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Laser Flash Photolysis of Carbamates Derived from 9-Fluorenone Oxime

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Abstract: The photochemistry of carbamates derived from 9-fluorenone oxime was investigated by laser flash photolysis and by product studies. Primary photocleavage of the excited carbamates leads to decarboxylation and concomitant generation of the 9-fluorenone ketimine-*N*-yl radical and an amino radical. In the case of 9-fluorenylideneamino *N*-(2,5-dimethoxyphenyl)carbamate the presence of 1,4-dimethoxybenzene in the product mixture as well as spectroscopic and kinetic evidence points to the intermediary formation of triplet (2,5-dimethoxyphenyl)nitrene, which in acetonitrile dimerizes to the corresponding azo compound. Analogously, the formation of *trans*-azobenzene upon photolysis of 9-fluorenylideneamino *N*-phenylcarbamate indicates the intermediacy of parent triplet phenylnitrene, which, until now, had not been observed in solution at ambient temperature.

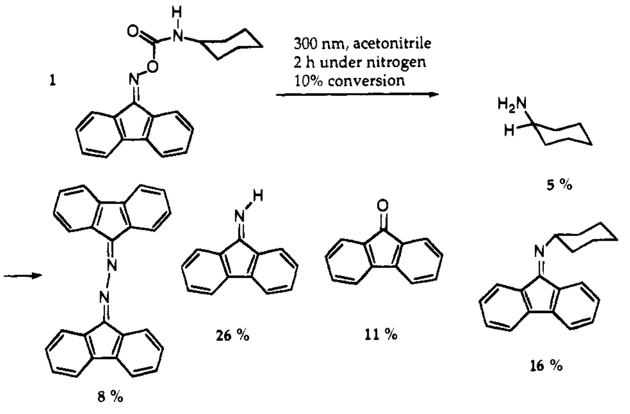
Introduction

Photogenerated acid has been an essential component in chemically amplified photoresists for some time.[1] The first class of compounds to be widely used for this purpose were the diazonaphthoquinones,[2] while more recently, vicinal dibromides proved to be excellent precursors for hydrogen bromide.[3,4] The idea of photochemically generating bases for use in photoresists, on the other hand, is a relatively new concept. The range of precursor molecules explored so far encompasses substances as diverse as cobalt amine complexes,[5] sulfonamides,[6] (*o*-nitrobenzyl)carbamates,[7] and methoxy-substituted cumylcarbamates.[8,9] While the quantum yield of base formation upon photolysis of carbamates may be satisfactory for practical applications, few detailed mechanistic studies to elucidate the reaction pathways have been published to date. In this contribution, we wish to report on the photochemistry of carbamates derived from 9-fluorenone oxime, which represents a novel class of photobases. The photochemistry of these carbamates and the model compounds 9-fluorenone *O*-acetyloxime and 9-fluorenone *N*-acetylketimine was investigated by product studies as well as by nanosecond time-resolved laser flash photolysis.

Results

Studies with 9-Fluorenylideneamino *N*-Cyclohexylcarbamate (1) and Model Compounds. 1. Product Studies. Product studies on **1** were performed in acetonitrile, using a Rayonet photoreactor (6 lamps, $\lambda_{exc} = 300$ nm). The efficiency of the photocleavage of **1** proved to be only moderate and irradiation times of >2 h were required to obtain more than 10% conversion. Evaluation of the GC chromatograms was complicated by the fact that **1** fragments cleanly in the injector block of the GC, yielding 9-fluorenone oxime and cyclohexyl isocyanate. For this reason, both the isocyanate and the oxime always appeared in the chromatograms. In order to assess whether these products were also produced photochemically, we irradiated one sample for an extended period of time (12 h, complete conversion). Due to secondary photochemistry of the primary products, the resulting product mixture was complex, but comparison of GC retention times with authentic samples of 9-fluorenone oxime and cyclohexyl isocyanate showed that these compounds were not present in significant amounts. Control experiments showed that cyclohexyl isocyanate is transparent at the irradiation wavelength, while fluorenone oxime is largely photostable under these conditions, leading only to modest yields of 9-fluorenone ketimine.

Scheme 1



The products formed by irradiation of **1** in acetonitrile under nitrogen ($\lambda_{exc} = 300$ nm, 2 h) are given in Scheme 1; further details are provided in the Experimental Section.

A significant fraction of the cyclohexylamine is probably lost by evaporation prior to analysis. Further, 9-fluorenone probably arises by hydrolysis of 9-fluorenone ketimine by traces of water.

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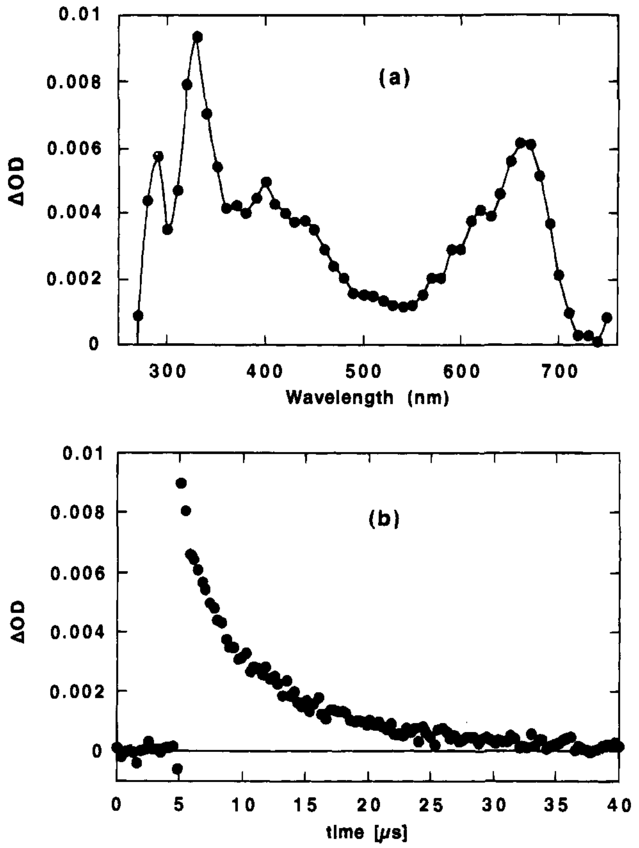
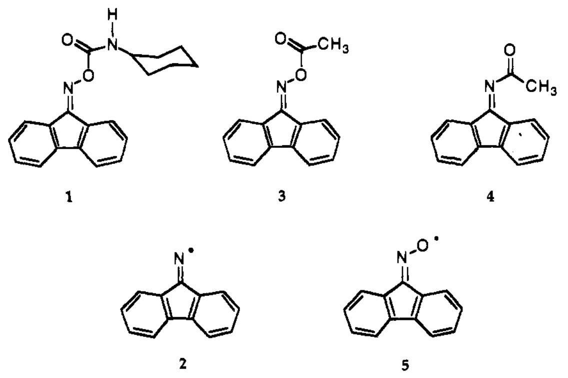


Figure 1. (a) Transient spectrum showing the difference in changes in optical density between the windows recorded 560 ns and 14 μs after laser flash photolysis of **1** in acetonitrile under N_2. (b) Transient decay trace recorded after laser flash photolysis (248 nm) of **1** in acetonitrile under N_2, monitored at λ = 660 nm.

Chart 1



As the predominant formation of 9-fluorenone ketimine in this photoreaction points to the generation of the ketiminyl radical **2**, we examined two model compounds as possible alternate sources for **2**. The photochemistry of 9-fluorenone *O*-acetyloxime (**3**) and 9-fluorenone *N*-acetylketimine (**4**) was therefore studied by product analysis following 300 nm irradiation in acetonitrile (see Chart 1). The slow conversion in these systems suggests a low quantum yield for primary photocleavage. 9-Fluorenone ketimine, and smaller amounts of 9-fluorenone were the primary products of the low-conversion (<5%, 30 min) irradiation of **3** (see Experimental Section). Similarly, **4** yielded 9-fluorenone ketimine and 9-fluorenone during low-conversion (<5%, 4 h) irradiation.

2. Laser Flash Photolysis. Laser photolysis of **1** in acetonitrile at 248 nm leads to a transient with absorption maxima at λ_{max} ≈660, 390, and 330 nm, which decayed with a lifetime of ~8 μs (Figure 1). We also observed a residual absorption due to a stable (or at least long-lived) product with λ_{max} = 350 nm. Neither transient nor residual absorption was affected by purging the solution with oxygen or by addition of 1% methanol.

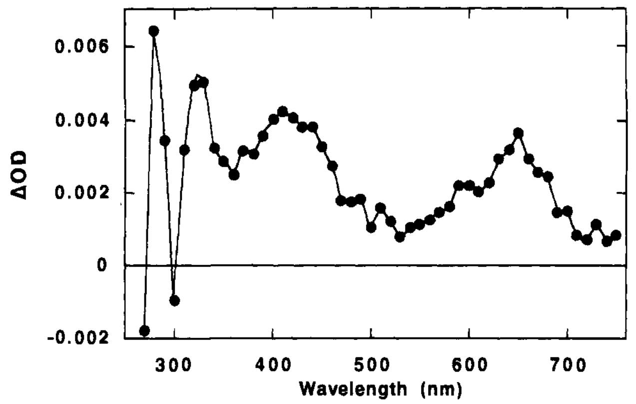


Figure 2. Transient spectrum, recorded 560 ns after laser flash photolysis (248 nm) of **3** in acetonitrile under N_2; the negative segments indicate bleaching of the precursor.

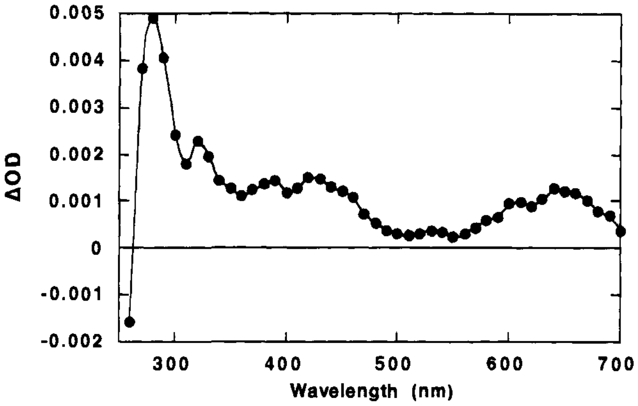
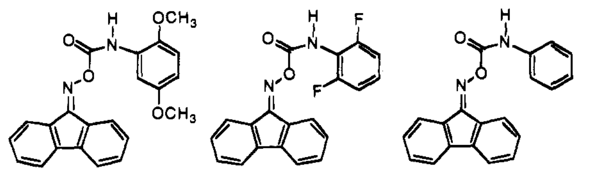


Figure 3. Transient spectrum, recorded 560 ns after laser flash photolysis (248 nm) of **4** in acetonitrile under N_2.

Laser flash photolysis (248 nm) of ester **3** in acetonitrile led to very similar results. We detected a transient with λ_{max} = 650, 410, and 320 nm, decaying with a lifetime of ~6.4 μs, which was not affected by oxygen (Figure 2). The transient spectrum is virtually identical to that observed after laser flash photolysis of **1**, and as both lifetime and behavior toward oxygen are similar, we conclude that the same species is formed in both cases. Laser excitation (248 nm) of **4** in acetonitrile gave very weak signals of a transient species with λ_{max} = 640, 430, 380, 320, and 280 nm and a lifetime $\tau \approx$ 11 μs (Figure 3). The weak nature of the signal leads to considerable uncertainty in the lifetime value. Again, purging the solution with oxygen had no effect on transient lifetime or intensity. As the transient spectrum is again very similar to those monitored after laser flash photolysis of **1** and **3**, it appears likely that the same reactive intermediate is formed in all three cases.

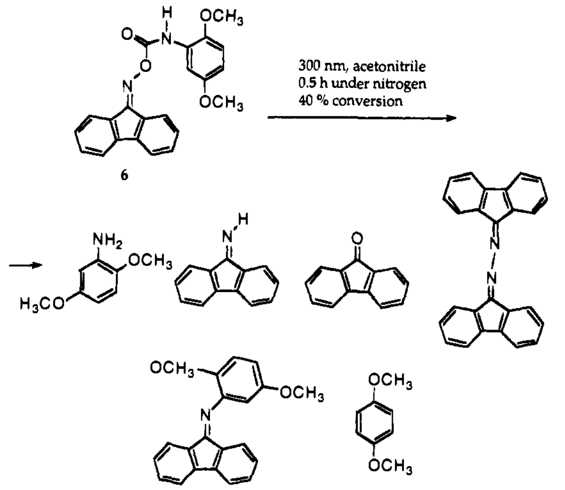
The laser flash photolysis experiments with **4** give us a clue on the nature of the transient species observed. Whereas both ketiminyl radical **2** and the 9-nitroso-fluorenyl radical **5** are reasonable candidates for the primary products formed upon laser flash photolysis of **1** and **3**, the only possible radical product to be observed following laser flash photolysis of **4** is the ketiminyl radical **2**. This assignment is in complete agreement with the results of our product studies. It is also consistent with the transient's lack of reactivity toward oxygen. Hence we assign the reactive intermediate observed upon laser flash photolysis of **1**, **3**, and **4** to be the 9-fluorenone ketimine-*N*-yl radical **2**. The rather long wavelength absorption of **2**

Chart 2



6 7 8

Scheme 2



suggests considerable involvement of the π system in this transition. While we cannot completely rule out the possibility of the generation of the nitroxy radical **5** upon laser flash photolysis of carbamate **1** or ester **3**, we note that neither the time-resolved experiments nor the product studies suggest this.

Studies with 9-Fluorenylideneamino *N*-Arylcarbamates 6–8. 1. Product Studies. Product studies were again complicated by the fact that the carbamates (see Chart 2) cleaved thermally in the injector block of the gas chromatograph, yielding 9-fluorenone oxime and the corresponding aryl isocyanate. However, long irradiation runs with complete conversion indicated that the oxime is not formed photochemically. Products were identified by comparison of GC retention times with authentic samples and by GC/MS analysis.

Irradiation of **6** in acetonitrile or methanol (300 nm) led to 2,5-dimethoxyaniline, 9-fluorenone ketimine, 9-fluorenone *N*-(2,5-dimethoxyphenyl)ketimine, 9-fluorenone, and 9-fluorenone ketazine as the main products (Scheme 2, see Experimental Section for details). In addition, we were surprised to find systematically small yields ($\leq$2%) of 1,4-dimethoxybenzene. 9-Fluorenone and its Schiff base [9-fluorenone *N*-(2,5-dimethoxyphenyl)-ketimine] were probably formed by thermal reactions of the reactive ketimine (which is more reactive than fluorenone) with trace amounts of water or photochemically formed 2,5-dimethoxyaniline.

In an attempt to determine if the formation of 1,4-dimethoxybenzene was mediated by the corresponding azo compound, some product studies were carried out under conditions of 308 nm laser excitation. Under these conditions, *trans*-2,2′,5,5′-tetramethoxyazobenzene accounted for 3% of the products. This and other evidence (*vide infra*) suggest the intermediacy of (2,5-dimethoxyphenyl)nitrene. While the almost total absence of 2,5-dimethoxyaniline in the product mixture at first seemed very surprising, it can be explained by the fact that the much higher transient concentrations occurring during laser flash photolysis will naturally favor products of radical–radical reactions, particularly if relatively unreactive radicals such as the 2,5-dimethoxyaniline-*N*-yl radical are involved. The remaining small amounts of 2,5-dimethoxyaniline being formed by H-abstraction by the anilino radical were then trapped by 9-fluorenone ketimine, yielding 6% of the corresponding Schiff base.

Irradiation of 9-fluorenylideneamino *N*-(2,6-difluorophenyl)-carbamate (**7**) in acetonitrile at 300 nm led to a mixture of 2,6-difluoroaniline, 9-fluorenone, 9-fluorenone ketimine, 9-fluorenone ketimine, and 9-fluorenone *N*-(2,6-difluorophenyl)ketazine. Again the ketone and the Schiff base are presumably formed by secondary thermal reactions of the primary photochemical product mixture.

Similarly, irradiation of 9-fluorenylideneamino *N*-phenylcarbamate (**8**) in acetonitrile yielded aniline, 9-fluorenone, 9-fluorenone ketimine, 9-fluorenone *N*-phenylketimine, and 9-fluorenone ketazine as main products. Additionally, a small amount of *trans*-azobenzene (4%) was detected. Again, the formation of the azo dye points to the intermediacy of a triplet nitrene, which would be parent triplet phenylnitrene in this case.

2. Laser Flash Photolysis. Laser flash photolysis (308 nm) of **6** in acetonitrile under nitrogen at ambient temperature led to the detection of a transient with λ_{max} = 640 nm, decaying with second-order kinetics and a first half-life of ~140 μs. Concomitant with the decay at λ = 640 nm, a growth with λ_{max} = 380 nm was observed; this growth was best fitted by second-order kinetics (Figure 4). In addition, we detected the instantaneous formation of a product with λ_{max} = 410 nm. Neither growth nor decay was affected by purging the solution with oxygen. Saturating the solution with triethylsilane also had no effect, whereas saturation with tributylstannane led to a decrease of the growth and decay lifetimes to ~90 μs (first-order kinetics). Using methanol as the solvent, we monitored both transients with unchanged λ_{max} but observed shorter lifetimes ($\tau \approx$ 110 μs, first-order kinetics).

Laser flash photolysis (248 nm) of carbamate **7** in acetonitrile at ambient temperature gave results that were very similar to those obtained with carbamate **1**, ester **3**, and ketimine **4**. We observed a transient with λ_{max} ~660, 400, and ~320 nm, which decayed with a lifetime of ~5.4 μs. Purging the solution with oxygen had no influence on transient lifetime. As the transient spectrum (Figure 5) is practically identical to the spectra recorded upon laser flash photolysis of compounds **1**, **3**, and **4**, we conclude that the ketiminyl radical **2** is also observed here. This assignment is consistent with the results of our product studies, which show that 9-fluorenone ketimine is one of the major products.

Laser flash photolysis (248 nm) of carbamate **8** at room temperature gave results that were reminiscent of those obtained with the methoxy-substituted carbamate **6**. We observed a transient growing in with second-order kinetics and a first half-life of ca. 150 μs with an absorption maximum at λ_{max} = 375 nm (Figure 6). Additionally, at $\lambda \approx$ 500 nm we were able to detect an extremely weak transient decaying within a time frame compatible with the growth at 375 nm. No signal could be monitored at λ > 550 nm. Traces recorded at λ = 370 nm were of "jump and growth" type; i.e., either some decaying transient or a stable product (or both) was absorbing in this region immediately after laser flash photolysis.

The photochemistry of the carbamates **1** and **7** provides a consistent picture where photolysis results in the formation of the ketiminyl radical **2**, which either abstracts a hydrogen atom from the solvent or dimerizes to form 9-fluorenone ketazine. The aminyl radicals which are formed at the same time are not readily observed in the laser flash photolysis experiments, but from our product studies we can conclude that hydrogen

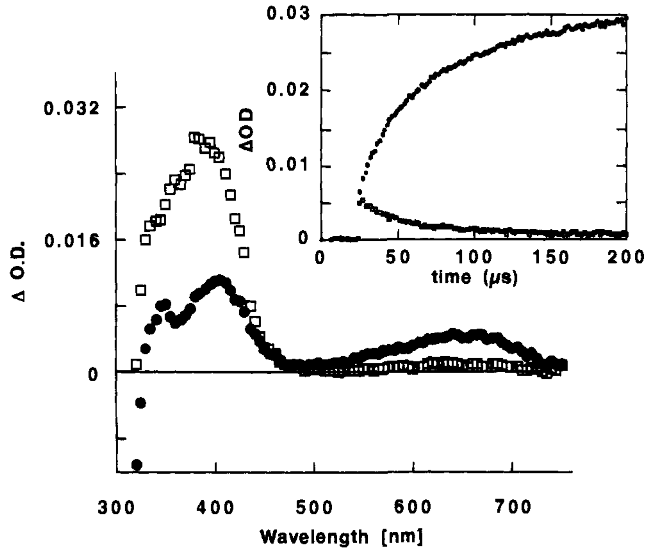


Figure 4. Transient spectra, recorded after laser flash photolysis (308 nm) of **6** in acetonitrile under N_2. Solid circles: time window between 160 and 960 ns after laser excitation. Light squares: time window between 94 and 150 μs after laser excitation. Inset: transient traces, recorded after laser flash photolysis (308 nm) of **6** in acetonitrile under N_2. Solid circles: decay, monitored at λ = 650 nm. Light squares: growth, monitored at λ = 390 nm.

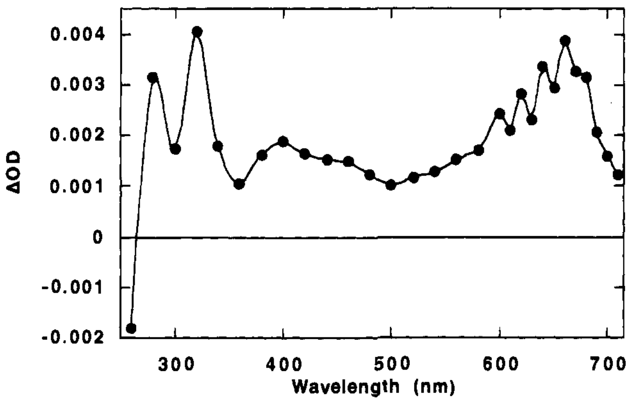


Figure 5. Transient spectrum showing the difference in changes in optical density between the windows recorded 560 ns and 13 μs after laser flash photolysis of **7** in acetonitrile under N_2.

abstraction to form the corresponding primary amine (cyclohexylamine or 2,6-difluoroaniline) must be their main mode of decay.

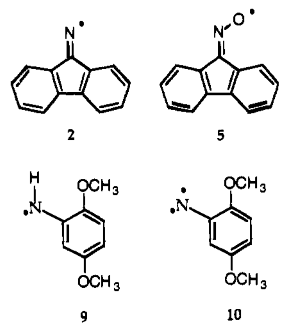
The results of the laser flash photolysis studies on carbamates **6** and **8** differ dramatically from those obtained with **1** and **7**. The transients observed are much longer lived and react according to second-order kinetics (in acetonitrile), and in addition, a growth leading to a stable product is also observed.

Which intermediates could conceivably account for the transient laser photolysis traces observed upon laser flash photolysis of **6**? Chart 3 depicts some of the reactive species which could be generated by photolysis of **6**.

Among these radicals, the ketiminyl radical **2** is clearly absent since we observed and characterized this species upon laser flash photolysis of compounds **1**, **3**, **4**, and **7**. Possible candidates are therefore the nitroxyl radical **5**, the anilyl radical **9**, and the nitrene **10**. The possibility of nitrene formation in this system a priori seems surprising; we will discuss mechanistic details in the Discussion section of this contribution.

A species that could be observed upon laser flash photolysis of **6** is the 2,5-dimethoxyaniline-*N*-yl radical **9**. We attempted

Chart 3



to generate this intermediate independently by hydrogen abstraction from 2,5-dimethoxyaniline (laser flash photolysis at 355 nm using 50% di-*tert*-butyl peroxide in benzene in the presence of 1 mM 2,5-dimethoxyaniline). A transient (λ_{max} = 640 and 420 nm) was observed growing-in with a growth lifetime of ca. 1 μs, followed by a decay with a lifetime of ca. 36 μs (Figure 7). Purging the solution with oxygen had only a minor effect, if any ($\tau \approx$ 30 μs under 1 atm O_2).

We assign the transient observed in this experiment to the 2,5-dimethoxyaniline-*N*-yl radical **9**. While an attack of the *tert*-butoxy radical at the methoxy groups is conceivable, the resulting carbon-centered radical would not be expected to absorb at 640 nm; it would also be expected to be readily quenched by oxygen. The species is clearly shorter lived than the decaying transient monitored upon laser flash photolysis of **6**, which however does not rule out its formation in this system as its decay may well be masked by the long-lived second-order decay which we observe. Methoxy substitution clearly leads to a substantial red shift of the absorption in relation to the parent anilino radical.[10]

An attempt to generate the iminoxyl (or 9-nitrosofluorenyl) radical **5** independently by hydrogen abstraction (by the *tert*-butoxy radical) from 9-fluorenone oxime failed due to the absorption of the oxime at 337 and 355 nm, both wavelengths where photolysis of di-*tert*-butyl peroxide is convenient.[11] Samples with sufficient concentrations of oxime (>10 mM) had optical densities which were far too high to allow for laser flash photolysis experiments using these laser wavelengths. As a model experiment, we studied the H-abstraction from benzophenone oxime by the *tert*-butoxy radical (Scheme 3). Laser flash photolysis (308 nm) of a solution containing 4% di-*tert*-butyl peroxide and 0.05 M benzophenone oxime in acetonitrile resulted in the growth ($\tau \approx$ 17 μs) of a transient with an absorption maximum at λ < 320 nm, tailing out to $\lambda \approx$ 550 nm (Figure 8). The intermediate decayed with a lifetime of $\tau \approx$ 0.6 ms and was not appreciably quenched by oxygen. The absorbance at 308 nm (the laser wavelength) was 1.0 (70% due to the oxime); in a separate experiment we therefore investigated the direct laser flash photolysis (266 nm) of benzophenone oxime. As we were unable to detect transient species in this control experiment, the intermediates monitored in the experiment with di-*tert*-butyl peroxide must result from reactions of the *tert*-butoxy radical. Since the *tert*-butoxy radical is not likely to abstract a hydrogen atom other than the oxime hydrogen from benzophenone oxime, we assume that the transient observed is the iminoxy radical (or nitrosodiphenylmethyl radical) **11**.

A clue toward the possible nature of both transients decaying following laser flash photolysis of **6** in acetonitrile and the product growing-in may be found in our product studies.

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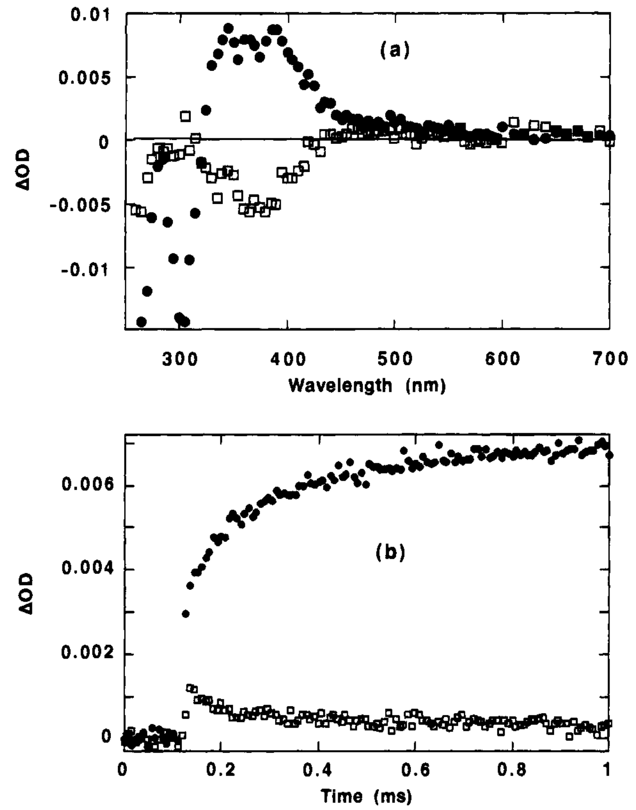


Figure 6. (a) Solid circles: transient spectrum, recorded 28 μs after laser flash photolysis (248 nm) of **8** in acetonitrile under N_2. Light squares: transient difference spectrum showing the difference in changes in optical density between the windows, recorded 28 and 650 μs after laser flash photolysis of **8** in acetonitrile under N_2; this substraction gives an inverted spectrum that, in this case, facilitates visualization. (b) Transient traces, recorded after laser excitation (248 nm) of **8** in acetonitrile under N_2. Solid circles: decay, monitored at λ = 500 nm. Light circles: growth, monitored at λ = 370 nm.

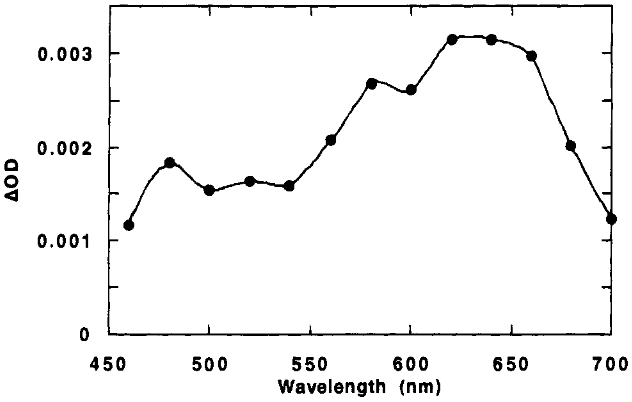


Figure 7. Transient spectrum, recorded 560 ns after laser flash photolysis (355 nm) of 50% di *tert*-butyl peroxide in benzene containing 1 mM 2,5-dimethoxyaniline under N_2.

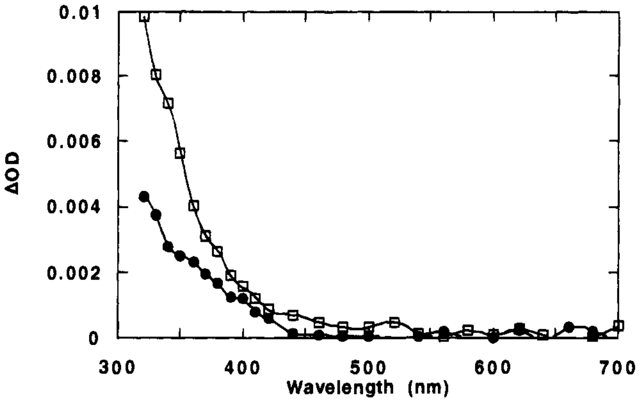
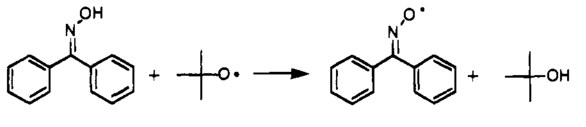


Figure 8. Transient spectra, recorded after laser flash photolysis (308 nm) of 4% di *tert*-butyl peroxide in acetonitrile containing 0.05 M benzophenone oxime under N_2. Solid circles: time window between 800 ns and 4.8 μs after laser excitation. Light squares: time window between 9.6 and 19.2 μs after laser excitation.

Scheme 3



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Among the products formed upon irradiation of **6** in acetonitrile, the presence of 1,4-dimethoxybenzene is particularly noteworthy, as it suggests the formation of the 2,5-dimethoxyphenyl radical. Phenyl radicals are high-energy species, and in general good leaving groups (such as the iodine atom or molecular nitrogen) are required for their formation to be feasible in photochemical reactions. In our system, cleavage of the carbon–nitrogen bond in an aniline derivative does not seem a likely reaction; however, a precursor for this radical could be 2,2′,5,5′-tetramethoxyazobenzene, which would have to be formed by dimerization of triplet (2,5-dimethoxyphenyl)nitrene. The efficiency of second-order radical–radical reactions is highly dependent on the irradiation intensity; consistently, steady-state irradiation at best gave trace amounts of this azo dye, while its yield was somewhat higher upon irradiation with the pulsed excimer laser. While the quantum yield for the formation of the 2,5-dimethoxyphenyl radical from 2,2′,5,5′-tetramethoxyazobenzene is expected to be low, it may be sufficient for conversion of the small—but strongly absorbing—concentrations of azo compound involved.

The following arguments can be invoked to rationalize the formation of nitrene **10** upon laser flash photolysis of carbamate **6**. (i) The behavior of the decaying transient (λ_{max} = 640 nm) is consistent with what is known about the behavior of triplet nitrenes;[12] previous studies had shown that the predominant mode of decay is its dimerization to azo dyes which follows a second-order rate law.[13] Moreover, the lack of reactivity toward oxygen and an overall sluggishness of reactions were reported.[12] We note that the maximum in the ΔOD spectrum, λ_{max} = 380 nm (measured for the product growing in), agrees well with the absorption maximum of an authentic sample of *trans*-2,2′,5,5′-tetramethoxyazobenzene (λ_{max} = 402 nm in acetonitrile). The λ_{max} determined in the laser flash photolysis experiment may be blue-shifted due to bleaching in the near-UV part of the spectrum. Alternatively, some cis azo compound could also be formed in the nitrene dimerization reaction. (ii) The 2,5-dimethoxyaniline-*N*-yl radical **9** is shorter lived than the rather long-lived transient observed upon laser flash photolysis of **6**. On the other hand, an absorption maximum λ_{max} = 640 nm for **9** supports an assignment of the weak long-lived transient as nitrene **10**, as **10** and **9** would be expected to have very similar absorption characteristics. (iii) Radicals containing the fluorene moiety can be excluded. This is evident in the case of the ketiminyl radical **2**, which is formed upon laser flash photolysis of compounds **1**, **3**, **4**, and **7** and which has properties different from the transient observed upon laser flash photolysis of **6**. The evidence against the iminoxy radical **5** is weaker, as

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[12] Schuster, G. B.; Platz, M. S. In *Advances in Photochemistry*; Volman, D. H., Hammond, G. S., Neckers, D. C., Eds.; John Wiley and Sons: New York, 1992; Vol. 17; p 69.

[13] Liang, T.-Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1987**, *109*, 7803.

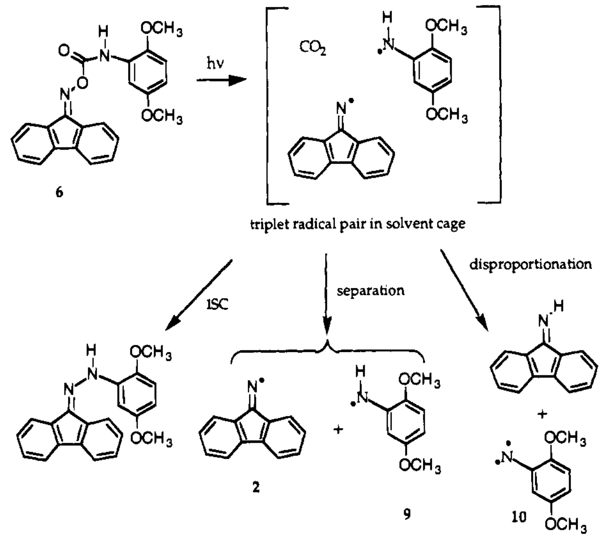
we have not been able to generate it independently. Model experiments on the hydrogen abstraction from benzophenone oxime showed that no growth could be observed concomitantly with the decay of the long-lived transient tentatively identified as the nitrosodiphenylmethyl radical **11**. This indicates that the situation should be similar in the case of the decay of radical **5** (no growth should be expected). Further, the presence of **5** should reveal itself in the product distribution. Fluorenone oxime, however, is apparently not formed from **6** photolytically (although it is formed by thermal cleavage of the carbamate). (iv) As the amount of 1,4-dimethoxybenzene and its azo dye precursor together was always well below 10% of the total amount of products formed, the process observed can only be a minor side reaction. Thus, the product formed must have a high extinction coefficient for its growth to be readily observable; this is the case for an azo compound as product. Consistently, irradiated samples of **6** (and **8**) in acetonitrile had a distinct yellow color after brief irradiation, while samples of all other compounds investigated stayed nearly colorless under the same conditions.

Similar arguments can also be brought up in support of the intermediacy of ground state[14] triplet phenylnitrene in the photolysis of carbamate **8**. The azo dye identified as a product points most strongly toward this intermediate; furthermore, the kinetic behavior (second-order growth of the product) is entirely consistent with the assignment. We note that an extremely weak band tailing out to $\lambda \approx 500$ nm agrees with what is known about triplet phenylnitrene from low-temperature matrix isolation work; as well, the spectrum observed immediately after the laser pulse resembles the published spectrum of triplet phenylnitrene (in an ether−pentane−alcohol, EPA, glass at 77 K) to some degree.[15] Finally, our failure to detect any transient absorption at wavelengths longer than 550 nm essentially excludes an assignment as an intermediate based on the fluorene moiety; in this case, transients observed upon laser flash photolysis of carbamates **6** and **8** would have had to be identical.

Discussion

The observation that triplet (2,5-dimethoxyphenyl)nitrene (**10**) may be formed in small amounts upon laser flash photolysis of carbamate **6** a priori seems surprising, as this reaction would involve hydrogen abstraction from a radical center. Hydrogen transfer reactions of carbon-centered radicals are quite common (disproportionation of radical pairs), but it is normally a β-hydrogen atom that is removed from a radical. The products formed in these reactions are a hydrocarbon molecule saturated at the former radical site plus an olefin, generated from the H-donor radical. On the other hand, disproportionation of a radical pair forming a free carbene and a saturated hydrocarbon is a very unlikely reaction. For example, the reaction of two diphenylmethyl radicals forming triplet diphenylcarbene and diphenylmethane is endothermic by about 7 kcal/mol.[16] In fact, diphenylcarbene is an excellent hydrogen abstractor, its reactions leading to the diphenylmethyl radical.[17,18] However, if the radical pair is unsymmetric, a sizable amount of energy could be liberated in such a reaction; a necessary condition for this to happen is a significant difference in the X−H bond energies of the species involved. Scheme 4 shows how the formation of **10** may be rationalized.

Scheme 4



According to Scheme 4, the triplet radical pair generated by primary photodecarboxylation of excited **6** can decay by three pathways: Intersystem crossing (ISC) to the singlet radical pair which subsequently collapses to form the (2,5-dimethoxyphenyl)hydrazone of 9-fluorenone; separation of the triplet radical pair; and disproportionation, giving 9-fluorenone ketimine and triplet (2,5-dimethoxyphenyl)nitrene (**10**). The relative yield of the disproportionation reaction will depend critically on the N−H bond energies in 9-fluorenone ketimine and the radical **9**. We calculated the reaction enthalpy of the H-transfer from **9** to **2** using the AM1/RHF method; it was predicted to be exothermic by 1.8 kcal/mol. When a similar calculation was carried out on the disproportionation of the triplet radical pair created by photolysis of **7**, the result was $\Delta H^\circ = -0.2$ kcal/mol. For comparison, for the disproportionation reaction in the photochemistry of **8**, ΔH was calculated to be −2.4 kcal/mol, supporting nitrene intermediacy in this system. The trend seen in the calculations is consistent with our experimental observations as we do not have evidence for the formation of triplet 2,6-difluorophenylnitrene from **7**. The most important result of our calculations is the finding that the reactions calculated should be approximately thermoneutral; small differences in energy may therefore decide whether the reaction is favored or not.

The traditional source for arylnitrenes has been the photolysis of the corresponding aryl azides.[12] Unfortunately, in most cases the initially formed singlet nitrenes undergo ring expansion to azacycloheptatetraene derivatives very readily so that low-temperature matrix isolation is required to obtain the triplet nitrenes.[12,15,19] In this context, our observation that triplet arylnitrenes may be formed upon laser flash photolysis of some of the carbamates involved in this study might indicate a useful alternate precursor for these intermediates in solution. Its limitations are revealed by the low yield of nitrene **10** obtained in our experiments and by our failure to generate triplet 2,6-difluorophenylnitrene from carbamate **7**. It should however be possible to modify the oxime moiety in these carbamates in a way which would increase the N−H bond energy in the ketimines formed, thereby making hydrogen transfer more favorable.

Another conclusion which can be drawn from the work presented here refers to practical applications of photobases in

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photoresist technology. The strongly reduced yields of 2,5-dimethoxyaniline upon laser flash photolysis of carbamate **6** (as opposed to steady-state photolysis) show that, at least in cases where the base is formed by hydrogen abstraction by a relatively unreactive radical, care has to be taken to avoid high light intensities—the use of pulsed lasers here may prove counterproductive.

Experimental Section

Materials. Carbamates **1** and **6** were obtained from the ABC library of rare chemicals (Aldrich) and were recrystallized from diethyl ether prior to use. 9-Fluorenone *O*-acetyloxime (**3**) was prepared by reaction of 9-fluorenone oxime with acetyl chloride in CH_2Cl_2 in the presence of pyridine; it was recrystallized from hexane prior to use. 9-Fluorenone *N*-acetylketimine (**4**) and 9-fluorenone ketimine were synthesized according to a literature procedure;[20] they were recrystallized from hexane twice prior to use. Carbamate **8** was synthesized by condensing 9-fluorenone oxime with excess phenyl isocyanate (Aldrich) as solvent. Its properties were in agreement with literature values.[21] 2,5-Dimethoxyaniline (Aldrich) was recrystallized several times from hexane in the presence of charcoal until the compound was colorless. 9-Fluorenone oxime and benzophenone oxime were prepared from the ketones and hydroxylamine hydrochloride (Aldrich). *trans*-Azobenzene was obtained from Aldrich, while 2,2′,5,5′-tetramethoxyazobenzene was synthesized by reduction of 2,5-dimethoxynitrobenzene with $LiAlH_4$ in dry diethyl ether.

Carbamate **7** was synthesized from 9-fluorenone oxime and 2,6-difluorophenyl isocyanate (Aldrich) in dry CH_2Cl_2 (48 h of stirring at room temperature, recrystallized from dry diethyl ether, mp 154 °C, moderate yield). Anal. Calcd for $C_{20}H_{12}N_2F_2O_2$: C, 68.57; H, 3.45; N, 8.00; F, 10.85. Found: C, 68.57; H, 3.51; N, 7.91; F, 10.66. MS: due to sample decomposition upon heating, FAB measurements were necessary; *m/e* 351.1 ($M^{\cdot +} + 1$), 196.1, 137.0. FTIR (in KBr, cm^{-1}): 3200.0 (s), 3052.4 (m), 3018.5 (m), 1957.3 (vw), 1921.6 (vw), 1733.3 (vs), 1599.3 (s), 1534.9 (vs), 1467.9 (vs), 1450.3 (s), 1384.4 (w), 1321.0 (m), 1299.6 (s), 1240.8 (vs), 1222.8 (vs), 1153.4 (m), 1090.5 (w), 1047.2 (m), 1032.0 (s), 1005.6 (vs), 961.4 (vs), 918.2 (w), 850.7 (w), 814.8 (w), 780.8 (s), 755.4 (w), 728.7 (s), 704.2 (m), 645.1 (m). NMR (Bruker, 500 MHz; ^{19}F 300 MHz, in $CDCl_3$): (a) ^{19}F $\delta = -41.905$ (t); (b) ^{13}C $\delta =$ 111.93 (d, $J_{CF} = 21$ Hz), 113.57 (t, $J_{CF} = 16$ Hz), 120.22, 120.36, 122.75, 128.12 (t, $J_{CF} = 10$ Hz), 128.32, 128.91, 131.15, 131.87 (d, $J_{CF} = 523$ Hz), 131.95, 132.98, 141.60, 142.45, 152.24, 156.57, 157.18, 159.18; (c) ^1H $\delta = 8.43$ (s, br, 1H), 8.01 (s, br, 1H), 7.79 (d, 1H, $J_o = 7.6$ Hz), 7.58 (m, 2H), 7.48 (dt, 1H, $J_o = 7.6$ Hz, $J_m = 1.0$ Hz), 7.44 (dt, 1H, $J_o = 7.6$ Hz, $J_m = 1.1$ Hz), 7.29 (m, 3H), 7.01 (m, 2H). Upon cooling to 250 K, the broad singlet at 8.43 ppm became a sharp doublet. An HMQC experiment showed that it belonged to a proton bound to an aromatic carbon atom. Therefore it is suggested that this proton resides in the 1-position in the fluorenone system and interacts with the oxime oxygen atom.

Acetonitrile, methanol, and benzene (all BDH Omnisolv) were used as received. Di-*tert*-butyl peroxide (BDH) was passed over an alumina column prior to use in order to remove residual *tert*-butyl hydroperoxide.

Product Studies. Irradiations were carried out in 50-mL Pyrex test tubes. The samples were deaerated by purging with a slow stream of nitrogen for 30 min. They were irradiated in a reactor equipped with six RPR-300 lamps. The temperature of the irradiation chamber was in the 30–35 °C range. Typically, a sample of 10 mg of substance in 50 mL of solvent was irradiated for a given time. After irradiation, the samples were concentrated to a volume of ca. 2 mL and analyzed by GC. Product identification was achieved by comparison of GC retention times with authentic samples and/or GC/MS analysis.

Irradiation of carbamate **1** in acetonitrile (2 h, 10% conversion under N_2) led to cyclohexylamine (ca. 5%) (significant amounts of this compound were probably lost upon evaporation of the solvent), 9-fluorenone ketimine (26%), 9-fluorenone (11%) (probably formed by hydrolysis of 9-fluorenone ketimine with traces of water), 9-fluorenone *N*-cyclohexylketimine (16%), and 9-fluorenone ketazine (8%). Further minor products were not identified.

Short irradiation time (30 min, <5% conversion) of ester **3** in acetonitrile led to 9-fluorenone ketimine (62%), 9-fluorenone (16%), and small amounts of unidentified products. Irradiation for 4 h (<30% conversion) led to 9-fluorenone ketimine (ca. 50%) as the main product. Some 9-fluorenone was also formed. The product mixture was complex. Irradiation for 12 h (ca. 80% conversion) led to a complex product mixture. Products include 9-fluorenone ketimine (ca. 20%), 9-fluorenone (ca. 4%), and 9-fluorenone ketazine (ca. 25%).

Irradiation of ketimine **4** in acetonitrile for 4 h (<5% conversion) led to 9-fluorenone ketimine (35%), 9-fluorenone (32%), and other unidentified products. Irradiation for 12 h (<10% conversion) led to 9-fluorenone ketimine (ca. 25%), 9-fluorenone (ca. 50%) and small amounts of unidentified products.

Irradiation of 9-fluorenylideneamino *N*-(2,5-dimethoxyphenyl)carbamate (**6**) in methanol (1 h, 100% conversion) led to the formation of 2,5-dimethoxyaniline (31%), 9-fluorenone (7%) (probably formed by hydrolysis of the ketimine), 9-fluorenone ketimine (43%), 9-fluorenone *N*-(2,5-dimethoxyphenyl)ketimine (3%) (probably formed by secondary condensation of 9-fluorenone ketimine with 2,5-dimethoxyaniline), and 9-fluorenone ketazine (5%).

Short irradiation of **6** in acetonitrile (20 min, ca. 40% conversion) led to 1,4-dimethoxybenzene (<2%), 2,5-dimethoxyaniline (31%), 9-fluorenone (5%), 9-fluorenone ketimine (11%), 9-fluorenone *N*-(2,5-dimethoxyphenyl)ketimine (23%), and 9-fluorenone ketazine (30%). There may be a trace (<0.5%) of *trans*-2,2′,5,5′-tetramethoxyazobenzene present and traces of other unidentified products.

Long irradiation of **6** in acetonitrile (90 min, >90% conversion) led to 1,4-dimethoxybenzene (4%), 2,5-dimethoxyaniline (30%), 9-fluorenone (5%), 9-fluorenone ketimine (4%), 9-fluorenone *N*-(2,5-dimethoxyphenyl)ketimine (8%), and 9-fluorenone ketazine (38%). Small amounts of unidentified products were also formed.

Pulsed excimer laser irradiation of **6** in acetonitrile (308 nm, ca. 1 min with a repetition rate of 10 Hz, ca. 100 mJ/pulse, 25% conversion) led to 1,4-dimethoxybenzene (ca. 1%), 9-fluorenone (19%), 9-fluorenone ketimine (43%), *trans*-2,2′,5,5′-tetramethoxyazobenzene (3%), 9-fluorenone *N*-(2,5-dimethoxyphenyl)ketimine (6%), and 9-fluorenone ketazine (24%). Traces of unidentified products were also formed. 2,5-Dimethoxyaniline was only present in trace amounts.

Irradiation of 9-fluorenylideneamino*N*-(2,6-difluorophenyl)carbamate (**7**) in acetonitrile (60 min, ca. 30% conversion) led to 2,6-difluoroaniline (22%), 9-fluorenone (13%), 9-fluorenone ketimine (33%), *N*-(2,6-difluorophenyl)-9-fluorenone ketimine (17%), and 9-fluorenone ketazine (6%). Traces of unidentified products were also formed.

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Irradiation of 9-fluorenylideneamino *N*-phenylcarbamate (**8**) in acetonitrile (15 min, >90% conversion) led to aniline (18%), *trans*-azobenzene (4%), 9-fluorenone (4%), 9-fluorenone ketimine (8%), 9-fluorenone *N*-phenylketimine (22%), and 9-fluorenone ketazine (14%). Traces of unidentified products were also formed.

Irradiation of 9-fluorenone oxime in acetonitrile (300 nm, 40 min) led to only very small amounts of 9-fluorenone ketimine.

Laser Flash Photolysis. The experimental setup used for the laser flash photolysis studies is similar to that described in detail elsewhere.[22,23] Samples were photolyzed using a Lumonics EX-510 excimer laser operated either with Xe/HCl/Ne (ca. 5 ns, ~100 mJ/pulse, 308 nm) or with Kr/F_2/He (ca. 5 ns, ~140 mJ/pulse, 248 nm). In some experiments, the third or fourth harmonic of a Surelite Nd-YAG laser (355 nm, ca. 6 ns, ~20 mJ/pulse or 266 nm, ca. 6 ns, ~10 mJ/pulse) was employed. Carbamate concentrations were ca. 3×10^{-5} M. A rapid flow of fresh sample solution was maintained during the experiments in order to avoid product buildup and sample depletion.

Calculations. Semiempirical calculations were carried out using the AM1 SCF-MO method as implemented in the MOPAC program supplied with a Tektronix CAChe workstation operating with software version 3.5.

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