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# Synthesis and Photochemistry of Tertiary Amine Photobase Generators

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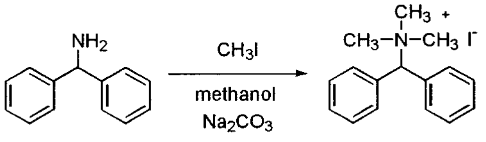
A family of tertiary amine photobase generators have been prepared and studied. The compounds investigated were quaternary ammonium salts of benzhydrylamine (aminodiphenylmethane) and 9-aminofluorene. The compounds were prepared by the following methods: methylation of the benzhydryl or fluorenylamines, reaction of a tertiary amine with 9-bromofluorene, and reaction of a primary or secondary amine with 9-bromofluorene followed by exhaustive methylation. Alkylation was limited to methylation in the benzhydryl system, as larger alkyl groups would not react. This appears to be a result of steric hindrance. The fluorenyl system allowed for a wider variation in the synthesis of tertiary amine photobase generators. Examination of the solution photochemistry by NMR spectroscopy supported a heterolytic mechanism for photodecomposition.

Photochemical sources for catalysts have a long history in polymer and materials science.[1] The development of chemically amplified photoresists[2] has stimulated interest in photochemical sources of acids[3] and more recently bases.[3−5] Most of the known photobase generators produce organic amine bases, and most of these have been primary and secondary amines. There have been only a few photobase generator systems that have allowed the generation of tertiary amines,[5,6] although certain applications could be favored by the use of tertiary amine catalysts.[7]

We report further developments in the synthesis and photochemical investigation of a family of photobase generators with a quaternary ammonium salt structure.[6] One of the substituents on the quaternized nitrogen is selected for the stability of the resulting carbocation. Upon photolysis, the bond between this substituent and the nitrogen is broken, liberating the free tertiary amine. In this report, we describe the synthesis and characterization of quaternary ammonium salts where the photolabile substituent is either benzhydryl or fluorenyl along with photochemical experiments that provide some insight on the mechanism of photobase generation for these compounds.

**Scheme 1. Synthesis of Trimethylbenzhydrylammonium Iodide 1**



**1**

## Results

Synthesis of trimethylbenzhydrylammonium iodide **1** was accomplished by exhaustive methylation of aminodiphenylmethane (benzhydrylamine) with iodomethane in refluxing methanol with sodium carbonate as a base.[8] This reaction is shown in Scheme 1. The reaction was optimized for yield of the quaternized product. As the reaction proceeds, the concentration of nucleophilic iodide increases, leading to formation of iododiphenylmethane **4** by displacement of the quaternized nitrogen. Optimum yield represents a balance between full conversion of the free amine to **1** and decomposition of **1**. The optimal time for the reaction was found to be 25 h in refluxing methanol with a 37% yield of trimethylbenzhydrylammonium iodide **1**. The structure of **1** was corroborated by IR and NMR spectroscopy and elemental analysis. Thermal and photochemical properties of these compounds are critical to their use as photobase

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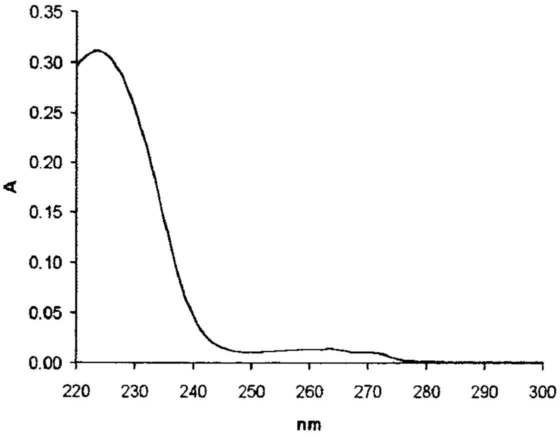
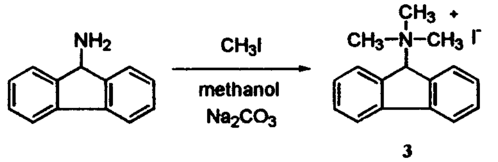


**Figure 1.** Electronic absorption spectrum of trimethylbenzhydrylammonium iodide **1** in ethanol.

**Scheme 2. Synthesis of Trimethylfluorenylammonium Iodide 3**



**3**

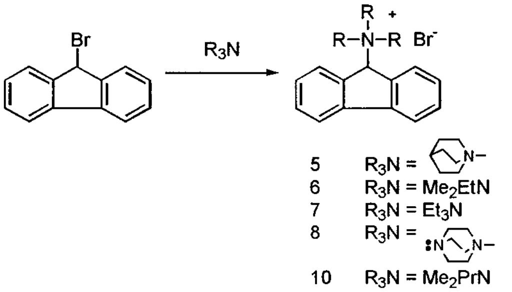
generators. Differential scanning calorimetry revealed a thermal decomposition temperature of 188 °C, which is sufficiently high for most applications. The electronic spectrum of **1** in ethanol is shown in Figure 1 and is typical of diphenylmethane derivatives.[9]

Attempts to use a similar strategy for the preparation of other trialkylbenzhydrylammonium derivatives were not successful. Other alkyl iodides (ethyl, propyl, butyl, and benzyl) failed to react with aminodiphenylmethane under a variety of conditions. Other alkylating schemes also failed, as did reductive amination. This failure can be understood in terms of the steric demands for reaction of the amine lone pair in aminodiphenylmethane and is discussed further below.

The trimethylbenzhydrylammonium photobase generator was then prepared with a non-nucleophilic counterion through an exchange process. Trimethylbenzhydrylammonium triflate **2** was prepared by dissolving trimethylbenzhydrylammonium iodide **1** in acetone and adding silver triflate dissolved in acetone. Precipitated silver iodide was removed by filtration, and product **2** was isolated from the filtrate.

Trimethylfluorenylammonium iodide **3** was prepared using the same exhaustive methylation strategy used in preparation of **1**. The reaction is shown in Scheme 2. The optimal reaction time for formation of **3** is 4 h at reflux giving **3** in 39% yield. As in the benzhydryl system, this is a compromise between product formation and decomposition of the product due to an $S_N2$ reaction with the iodide anion to form 9-iodofluorene. It is interesting that the optimal yields for **1** and **3** are identical within experimental error, but the optimum reaction time is much shorter for **3**. This suggests that **3** both forms faster and decomposes faster than **1**, consistent with less steric hindrance for **3**. Differential scanning calorimetry revealed a decomposition temperature of 193 °C.

**Scheme 3. Synthesis of Trialkylfluorenylammonium Bromides from 9-Bromofluorene**



The other fluorenyl photobase generators were made by an alternative strategy: reaction of 9-bromofluorene with tertiary amines. This approach was successful with a variety of tertiary amines, including quinuclidine, dimethylethylamine, triethylamine, and 1,4-diazabicyclo[2.2.2]octane (DABCO). Isolated yields ranged from 20 to 90%. This chemistry and the resulting photobase generators are shown in Scheme 3. The two synthetic strategies can also be combined, as demonstrated in the preparation of 9′-fluorenyldimethylpropylammonium iodide **10**. Here, reaction of 9-bromofluorene with propylamine gives the intermediate 9′-fluorenylpropylamine **9** in 70% yield, and **9** is then exhaustively methylated with iodomethane to give **10**. The exhaustive methylation has a rather low yield of 20%, giving an overall yield of 14%. Generally, reaction of tertiary amines with 9-bromofluorene is the most efficient route to the quaternary ammonium fluorenyl photobase generators.

The solution photochemistry of trimethylbenzhydrylammonium iodide **1** was analyzed by NMR spectroscopy following photolysis in nucleophilic and non-nucleophilic solvents and with nucleophilic and non-nucleophilic counterions. There are several possible mechanisms for the photochemical generation of the tertiary amine from the quaternary ammonium salt, and these experiments were aimed at eliminating some of these possibilities. The most likely mechanisms for reaction of the excited state are shown in Scheme 4, where Ar represents the benzhydryl or fluorenyl group (but could represent any other group leading to a stable cation or radical) and R represents the alkyl groups. The first mechanism, which we label “photo-$S_N1$”, consists of photochemical heterolysis to give the tertiary amine and the carbocation followed by reaction of the cation with a nucleophile. This is the mechanism favored by earlier work on the photosolvolysis of trialkylbenzylammonium salts in water and alcohols.[10] Homolytic variants of this chemistry are possible, but these generally result in different products, such as radical coupling and hydrogen abstraction products.[10] A “photo-$S_N2$” mechanism consists

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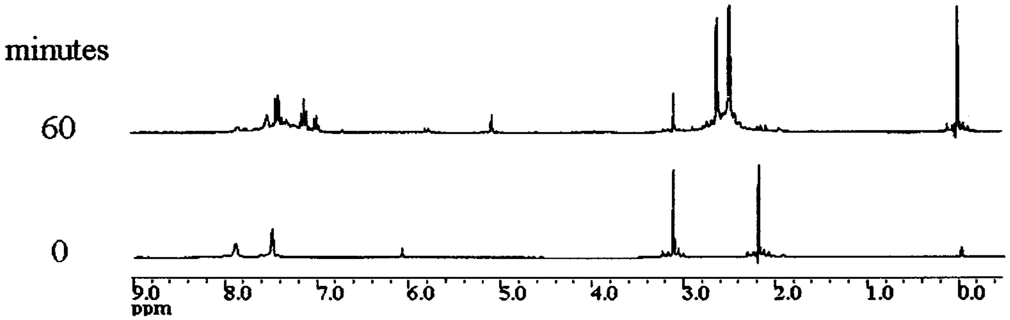
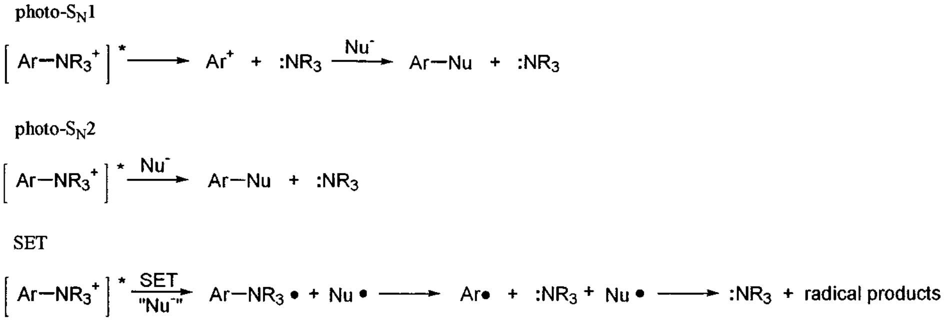


**Figure 2.** NMR spectra of **1** in acetonitrile-$d_3$ after 0 and 60 min of irradiation at 254 nm.

**Scheme 4. Possible Mechanisms for Generation of Tertiary Amine Bases from Benzhydryl-trialkylammonium Salts (Ar = Benzhydryl Group, R = Alkyl Groups).**



of direct displacement of the tertiary amine in the excited state. Finally, an electron-transfer mechanism ("SET") could occur,[5] where single-electron transfer from the anion ("Nu$^-$") to the aromatic system of the ammonium cation is followed by dissociation to the benzhydryl (or fluorenyl) radical and the free amine. The benzhydryl radical then recombines with the radical arising from the anion or reacts to give other radical products. Note that the homolytic dissociation mechanism (not shown) leads to different products,[10] and the photo-S$_N$2 and SET mechanisms should be sensitive to changes in counterion. These differences might be used to discriminate between these mechanisms.

Initial photochemical studies of trimethylbenzhydrylammonium iodide **1** were made in deuterated acetonitrile, which had been dried with activated aluminum oxide.[6] Photolysis using 254 nm light was followed over time and was found to be complete after 60 min. The NMR spectra before and after 254 nm exposure for 1 h in this relatively non-nucleophilic solvent is shown in Figure 2. The resonance for **1** near 6.0 ppm due to the benzhydryl proton decreases with photolysis, as does the resonance at 3.1 ppm due to the methyl protons of **1**. New resonances appear at 5.1 ppm, due to the formation of iododiphenylmethane **4,** and at 2.4 ppm, due to the formation of free trimethylamine, in equilibrium with residual water. (The peak for residual water at 2.2 ppm also shifts to 2.6 ppm.)

The photochemistry of **1** was also analyzed in a nucleophilic solvent, methanol, which is one of the solvents used in the early work of Kochi and McKenna on the related benzyl systems.[10] Photobase generator **1** was irradiated with 254 nm light in deuterated methanol, and the photolysis was again found to be complete after 60 min. The benzhydryl proton resonance of **1** near 6.00 ppm decreases with increasing exposure time along with the methyl proton resonance of **1** at 3.35 ppm. A resonance grows in at 2.80 ppm for trimethylamine, in equilibrium with water and HI. The other product of photodecomposition was isolated and found to be benzhydryl methyl ether by comparison with an authentic sample. In a nucleophilic solvent such as methanol, the solvent can effectively compete with the nucleophilic iodide and so the solvent reacts most rapidly with the diphenylmethyl cation. The time required for photolysis is essentially the same as for the photodecomposition in acetonitrile.

It is possible that the benzhydryl methyl ether isolated from photolysis of **1** in methanol is not the primary photoproduct. Iododiphenylmethane **4** could be the primary photoproduct and could then undergo secondary photosolvolysis to form the benzhydryl methyl ether. To eliminate this possibility, iododiphenylmethane **4** was prepared by reaction of chlorodiphenylmethane with sodium iodide at room temperature. Iododiphenylmethane **4** dissolved in methanol was irradiated at 254 nm for 1 h. No reaction was observed, suggesting that benzhydryl methyl ether is indeed the primary photoproduct.

If the reaction truly resembles a photo-S$_N$1 photoheterolysis, then the solution photochemistry should remain the same with a non-nucleophilic counterion as with the nucleophilic iodide counterion. Analysis of the solution photochemistry was made with a photobase generator containing the non-nucleophilic triflate anion. Irradiation of trimethylbenzhydrylammonium triflate **2** was completed in acetonitrile which had been dried over activated aluminum oxide. The irradiation of the triflate salt **2** is very similar to irradiation of the iodide salt **1**. The resonance due to the benzhydryl proton and the resonance for the methyl protons both decrease over 60 min of photolysis. A new resonance grows in due to the production of trimethylamine, in equilibrium with residual water and triflic acid. The other main product

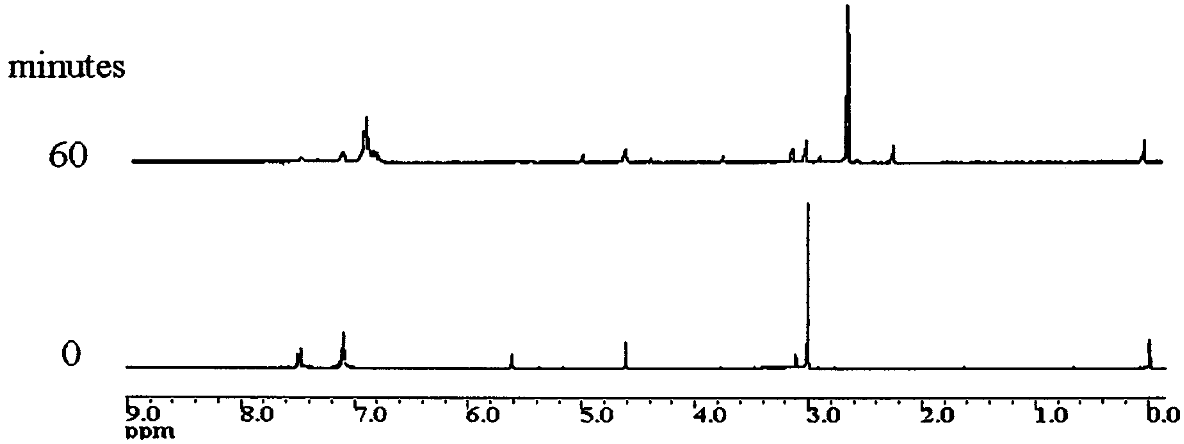


**Figure 3.** NMR spectra of **3** in acetonitrile-$d_3$ after 0 and 60 min of irradiation at 254 nm.

isolated following photolysis of **2** is benzhydryl alcohol. The generation of benzhydryl alcohol is a result of the reaction of the diphenylmethyl cation with trace amounts of water in the sample. The cation reacts with the best nucleophile available, and the fastest reaction is with trace water present in the acetonitrile. The reaction of the diphenylmethyl cation with water is very fast. Literature flash photolysis studies report that the pseudo-first-order rate of reaction for the diphenylmethyl cation with trace amounts of water (up to 0.15 M) in acetonitrile is on the order of $1.3 \times 10^8$ $s^{-1}$, while that for the cation decay in pure acetonitrile with no water is $4.0 \times 10^6$ $s^{-1}$.[11] Reaction with the iodide or bromide anions is much faster. The bimolecular rate constant for reaction of bromide with the diphenylmethyl cation in acetonitrile has been measured as $2.0 \times 10^{10}$ $M^{-1}$ $s^{-1}$.[12]

Photochemical studies were also completed on the quaternary ammonium salts of the fluorenyl system. The photochemistry of trimethylfluorenylammonium iodide **3** was examined in non-nucleophilic acetonitrile. Solutions of **3** were made in deuterated acetonitrile which had been dried with activated aluminum oxide. The exposure wavelength was 254 nm, and irradiation was followed over 60 min by NMR spectroscopy. The NMR spectra (Figure 3) show the disappearance of the starting material **3** (resonances at 5.75 and 3.18 ppm) and the appearance of trimethylamine in equilibrium with trace water (2.3−2.5 ppm) along with formation of the other product, 9-iodofluorene (3.90 ppm).

## Discussion

A number of different photobase generator molecules with the trialkylbenzhydrylammonium motif were synthesized. This motif was originally selected for several reasons. To generate tertiary amines by photolysis leading to C−N bond cleavage of quaternary ammonium salts, one substituent on the ammonium must be a stable cation (or radical for electron-transfer mechanisms). Aryl-substituted methyl cations were favored since elimination reactions are not possible and cannot compete with nucleophilic displacement of the amine. From previous literature reports and from cation stability data, it was believed that the benzyl cation would not be sufficiently stable for our purposes, while the triphenylmethyl and xanthenyl cations would be too stable, resulting in ammonium salts prone to thermal decomposition.[13] The benzhydryl or diphenylmethyl system also has steric constraints between the benzyl and triphenylmethyl systems. A system based on a stable cation with too few steric demands would be prone to decomposition by $S_N2$ pathways and also to recombination. If the steric demands are too great, then synthesis of the system will be difficult, and the sterics may also destabilize the system for thermal decomposition.

The results of our synthetic efforts demonstrate some of these effects. For the benzhydryl (diphenylmethyl) system itself, only the trimethylbenzyhydrylammonium cation could be prepared by any route. This reveals the steric limitations of the benzhydryl system. Molecular modeling of benzhydrylamine revealed that the nucleophilic nitrogen lone pair lies between two “guarding” hydrogens on the phenyl rings and is not readily accessible to an electrophile.[14] The fluorenyl system is forced to be nearly planar by the coupling of the two phenyl rings and therefore has fewer steric demands. Many more trialkylfluorenylammonium derivatives could therefore be prepared. Alkylation of tertiary amines by 9-bromofluorene proved to be the most versatile method for the synthesis of the trialkylfluorenylammonium salts. Standard techniques for counterion metathesis can be used to change the counterion of these salts. For example, treatment of the halide salt **1** with silver triflate gave salt **2** with the non-nucleophilic triflate counterion.

Thermal analysis by differential scanning calorimetry (DSC) showed that the trimethylbenzhydrylammonium iodide decomposed at 188 °C, while the trimethylfluor-

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enylammonium iodide decomposed at 193 °C. The lower decomposition temperature of the benzhydryl system may be attributable to the greater stability of the benzhydryl cation (since the fluorenyl cation may be less stable due to antiaromaticity[13]), or this may be attributable to steric destabilization of the benzhydryl-substituted ammonium cation. The thermal stabilities are sufficiently high that processing temperatures of up to 150 °C can be used, making these compounds useful for many applications in materials.

Some basic photochemistry of these ammonium salts was then explored. The electronic absorption spectra are minimally perturbed by the substitution, as seen in the spectrum of **1** (Figure 1) which is nearly identical to the spectrum of diphenylmethane.[9] The trimethylbenzydrylammonium and trimethylfluorenylammonium iodides when irradiated in acetonitrile gave trimethylamine and the benzhydryl or fluorenyl iodide as the only products by NMR. This demonstrated that photodecomposition to give the free amine is the primary photochemistry for these compounds.

Further photochemical experiments were pursued to answer questions about the mechanism of the photodissociation. As described above, there are a number of mechanistic possibilities, including the photo-$S_N1$, photo-$S_N2$, and SET mechanisms. The results from the photolysis of the trimethylbenzhydrylammonium triflate **2** eliminate the SET mechanism from serious consideration. The triflate anion is not a good electron donor, so one would not expect **2** to readily photodissociate if the SET mechanism were occurring. Since photolysis of **2** does lead to photodissociation, some other mechanism must be occurring. Our results cannot conclusively eliminate either the photo-$S_N1$ or photo-$S_N2$ mechanism although we believe that the evidence and literature precedent[10-12] favors the photo-$S_N1$. There are experiments that may be able to distinguish between the photo-$S_N1$ and photo-$S_N2$.[10-12] Chiral benzhydryl or fluorenyl substituents could be used to compare conversion to racemization, since the photo-$S_N1$ should lead to racemic products while the photo-$S_N2$ should give inversion. Earlier studies of chiral benzyl systems gave mostly racemization of the products and very little racemization of the recovered starting material, primarily indicating a photo-$S_N1$ type mechanism.[10] Since the benzhydryl and fluorenyl cations are more stable than the benzyl cation, they would be expected to even more likely follow a photo-$S_N1$ mechanism. Transient absorbance experiments could also establish if the fluorenyl or benzhydryl cations are formed on flash photolysis, as is known for other benzhydryl compounds.[11,12]

In summary, we have explored the synthesis and photochemistry of a family of photobase generators based on quaternary ammonium salts with one benzhydryl or fluorenyl substituent. The fluorenyl compounds can be readily prepared by reaction of 9-bromofluorene with tertiary amines. Mechanistic studies suggest that photoamine generation follows a photo-$S_N1$ pathway. These compounds may find use in a variety of applications in materials, such as photoresists.[14]

## Experimental Section

**General.** Reagents and solvents were purchased from Aldrich Chemical Co. and used as received with the exception of tetrahydrofuran, which was distilled from sodium/benzophenone. Nuclear magnetic resonance (NMR) spectra were acquired on a General Electric QE−300 FT-NMR and are reported in $\delta$ units referenced to tetramethylsilane (TMS). NMR data are reported in this order: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and number of protons. All reactions were run under a positive pressure of argon unless otherwise noted. IR spectra were acquired on a MIDAC Model PRS FT-IR at 4 cm$^{-1}$ resolution. UV−vis spectra were obtained on a Hewlett-Packard (model 8452A) diode array spectrophotometer. Thermal analyses were obtained on a Perkin-Elmer DSC-4 differential scanning calorimeter and TGA-7 thermogravimetric analyzer. Melting points were determined on a Mel-Temp from Laboratory Devices. Chemical analyses were performed by Schwarzkopf Microanalytical Laboratories, Inc., Woodside, NY.

**Synthesis.** *Trimethylbenzhydrylammonium iodide* (*1*).[8] To a solution of 1.0 g (4.6 mmol) of aminodiphenylmethane hydrochloride in 100 mL of methanol, 3.85 g (36 mmol) of anhydrous sodium carbonate and 2.26 mL (36 mmol) of iodomethane were added. The mixture was refluxed for 25 h under argon and then allowed to cool to room temperature, when 30 mL of 1 M sodium thiosulfate was added, and the mixture stirred for 10 min. The solution was gravity filtered, and 10 g of potassium iodide was added and stirred for 15 min. The solution was transferred to a separatory funnel, and 50 mL of methylene chloride and 50 mL of water were added. Two additional 50 mL extractions were made with methylene chloride, and the organic layers were collected, dried with anhydrous sodium sulfate, and concentrated under reduced pressure to ca. 10 mL. The residue was recrystallized from boiling ethanol affording 0.61 g (37%) of **1** as white crystals, mp 136−140 °C. The thermal decomposition temperature was measured as 188 °C by DSC. UV−vis (ethanol) $\lambda_{max}$ 224 nm ($\epsilon$ = 9600), 264 nm ($\epsilon$ = 450). NMR ($CD_3CN$, TMS): $\delta$ 7.87 (m, 4H), 7.51 (m, 6H), 5.92 (s, 1H), 3.11 (s, 9H). IR (KBr pellet, 3057, 3027, 2958, 1582, 1484, 1451, 1411, 1273, 1205, 1092, 966, 852, 816, 797, 741, 712, 703,655 cm$^{-1}$). Anal. Calcd. for $C_{16}H_{20}NI$: C, 54.38; H, 5.71; N, 3.97; I, 35.94. Found: C, 54.16; H, 5.81; N, 3.79; I, 35.97.

*Trimethylbenzhydrylammonium triflate* (*2*). To a solution of 1.0 g (28 mmol) of trimethylbenzhydrylammonium iodide in 30 mL of acetone, a 30 mL acetone solution containing 0.73 g (28 mmol) of silver trifluoromethane sulfonate was added. The bright yellow solid that precipitated immediately from solution was indicative of AgI. The solution was stirred for 15 min, gravity filtered, and concentrated under reduced pressure. No further purification was required affording 1.1 g (100%) of **2** as white crystals, mp 135−136 °C. NMR ($CD_3CN$, TMS): $\delta$ 7.79 (m, 4H), 7.51 (m, 6H), 5.60 (s, 1H), 3.07 (s, 9H).

*Trimethylfluorenylammonium iodide* (*3*). To a solution of 1.0 g (4.6 mmol) of 9-aminofluorene hydrochloride in 50 mL of methanol, 4 equiv (18.4 mmol) of anhydrous sodium carbonate and 10 equiv (46 mmol) of iodomethane were added. The mixture was refluxed for 4 h under argon and then allowed to cool to room temperature. After the addition of 25 mL of 1 M sodium thiosulfate, the mixture was stirred for 10 min. The solution was gravity filtered, and 10 g of potassium iodide was added and stirred for 15 min. The solution was transferred to a separatory funnel, and 50 mL of methylene chloride and 50 mL of water were added. Two additional 50 mL extractions were made with methylene chloride, and the organic layers were collected, dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was recrystallized from boiling ethanol affording 0.63 g (39%) of **3** as white crystals, mp 132−134 °C. The thermal decomposition temperature was measured as 193 °C by DSC. NMR ($CD_3CN$, TMS): $\delta$ 7.88 (m, 2H), 7.78 (m, 2H), 7.62 (m, 2H), 7.43 (m, 2H), 5.51(s, 1H), 3.07 (s, 9H). Anal. Calcd. for $C_{16}H_{18}NI$: C, 54.71; H, 5.17; N, 3.99; I, 36.13. Found: C, 54.75; H, 5.07; N, 3.80; I, 35.84.

*Iododiphenylmethane* (*4*). To 1 mL (5.60 mmol) of chlorodiphenylmethane, 25 mL of acetonitrile was added. To this solution, 0.843 g (5.60 mmol) of sodium iodide was added. The solution was stirred for 48 h at room temperature under argon.

The solution was then concentrated to ca. one-half of the volume under reduced pressure, and 75 mL of diethyl ether was added. The reaction solution was washed (3 × 100 mL) with saturated NaCl solution, and the organic layers were collected, dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The product was purified by column chromatography on silica gel (toluene as eluent) followed by recrystallization from hexanes affording 1.52 g (92%) of **4** as pale yellow crystals, mp 96−97 °C. NMR ($CD_3CN$, TMS): $\delta$ 7.20 (m, 10H), 5.20 (s, 1H).

*9′-Fluorenylquinuclidinium bromide* (*5*). To a solution of 1.19 g (4.9 mmol) of 9-bromofluorene in 150 mL of toluene, 0.60 g (5.4 mmol) of quinuclidine was added. The reaction mixture was stirred at room temperature under argon for 12 h. The precipitated product was isolated by vacuum filtration from the reaction solution and washed three times with 30 mL of cold toluene. The crystals were recrystallized from ethanol affording 1.61 g (97%) of **5** as white crystals, mp 217−218 °C. NMR ($CD_3CN$, TMS): $\delta$ 7.72 (m, 2H), 7.51 (m, 2H), 7.28 (m, 2H), 7.10 (m, 2H), 5.31 (s,1H), 3.26 (m,6H), 1.65 (m, 6H), 1.57 (m, 1H). Anal. Calcd. for $C_{20}H_{22}NBr$: C, 64.18; H, 6.42; N, 3.74; Br, 21.35. Found: C, 64.67; H, 6.13; N, 3.62; Br, 20.29.

*Dimethylethyl-9-fluorenylammonium bromide* (*6*). To a solution of 10 mL of *N*,*N*-dimethylethylamine (92 mmol) in 150 mL toluene, 0.45 g (1.8 mmol) of 9-bromofluorene was added. The reaction mixture was heated gently under Ar for 25 h. The reaction mixture was concentrated under reduced pressure to ca. one-quarter of the original volume. To this mixture, 30 mL of acetone was added, and the mixture was stirred for 15 min. The product was isolated by vacuum filtration and recrystallized from hexanes affording 0.12 g (21%) of **6** as white crystals, mp 166−167 °C. NMR ($CDCl_3$, TMS): $\delta$ 7.75 (m, 2H), 7.70 (m, 2H), 7.50 (m, 2H), 7.30 (m, 2H), 6.35 (s, 1H), 3.70 (quart, 2H, $J = 7$ Hz), 3.40 (s, 6H), 1.50 (t, 3H, $J = 7$ Hz). Anal. Calcd. for $C_{17}H_{20}NBr$: C, 60.73; H, 6.54; N, 4.17; Br, 23.76. Found: C, 61.51; H, 6.14; N, 4.10; Br, 22.82.

*Triethyl-9-fluorenylammonium bromide* (*7*). To 0.245 g (1.0 mmol) of 9-bromofluorene, 3 mL of toluene and 3.03 g (30 mmol) of triethylamine were added. The solution was stirred at room temperature under Ar. After 24 h, an additional 1.01 g (10 mmol) of triethylamine was added and the reaction mixture was gently heated for 24 h. The solution was allowed to cool to room temperature and concentrated to ca. one-half the volume affording an oily residue. This was recrystallized from hexanes producing 0.08 g (23%) of **7** as white crystals, mp 209−212 °C. NMR ($CD_3CN$, TMS): $\delta$ 7.63 (m, 2H), 7.48 (m, 2H), 7.35 (m, 2H), 7.18 (m, 2H), 5.39 (s, 1H), 2.82 (q, 6H, $J = 7$ Hz), 1.05 (t, 9H, $J = 7$ Hz).

*9′-Fluorenyl-1,4-Diazobicyclo[2.2.2]octane ammonium bromide* (*8*). To a solution of 0.15 g (1.3 mmol) of DABCO in 50 mL of acetonitrile, 0.25 g (1.0 mmol) of 9-bromofluorene was added. The reaction mixture was heated under argon and refluxed for 24 h, followed by gentle heating for an additional 48 h. After being cooled, the reaction mixture was concentrated under reduced pressure to ca. one-half of the original volume. After the addition of 300 mL of toluene, the mixture was stirred for 1 h. The precipitated product was isolated by vacuum filtration from the solution affording 0.09 g (25%) of **8** as white crystals, mp 204−205 °C. No further purification was needed. NMR ($CD_3CN$, TMS): $\delta$ 7.84 (m, 2H), 7.77 (m, 2H), 7.59 (m, 2H), 7.42 (m, 2H), 5.64 (s, 1H), 3.45 (t, 6H, $J = 4$ Hz), 3.06 (t, 6H, $J = 4$ Hz). Anal. Calcd. for $C_{19}H_{21}N_2Br$: C, 63.17; H, 6.42; N, 7.75; Br, 22.12. Found: C, 63.47; H, 5.84; N, 7.70; Br, 18.84.

*N-Propyl-9-aminofluorene* (*9*). To 1.02 g (4.16 mmol) of 9-bromofluorene, 10.3 mL (125 mmol) of *n*-propylamine was added, and the mixture was stirred under argon and refluxed for 24 h. The reaction was allowed to cool to room temperature and poured into a separatory funnel to which were added 50 mL of diethyl ether and 100 mL of 0.1 M sodium carbonate solution. The mixture was extracted with ether (3 × 50 mL). The organic layers were collected, dried with anhydrous sodium sulfate, and concentrated under reduced pressure to give 0.65 g (70%) of **9** as a yellow oil. NMR ($CD_3CN$, TMS): $\delta$ 7.80 (m, 2H), 7.60 (m, 2H), 7.30 (m, 4H), 4.90 (s, 1H), 2.25 (t, 2H, $J = 7$ Hz), 2.10 (s, 1H), 1.35 (m, 2H), 0.80 (t, 3H, $J = 8$ Hz).

*9′-Fluorenyldimethylpropylammonium iodide* (*10*). To 0.14 g (0.627 mmol) of *N*-propyl-9-aminofluorene **(9)**, 25 mL of methanol was added. After the addition of 0.13 g (12.5 mmol) of anhydrous sodium carbonate, the solution was stirred at room temperature under Ar. After 10 min, 0.4 mL (6.27 mmol) of iodomethane was added and the solution was stirred at room temperature for 24 h followed by refluxing for 24 h. The reaction mixture was allowed to cool to room temperature, 10 mL of 1 M sodium thiosulfate was added, and the mixture was stirred for 20 min. The solution was then gravity filtered. To the filtered solution, 1.0 g of potassium iodide was added; stirring was continued for 30 min, and the solution was gravity filtered once again. The solution was transferred to a separatory funnel, and 30 mL of methylene chloride and 50 mL of water were added. The solution was extracted with methylene chloride (3 × 50 mL). The organic layers were collected and dried with anhydrous sodium sulfate. They were then concentrated under reduced pressure, and the residue was recrystallized from ethanol affording 0.05 g (21%) of **10** as white crystals, mp 138−140 °C. NMR ($CDCl_3$, TMS): $\delta$ 7.75 (m, 4H), 7.50 (m, 2H), 7.40 (m, 2H), 6.3 (s, 1H), 3.38 (s, 6H), 2.10 (m, 2H), 1.60 (m, 2H), 1.10 (t, 3H, $J = 8$). Anal. Calcd. for $C_{18}H_{22}NI$: C, 57.00; H, 5.84; N, 3.69; I, 33.46. Found: C, 56.68; H, 5.72; N, 3.53; I, 33.22.

**Photochemical Product Analysis.** Samples of the photobase generators were recrystallized a second time prior to photochemical experiments. Samples were prepared in deuterated solvents and divided among four quartz NMR tubes. One sample was set aside as a control (no irradiation), and the NMR spectrum was obtained. The remaining samples were irradiated in a Rayonet photochemical reactor with 254 nm lamps. At intervals, a sample tube was removed and the NMR spectrum was measured. Product peaks (benzhydryl iodide, benzhydrol, benzhydryl methyl ether, and trimethylamine) were checked against authentic samples for identification.

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