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Photoreaction of Vicinal Dibromides with Alcohols: Chain-Amplified Generation of Hydrogen Bromide

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The results reported here show that vicinal dibromides undergo photodecomposition in the presence of alcohols via a free radical chain reaction generating HBr with high quantum yields. The chain steps in this reaction involve the rapid debromination of radicals of the type $R\dot{C}HCH_2Br$ to yield bromine atoms that abstract hydrogen from alcohols, thus leading to the formation of ketyl radicals. Ketyl radicals of the type $R_2\dot{C}OH$, in turn, reduce the vicinal dibromides in a reaction that is probably the rate determining step in the overall process. The rate constants for some of these reactions have been determined by laser and conventional flash photolysis techniques. Chemically amplified resists play an important role in modern microlithography; the new mechanism reported here opens the possibility of amplification in the initial photoinduced acid generation step and has the potential to lead to a dramatic increase in photospeed.

Introduction

Vicinal dibromides are efficient photochemical sources of hydrogen bromide. In fact, several acid-hardened photoresist systems developed over the years are based on the use of vicinal dibromides as UV photoacid generators.[1,2] The photoinduced mechanism involved in these systems, however, is not yet completely understood.

Previous work from this laboratory has been directed toward the study of the direct photochemistry of vicinal dibromides. Studies were carried out based mainly on the application of time-resolved laser flash photolysis techniques,[3,4] using 1,2-dibromoethane (**1**), 1,2-dibromodecane (**2**), and tris(2,3-dibromopropyl) isocyanurate (**3**) as vicinal dibromides; the latter compound being used in photoresist compositions. These studies demonstrated that the deep-UV (266 nm) photodecomposition of vicinal dibromides in solution involves the formation of bromine atoms with a quantum yield of 2.0. In the absence of resonance stabilized moieties, the quantum yields show no dependence on molecular structure.[4] These observations were interpreted as the result of an efficient primary photocleavage of a C−Br bond, followed by a further elimination of a second bromine atom from radicals of the type $R\dot{C}HCH_2Br$ and concomitant formation of a C−C double bond (reactions 1 and 2).

$$RCHBrCH_2Br \xrightarrow{h\nu} R\dot{C}HCH_2Br + Br^\bullet \qquad (1)$$

$$R\dot{C}HCH_2Br \xrightarrow{k_2} RCH{=}CH_2 + Br^\bullet \qquad (2)$$

For these experiments, bromine atoms were "made visible" by complexation with bromide ions to yield $Br_2^{\bullet-}$, a species having a characteristic absorption band centered at 370 nm.[5,6]

Further evidence to the mechanism represented by reactions 1 and 2 came from quantum yield determinations of alkene formation measured under steady-state conditions. Thus, irradiation (254 nm) of **2** led to the formation of 1-decene with a quantum yield of approximately 1.0. confirming that each photon leads to the formation of a C−C double bond.[4]

As part of these studies it was also found that, upon irradiation in the presence of hydrogen donors, solutions of vicinal dibromides became strongly acidic. This observation was ascribed to the formation of HBr (reaction 3) as a result of hydrogen abstraction from the media by bromine atoms produced according to reactions 1 and 2.

$$Br^\bullet + RH \rightarrow HBr + R^\bullet \qquad (3)$$

To gain insight the role of hydrogen abstraction in the ultimate generation of HBr, efforts were directed towards studies in hydrogen-donor-containing systems. The results of these investigations are reported here.

Results and Discussion

Solutions containing compounds **1**, **2**, **3**, or tris(2,3-dibromopropyl) phosphate (**4**) in solvents such as acetonitrile, diglyme, and alcohols were irradiated (254 nm) under steady-state conditions. Quantum yields of HBr formation were then determined based on acid−base titrations.

[⊗] Abstract published in *Advance ACS Abstracts*. April 15. 1995.

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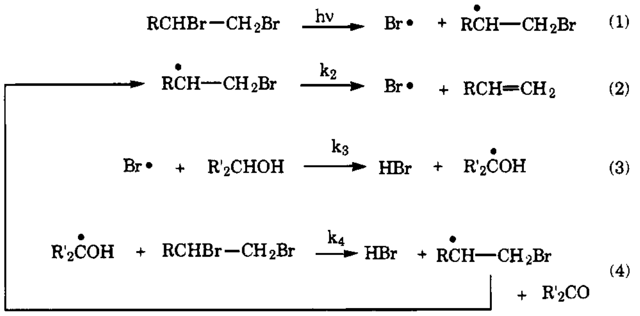
Table 1. Quantum Yields of HBr Formation in Alcohol Solutions

	methanol		1-propanol		2-propanol		
dibromide	air	N_2	air	N_2	O_2	air	N_2
1[a]	6.3	10	8.1	21	3.8	12	38
4[b]	7.0	13	7.4	22	3.1	15	41

[a] [1] = 0.12 M. [b] [4] = 0.04 M.

Scheme 1

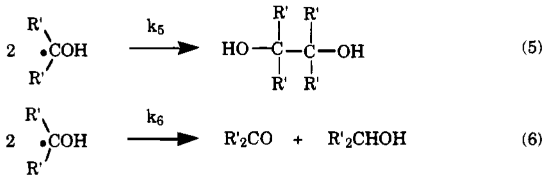


In diglyme solutions, for example, quantum yields of HBr formation were systematically around 2.0, whereas in acetonitrile (a poor hydrogen-donor solvent) yields of HBr were significantly lower (<0.1) as a result of an efficient formation of Br_2. However, both in diglyme and in acetonitrile solutions, irradiation of **2** led to the formation of 1-decene with a quantum yield (as determined by GC analyses) of 1.0 confirming, as already mentioned, that each photon leads to the loss of two bromine atoms and consequently, to the formation of a C−C double bond. In alcohol-containing systems, however, quantum yields of HBr formation were systematically higher than 2.0. In addition, these quantum yields were found to decrease in the presence of oxygen. Table 1 summarizes the quantum yields of HBr formation obtained when using **1** and **4** as vicinal dibromides.

A reaction mechanism such as the one represented by reactions 1−3 can explain only quantum yields of HBr formation equal to or lower than 2.0. As already indicated, quantum yields of acid formation lower than 2.0 frequently result as a consequence of an efficient recombination of bromine atoms to yield Br_2. In addition, McGimpsey et al. have recently shown that resonance stabilized systems (leading to benzylic radical centers) frequently cleave only one C−Br bond, i.e., reaction 2 is slow.[7] Quantum yields higher than 2.0, such as those observed in alcohol-containing systems, clearly indicate that an additional source of HBr generation must be available. The observation of quantum yields of HBr formation greater than two supports a mechanism involving a chain reaction; the inhibiting effect of oxygen suggests that such a mechanism must involve species reactive towards oxygen, such as carbon-centered free radicals. In the presence of alcohols, hydrogen abstraction as represented by reaction 3 will lead to the formation of ketyl radicals. These free radicals are known to be excellent reducing agents, and ketyl-mediated chain processes have been documented.[8] Further, ketyl radicals are expected to react readily with molecular oxygen.

Reduction of bromoalkanes by ketyl radicals can lead to the formation of carbon centered radicals by loss of bromide.[9,10] The proposed mechanism for the chain-amplified generation of HBr from vicinal dibromides in the presence of alcohols can be represented as shown in Scheme 1.

Chain termination would occur mainly by self-reaction and disproportionation of ketyl radicals (reactions 5 and 6); the predominant reaction being dependent of the type on ketyl radical.[11]



$$2\,R'_2\dot{C}OH \xrightarrow{k_5} HO-CR'_2-CR'_2-OH \quad (5)$$

$$2\,R'_2\dot{C}OH \xrightarrow{k_6} R'_2CO + R'_2CHOH \quad (6)$$

Thus, inhibition by oxygen (Table 1) is attributed to scavenging of ketyl radicals in competition with reactions 4−6.

The formation of ketone (reaction 4) was verified for the photolysis of **3** in 2-propanol, where acetone was identified by HPLC, along with the expected debromination products from **3**.

To fully characterize the proposed mechanism for the chain-amplified formation of HBr, efforts were directed toward the determination of absolute rate constants for the individual processes (reactions 2−4) involved in the propagation steps of the chain reaction.

***β*-Cleavage (Reaction 2).** In previous work, we have shown that *β*-cleavage from radicals of the type $R\dot{C}HCH_2Br$ derived from **1**, **2** and **3** leads to the loss of bromine atom (reaction 2) within the time resolution of our system ($\tau \approx 20$ ns).[4] Consequently, a conservative lower limit for this process is $k_2 \geq 5 \times 10^7\ s^{-1}$. We remain interested in the dynamics of this reaction, but at this point it is clear that this process will not be the rate-determining step for chain propagation.

Hydrogen Abstraction by Bromine Atoms (Reaction 3). As already reported,[4] formation of $Br_2^{\bullet -}$ can be used as a probe to determine absolute rate constants for hydrogen abstraction (k_3) by bromine atoms. The rate of formation of the signal due to $Br_2^{\bullet -}$ (k_{growth}), was determined by time-resolved laser flash photolysis techniques and is related to the kinetics of reaction 3 according to eq 7, where k_0 represents the rate constant

$$k_{growth} = k_0 + k_3[RH] \qquad (7)$$

for bromine atom decay in the absence of added RH. Values of k_3 are then obtained from the slope of linear plots of k_{obs} vs [RH] (Figure 1). Representative values thus obtained are 9.3×10^5, 4.1×10^7, and $4.1 \times 10^9\ M^{-1}\ s^{-1}$ for methanol,[4] 2-propanol,[4] and benzhydrol, respectively. Clearly, these rate constants follow the known relative order of reactivity as determined by the C−H bond dissociation energy at the alcohol moiety.[12] When the hydrogen donor has a significant absorption in the UV region (e.g, benzhydrol), the direct photo-

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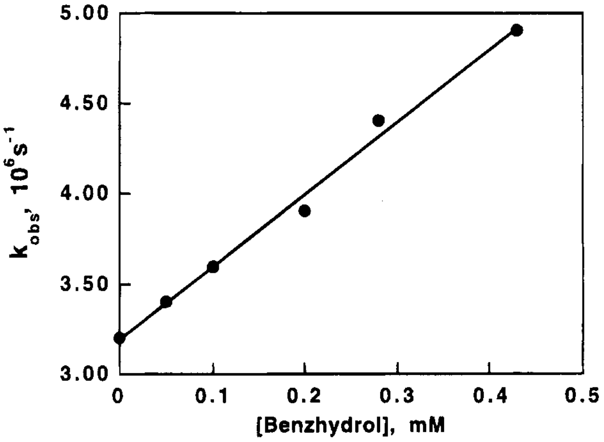
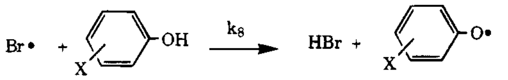


Figure 1. Plot according to eq 7 for reaction of bromine atoms with benzhydrol.

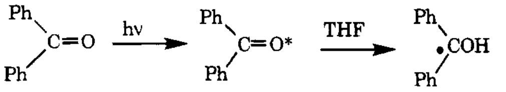
decomposition of vicinal dibromides can be inefficient as a result of UV screening by the donor. In these cases α-bromoacetophenone[13] was employed as a bromine atom precursor, since its absorption extends well into the 350 nm region.

Interestingly, hydrogen abstraction by bromine atoms from *p*-cresol was found to be diffusion controlled in acetonitrile solution (i.e., $k_8 = 3 \times 10^{10}\ M^{-1}\ s^{-1}$),[4] and therefore this process is 1–4 orders of magnitude more rapid than hydrogen abstraction from alcohols. Thus, in phenol-containing systems—such as typical photoresist compositions—chain transfer to phenolic groups (eq 8) may represent a major limitation to the chain amplified generation of HBr by alcohols.



(8)

Reduction of Vicinal Dibromides by Ketyl Radicals (Reaction 4). To determine k_4 values, ketyl radicals were generated by photoreduction of ketones in a hydrogen donor solvent unable to carry the chain reaction, such as tetrahydrofuran. Ketone photoreduction is known to be mediated by the triplet state of the carbonyl chromophore and is an efficient process when this triplet has n,π^* character.[14] In our initial experiments we have employed benzophenone as a precursor of ketyl radicals (reaction 9). These radicals are the same ones generated when benzhydrol is used as hydrogen donor in reaction 3 (Scheme 1).



$$Ph_2C{=}O \xrightarrow{h\nu} Ph_2C{=}O^* \xrightarrow{THF} Ph_2\dot{C}OH \qquad (9)$$

The rate of decay of ketyl radicals (k_{decay}), measured by means of conventional flash photolysis, is related to the kinetics of reaction 4 according to eq 10, where k_0 represents the rate constant for decay of ketyl radicals in the absence of added vicinal dibromide and, therefore, being dominated by second order kinetics. The observed

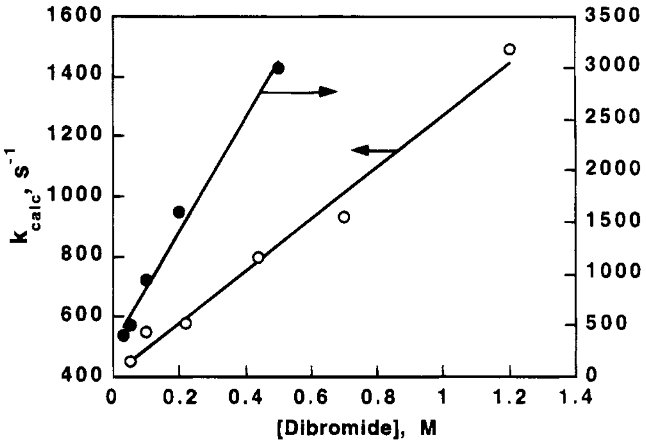


Figure 2. Plot of k_{calc} for reaction of ketyl radicals with vicinal dibromides (○, **1**; ●, **4**).

$$k_{decay} = k_0 + k_4[\text{dibromide}] \qquad (10)$$

decay traces measured as a function of [dibromide] were fitted to competitive first and second order processes. Values of k_4 where then obtained from the slopes of linear plots of the calculated pseudo-first-order rate constants (k_{calc}) against the concentration of dibromide (Figure 2). The rate constants obtained in this manner are given in Table 2. These rate constants suggest that, under our experimental conditions, the reduction of vicinal dibromides by ketyl radicals is the rate determining step in the chain process of Scheme 1. To verify this conclusion, 1-decene concentrations were determined as a function of the total concentration of **2** in two 2-propanol solutions with identical absorbances at 254 nm (i.e., constant initiation rate); the latter being achieved using concentrations of **2** inversely proportional to the diameter of the quartz test tubes employed for these experiments. If the electron-transfer process is the rate-limiting step, the concentration of 1-decene will increase as the total initial concentration of **2** increases. On the other hand, if hydrogen abstraction were the rate-limiting step, the concentration of 1-decene would be independent of the total initial concentration of vicinal dibromide. On the basis of GC analysis it was found that the concentration of 1-decene increases from 5.8 to 14 mM as the total initial concentration of **2** was varied from 0.028 to 0.095 M.

Chain Lengths. Direct irradiation (254 nm) of vicinal dibromides in alcohol solutions leads to the quantum yields of HBr formation (Φ_{Br}) reported in Table 1. According to the proposed mechanism, the quantum yield of bromine atom formation equals twice the chain lengths (i.e., chain length, $\nu = \Phi_{Br}/2$). These chain lengths range from 6 in methanol to 20 in 2-propanol under our experimental conditions. Chain lengths based on quantum yields of alkene formation (i.e., chain length = Φ_{alkene}) are in full agreement with those obtained from HBr analysis. These experiments were based on the use of **2** as vicinal dibromide and quantification of 1-decene by GC analyses. Quantum yields of 1-decene formation were found to be one-half of the corresponding quantum yields of HBr formation, as expected.

Alcohols such as benzhydrol, however, absorb significantly at 254 nm and compete with the vicinal dibromides for absorption at this wavelength. In these cases one needs an alternate way to trigger the chain-

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[12] Reported C–H bond dissociation energies for methanol and 2-propanol are 94 and 91 kcal/mol, respectively (McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493), while for benzhydrol reported values range from 75.4 to 87 kcal/mol (Arnaut, L. G.; Caldwell, R. A. *J. Photochem. Photobiol. A: Chem.* **1992**, *65*, 15. Poston, P. E.; Harris, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 644).

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Table 2. Rate Constants for Reaction of Benzophenone Ketyl Radicals with Vicinal Dibromides in Tetrahydrofuran

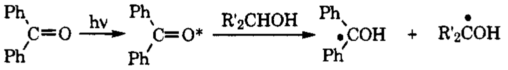
compound	k_4 (M^{-1} s^{-1})
1	8.9×10^2
2	3.7×10^3
3	4.8×10^3
4	5.6×10^3

Table 3. Sensitized Quantum Yields of 1-Decene Formation in the Presence of Alcohols[a]

expt	solvent	Φ_{alkene}
1[b]	methanol	0.7
2[b]	2-propanol	1.3
3[b]	1 M methanol in benzene	0.0045
4[b]	1 M 2-propanol in benzene	0.0074
5[b]	1 M benzhydrol in benzene	0.0028
6[c]	2-propanol	6

[a] [**2**] = 0.020 M. [b] Benzophenone (0.023 M) as sensitizer; 350-nm lamp irradiation. [c] Acetone as sensitizer; 300-nm lamp irradiation.

amplified generation of HBr. This can be achieved, for example, by generating the ketyl radicals by photoreduction of benzophenone in the presence of aliphatic alcohols (reaction 11).


(11)

Reaction 11 produces aliphatic and aromatic ketyl radicals. Both are expected to reduce vicinal dibromides according to reaction 4, thus triggering the chain mechanism of Scheme 1. The rate constants for the aliphatic ketyl radicals (for reaction 4) are probably faster than for their aromatic counterparts, reflecting the thermodynamic changes. Thus, the enthalpy changes for H-atom loss ($R_2\dot{C}OH \rightarrow R_2CO + H$) are 35, 30.3, and 27.2 kcal/mol for the radicals from benzhydrol, methanol, and 2-propanol, respectively.[15,16]

Sensitized quantum yields are defined as the ratio between the number of moles of product formed (i.e., alkene in the case of these experiments) and the number of photons absorbed by the sensitizer. Table 3 (entries 1−5) summarizes sensitized quantum yields of alkene formation when using **2** as vicinal dibromide and benzophenone as sensitizer. These quantum yields are significantly lower than those determined by direct irradiation of vicinal dibromides; in fact, no chain reaction is observed. These results suggest that some other reaction routes for the ketyl radicals intermediates which have detrimental effects on the chain-amplified formation of HBr are involved in these cases.

The mechanism of photoreduction of benzophenone by aliphatic alcohols has been widely investigated.[14,17] In the case of 2-propanol as solvent, hydrogen abstraction by benzophenone triplets (reaction 11, R′ = CH_3) leads to the formation of diphenyl and dimethyl ketyl radicals. These radicals may either combine or disproportionate (e.g, reaction 12) and thus contribute to the termination of the chain-amplified formation of HBr. Furthermore, radical−radical recombination such as reactions 5 and 6 may compete better as the steady-state concentration of radicals increases. These types of processes have absolute rate constants in the 10^8−10^9 M^{-1} s^{-1} range.[18]

Of relevance to the quenching of the chain mechanism, however, is the exchange of hydrogen atoms between ketyl radicals and ketones,[11,19−21] such as the reduction of benzophenone by dimethyl ketyl radicals (reaction 13). This process leads to the formation of

$$Ph_2\dot{C}OH + (CH_3)_2\dot{C}OH \xrightarrow{k_{12}} Ph_2CO + (CH_3)_2HCOH \tag{12}$$

$$Ph_2CO + (CH_3)_2\dot{C}OH \xrightarrow{k_{13}} Ph_2\dot{C}OH + (CH_3)_2CO \tag{13}$$

diphenyl ketyl radicals (which in general are an order of magnitude less reactive than dialkyl ketyl radicals) with an absolute rate constant of the order of 10^4−10^5 M^{-1} s^{-1}.[11,19,20] Therefore, under our experimental conditions, this reaction is more efficient than reaction 4.

Benzophenone triplet, on the other hand, is found to be quenched by dibromodecane with a rate constant of 1.7×10^6 M^{-1} s^{-1} in acetonitrile solutions. The contribution of this quenching process will be more significant as the concentration of alcohol decreases (e.g., Table 3, entries 3−5).

Hydrogen atom exchange between dimethyl ketyl radicals and benzophenone (i.e., reaction 13) appears to play a key role in the inhibition of the sensitized formation of HBr by benzophenone. We reasoned that this detrimental effect could be avoided if one uses acetone as sensitizer instead. Under these conditions, reactants and products of reaction 13 are a dimethyl ketyl radical and acetone. A sensitized quantum yield of 1-decene formation and consequently, a chain length of six is obtained in a 2-propanol solution of **2** (Table 3, entry 6). Acetone triplet quenching by **2** in acetonitrile solution is similar to that of benzophenone triplet (1.9×10^6 M^{-1} s^{-1}). The inhibiting effect is mainly attributed in this case to an increase of the relative contribution of ketyl radical−ketyl radical reactions which, as mentioned before, compete better as the steady-state concentration of radicals increases.

Conclusion

The results reported here show that vicinal dibromides undergo photodecomposition in the presence of alcohols via a free-radical chain reaction that generates two molecules of HBr per propagation cycle. The reaction follows the mechanism of Scheme 1 with the reduction of vicinal dibromides by ketyl radicals (reaction 4) as the likely rate determining step. Chemically amplified resists play an important role in modern microlithography; the new mechanism reported here opens the possibility of amplification in the initial photoinduced acid generation step and has the potential to lead to a dramatic increase in photospeed.

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Experimental Section

Materials. 1,2-Dibromoethane (**1**), tris(2,3-dibromopropyl) isocyanurate (**3**), α-bromoacetophenone, and benzhydrol, all from Aldrich, and tris(2,3-dibromopropyl) phosphate (**4**), from ICN, where used as received. 1,2-Dibromodecane (**2**) was prepared and purified as previously reported.[4] All solvents, spectra grade from BDH, were used as received.

General Techniques. UV–visible spectra were recorded using a Hewlett-Packard 8451 diode array spectrometer. Gas chromatographic analyses were carried out on a Perkin-Elmer Model 8320 capillary instrument fitted with a 15-m DB-5 bonded-phase column from J&W Scientific. 1,2-Dibromodecane showed no thermal decomposition under the conditions of these analyses. HPLC analyses were performed on a Varian Instrument fitted with a 15-cm column (Varian) type Micro-Pack SP-C18.

Steady-state irradiations were performed in a photoreactor equipped with RPR-254 or RPR-350 lamps from the Southern New England Ultraviolet Co. The temperature in this reactor was typically between 32 and 35 °C. The samples were contained in quartz cells of the same type used for laser flash experiments and were rotated with a "merry-go-round" apparatus to ensure that all samples received the same irradiation dose.

HBr Quantum Yield Determination. Solutions of dibromides having the same concentration of vicinal dibrominated moieties (e.g., 0.12 M for **1** or **2** and 0.04 M for **3** or **4**) were prepared in various hydrogen donor solvents. 2 × 3 mL samples of these solutions were deaerated by bubbling with oxygen-free nitrogen (20–30 min) in quartz cells and then irradiated (e.g., 15 min when using alcohols) at 254 nm using only one lamp in the photoreactor. HBr concentrations were determined by duplicate acid–base titrations in methanol solutions using phenolphthalein as indicator. A 0.01 M solution of NaOH in methanol was used as titrant. For these studies, valerophenone was used as an actinometer.[22]

Conventional Flash Photolysis. Kinetics measurements were carried out on a PRA flash photolysis apparatus (Model FP1000). Data were acquired by a Tektronix Model 2332 digital oscilloscope interfaced to a Macintosh Quadra 650 computer. The programs that control the experiment were developed using LabVIEW-2.2 software from National Instruments.

A cylindrical Pyrex sample cell 10 cm long (optical path) and 1.5 cm o.d. with flat windows fused to the ends was employed. The cell was connected by side arms to a reservoir where solutions were contained during the degassing procedure. Solutions were deaerated by purging with oxygen-free argon for 20–30 min. Cutoff filters at 345 nm were used both in front of the monitoring source and the flash lamps. Diphenyl ketyl radical decay traces were recorded by monitoring changes in absorbance at 540 nm.

Laser Flash Photolysis. The few experiments with α-bromoacetophenone and those regarding ketone triplet quenching were carried out using a Lumonics EX-510 excimer laser (Xe/HCl, 308 nm, ~6 ns, ≤40 mJ/pulse) for excitation. The system is controlled by a Macintosh II-ci computer running LabVIEW-2.2 software from National Instruments. This computer is also interfaced (GPIB) to a Tektronix Model 2440 digital oscilloscope used for data acquisition.

Solutions were contained in quartz cells constructed of 7 × 7 mm^2 Suprasil tubing, and deaerated by bubbling with oxygen-free nitrogen. All measurements were performed at room temperature.

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