Remarkable kinetic stability of α-thiocarbamoyl substituted 4-methoxybenzyl cations

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Abstract: 4-Methoxybenzyl cations bearing α -(*N*,*N*-dimethylcarbamoyl) and α -(*N*,*N*-dimethylthiocarbamoyl) substituents have been generated photochemically upon irradiation of precursors with pentafluorobenzoate or 4-methoxybenzoate leaving groups. The ions have been observed with flash photolysis in 40:60 acetonitrile:water and in 50:50 methanol:water, and rate constants were measured for their decay in solvent alone and for their capture by azide ion. The cations so studied and their lifetimes in 40% acetonitrile are **6**, ArC⁺H-CONMe₂, 0.6 µs; **2**, ArC⁺H-CSNMe₂, 7 ms; and **4**, ArC⁺(CH₃)-CSMe₂, 6 ms, where Ar = 4-MeOC₆H₄. The cation **4** reacts with solvent by elimination of a proton from the α -methyl group, and the rate constant for solvent addition must be less than 1 s⁻¹. The CSNMe₂ substituted cations are 10⁵-10⁷-fold longer lived than analogs where the thioamide group has been replaced with an α methyl. The UV–visible absorption spectra of these two cations also show significant differences from those of typical 4-methoxybenzyl cations. Thus, both the lifetimes and spectra point to a strong interaction of the benzylic centre with the thioamide group.

Key words: flash photolysis, thiocarbamoyl stabilized carbocation, photosolvolysis.

Résumé : L'irradiation de précurseurs appropriés portant des groupes partant pentafluorobenzoate ou 4méthoxybenzoate permet de générer photochimiquement des cationns 4-méthoxybenzyle portant des substituants α -(*N*,*N*-diméthylcarbamoyle) et α -(*N*,*N*-diméthylthiocarbamoyle). On a observé les ions par photolyse éclair dans des mélanges 40 : 60, acétonitrile : eau et de 50 : 50, méthanol : eau et on a mesuré les constantes de décroissance dans les solvants seuls ainsi que pour leur capture par l'ion azoture. Les cations ainsi étudiés et leurs temps de vie dans l'acétonitrile à 40% sont : **6**, ArC⁺H-CONMe₂, 0,6 µs; **2**, ArC⁺H-CSNMe₂, 7 ms et **4**, ArC⁺CH₃-CSNMe₂, 6 ms dans lesquels Ar = 4-MeOC₆H₄. Le cation **4** réagit avec le solvant pour donner une élimination de proton provenant du groupe méthyle en α et la constante de vitesse pour l'addition du solvant doit être inférieure à 1 s⁻¹. Les temps de vie des cations substitués par CSNMe₂ sont de 10⁵–10⁷ fois plus grandes que celles de leurs analogues dans lesquels le groupe thioamide a été remplacé par un α -méthyle. Les spectres d'absorption UV–visible de ces deux cations présentent des différences importantes par rapport à ceux des cations 4-méthoxybenzyles typiques. Les temps de vie et les spectres suggèrent donc tous les deux qu'il existe une forte interaction entre le centre benzylique et le groupe thioamide.

Mots clés : photolyse éclair, carbocation stabilisé par un groupe thiocarbamoyle, photosolvolyse.

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There have been several recent studies of solvolysis reactions involving carbocations substituted at the C⁺ center with a thioamide functional group such as CSNMe₂ (1–9). There is good evidence that the reactions do occur by a stepwise $D_N + A_N (S_N 1)$ mechanism proceeding via a carbocation intermediate (2, 4, 7). Rate constants for the formation of the α -thioamido substituted cation relative to an analog with α methyl vary. In some cases the former forms slightly more

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¹Author to whom correspondence may be addressed. Telephone: (416) 978-3592. Fax: (416) 978-3592. E-mail: rmcclell@alchemy.chem.utoronto.ca slowly, in some cases somewhat more quickly, and in some cases considerably more quickly. On the other hand, an α -CONMe₂ substituted cation generally forms considerably more slowly than its α -methyl analog.

Less is known about the rate constants for solvent capture of the fully formed cations. The 9-thioamidofluorenyl cation **1** has been claimed as a transient intermediate in a laser flash photolysis experiment in 2,2,2-trifluoroethanol (TFE) (6). There are, however, now serious concerns over the structural assignment in this study, since the chloro precursor that was supposedly employed decomposes instantly when dissolved in TFE (9).



Table 1. Rate constants for solvent decay and azide quenching of 4-methoxybenzyl cations $4-\text{MeOC}_6\text{H}_4\text{C}^+\text{R}_1,\text{R}_2$ generated by flash photolysis of **7–9**. Experiments at 20°C in 40:60 acetonitrile:water at ionic strength zero and in 50:50 methanol:water at ionic strength 0.5 with NaClO₄.

	7 ightarrow 6	8 ightarrow 2	9 ightarrow 4
Constant	CONMe ₂ , H	CSNMe ₂ , H	CSNMe ₂ , Me
$k_{\rm s}$ (40% AN), s ⁻¹	$(1.6\pm0.1) \times 10^{6}$	$(1.5\pm0.2) \times 10^2$	$(1.8\pm0.2) \times 10^2$
$k_{\rm az}$ (40% AN), M ⁻¹ s ⁻¹	$(5.4\pm0.3) \times 10^9$	$(6.3\pm0.2) \times 10^7$	Not measured
$k_{\rm s}$ (50% MeOH), s ⁻¹	$(8.6\pm0.4) \times 10^{6}$	$(2.4\pm0.1) \times 10^2$	$(2.1\pm0.1) \times 10^2$
$k_{\rm az}$ (50% MeOH), M ⁻¹ s ⁻¹	$(2.1\pm0.3) \times 10^9$	$(1.03\pm0.03) \times 10^7$	$(4.9\pm0.2) \times 10^4$
$k_{\rm az}:k_{\rm s}$ (50% MeOH), M ⁻¹	$(2.4\pm0.4) \times 10^2$	$(4.3\pm0.2) \times 10^4$	$(2.3\pm0.2) \times 10^2$
$k_{az}:k_s$ (50% MeOH-sol), ^{<i>a</i>} M ⁻¹	2.1×10^2	7×10^4	$1.8 \times 10^{2} {}^{b}$

^a Ratio obtained from analysis of products of ground state solvolysis (7).

^b Solvent reaction is elimination. Azide reaction is sum of elimination and addition.

In a second study, competition kinetics in 50:50 methanol:water revealed that the benzylic derivative 2 has an azide:solvent selectivity $k_{az}:k_s$ of 7×10^4 M⁻¹ (7). This is 10⁴-fold greater than the $k_{az}:k_s$ of 7.2 M⁻¹ for the 4-methoxyphenethyl cation 3 in the same solvent (7). With the assumption that the azide combination is a diffusion-limited process (10), so that k_{az} is the same for both cations (~5 × 10⁹ M^{-1} s⁻¹), the lifetime $(1/k_s)$ of the thioamido-substituted cation is 10 000-fold longer. Unexpected behavior is also seen with α -thioamido, α -methyl substituted cations (4, 7). The cation 4, for example, reacts with solvent to give exclusively the alkene product derived from elimination of one of the α -protons (7). Elimination even occurs with azide although, with this ion, addition to the C⁺ center also occurs. Such behavior contrasts with that of the cumyl cation analog 5, where only nucleophilic addition is observed (e.g., less than 1% elimination in the reaction with solvent in 50:50 methanol:water) (7).



As noted in the original paper (7), the large k_{az} : k_s ratio for 2 leads to concerns about the applicability of the azide clock assumption. The competing elimination/addition with 4 raises this question even more with this system. In consequence, we have performed flash photolysis experiments so as to obtain the absolute rate constants for these cations. The α -amido substituted 6 was included for comparison purposes. It transpires that these cations can be generated from the same precursors employed in the studies of the ground solvolysis. Moreover, the α -thioamido cations are remarkably long-lived.

Results

The substituted benzoates **7–9** were employed as photochemical precursors of the cations **6**, **2**, and **4**, respectively. These esters undergo ground state solvolysis with half-lives of 100 h (**7**), 130 s (**8**), and 5.2 h (**9**) in 50:50 methanol:water at 25°C (**7**). With **8** this meant that the flash photolysis experiments needed to be carried out immediately after preparation of the solution. It in fact proved possible to prepare the solution and irradiate within 20 s.



Flash photolysis spectra obtained with 7-9 in 40% acetonitrile are shown in Fig. 1. The benzoate 7 produces a transient species with λ_{max} around 350 nm, which decays over 5–10 µs to essentially zero OD. The decay is first order, with the same rate constant being obtained across the entire spectrum consistent with the presence of a single transient species. Absorbing species are also observed with 8 and 9. However, these show no decay up to times as long as 500 μ s, the longest time that can be reliably employed with the laser flash photolysis apparatus. Decay is seen, however, using a lamp photolysis apparatus. Like 7, these decays are first order with the same rate constant throughout the spectrum. The λ_{max} of the transients with $\boldsymbol{8}$ and $\boldsymbol{9}$ lie in the range 310-325 nm, being slightly higher with 9. There is, however, some distortion of the spectra, since the thioamido precursors absorb below 310 nm. (Note that these experiments measure a $\triangle OD$, the OD after the laser pulse minus the OD before.) With 9, there is a second weaker absorption with λ_{max} around 500 nm. This is due to the same transient as the absorbance at lower wavelength, since the decay here has the same rate constant. It can be noted that with 8, aged solutions that had undergone solvolysis to the alcohol failed to produce any transient.

Azide ion accelerates the decay of all three transients, with linear plots of the observed rate constant versus azide concentration. Values of k_s , the first-order rate constant for decay in solvent alone, and k_{az} , the second-order rate constant for the quenching by azide ion, are given in Table 1. Two solvents were employed, 40:60 acetonitrile:water, and 50:50 methanol:water. The former was chosen to provide comparisons with rate constants measured by flash photolysis for other benzylic cations. The latter was the solvent



employed in the analysis of the products of the ground state solvolysis of these esters.

The final products of the irradiation were examined in 40% aqueous acetonitrile. These experiments were carried out by preparing a solution of the precursor benzoate of concentration ~100 μ M, which was then split in two. One half was irradiated at 254 nm, while the other was kept in the dark under conditions sufficient for complete ground state solvolysis. The HPLC chromatograms of the two were then compared, along with the chromatograms of the authentic products of the ground state hydrolysis.

With **8**, which undergoes a relatively rapid ground state solvolysis, the solvent was cooled to 0° C before addition of the substrate. After substrate addition, half was irradiated at this temperature for 30 s, a time sufficient to remove 95% of the precursor. The other half was warmed to room temperature and allowed to stand for a total time of 1 h. (The half-life at 20°C is 4 min.) The products observed in both the excited state and ground state reactions were the alcohol **10** and pentafluorobenzoic acid (eq. [1]). Based on the relative areas of the peaks (with a small correction for remaining precursor), the yield of the the alcohol in the irradiated solution was 102% of that in ground state. Thus, within experimental error, there was quantitative formation of the same product of the ground state solvolysis.

The same conclusion was reached with **9**. Again, 30 s irradiation was sufficient to photolyze 95% of the precursor. Four hours at 50°C was required for the ground state reaction. The observed products from both were the alkene **12** and 4-methoxybenzoic acid (eq. [2]). The yield of alkene in the irradiated solution was 97% of that of the solvolyzed one.

With **9**, the situation was more complicated. The photolysis was considerably less efficient, 3 min of irradiation for example only reacting 45% of the starting material. A consequence was that the products were not stable, unlike the situation with the two thioamides, but underwent further photochemistry. The solvolysis reaction required overnight at 50°C for completion, and gave the expected alcohol **11** and pentafluorobenzoic acid (eq. [1]). These were also the major products in the irradiated solution, but their yields expressed as a percentage of reacted **7** decreased with increased irradiation time. Based on a three-point extrapolation to zero irradiation, the yield of alcohol is 60–70%. The HPLC chromatogram of the irradiated solution did have other peaks, but these were not identified.

Discussion

Identification of transients as benzylic carbocations

While there is no spectrum of an authentic cation available for comparison, there is good evidence that the transients observed with the three esters 7-9 are cations forming by photoheterolytic cleavage of the α -carbon-oxygen bond. Firstly, the stable products of irradiation are those expected of a photosolvolvsis. In the case of the thioamides 8 and 9 in fact, there is a very efficient conversion to exactly the same products obtained in the ground state solvolysis reaction. Secondly, the transients are quenched by azide ion, a typical carbocation trap. More importantly, the absolute rate constants k_{az} and k_s obtained by flash photolysis give selectivities $k_{az}:k_s$ that are essentially the same as those obtained in the ground state solvolysis (7). This comparison was made in 50:50 methanol:water and is shown in Table 1. In the case of the cations 4 and 6, the flash photolysis ratio is slightly larger but the difference is not outside experimental error. With 2, the flash photolysis ratio is about two thirds of that obtained in the competition experiment. The latter was, however, obtained with azide ion concentrations in the range 0.5-1.0 mM, where >95% of the products arise from azide trapping (7). This means that the amount of alcohol product being measured is quite small, creating some uncertainty in the final ratio.

Rate constants for addition and elimination in cation 4 The reaction of the cation **4** gives only alkene product in 50:50 methanol:water (7). Thus the decay of this ion observed in the flash photolysis experiments represents the reaction with solvent acting as a base, and the k_s of 210 s⁻¹ is equal to $k_s(B)$ of eq. [3]. There is less than 1% of the ether and alcohol products that would arise form nucleophilic addition of solvent. Thus $k_s(Nu) < 2 \text{ s}^{-1}$.

With azide ion, both elimination and addition occur. The azide-catalyzed elimination is seen in the observation that the alkene:RN₃ ratio does not approach zero at high concentrations of azide, but plateaus, in fact, with a greater amount of alkene (7). The limiting [alkene]:[RN₃] is 1.69; this is equal to the ratio of rate constants for azide acting as a base and a nucleophile, $k_{az}(B):k_{az}(Nu)$. The quenching that is observed with azide ion in the flash photolysis studies represents the sum of these two processes, i.e., k_{az} (flash photolysis) = $k_{az}(B) + k_{az}(Nu)$. Since the ratio is known from the product analysis, the absolute values of the two can be calculated. Thus $k_{az}(B) = 3.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{az}(Nu) =$

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R_1	R ₂	$(1/k_{\rm s})$ in TFE	$(1/k_s)$ in W:AN ^a	Ref.	
Н	Н	0.2 µs		12	
Н	CH_3	2.5 µs		12	
CH ₃	CH ₃	60 µs	25 ns	12	
Н	COOMe	6 µs	50 ns	13	
Н	CONMe ₂		0.6 µs	This work	
Н	CSNMe ₂		7 ms	This work	
CH ₃ CSNMe ₂	CSNMe ₂		6 ms (elim.)	This work	
			>1 s (add)		

Table 2. Lifetimes of 4-methoxybenzyl cations 4-MeOC₆H₄C⁺R₁R₂ measured by flash photolysis.

^{*a*} The lifetimes of carbocations in aqueous acetonitrile solutions (0–60% acetonitrile) do not change by more than 10–20% with changing acetonitrile content (14).

$$[3] 4-MeOC_{6}H_{4} - \underset{+}{\overset{C}{\overset{}_{\text{H}_{2}}(B)[N_{3}^{-}]}{\overset{}_{\text{K}_{8}(B)}}} \xrightarrow{CH_{2}S} \\ \underbrace{\overset{K_{82}(B)[N_{3}^{-}]}{\overset{K_{82}(B)}} 4-MeOC_{6}H_{4} - \underset{-}{\overset{C}{\overset{}_{\text{C}}(B)}} \\ \underbrace{\overset{K_{82}(Nu)[N_{3}^{-}]}{\overset{K_{82}(Nu)[N_{3}^{-}]}} \\ \underbrace{\overset{K_{82}(Nu)[N_{3}^{-}]}{\overset{K_{82}(Nu)}} 4-MeOC_{6}H_{4} - \underset{-}{\overset{C}{\overset{}_{\text{C}}(B)}} \\ \underbrace{\overset{K_{82}(Nu)[N_{3}^{-}]}{\overset{K_{82}(Nu)}} \\ \underbrace{\overset{K_{82}(Nu)[N_{3}^{-}]}{\overset{K_{82}(Nu)}} \\ \underbrace{\overset{K_{82}(Nu)[N_{3}^{-}]}{\overset{K_{82}(Nu)[N_{3}^{-}]}} \\ \underbrace{\overset{K_{82}(Nu)[N_{8}(Nu)[N_{8}^{-}]}} \\ \underbrace{\overset{K_{82}(Nu)[N_{8}(Nu)[N_{8}^{-}]} \\ \underbrace{\overset{K_{82}(Nu)[N_{8}(Nu)[N_{8}^{-}]}} \\ \underbrace{\overset{K_{82}(Nu)[N_{8}(Nu)[N_{8}^{-}]} \\ \underbrace{\overset{K_{82}(Nu)[N_{8}(Nu)[N_{8}^{-}]} \\ \underbrace{\overset{K_{82}(Nu)[N_{8}(Nu)[N_{8}^{-}]} \\ \underbrace{\overset{K_{82}(Nu)[N_{8}(Nu)[N_{8}^{-}]} \\ \underbrace{\overset{K_{82}(Nu)[N_{8}(Nu)[N_{8}^{-}]} \\ \underbrace{\overset{K_{82}(Nu)[N_{8}(Nu)[N_{8}^{-}]} \\ \underbrace{\overset{K_{82}(Nu)[N_{8}(Nu)[N_{8}(Nu)[Nu]]} \\ \underbrace{\overset{K_{82}(Nu)[N_{8}(Nu)[N$$

 1.8×10^4 M⁻¹ s⁻¹. The latter is a remarkably low number for the addition of azide ion to a carbocation. Even the tris(4-methoxyphenyl)methyl cation reacts with $k_{\rm az}$ around 10^7 M⁻¹ s⁻¹ (11).

It is also worth noting that for stabilized triarylmethyl cations k_{az} : k_s is approximately constant with changing reactivity (11), although the ratio starts to sharply decrease when the azide reaction approaches the diffusion limit. For the cation **2**, where both azide and solvent react as nucleophiles, k_{az} : $k_s = 4.5 \times 10^4$. If the same ratio were to apply to the nucleophilic reactions of **4**, then k_s (Nu) for this cation would be 0.4 s⁻¹, only 0.2% of the k_s (B) value.

Lifetimes of 4-methoxybenzyl cations

As suspected in the earlier study (7), the assumption of diffusion control for the reactions of azide ion with the cations **2** and **4** is incorrect. The reactions with azide are considerably slower than diffusion, and the lifetimes of these two cations are substantial. A comparison with other 4-methoxybenzylic cations whose rate constants have been directly determined by flash photolysis is presented in Table 2. In the case of the parent 4-methoxybenzyl and the derivative with one α -methyl group, the lifetimes are too short in aqueous solutions for the cations to be studied by ns laser flash photolysis. These cations can, however, be observed in the less nucleophilic TFE.

As was observed previously with an α -COOMe derivative (13), the α -CONMe₂ cation **6** examined in this work is longer lived than its α -methyl analog. The differences, however, are not large. The amide is an order of magnitude longer lived than the ester, which in turn is probably about another order of magnitude longer lived in water than the α -methyl derivative (7, 10). These kinetic stabilizations occur in spite of the fact that the α -CO cations are much less thermodynamically stable. Such observations are also made with cations bearing α -CF₃ substituents. Explanations for this behaviour have been proposed in the literature and need not be repeated here (7, 13, 15, 16).

The cations bearing α -CSNMe₂ on the other hand are extraordinarily long-lived. The secondary ion **2**, for example, is 10⁴ longer lived than its CONMe₂ analog and 10⁶–10⁷ longer lived than the 4-methoxyphenethyl cation. The tertiary **4** is 10⁵ longer lived than the 4-methoxycumyl cation. If this comparison involves only solvent addition to the α -C⁺ center, this factor rises to 10⁷.

There are two possible interactions that could account for the stabilization. One involves a resonance interaction as shown in structure **13b** where the positive charge is delocalized to the sulfur atom. A large fraction of this interaction would be lost in the transition state for solvent capture, leading to an unusually low reactivity (15, 16). The second possibility is the formation of a bridged ion, shown as the resonance structures **13c** and **13d**.



Fig. 1. Flash photolysis spectra obtained on irradiation of **7** (*a*), **8** (*b*), and **9** (*c*) in 40:60 acetonitrile:water. Figure 1(*a*) was obtained with 248 nm laser flash photolysis; Figs. 1(*b*) and 1(*c*) were obtained with lamp flash photolysis. In each figure the uppermost spectrum is the Δ OD measured immediately after the laser or lamp flash, the middle spectrum is the Δ OD at a time corresponding to one half-life of the decay, and the bottom spectrum is the Δ OD at the completion of the decay (6–8 halflives). The points drawn as full squares in Fig. 1(*b*) were obtained with the laser flash photolysis apparatus, and represent the Δ OD immediately after the laser flash, normalized to the same Δ OD's obtained in the lamp flash photolysis experiment.



Ab initio calculations have found that an α-thioamido cation where $R_1 = H$ and $R_2 = H$ is stabilized by 35.7 kcal/mol by the first interaction, but a further 47.2 kcal/mol stabilization accompanies conversion to the cyclic structure (17). The cation 13 with $R_1 = H$ and $R_2 = 3,5$ -bis(trifluoromethyl)phenyl reacts predominantly as a closed ion, giving 86% of a product that has arisen from reaction of solvent (acetic acid) at the thioamide carbon (2). The cation 2 of this study, however, reacts to give products of addition at the α -carbon (7). This cation of course has the strongly electron-donating 4-methoxy group, which would favour the open structure, and the contrasting behaviour with the bis-CF3 cation implies it must be reacting through this form. There is the possibility that the open cation is a minor species in an equilibrium mixture with an unreactive closed form (7). This, however, cannot account for all of the kinetic stabilization. This conclusion is based on the measured k_{az} for 2 in aqueous acetonitrile, which is about 1% of the k_{az} of a diffusioncontrolled combination (e.g., the k_{az} for **6**). Providing azide ion reacts with the open cation (as the azide product implies) there must be at least 1% of the open cation in the mixture with the closed one. A percentage less than 1% requires k_{az} to be greater than the encounter limit. This in turn means that $k_{\rm w}$ for the open cation must still be less than 10⁴ s⁻¹. This is still two orders of magnitude lower than the $k_{\rm w}$ for 6 and 10^4 lower than the value for the α -methyl cation.

The UV–visible spectra observed for the three cations in this study (Fig. 1) are also interesting in the context of the structural issue. The spectrum for the α -amido cation **6** is typical of 4-methoxybenzyl cations. The 4-methoxyphene-thyl and 4-methoxycumyl ions, for example, have similarly shaped absorption bands (somewhat narrower) with λ_{max} at 340 and 360 nm, respectively (12), in the same region as **6**. With this cation, therefore, there is no indication of anything highly unusual that could be attributed to a strong interaction with the α -carbonyl group.

This, however, cannot be said for the α -CSNMe₂ cations. With 2 the λ_{max} is shifted to a lower wavelength, perhaps not highly unusual for a benzyl cation, but there is a long tailing absorbance, and cation decay is even observed at 550 nm. The methyl cation 4 has a similar λ_{max} at the lower wavelength, and the absorbance at higher λ has now become so pronounced that there is a second band centered around 500 nm. These spectra are clearly different from the spectrum for **6**, and also from those of other benzylic derivatives. It is tempting to ascribe the high-wavelength absorption observed with 4 to increased delocalization, in other words to a strong resonance interaction of the type $13a \leftrightarrow 13b$ in an open cation. The same absorption is seen with 2, but it is much weaker. This suggests the possibility that there is less open cation in this system, although clearly there is still some. Such conclusions are highly speculative, since there are no suitable models that allow unambiguous comparisons to be made. What can certainly be concluded is that the behaviours of the α -CSNMe₂ cations are unusual, and this is paralleled in both the absorption spectra and the kinetic stabilities.

Experimental section

The photochemical precursors 7-9 and the solvolysis

products **10–12** were from a previous study (7). Laser flash photolysis experiments involved ca. 20 ns pulses at 248 nm (60-120 mJ / pulse) from a Lumonics excimer laser (KrF) emission. A pulsed Xenon lamp provided monitoring light. After passing through a monochromator, the signal from the photomultiplier tube was digitized and sent to a computer for analysis. Conventional flash photolysis experiments were performed with equipment previously described (18), with the sample being irradiated with a broad-band flash lamp of ca. 100 ms duration.

The products of irradiation were determined by preparing 5 mL of a solution of 7-9 in 40% aqueous acetonitrile of concentration 100 μ M. With 8, the solvent had been cooled to 0°C in an ice bath before the substrate was added. One half (2.5 mL) of these solutions were placed in a UV cuvette, the other 2.5 mL in a capped vial wrapped in tin foil. The former were immediately irradiated at 254 nm in a spinning merry-go-round in a Rayonet reactor, then immediately analyzed by HPLC. The latter solutions were left under such conditions that no precursor remained (see Results), as shown by HPLC. Identical volumes of the irradiated and solvolyzed solutions were injected into a Waters HPLC, eluting with 60:40 water: acetonitrile through a C18 column. Products were identified by comparison with known standards. The yields of the products in the irradiated solutions were calculated from the relative peak areas of the irradiated and solvolyzed solutions.

Acknowledgments

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