to N), 7.47 (d, *J* 7.4, 2H, aromatic attached to N), 7.35 (m, 10H, *ortho* to B and benzophenone moiety), 6.92 (t, *J* 7.4, 8H, *meta* to B), 6.78 (t, *J* 7.0, 4H, *para* to B), 5.19 (s, 2H), 3.75 (s, 6H), 2.42 (s, 3H). (Calcd. for $C_{47}H_{44}BNO$: C, 86.94; H, 6.78; N, 2.16%. Found: C, 87.22; H, 6.78; N, 2.17).

***p*-(Benzoyl)benzyl-*N*,*N*-dimethyl-*N*-(butanoyloxyethyl)-ammonium triphenyl-*n*-butylborate (3g).** Mp 110–111 °C (ethyl acetate). δ_H(CD_3CN) 7.83 (t, *J* 8.0, 4H, aromatic protons *ortho* to C=O), 7.70 (m, 1H, aromatic proton *para* to C=O), 7.59 (m, 4H, aromatic protons *meta* to C=O), 7.26 (m, 6H, *ortho* to B), 6.96 (t, *J* 8.0, 6H, *meta* to B), 6.79 (t, *J* 6.5, 3H, *para* to B), 4.51 (s, 2H, Ar–CH_2), 4.49 (m, 2H, O–CH_2), 3.65 (m, 2H, N–CH_2), 2.94 (s, 6H, N–CH_3), 2.62 (m, 1H), 1.93 (m, 2H, B–CH_2), 1.16 (d, 6H), 0.90 (m, 4H), 0.77 (t, *J* 6.5, 3H). (Calcd. for $C_{44}H_{52}BNO_3$: C, 80.89;. H, 7.96; N, 2.14%. Found: C, 80.72; H, 7.93; N, 2.17).

***p*-(Benzoyl)benzyl-*N*,*N*-dimethyl-*N*-(*p*-bromophenyl)-ammonium triphenyl-*n*-butylborate (3f).** Mp 76–78 °C (ethanol–hexanes). δ_H(CD_3CN) 7.70 (m, 6H), 7.55 (m, 3H), 7.45 (d, *J* 8.4, 2H), 7.27 (m, 6H, *ortho* to B), 7.16 (d, *J* 8.4, 2H), 6.96 (t, *J* 7.2, 6H, *meta* to B), 6.79 (t, *J* 7.4, 3H, *para* to B), 4.79 (s, 2H), 3.43 (s, 6H), 1.21 (m, 2H, B–CH_2), 0.91 (m, 4H), 0.77 (t, *J* 7.4, 3H). (Calcd. for $C_{44}H_{45}BNBrO$: C, 76.13; H, 6.48; N, 2.02; Br, 11.51%. Found: C, 75.91; H, 6.45; N, 2.00; Br, 11.67).

***p*-(Benzoyl)benzyl-*N*,*N*-dimethyl-*N*-(*p*-bromophenyl)-ammonium tetraphenylborate (2f).** Mp 108–110 °C (ethanol–acetone). δ_H(CD_3CN) 7.72 (m, 6H, benzophenone moiety), 7.59 (m, 3H, benzophenone moiety), 7.46 (d, *J* 8.2, 2H), 7.26 (m, 8H, *ortho* to B), 7.17 (d, *J* 8.2, 2H), 6.99 (t, *J* 7.4, 8H, *meta* to B), 6.83 (t, *J* 7.0, 4H, *para* to B), 4.82 (s, 2H), 3.45 (s, 6H). (Calcd. for $C_{46}H_{41}BNBrO$: C, 77.36; H, 5.74; N, 1.96; Br, 11.19%. Found: C, 76.94; H, 5.72; N, 1.96; Br, 11.30).

***p*-(Benzoyl)benzyl-*N*,*N*,*N*-tributylammonium tetrafluoroborate (7c).** 0.21 g (0.45 mmol) of *p*-(benzoyl)benzyl-*N*,*N*,*N*-tributylammonium bromide was dissolved in 10 ml water at 50–55 °C. Insoluble dust materials were filtered out. 0.5 ml 48% by wt. of fluoroboric acid in water was added at 50 °C drop by drop with stirring. Precipitate was formed immediately. 10 ml water was added to it and stirred for 30 min. Product was filtered and washed with water. 0.16 g (80% yield) of white solid was obtained: mp 78–79 °C. (Calcd. for $C_{26}H_{38}BF_4NO$: C, 66.86; H, 8.14; Br, 0.0%. Found: C, 66.93; H, 8.19; Br, 0.0).

Acknowledgements

We thank the National Science Foundation (DMR-9526755) and the Office of Naval Research (Navy N00014-91-J-1921) for financial support of this work and Dr George S. Hammond for useful discussions. Alexander Mejiritski was a Fellow of the McMaster Endowment. Adrian Lungu was supported by a grant from Argonne National Laboratories.

References

1 Contribution #352 from the Center for Photochemical Sciences.
2 J. M. J. Frechet, *Pure Appl. Chem.*, 1992, **64**, 1239.
3 (*a*) A. Mochizuki, T. Teranishi and M. Ueda, *Macromolecules*, 1995, **28**, 365; (*b*) J. D. Davies, W. H. Daly, Z. Wang and C. Kutal, *Chem. Mater.*, 1996, **8**, 850; (*c*) D. Y. Pai, S. S. Rodriguez, K. J. Chetham, G. S. Calabrese and R. F. Sinta, Eur. Patent 0 555 749/1993; *Chem. Abstr.*, 1994, **120**, 65918w.
4 (*a*) M. K. Leung, J. M. J. Frechet, J. F. Cameron and C. G. Willson, *Macromolecules*, 1995, **28**, 4693; (*b*) D. R. McKean, G. M. Wallraff, W. Volksen, N. P. Hacker, M. I. Sanchez and J. W. Labadie, *Polym. Mater. Sci. Eng.*, 1992, **66**, 237.
5 (*a*) K. Ito, M. Nishimura, M. Sashio and M. Tsunooka, *J. Polym. Sci., Polym. Chem.*, 1994, **32**, 2177; (*b*) K.-H. Sonk, M. Tsunooka and M. Tanaka, *J. Photochem. Photobiol. A*, 1988, **44**, 197; (*c*) C. Kutal and C. G. Willson, *J. Electrochem. Soc.*, 1987, **134**, 2280.
6 (*a*) J. F. Cameron and J. M. J. Frechet, *J. Am. Chem. Soc.*, 1991, **113**, 4303; (*b*) J. F. Cameron and J. M. J. Frechet, *J. Org. Chem.*, 1990, **55**, 5919; (*c*) J. F. Cameron, C. G. Willson and J. M. J. Frechet, *J. Chem. Soc., Chem. Commun.*, 1995, 923; (*d*) M. C. Pirrung and C. Y. Huang, *Tetrahedron Lett.*, 1995, **36**, 5883; (*e*) J. F. Cameron, C. G. Willson and J. M. J. Frechet, *J. Am. Chem. Soc.*, 1996, **118**, 12 925.
7 J. E. Hanson, K. H. Jensen, N. Garguilo, D. Motta, D. A. Pingor, A. E. Novembre, D. A. Mixon, J. M. Kometani and C. Knurek, in *Microelectronics Technology*; *ACS Symp. Ser. 614*, 1995, p. 137.
8 S. E. Drewes and G. H. P. Roos, *Tetrahedron*, 1988, **44**, 4653.
9 (*a*) T. Sakurai, S. Kojima and H. Inoue, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 3141; (*b*) T. Sakurai, S. Yamada and H. Inoue, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 2666.
10 (*a*) J. Y. Lan and G. B. Schuster, *J. Am. Chem. Soc.*, 1985, **107**, 6710; (*b*) S. Chatterjee, P. Gottschalk, P. D. David and G. B. Schuster, *J. Am. Chem. Soc.*, 1988, **110**, 2326; (*c*) S. Chatterjee, P. D. Davis, P. Gottschalk, M. E. Kurtz, B. Sauerwein, X. Yang and G. Schuster, *J. Am. Chem. Soc.*, 1990, **112**, 6329.
11 (*a*) A. Mejiritski, A. Y. Polykarpov, A. M. Sarker and D. C. Neckers, *Chem. Mater.*, 1996, **8**, 1360; (*b*) A. M. Sarker, A. Mejiritski, B. R. Wheaton and D. C. Neckers, *Macromolecules*, 1997, **30**, 2269; (*c*) A. Mejiritski, A. M. Sarker, B. R. Wheaton and D. C. Neckers, *Chem. Mater.*, 1997, **9**, 1488.

12 (*a*) D. F. Eaton, *Adv. Photochem.*, 1986, **13**, 427; (*b*) M. C. Etter, B. N. Holmes, R. B. Kress and G. Filipovich, *Isr. J. Chem.*, 1985, **25**, 264; (*c*) A. M. Sarker, A. Lungu and D. C. Neckers, *Macromolecules*, 1996, **29**, 8047.

13 (*a*) S. Hassoon, A. Sarker, M. A. J. Rodgers and D. C. Neckers, *J. Am. Chem. Soc.*, 1995, **117**, 11369; (*b*) S. Hassoon, A. Sarker, A. Y. Polykarpov, M. A. J. Rodgers and D. C. Neckers, *J. Phys. Chem.*, 1996, **100**, 12 386.

14 E_{ox} (Br^-) = 1.5 V (irreversible) *versus* SCE; H. G. O. Becker, G. Israel, B. Oertel and H. V. Vetter, *J. Prakt. Chem.*, 1985, **327**, 399.

15 I. Carmichael and G. S. J. Hug, *J. Phys. Chem. Ref. Data*, 1986, **15**, 1.

16 P. J. Wagner, R. J. Truman, A. E. Puchalski and R. Wake, *J. Am. Chem. Soc.*, 1986, **108**, 7727.

17 W. M. Moore, G. S. Hammond and R. P. Foss, *J. Am. Chem. Soc.*, 1961, **83**, 2789.

18 E_{ox} (n-$BuPh_3B^-$) = 0.70 V (irreversible) *versus* SCE and E_{ox} (Ph_4B^-) = 0.90 V (irreversible) *versus* SCE.[10c]

19 S. Murphy, X. Yang and G. B. Schuster, *J. Org. Chem.*, 1995, **60**, 2411.

20 S. T. Murphy, C. Zou, J. B. Mierj, R. M. Ballew, D. C. Dlott and G. B. Schuster, *J. Phys. Chem.*, 1993, **97**, 13 152.

21 H. C. Brown, *Boranes in Organic Chemistry*, Cornell University Press, Ithaca, NY, 1972, ch. 5–8.

22 A. Mejiritski, A. Y. Polykarpov, A. M. Sarker and D. C. Neckers, *J. Photochem. Photobiol. A*, 1997, **108**, 289.

23 (*a*) H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill Book Company, New York, 1967; (*b*) T. Nishikubo, E. Takehara and A. Kamayama, *J. Polym. Sci.*, *Polym. Chem.*, 1993, **31**, 3013.

24 The triplet state of **7c** is quenched by tetrabutylborate tetrabutylammonium salt in acetonitrile at a rate of 5.65×10^9 M^{-1} s^{-1}. Previously, similar quenching was observed by triphenyl-*n*-butylborate at the diffusion controlled limit (8.8×10^9 M^{-1} s^{-1} in acetonitrile).[13b]

25 $\Delta G = -0.62$ eV for **2c** as calculated from Rehm–Weller equation: D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259.

Paper 8/00469B