Photochemical Properties Of 4-Benzoylbenzylammonium Borates

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Several new 4-benzoylbenzylammonium borates were prepared in order to study their photochemical properties. It was found that a quantitative yield of biphenyl and a small amount of benzene are formed from photolysis of the title compounds as tetraphenylborates in the absence of oxygen. In addition, amines and methylbenzophenone were detected after the steady-state photolysis. The quantum yields of the photolysis of the title compounds and the formation of biphenyl, amines, and methylbenzophenone were determined. Radical trapping experiments showed that the photogenerated amine is converted to an α-aminoalkyl radical, which is an important initiating species for the polymerization of acrylates when tetraphenylborate is chosen as a counteranion. It was found that even 1-(4-benzoylbenzyl)pyridinium tetraphenylborate is an active photoinitiator, however, indicating that α-aminoalkyl radical is not the only initiating species formed from 4-benzoylbenzylammonium tetraphenylborates. The effect of structure on initiating activity was determined and discussed.

Introduction

Tetraalkylammonium butyltriphenylborate salts have been used extensively as coinitiators for acrylate polymerization.[2−4] When paired with a reactive light absorber such as a carbocyanine dye, butyltriphenylborates undergo photoinduced single-electron transfer but only when dissolved in solvents in which they form tight ion pairs.[5−7] The resulting oxidized borate, the butyltriphenylboranyl radical, has a lifetime of about 250 fs[8] before it decomposes to butyl radical and, presumably, triphenylboron. The butyl radical there formed initiates the chain polymerization of the acrylate monomer. The cyanine cation radical appears to play no role in the polymerization in the simplest cases, though there is limited experimental information on this point.

Recently, we and others have isolated onium borate salts (e.g., diphenyliodonium butyltriphenylborate)[9,10] and, after light absorption in the charge transfer complex there formed and subsequent single-electron transfer, both the onium cation and borate anion produce free radicals. One to one, as well as more complex, adducts of these radicals have been isolated with methyl methacrylate.[9]

Tetraalkylammonium tetraarylborates, in contrast, have been reported to be inefficient coinitiators when used as electron-transfer donors in bimolecular processes.[7,9] However, we have reported that when paired with ammonium ions that are unstable after reduction, even tetraphenylborate salts may be viable sources of radicals for acrylate polymerization.[11] Ketoneammonium tetraphenylborates are almost as good initiators as ketoneammonium triphenylalkylborates.[12,13] Since these systems are substantially better initiators than their bimolecular counterparts, we have postulated that the α-aminoalkyl radical formed in a secondary process from the amine that is formed is also an important initiating species in these cases. This hypothesis could explain why ketoneammonium tetraphenylborates are initiators but does not explain why there is so little difference between ketoneammonium tetraphenylborates and their butyltriphenylborate counterparts.

In this paper, we report studies of the photochemistry and photoreactivity of such borates with particular concentration on the structure of the amine in 4-benzoylbenzylammonium borates that differ in no other way. The objective is to identify all of the radical, hence initiating species formed, and to outline the differences in reactivity that result.

Results and Discussion

Preparations: Activity as Photoinitiators. The procedure for the preparation of the borates is similar to that described previously.[11] From 4-bromomethylbenzophenone, different amines were used to produce 4-benzoylbenzylammonium bromides. The target borates were obtained by metathesis with either the sodium borate salts or the tetramethylammonium borate salts. *N*-benzoylbenzyl-*N*,*N*-dimethylbenzylammonium butyltriphenylborate (DMBzBB) and *N*-benzoylbenzyl-*N*,*N*-

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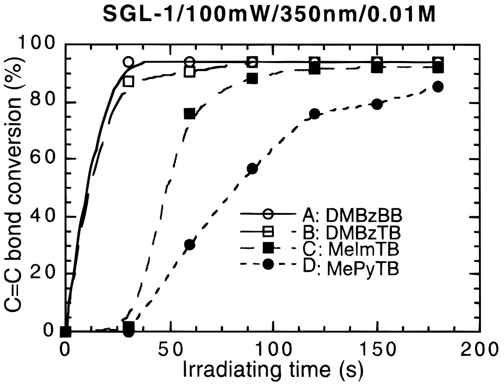
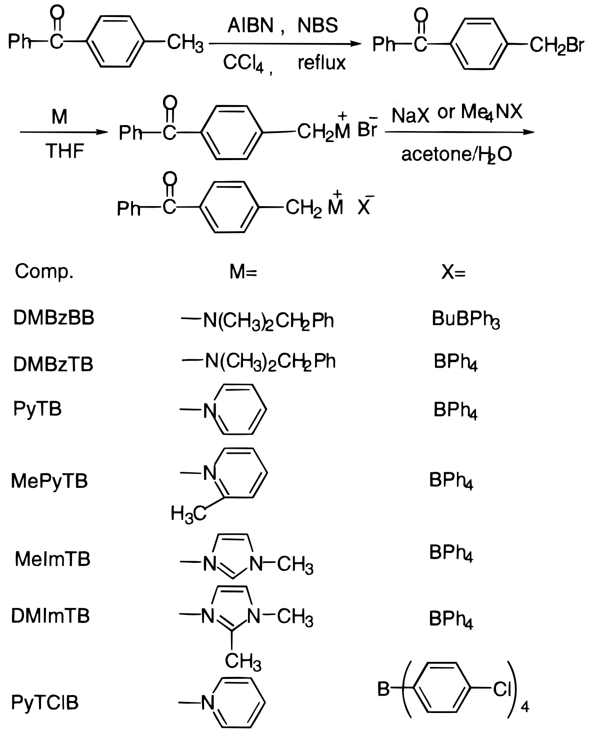


Figure 1. Photopolymerization of SGL-1 resin with 0.01 M borates.

Scheme 1



dimethylbenzylammonium tetraphenylborate (DMBzTB)-were prepared to compare the ketoneammonium butyltriphenylborates and ketoneammonium tertaphenylborates as photoinitiators. (Scheme 1). We suspected that α-aminoalkyl radicals formed in a secondary photoprocess from the amine to be important initiating species and that these α-aminoalkyl radicals initiate polymerization. In order to avoid formation of such an α-aminoalkyl radical, 1-(4-benzoylbenzyl)pyridinium tetraphenylborate (PyTB), 1-(4-benzoylbenzyl)-2-methylpyridinium tetraphenylborate (MePyTB), 1-(4-benzoylbenzyl)-3-methylimidazolium tetraphenylborate (MeImTB), and 1-(4-benzoylbenzyl)-2,3-dimethylimidazolium tetraphenylborate (DMImTB) were prepared. In addition, 1-(4-benzoylbenzyl)pyridinium tetrakis(4-chlorophenyl)borate (PyTClB) was prepared to determine the source of the biphenyl and benzene in these systems.

DMBzBB, DMBzTB, MeImTB, and MePyTB were tested as photoinitiators in a standard acrylate resin (Figure 1). PyTB and DMImTB were insoluble in the standard resin. FTIR was used to measure double-bond conversion in the photopolymer-forming processes.

Steady-State Photolysis. Each compound was irradiated at 350 nm. Biphenyl, methylbenzophenone, the amines, and a small amount of benzene were formed. 4-Pentylbenzophenone, the coupling product, formed only in the case of DMBzBB. No unexpected side products were detected even after several hours of irradiation. Quantum yields of the photolysis of the title compounds, and for the formation of three major photolytic products, were determined.

DMBzBB and DMBzTB have much higher quantum yields of decomposition than either PyTB or MeImTB, Table 1. We believe the introduction of the methyl group in the amine elevates these quantum yields in that dimethylbenzylamine is more sterically crowded than either pyridine or imidazole. As Schuster has reported,[8] the lifetime of the butyltriphenylboranyl radical (250 fs) is shorter than that of the tetraphenylboranyl radical (40 ps). Thus, the butyltriphenylborates have higher quantum yields for decomposition than tetraphenylborates even when paired with the same chromophore.[11,13] When tetraphenylborate was used as the counterion, biphenyl was the major product, Table 1. This is not unexpected since both electrochemical[14,15] and photochemical studies[16] have demonstrated that the tetraphenylborate salts give quantitative amounts of biphenyl. We have found that each of the tetraphenylborates gives almost the same quantum yield of biphenyl formation and that this is independent of the structure of the amine. This suggests that the C−N cleavage after electron transfer is faster than either back-electron transfer or the decomposition of tetraphenylboranyl radical.

Polykarpov previously observed[17] biphenyl formation from the photooxidation of butyltriphenylborate or dibutyldiphenylborate by benzophenone triplets. After a long irradiation, small amounts of biphenyl are also formed likely as secondary products from the primary boron-containing products. Thus, more than quantitative quantities of biphenyl may result under our experimental conditions.

Methylbenzophenone was another major product. In the case of DMBzBB, the high photolysis quantum yield ($\phi_{\mathrm{photolysis}}$) and high quantum yield (ϕ_{amine}) of amine formation indicate a strong possibility of rate-limiting C−N bond cleavage. It is a little surprising that the quantum yield of formation of methylbenzophenone (ϕ_{MeBP}) is low.

Amine was detected from each borate photolyzed. Since it is well known that triphenylborane or diphenylborane form acid/base complexes with amines and, in the case of MeImTB and DMImTB, the GC peak of the imidazole derivatives was too broad and flat to be integrated, these results must be considered nonquantitative likely because the imidazole probably forms a relatively stable complex with one of the Lewis acid, boron-containing products. In the case of DMBzBB and DMBzTB, the concentration of dimethylbenzylamine reaches a maximum after 20 min of irradiation, Figure 2. With an increase in the irradiation time, this concentration decreases gradually, suggesting that the electron-transfer reaction occurs between the benzophenone chromophore (from unreacted starting materials and the newly pro-

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Table 1. Quantum Yields of the Photolysis of the Title Compounds and the Quantum Yields of the Formation of Three Major Photolytic Products

compds	$\phi_{\text{photolysis}}$ by NMR	ϕ_{amine} by GC	ϕ_{MeBP} by GC	ϕ_{biphenyl} by GC
PyTB	0.42	0.07	0.07	0.42 (103)[a]
MePyTB	0.50	0.14	0.07	0.40 (106)
MeImTB	0.43		0.16	0.42 (112)
DMImTB	0.56		0.20	0.40 (104)
DMBzTB	0.61	0.45	0.16	0.41 (102)
DMBzBB	0.67	0.54	0.02	0.21 (26)
PyTBCl	0.09	0.01	0.02	0.07 (86)
BPPyBr		no photoreaction in 1 h irradiation		

[a] The number in parentheses is the amount (%) of biphenyl formed after 14 h irradiation.

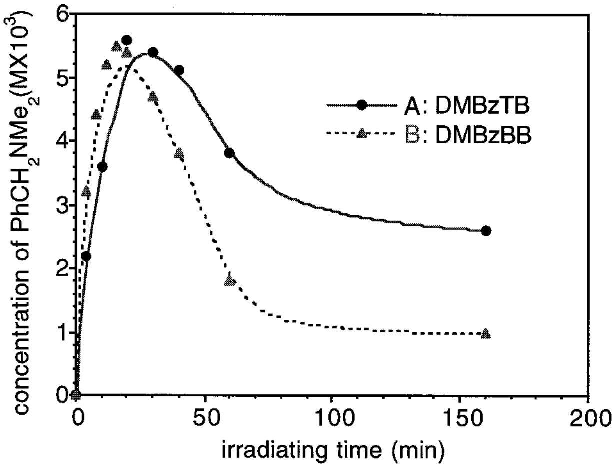


Figure 2. Formation of dimethylbenzylamine in the photolysis of DMBzTB and DMBzBB.

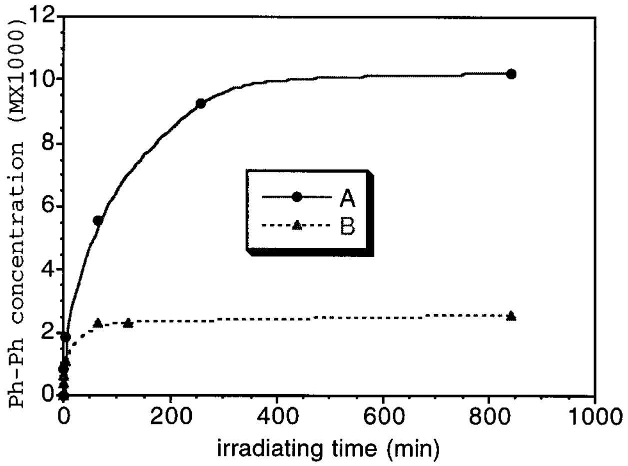
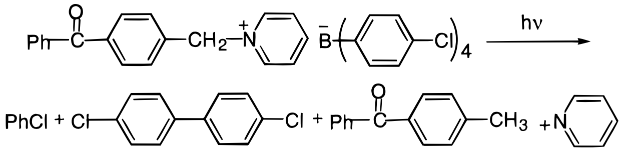


Figure 3. Biphenyl formation in the photolysis of DMBzTB (A) and DMBzBB (B).

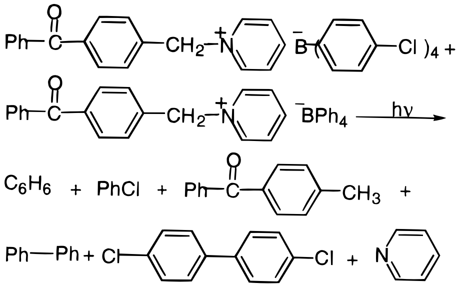
duced methylbenzophenone) and the photogenerated dimethylbenzylamine. This reaction produces an α-aminoalkyl radical as an initiating species.

When butyltriphenylborate is used as the counteranion, the formation of butyl radical as the main elimination product from the borate is to be anticipated[5,18] The yields of biphenyl as a function of irradiation time from DMBzBB and DMBzTB are shown in Figure 3. The fact that most of the biphenyl is formed at an early stage of the irradiation of DMBzBB indicates that most of the biphenyl is formed from the butyltriphenylboranyl radical directly.

Scheme 2



Scheme 3



Benzene was also detected after long periods of irradiation. When PyTClB was irradiated, only chlorobenzene was detected. This indicates the benzene is not formed from the benzophenone chromophore, but from the borate (Scheme 2).

That 4,4'-dichlorobiphenyl is formed at room temperature in the absence of oxygen is demonstrated by comparing the NMR (both proton and carbon) of the photolysis mixture with that of pure 4,4'-dichlorobiphenyl, which we obtained from the photolysis of PyTClB. As expected, the electron-withdrawing Cl atom retards the electron-transfer process.

Crossover experiments employing a 1:1 mixture of PyTB and PyTClB show that only biphenyl and 4,4'-dichlorobiphenyl form under these conditions. Coinciding with Schuster's results, [16] this means that the biphenyl is formed directly from the tetraphenylboranyl radical, and the bond between the rings of those biphenyls are formed from carbons that are bonded to boron. It also demonstrated that although PyTClB decomposes more slowly, it undergoes the same decomposition as the other borates upon irradiation (Scheme 3).

Radical Trapping. When paired with electron-acceptor chromophores, alkyltriarylborate salts can be used as free radical initiators with either UV or visible light. Butyl radicals have been shown to be the primary initiating species when butyltriphenylborate was used as the counteranion.[5,9,17,18] In a trapping experiment in which DMBzBB was photolyzed in the presence of methyl methacrylate (MMA), methyl 2-methylheptanoate (*n*-Bu-MMA) and methyl 2,4-dimethylhexanoate (*s*-Bu-MMA) are formed from one butyl radical or a second butyl radical addition to MMA by comparison of the MS spectra of these products and the known compounds.[9] Both

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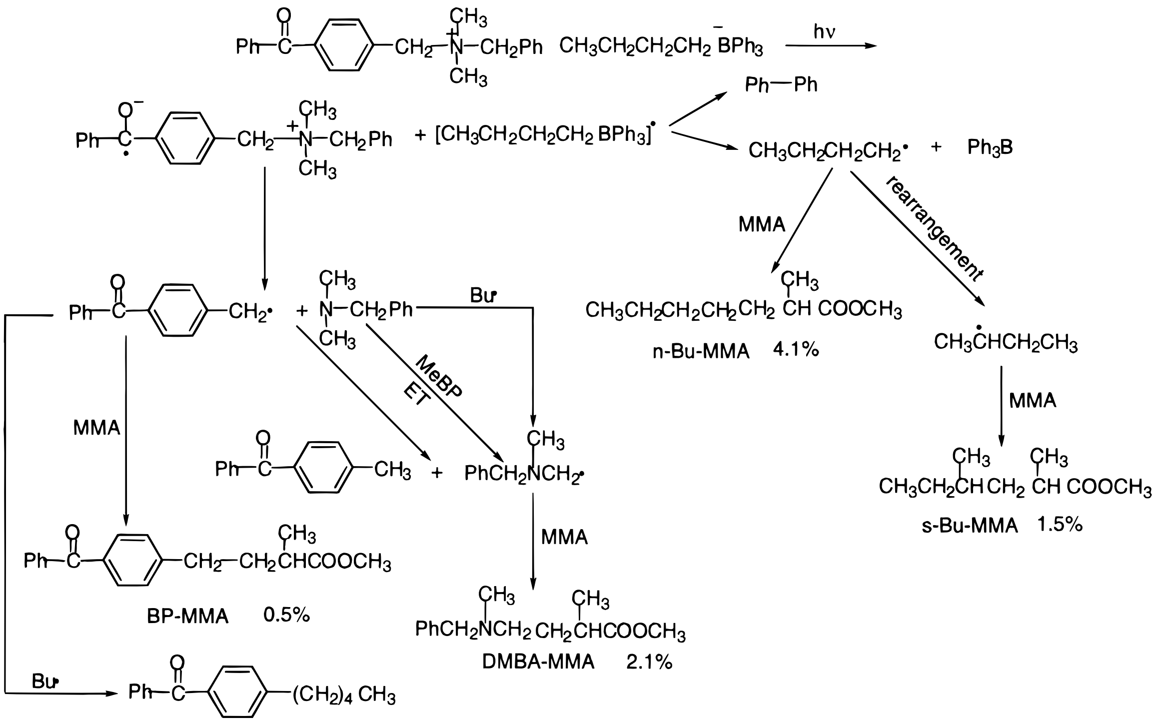
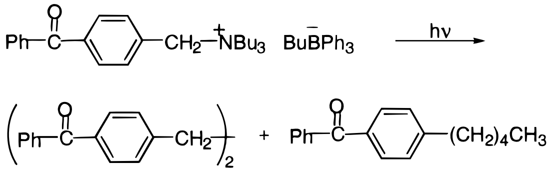
Scheme 4. Results of Radical Trapping of DMBzBB



Scheme 5



radical adducts with two and three molecules of MMA were also found.

The other two products are formed from the addition of the *N*,*N*-dimethylbenzylamine radical with MMA, [methyl 2-methyl-4-(*N*-methylbenzylamino)butanoate (DMBA−MMA)] and from the benzoylbenzyl radical with MMA, [methyl 2-methyl-4-[4-(benzoylphenyl)]butanoate (BP−MMA)]. Previous work[11] had suggested the existence of benzoylbenzyl radical because the coupling product of two such radicals was detected, Scheme 5. In the MS spectrum of DMBA−MMA, the $m/z = 91$ peak (benzyl cation) is the base peak. Thus, the structure of DMBA−MMA is that shown in Scheme 4. Although the *N*,*N*-dimethylaminobenzyl radical is more stable and more easy to form than the *N*-benzyl-*N*-methylaminomethyl radical, the fomer may be too crowded to be trapped by MMA. The *N*-benzyl-*N*-methylaminomethyl radical may be formed from electron transfer of DMBA to methylbenzophenone (MeBP) or formed from the hydrogen abstraction by benzoylbenzyl or butyl radicals.

Small quantities of benzobenzyl radical coupling product with butyl radical are formed from DMBzBB. No isomers of 4-pentylbenzophenone were observed. The low quantum yield of methylbenzophenone formation (Table 1) and small trapping yield of benzobenzyl radical in the case of DMBzBB suggest these coupling processes (see Scheme 5) likely decrease the initiating activity of DMBzBB. This suggests the reason there is little activity difference between DMBzTB and DMBzBB. The rearrangement of the butyl radical occurs when it escapes from the solvent cage before it is trapped by MMA.

Table 2. Radical Products Detected by GC−MS

	Ph−Ph	Ph−MMA	BP−MMA	DMBA−MMA
PhTB	100	0.3	1.8	
MePyTB	100	2.4	3.2	
MelmTB	100	0.3	2.4	
DMlmTB	100	0.4	2.8	
DMBzTB	100	0.8	1.6	4.8
DMBzBB[a]	25	trace	0.5	2.1 Bu−MMA 5.6
PyTCIB	100[b]	0.7[c]	0.9	

[a] Choose the amount of biphenyl formed in the case of DMBzTB as external standard. [b] 4,4′-Dichlorobiphenyl. [c] Methyl 3-(4-chlorophenyl)-2-methylpropanoate.

In the case of DMBzTB, free radical adducts identical to those of MMA were observed. The observation of the amine−MMA adduct also implicates the α-aminoalkyl radical as the initiating species in this case (Table 2). A small amount of phenyl adduct, methyl 2-methyl-3-phenylpropanoate (Ph-MMA), was also detected. Phenyl adducts with two molecules of MMA, namely dimethyl 2,5-dimethyl-3-phenylhexandioate and dimethyl 2,4-dimethyl-2-benzylpentandioate, have also been detected. When PyTClB was irradiated under similar conditions, methyl 3-(4-chlorophenyl)-2-methyl-3-phenylpropanoate as well as 4-chlorophenyl adducts with two molecules of MMA were observed, but no phenyl radical adduct was detected. When a reaction mixture of 4,4'-dimethylbenzophenone (0.013 M), sodium tetraphenylborate (0.013 M), and MMA (0.13 M) was irradiated in the same solvents under identical conditions, similar Ph−MMA adducts (0.5% compared to biphenyl) were obtained. All these results mean Ph-MMA is formed from phenyl radical addition with MMA and the phenyl arising from the borate moieties and not from the benzophenone chromophore. Whether the phenyl radical as well as the benzene form directly from the tetraphenylboranyl radical or from the secondary boron-containing product is still unknown and under study.

Therefore, according to the results of radical-trapping experiments and the relative activity as a photoinitiator, we suggest that the α-aminoalkyl radical is the active initiating species. Several other radicals that were investigated also have the ability to initiate the polymerization of acrylates, and this may explain why some compounds such as MePyTB also show some activity as initiators. This also explains why a slight difference was observed between ketylammonium butyltriphenylborate and tetraphenylborate in terms of photoinitiating capability.

Conclusions

Direct formation of biphenyl from the butyltriphenylboranyl radical has been demonstrated. The α-aminoalkyl radical and other radicals formed were successfully trapped, indicating the α-aminoalkyl radical is not the only initiating species, but the α-aminoalkyl radical is the most active initiating species formed from these compounds according to the yields of radical adducts and rate of polymerization.

Experimental Section

General Procedures. ^{11}B NMR spectra were recorded in DMSO-d_6 with B(OMe)$_3$ ($\delta = 0$ ppm) as an external standard. The GC was programmed from 50 to 200 °C at a heating rate of 5 °C/min with the injection port temperature at 150 °C. Other determinations were performed in accord with the literature.[9]

Photopolymerizations. MePyTB, MeImTB, DMBzTB, and DMBzBB were added, respectively, to SGL-1 resin[9] at a concentration of 1×10^{-2} M and kept at 40-50 °C for 1 day in an ultrasonic apparatus to dissolve the initiator completely in the resin. A drop of formulated resin was placed between rectangular NaCl plates using a 15 μm Teflon spacer and then irradiated using a 200 W medium-pressure Hg lamp as the UV light source.

Double-bond conversion (DC) was monitored by following the disappearance of the peak at 811 cm^{-1} (corresponding to C−H out of plane vibration of methacrylate) in the FTIR absorption spectrum and calculated according to the formula

$$\mathrm{DC} = (A_0 - A_i)/A_0 \times 100\%$$

where A is the absorption adjusted by using the absorption of C−H stretching vibration at 2800−3010 cm^{-1} as a reference.

Steady-State Photolysis and Quantum Yields Determination. All photolysis experiments were carried out in a Rayonet model photochemical reactor fitted with 16 × 20 W filter-coated mercury lamps (300-400 nm) with an output maximum at 350 nm. The photoproducts and the radical adducts were detected by GC and GC−MS.

The actinometer solution (3 mL) containing benzophenone and benzhydrol, 0.1 M each, in benzene in a 4 mL Pyrex sample vial was degassed with three freeze−pump−thaw cycles. The sample was irradiated for 20 min and the amount of the benzophenone reacted determined from the change of its UV absorption at 344 nm, using the calibration $\phi_{\mathrm{act}} = 0.68$.[19] The light intensity was calculated to be 3.72×10^{18} photons/min. Under exactly the same conditions, a 1×10^{-2} M solution of borates in the same container was irradiated for 1 min only to avoid secondary reactions. The quantities of the products formed were detected by GC calibrated by reference standard, and the disappearance of these borates was determined by the decrease of ^{1}H NMR signal of CH$_2$ group using the aryl hydrogen signal as internal standard.

Isolation and Identification of 4,4′-Dichlorobiphenyl. PyTClB (73.1 mg) dissolved in 1 mL of CD$_3$CN in an NMR tube was irradiated for 30 h. The reaction mixture was analyzed by ^{1}H and ^{13}C NMR as well as GC−MS and then distilled to dryness under reduced pressure. The solid was extracted with hexane and dried again, and the white needle crystals were recrystallized from CH$_3$CN to afford 4,4′-dichlorobiphenyl: mp 143−5 °C (lit.[20] mp 146.5−7 °C); ^{1}H NMR (CD$_3$CN) δ 7.62 (d, 2H, $J = 8.8$ Hz), 7.47 (d, 2H, $J = 8.8$ Hz); ^{13}C NMR (CD$_3$CN) δ 139.1, 137.1, 129.8, 129.3; m/z (abundance) 222 (M$^{\bullet,+}$, 100), 224 (M$^{\bullet,+}$ + 2, 63), 226 (M$^{\bullet,+}$ + 4, 11), 186 (7), 152 (73).

Radical Trapping Experiments. In a 4 mL Pyrex sample vial, a solution of 0.013 M borates and 0.13 M methylmethacrylate (MMA) in 3 mL of acetonitrile and benzene (1:4 v/v) was purged with argon for 10 min, sealed, and irradiated for 2.5 h. The reaction mixtures were concentrated and analyzed by GC−MS. The addition products and relative ratios are listed in Table 2; methyl 2-methylheptanoate (*n*-Bu-MMA) (m/z (abundance) 127 (M$^{\bullet,+}$ − CH$_3$O$^\bullet$, 3), 101 (18), 88 (100)); methyl 2,4-dimethylhexanoate (*s*-Bu-MMA) (m/z (abundance) 127 (M$^{\bullet,+}$ − CH$_3$O$^\bullet$, 16), 101 (100), 88 (38); methyl 2-methyl-3-phenylpropanoate (Ph-MMA), m/z (abundance) 178 (M$^{\bullet,+}$, 15), 147 (4), 118 (39), 91 (100)); methyl 2-methyl-4-(*N*-methylbenzylamino)butanoate (DMBA−MMA) (m/z (abundance) 235 (M$^+$, 2), 134 (65), 120 (5), 91 (100)); methyl 2-methyl-4-[4-(benzoylphenyl)]butanoate (BP-MMA) (m/z (abundance) 296 (M$^{\bullet,+}$, 22), 265 (6), 209 (100), 131 (40), 105 (81), 88 (62)); methyl 2-methyl-3-(4-chlorophenyl)propanoate (m/z (abundance) 212 (M$^{\bullet,+}$, 9), 214 (M$^{\bullet,+}$ + 2, 3), 181 (3), 152 (23), 154 (8), 125 (100), 127 (34)); dimethyl 2,5-dimethyl-3-phenylhexandioate (m/z (abundance) 278 (M$^{\bullet,+}$, 2), 246 (4), 218 (17), 187 (25), 178 (19), 131 (22), 91 (100)); dimethyl 2,4-dimethyl-2-benzylpentandioate (m/z (abundance) 278 (M$^{\bullet,+}$, 1), 246 (2), 218 (17), 187 (22), 178 (<1), 131 (22), 91 (100)); 4-pentylbenzophenone (m/z (abundance) 252 (M$^{\bullet,+}$, 25), 196 (7), 181 (13), 175 (100), 105 (80)).

Synthesis. 1-(4-Benzoylbenzyl)pyridinium Bromide (PyBr). Pyridine, 3.1 mL (40 mmol), was added to a solution of 5.5 g (20 mmol) of 4-(bromomethyl)benzophenone[21] in 100 mL of THF, and the mixture was kept at room temperature for 60 h. The white precipitate was filtered and washed with THF. After drying under vacuum, PyBr was obtained as white needles (83%); mp 195−196 °C; ^{1}H NMR (CDCl$_3$) δ 9.82 (d, 2H), 8.56 (t, 1H), 8.10 (t, 2H), 7.45−7.96 (m, 9H), 6.56 (s, 2H).

1-(4-Benzoylbenzyl)-3-methylimidazolium Bromide (MeImBr). MeImBr was prepared as above: yield 88%; mp 93−94 °C; ^{1}H NMR (CDCl$_3$) δ 10.48 (s, 1H), 7.45−7.78 (m, 11H), 5.78 (s, 2H), 4.08 (s, 3H).

1-(4-Benzoylbenzyl)pyridinium Tetraphenylborate (PyTB). Sodium tetraphenylborate (3.42 g, 0.01 mol) in 10 mL of acetone was added to a solution of 3.54 g (0.01 mol) of PyBr in 50 mL of acetone and 5 mL of water. Then water was added slowly to the reaction mixture and white crystals formed directly. After filtration and washing with water, 6.4 g of PyTB was obtained (86%). The product was recrystallized from butanone: mp 195−197 °C; $\lambda_{\max}$ (log ϵ) nm 248 (4.52), 338 (2.21); ^{1}H NMR (CD$_3$COCD$_3$) δ 9.05 (d, 2H), 8.66 (t, 1H), 8.24 (t, 2H), 7.45−7.90 (m, 9H), 7.35 (m, 8H), 6.72−6.96 (m, 12H), 6.02 (s, 2H); ^{13}C NMR (DMSO-d_6) 195.4, 163.5 (q, $J_{\mathrm{C-B}} = 49.4$ Hz), 146.3, 145.2, 138.5, 137.9, 136.8, 135.7, 133.2, 130.5, 129.9, 129.0, 128.8, 128.7, 125.6 (q, $J_{\mathrm{C-B}} = 2.8$), 121.8, 63.0; ^{11}B NMR −25.16. Anal. Calcd for C$_{43}$H$_{36}$BNO: C, 87.01; H, 6.11; N, 2.38. Found: C, 87.05; H, 6.13; N, 2.37.

1-(4-Benzoylbenzyl)-3-methylimidazolium Tetraphenylborate (MeImTB). This preparation was identical to that used in the preparation of PyTB: yield 94%, recrystallized from butanone; mp 147−148 °C; $\lambda_{\max}$ (log ϵ) nm 246 (4.52), 340 (2.17); ^{1}H NMR (CD$_3$COCD$_3$) δ 8.28 (s, 1H), 7.44−7.86 (m, 11H), 7.36 (m, 8H), 6.72−6.96 (m, 12H), 5.41 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (DMSO-d_6) 195.5, 163.5 (q, $J_{\mathrm{C-B}} = 49.4$ Hz), 139.3, 137.4, 136.9, 135.7, 133.1, 130.4, 129.8, 128.8, 128.5, 125.6 (q, $J_{\mathrm{C-B}} = 2.7$ Hz), 124.2, 122.6, 121.7, 51.6, 36.0; ^{11}B NMR −25.18. Anal. Calcd for C$_{42}$H$_{37}$BN$_2$O: C, 84.56; H, 6.25; N, 4.70. Found: C, 84.42; H, 6.20; N, 4.66.

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***N*-(4-Benzoylbenzyl)-*N*,*N*-dimethylbenzylammonium Tetraphenylborate (DMBzTB).** 4-(Bromomethyl)benzophenone (3.5 g, 12.7 mmol) and 3 mL (20 mmol) of *N*,*N*-dimethylbenzylamine were dissolved in 30 mL of THF. After being stirred at room temperature for 40 h, 4.34 g (12.7 mmol) of sodium tetraphenylborate in 20 mL of acetone was added. Cold water was added slowly to the reaction mixture, and a white precipitate formed directly. After filtration and washing with water, the product was recrystallized from acetonitrile and ethanol to give 6.7 g of DMBzTB (yield 81%): mp 165−167 °C; λ_{max} (log ϵ) nm 246 (4.52), 340 (2.18); ^{1}H NMR (CD_3COCD_3) δ 7.50−7.92 (m, 14H), 7.34 (m, 8H), 6.74−6.96 (m, 12H), 4.77 (s, 2H), 4.72 (s, 2H), 3.06 (s, 6H); ^{13}C NMR (DMSO-d_6) 195.6, 163.5 (q, $J_{C-B} = 49.4$ Hz), 138.7, 136.7, 135.7, 133.6, 133.4, 132.3, 130.6, 130.1, 130.0, 129.2, 128.9, 128.0, 125.5 (q, $J_{C-B} = 2.8$), 125.4, 121.7, 67.6, 66.7, 48.5; ^{11}B NMR −25.22. Anal. Calcd for $C_{47}H_{44}BNO$: C, 86.89; H, 6.83; N, 2.16. Found: C, 86.92; H, 6.90; N, 2.17.

1-(4-Benzoylbenzyl)-2-methylpyridinium Tetraphenylborate (MePyTB). Prepared as above (75%) and recrystallized from butanone: mp 199−200 °C; λ_{max} (logϵ) nm 248 (4.53), 338 (2.22); ^{1}H NMR (CD_3COCD_3) δ 8.96 (d, 1H), 8.58 (t, 1H), 8.10 (m, 2H), 7.45−7.90 (m, 9H), 7.35 (m, 8H), 6.72−6.96 (m, 12H), 6.07 (s, 2H), 2.91 (s, 3H); ^{13}C NMR (DMSO-d_6) 195.4, 163.5 (q, $J_{C-B} = 49.4$ Hz), 155.9, 146.4, 146.2, 137.6, 137.5, 136.8, 135.8, 133.2, 130.6, 129.8, 128.8, 127.7, 126.2, 125.5 (q, $J_{C-B} = 2.8$ Hz), 121.8, 60.1, 20.2; ^{11}B NMR −25.19. Anal. Calcd for $C_{44}H_{38}BNO$: C, 86.98; H, 6.30; N, 2.31. Found: C, 86.89; H, 6.33; N, 2.25.

1-(4-Benzoylbenzyl)-2,3-dimethylimidazolium Tetraphenylborate (DMImTB). Prepared as above (77%) and recrystallized from butanone and ethyl acetate (1:3): mp 156−157 °C; λ_{max} (log ϵ) nm 246 (4.48), 340 (2.18); ^{1}H NMR (CD_3COCD_3) δ 7.48−7.86 (m, 11H), 7.35 (m, 8H), 6.72−6.96 (m, 12H), 5.57 (s, 2H), 3.86 (s, 3H), 2.69 (s, 3H); ^{13}C NMR (DMSO-d_6) 195.4, 163.5 (q, $J_{C-B} = 49.4$ Hz), 145.0, 139.2, 137.2, 136.9, 135.7, 133.1, 130.4, 129.8, 128.8, 127.8, 125.5 (q, $J_{C-B} = 1.8$ Hz), 123.0, 121.7, 121.5, 50.4, 35.0, 9.6; ^{11}B NMR −25.18. Anal. Calcd for $C_{43}H_{39}BN_2O$: C, 84.58; H, 6.44; N, 4.59. Found: C, 84.42; H, 6.46; N, 4.61.

1-(4-Benzoylbenzyl)-*N*,*N*-dimethylbenzylammonium Butyltriphenylborate (DMBzBB). Prepared using a procedure similar to that of DMBzTB except tetramethylammonium butyltriphenylborate was used instead of sodium tetraphenylborate: yield 80% recrystallized from ethanol; mp 126-127 °C; λ_{max} (log ϵ) nm 246 (4.54), 340 (2.18); ^{1}H NMR (CD_3COCD_3) δ 7.50-7.92 (m, 14H), 7.36 (m, 6H), 6.74-6.93 (m, 9H), 4.70 (br, 4H), 3.04 (br, 6H), 0.9-1.3 (m, 6H), 0.77 (t, 3H); ^{13}C NMR (DMSO-d_6) 195.6, 163.5 (q, $J_{C-B} = 49.4$ Hz), 138.7, 136.7, 135.7, 134.6, 133.6, 133.4, 132.3, 130.6, 130.0, 129.9, 129.2, 128.9, 128.0, 125.4, 121.7, 121.2, 67.6, 66.8, 48.5, 30.5, 27.7, 14.8; ^{11}B NMR −28.74. Anal. Calcd for $C_{45}H_{48}BNO$: C, 85.83; H, 7.68; N, 2.22. Found: C, 85.68; H, 7.62; N, 2.20.

1-(4-Benzoylbenzyl)pyridinium Tetrakis(4-chlorophenyl)borate (PyTClB). PyTClB was prepared using a procedure similar to that for PyTB except tetramethylammonium tetrakis(4-chlorophenyl)borate[22] was used instead of sodium tetraphenylborate: (82% recrystallized from acetone and water; mp 201−202 °C; λ_{max} (log ϵ) nm 244 (4.64), 340 (2.18); ^{1}H NMR (CD_3COCD_3) δ 9.34 (d, 2H), 8.80 (t, 1H), 8.34 (t, 2H), 7.52−7.89 (m, 9H), 7.18 (m, 8H), 6.99 (d, 8H), 6.23 (s, 2H); ^{13}C NMR (DMSO-d_6) 195.4, 160.6 (q, $J_{C-B} = 49.4$ Hz), 146.4, 145.3, 138.5, 137.9, 137.0, 136.8, 133.2, 130.5, 129.9, 129.0, 128.9, 128.8, 127.4, 125.8 (q, $J_{C-B} = 2.7$ Hz), 63.0; ^{11}B NMR −26.05. Anal. Calcd for $C_{43}H_{32}Cl_4BNO$: C, 70.62; H, 4.41; N, 1.92; Cl, 19.39. Found: C, 70.50; H, 4.40; N, 1.87; Cl, 19.29.

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