JOC Article

Photolysis of α-Azidoacetophenones: Direct Detection of Triplet Alkyl Nitrenes in Solution

Pradeep N. D. Singh, Sarah M. Mandel, Rachel M. Robinson, Zhendong Zhu, Roberto Franz, Bruce S. Ault, and Anna D. Gudmundsdóttir*

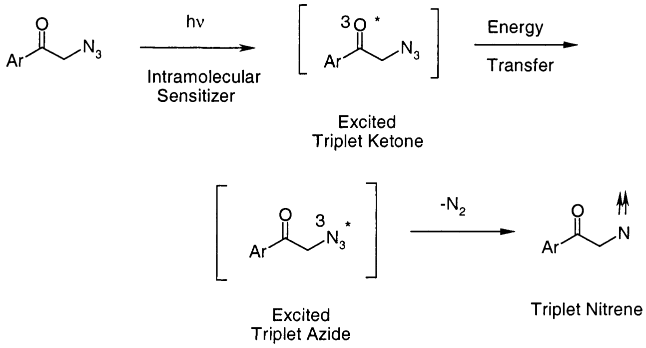
Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221-0172

anna.gudmundsdottir@uc.edu

Received May 20, 2003

We report the first detection of triplet alkyl nitrenes in fluid solution by laser flash photolysis of α-azido acetophenone derivatives, **1**. Azides **1** contain an intramolecular triplet sensitizer, which ensures formation of the triplet alkyl nitrene by bypassing the singlet nitrene intermediate. At room temperature, azides **1** cleave to form benzoyl and methyl azide radicals in competition with triplet energy transfer to form triplet alkyl nitrene. The major photoproduct **3** arises from interception of the triplet alkyl nitrene with benzoyl radicals. The triplet alkyl nitrene intermediates are also trapped with molecular oxygen to yield the corresponding 2-nitrophenylethanone. Laser flash photolysis of **1** reveals that the triplet alkyl nitrenes have absorption around 300 nm. The triplet alkyl nitrenes were further characterized by obtaining their UV and IR spectra in argon matrices. ^{13}C and ^{15}N isotope labeling studies allowed us to characterize the C−N stretch of the nitrene intermediate at 1201 cm^{-1}.

The pursuit of organic magnetic materials has sparked renewed interest in triplet nitrene intermediates, which are ideal candidates because of their high-spin properties.[1] It is presumed that the direct photolysis of alkyl azides does not lead to the formation of triplet alkyl nitrene intermediates; instead, alkyl azides are considered to undergo a rearrangement from the excited state of the azide to form imine derivatives with loss of nitrogen.[2] This is supported by the fact that there are only a few examples where products have been isolated that could be attributed to the decomposition of alkyl azides into alkyl nitrene intermediates.[3] However, physical measurements have been reported that support the existence of triplet alkyl nitrenes in matrices and in the gas phase.[4−8] Wasserman, for example, obtained EPR spectra of triplet alkyl nitrenes in a matrix by sensitized photolysis of alkyl azides.[4] Engelking and co-workers allowed methyl azide to react with metastable N_2 in a flowing afterglow and were then able to obtain and analyze the UV emission spectrum of triplet methyl nitrene in the gas phase.[6] Ferrante[8] and Platz et al. have obtained a UV absorption spectrum of triplet alkyl nitrene in matrices at low temperature.[9]



By photolyzing azidoaryl ketone derivatives, which contain an intramolecular triplet sensitizer, we have succeeded in obtaining products that can be attributed to the trapping of alkyl nitrenes in bimolecular reactions.[10] The intramolecular triplet sensitization ensures efficient formation of the triplet alkyl nitrene by bypass-

---

[1] (a) Rajca, A. *Chem. Rev.* **1994**, *94*, 871. (b) Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179. (c) *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999. (d) Nicolaides, A.; Tomioka, H.; Murata, S. *J. Am. Chem. Soc.* **1998**, *120*, 11530. (e) Subhan, W.; Rempala, P.; Sheridan, R. S. *J. Am. Chem. Soc.* **1998**, *120*, 11528.

[2] (a) Abramovitch, R.; Kyba, E. P. *J. Am. Chem. Soc.* **1971**, *93*, 1537. (b) Moriarty, R. M.; Serridge, P. *J. Am. Chem. Soc.* **1971**, *93*, 1534. (c) Moriarty, R. M.; Reardon, R. C. *Tetrahedron* **1970**, *26*, 1379.

[3] (a) Banks, R. E.; Berry, D.; McGlinchey, M. J.; Moore, G. J. *J. Chem. Soc. C* **1970**, 1017. (b) Pancrazi, A.; Khuong-Huu, Q. *Tetrahedron* **1975**, *31*, 2041

[4] (a) Barash, L.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1967**, *89*, 3931. (b) Wasserman, E.; Smolinsky, G.; Yager, W. A. *J. Am. Chem. Soc.* **1964**, *86*, 3166. (c) Smolinsky, G.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 3220.

[5] Radziszewski, J. G.; Downing, J. W.; Jawdosiuk, M.; Kovacic, P.; Michl, J. *J. Am. Chem. Soc.* **1985**, *107*, 594.

[6] (a) Chapell, E. L.; Engelking, P. C. *J. Chem. Phys.* **1988**, *89*, 6007. (b) Carrick, P. G.; Brazier, C. R.; Bernath, P. F.; Engelking, P. C. *J. Am. Chem. Soc.* **1987**, *109*, 5100. (c) Carrick, P. G.; Engelking, P. C. *J. Chem. Phys.* **1984**, *81*, 1661.

[7] (a) Shang, H. R.; Gao, R. M.; Ying, L. M.; Zhao, X. S.; Tang, Y. Q. *Chem. Phys. Lett.* **1997**, *267*, 345. (b) Ying, L. M.; Xia, Y.; Shang, H. R.; Zhao, X. S.; Tang, Y. Q. *J. Chem. Phys.* **1996**, *105*, 5798.

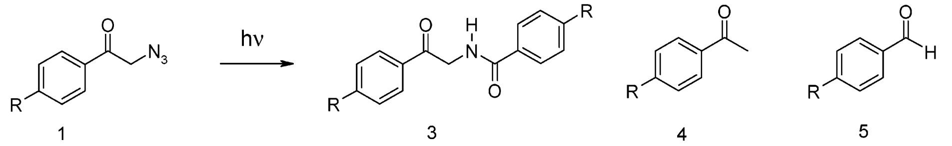
[8] Ferrante, R. F. *J. Chem. Phys.* **1987**, *86*, 25.

[9] Gritsan, N. P.; Likhotvorik, I.; Zhu, Z.; Platz, M. S. *J. Phys. Chem. A* **2001**, *105*, 3039.

[10] Mandel, S. M.; Krause Bauer, J. A.; Gudmundsdottir, A. D. *Org. Lett.* **2001**, *3*, 523.

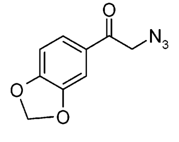
10.1021/jo034674e CCC: $25.00

SCHEME 1



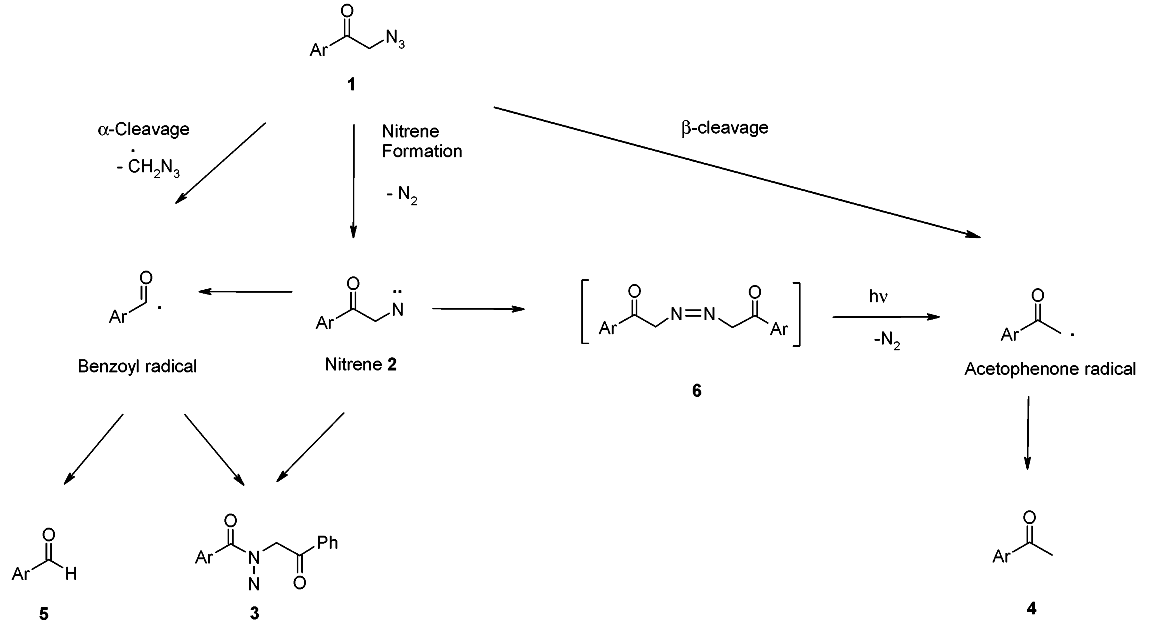
	Triplet Energy (kJ/mol)	Product Ratio		
a: R=H	310	90	7	3
b: R=Cl,	302	100		
c: R=Br,	297	90	10	
d: R=CN,	283	71	12	3
e: *	280	76	24	
f: R=Ph	255	77	16	7

*



1e

SCHEME 2



ing the singlet manifold of the azide precursor. Triplet alkyl nitrenes are presumably the ground state, as triplet methyl nitrene is 31 kcal/mol lower in energy than singlet methyl nitrene.[11] Since a spin barrier prohibits the triplet nitrenes from rearranging to singlet imine products, triplet alkyl nitrenes can be expected to be long-lived and thus directly detectable. In this present study we have extended our previous work[10] and set out to detect triplet alkyl nitrenes directly in fluid solution with time-resolved laser flash photolysis and to further characterize these intermediates by obtaining their UV and IR spectra in matrices. We specifically wanted to characterize the C−N stretch in the alkyl nitrene intermediates by using ^{15}N and ^{13}C labeling.

Results and Discussion

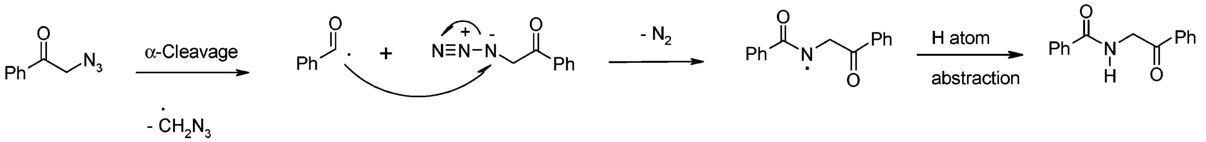
Product Studies. We photolyzed azides **1a**−**f** in toluene solutions at ambient temperature and kept the conversion below 20%. In all instances amide **3** was formed as the major product along with some acetophenone **4** and benzaldehyde, **5** (see Scheme 1). We have previously reported the product studies from photolysis of **1a** and **1c** but these compounds are included here for comparison.[10] Formation of amide **3** suggests that azides **1** undergo α-cleavage to form benzoyl radicals in competition with nitrene formation (see Scheme 2). Benzoyl radicals do not readily abstract H atoms from appropriate solvents but are quenched rapidly by molecular oxygen.[12]

---

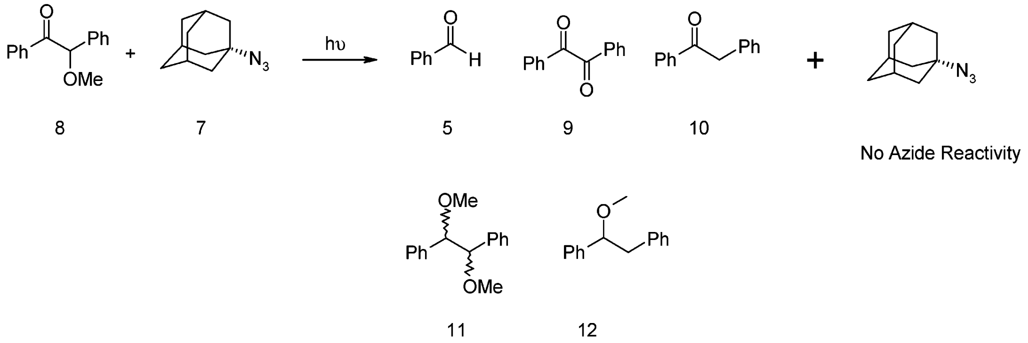
[11] Travers, M. J.; Cowles, D. C.; Clifford, E. P.; Ellison, G. B. *J. Chem. Phys.* **1999**, *111*, 5349.

[12] (a) Neville, A. G.; Brown, C. E.; Rayner, D. M.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 1869. (b) Brown, C. E.; Neville, A. G.; Rayner, D. M.; Ingold, K. U.; Lusztyk, J. *Aust. J. Chem.* **1995**, *48*, 363.

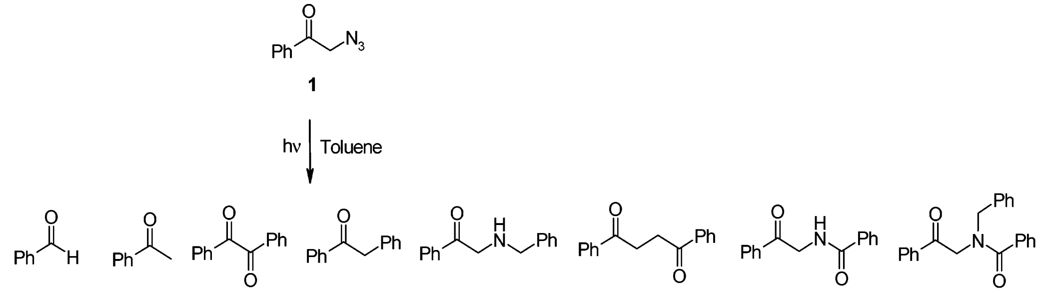
SCHEME 3



SCHEME 4



SCHEME 5



Product Ratio	5a	4a	9	10	11	12	3a	13
100°C	6		3	18	1		46	26
-63°C		8				26	60	6

Thus **3** can be formed similarly from interception of triplet nitrene, **2**, by a benzoyl radical, whereas benzoyl radicals slowly abstract an H atom from toluene to form a minor amount of benzaldehyde, **5**. It is also possible that triplet alkyl nitrenes **2** fragments into benzoyl and imine radical. Acetophenone **4** can be formed as a secondary photoproduct from photolysis of azo dimer **6**, which is presumably formed by dimerization of two triplet nitrene intermediates. We were, however, not successful in isolating azo dimer **6**, presumably because the concentration of **6** is minimal since it reacts efficiently. Nevertheless, triplet alkyl nitrenes can be expected to dimerize to form azo dimers in a manner similar to triplet phenyl nitrenes.[13] It is, however, also possible that acetophenone is formed from β-cleavage of azide **1a**.

It is also likely that **3** can be formed through a nonnitrene mechanism if the benzoyl radical formed from the irradiation of azide **1** reacts with a second azide molecule (see Scheme 3). To test this hypothesis we formed benzoyl radicals in the presence of admantanyl azide, **7**. Since azide **7** does not absorb light above 350 nm, benzoyl radicals can be formed in its presence by irradiating through the 349 nm filter benzoin methyl ether, **8**, that undergoes α-cleavage readily. We specifically selected **8** as the precursor for the benzoyl radical, since its excited state has been estimated to decay with a rate of more than 10^{10} s^{-1} and thus intermolecular triplet sensitization of azide **7** with **8** can be minimized.[14,15] Photolyzing **8** in the presence of **7** did not lead to any azide reactivity, but only the expected photoproducts from **8** (see Scheme 4). The photoproducts from **8**, **5**, **9**, **10**, **11**, and **12** were formed in the same ratio as when azide was not present. In contrast, we have shown that triplet-sensitized photolysis of azide **7** mainly leads to formation of di-adamantan-1-yl-1,2-diazene, presumably via triplet adamantyl nitrene formation.[15]

Effect of Temperature on Product Formation. We investigated how the temperature of the photolysis affected the product ratio (see Scheme 5). Photolysis at 100 °C yielded benzaldehyde and **3a** as at room tem-

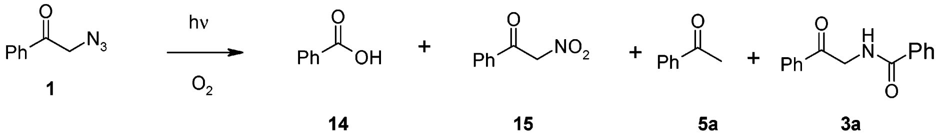
---

(13) (a) Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 5228. (b) Marcinek, A.; Levya, E.; Whitt, D.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 8609. (c) Schuster, G. B.; Platz, M. S. *Adv. Photochem.* **1992**, *17*, 70.

(14) Lewis, F. D.; Lauterbach, R. T.; Heine, H. G.; Hartmann, W.; Rudolph, H. *J. Am. Chem. Soc.* **1975**, *97*, 1519.

(15) R. F. Klima and A. D. Gudmundsdottir. Unpublished results. Triplet sensitization of 1-azidoadamantane with acetophenone yields mainly di-adamantan-1-yl-1,2-diazene.

SCHEME 6



Product Ratio	14	15	5a	3a
30°C	47	11		42
-63°C	14	64	14	8

pereature, but in addition products **9**, **10**, and **12** were formed. These compounds must originate from benzoyl radicals. Dibenzyl **9** is presumably formed from dimerization of two benzoyl radicals, and **10** must come from trapping of a benzoyl radical with toluene radicals. Similarly, **13** must come from trapping of the nitrene **2a** with two benzoyl radicals. Thus at higher temperature α-cleavage must be favored over triplet energy transfer since more of the products can be attributed to formation of benzoyl radicals. Photolysis at −63 °C gave **4a**, **3a**, and **12** as the major products. Diketone **12** must come from dimerization of two acetophenone radicals. Hence, photolysis at lower temperature yielded less of products coming from α-cleavage and more of products that must come from formation of acetophenone radicals. The product ratio indicates that the activation energy of α-cleavage must be higher than that for energy transfer to form triplet alkyl nitrene and the presumable β-cleavage.

Oxygen Trapping of the Reactive Intermediates Formed upon Photolysis of Azide 1a. We studied the photolysis of azide **1a** in oxygen-saturated solutions to trap the intermediates formed with oxygen. Irradiating azide **1a** in an oxygen-saturated toluene solution at ∼25 °C yielded benzoic acid as the major product and lesser amounts of acetophenone **5a** and 2-nitrophenylethanone, **15** (see Scheme 6). Formation of benzoic acid is expected since benzoyl radicals are efficiently trapped by molecular oxygen.[12] Formation of **15** demonstrates that we have trapped triplet alkyl nitrene **2a** with oxygen just as triplet aryl nitrenes are trapped with molecular oxygen to form nitroaryls.[16] Photolysis at ca. −63 °C of azide **1a** in toluene saturated with oxygen yielded nitro compound **15** as the major product. Thus, the major intermediate formed at ca. −63 °C must be nitrene **2a**, which is trapped by molecular oxygen to yield **15**. Additionally, since the combined yield of **4a** and **12** decreases in the presence of molecular oxygen we can speculate that these acetophenone-based products are not formed directly by β-cleavage of **1** but rather result from nitrene **2a**. Presumably, nitrene **2a** undergoes dimerization to form **6** in the absence of molecular oxygen, whereas in the presence of oxygen nitrene **2a** is trapped and thus any secondary photoproducts that might come for dimer **6** are decreased.

Electron Configuration of the Excited States of Azide 1 and Product Formation. We analyzed the product formation taking into account the electron configuration of the triplet excited state of the ketone in azides **1**, since α-cleavage is generally thought to arise from the n,π* excited state, whereas triplet energy transfer can take place from both the n,π* and the π,π* manifolds. We estimated that the triplet energy and the electronic configuration of the lowest excited ketone in azides **1** are the same as for the analogous ketones without azido substituents (see Scheme 1).[22] Thus the first excited triplet state of azides **1a**−**c** can be expected to have an n,π*configuration whereas in azides **1d**−**f** the π,π* excited state is lower in energy. We speculate that in azides **1**, the α-cleavage comes from the n,π* triplet excited states whereas the triplet energy transfer takes place from the π,π* excited state. Photolysis of azides **1** yields a similar amount of α-cleavage products, presumably since the first and second triplet excited states are in equilibrium with each other,[17] and thus we observe reactivity from both. Even though azides **1d**−**f** have the first excited triplet state with a π,π* configuration, they do not yield less of α-cleavage products, because the triplet energy of their π,π* state is lower than that in azides **1a**−**c** and thus the triplet energy transfer is more endothermic and slower, allowing for the α-cleavage to compete. Azides **1** can be compared to substituted valerophenone derivatives, which undergo intramolecular H-atom abstraction from their n,π* excited triplet state, whether the electron configuration of the first excited triplet state is n,π* or π,π*.[17] However, it possible that triplet alkyl nitrenes **2** fragment into benzoyl and imine radicals and thus care should be taken in correlating the product ratio from azides **1** with the electron configuration of the lowest triplet excitated state of the ketone.

Laser Flash Photolysis: Transient Spectra. We studied azide **1a** by laser flash photolysis in methylene chloride (Lambda Physik, excimer laser, 17 ns, 150 mJ, 308 nm), recording the spectrum immediately after the laser pulse over a window of 600 ns. A moderately broad transient with a maximum around 300 nm was observed upon irradiating azide **1a** (Figure 1). We have assigned this absorbance to the triplet alkyl nitrene **2a** ($\lambda_{max} \sim 300$ nm) and benzoyl radical ($\lambda_{max} = 370$ nm) based on the following:

The most intense absorption band near 300 nm in both triplet phenyl nitrene and NH radicals has been attributed mainly to the $n_z \rightarrow n_y$ transition on the nitrogen

---

[16] Abramovitch, R. A.; Challand, S. R. *J. Chem. Soc., Chem. Commun.* **1972**, 964.

[17] (a) Wagner, P. J.; Park, B.-S. Photoinduced Hydrogen Atom Abstraction by Carbonyl Compound. In *Org. Photochem.* **1991**, *11*, 227. *Ed. A. Padwa, New York, M. Dekker.* (b) Wagner, P. J.; Sibert, E. J. *J. Am. Chem. Soc.* **1981**, *103*, 7329. (c) Wagner, P. J.; Kemppainen, A. E.; Schott, H. E. *J. Am. Chem. Soc.* **1973**, *95*, 5604.

[18] Huggenberger, C.; Lipscher, J.; Fischer, H. *J. Phys. Chem.* **1980**, *84*, 3467.

[19] Gudmundsdottir, A. D. Unpublished results. Laser flash photolysis of β-azides propiophenone gives a transient spectrum that does not have any benzoyl radical absorption present.

[20] Fairchild, P. W.; Smith, G. P.; Crosley, D. R.; Jeffries, J. B. *Chem. Phys. Lett.* **1984**, *107*, 181.

[21] Gritsan, N. P.; Zhu, Z.; Hadad, C. M.; Platz, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 1202.

[22] Murov, S. T.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.;, Marcel Dekker: New York, 1993.

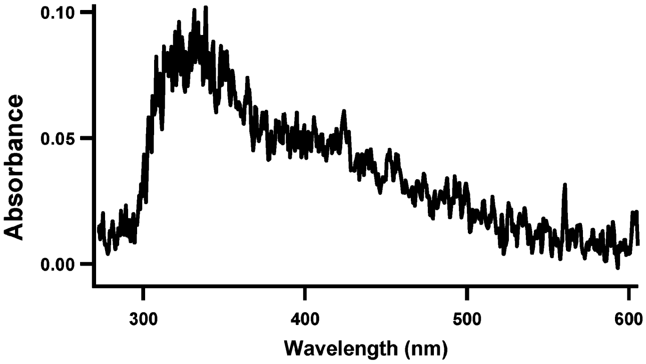
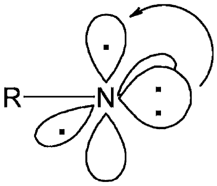


FIGURE 1. Transient spectra of azide **1a**.

SCHEME 7



atom (see Scheme 7) and does not involve the benzylic π-system in phenyl nitrene.[20,21] Therefore, we can expect triplet alkyl nitrene to absorb somewhat similarly as triplet phenyl nitrenes despite the fact that alkyl nitrene lacks a π-system. Furthermore, the absorption spectra of triplet trifluoromethyl nitrene and triplet methyl nitrene in matrices also have absorptions around 300 nm.[8,9] Triplet methyl nitrene has maximum absorption at 280 nm in matrices. The laser flash apparatus used in our studies is limited to detection above 300 nm and thus we cannot determine whether nitrene **2a** also absorbs strongly at 280 nm in solution. Benzoyl radicals have a weak UV absorbance with $\lambda_{\max} = 370$ nm that extents to 600 nm thus giving the transient spectra of **1a** a broad appearance compared to that of the triplet aryl nitrenes.[18,19] On a microsecond time scale, the transient with a maximum absorbance around 300 nm is unaffected in solutions saturated with oxygen. It can be concluded that the rate of interception of the triplet alkyl nitrene with oxygen must be slower than 10^4 s^{-1}. In contrast, when we obtained transient spectra 200 ns after the laser pulse in oxygen-saturated solutions, the benzoyl radical absorption is depleted (see Figure 2).

The transient spectrum of azide **1a** in methylene chloride does not exhibit absorption due to the triplet ketone, presumably because the triplet energy is efficiently transferred to the azido group at a rate faster than the time resolution of the laser flash apparatus. In contrast (Figure 3), the transient spectrum of azide **1f**, taken immediately after the laser pulse in a 200-ns window, reveals transient absorption of both the triplet ketone ($\lambda_{\max} = 420-450$ nm) and the triplet alkyl nitrene ($\lambda_{\max} \approx 300$ nm). A transient spectrum acquired 6900 ns after the laser pulse, in a 600-ns window, shows only the triplet alkyl nitrene and benzoyl radical absorption. Assuming that the triplet energy of the ketone moieties in azides **1** is the same as in the analogous ketones, the triplet energy of the ketone moiety in **1a** and **1f** is 311 and 254 kJ/mol, respectively.[22] Thus the lower triplet ketone energy in **1f** makes the triplet energy transfer less exothermic and slower than that in **1a**, enabling the triplet ketone absorption and the triplet nitrene to be detected.

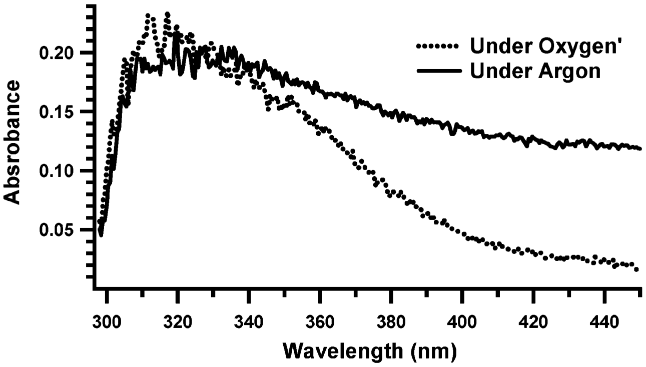


FIGURE 2. Transient spectrum of **1a** 200 ns after the laser pulse under O_2 and Ar.

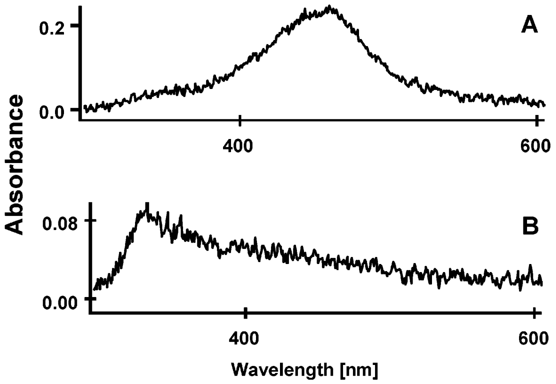


FIGURE 3. Transient spectra of **1f**: (A) immediately after the laser pulse and (B) 6900 ns after the laser pulse.

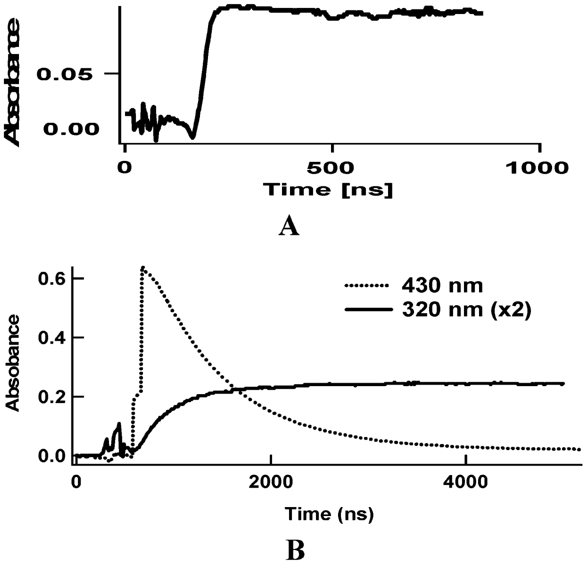


FIGURE 4. Kinetic traces (A) of **1a** at 320 nm and (B) of **1f** at 320 and 430 nm.

Kinetics. The absorption of nitrene **2a** was monitored at 320 nm and it formed faster than the time resolution of the laser flash photolysis apparatus (see Figure 4a). Therefore energy transfer from the triplet ketone to the azido group must be faster than 17 ns. Stern−Volmer

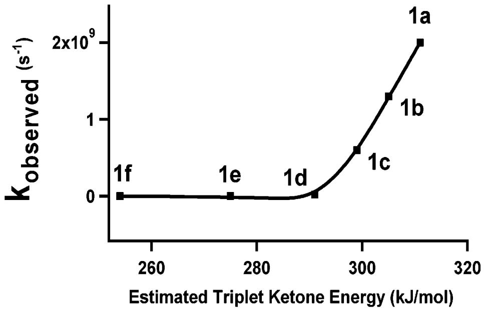


FIGURE 5. Rate of triplet energy transfer in azides **1**.

treatment of the quenching of the absorbance at 320 nm with isoprene in ethanol gave a linear plot with a slope of 0.9. Assuming that the energy transfer is diffusion controlled or k_q is between 1 and 10 × 10^9 M^{-1} s^{-1}, the lifetime of the triplet ketone can be estimated to be between 0.9 and 0.09 ns. For azide **1f**, the triplet ketone absorbance at 430 nm decays with a rate of 2 × 10^6 s^{-1} in methylene chloride (see Figure 4b) and the nitrene absorption at 320 nm forms at the same rate. The triplet ketone moieties in azides **1a** and **1f** are substantially shorter lived than the triplet ketone in the analogous acetophenone and *p*-phenylacetophenone, which have a lifetime of 0.3 and 5 μs, respectively, in methylene chloride. The short triplet lifetimes of the ketone azides are presumably due to efficient energy transfer to the azido moiety.

The triplet energy transfer in azide **1f** must be endothermic, which allows the energy transfer in azide **1f** to be measured. We set out to estimate the triplet energy of the azido group in azides **1** by measuring the rate of triplet energy transfer in azides **1** and comparing it to their triplet ketone energies. For azides **1b** and **1c** we used Stern−Volmer quenching with isoprene to estimate the lifetime of the triplet ketone, whereas for azides **1d** and **1e** we measured directly the rate of the energy transfer. As these compounds do not show any phosphorescence emission due to the efficient intramolecular quenching of the triplet ketone, we estimate that the triplet energies of the ketones are the same as those of the analogous ketones without α-azido substituents.[22] In Figure 5 we have plotted the rates of triplet energy transfer versus the triplet energy of the ketone. From this graph we can approximate that the triplet energy of the alkyl azide group must be slightly higher than 310 kJ/mol. This is in an agreement with Lewis et al., who estimated the triplet energy of simple alkyl azides to be between 314 and 335 kJ/mol.[23]

Theoretical Calculations

To identify possible intermediates in this study, we did theoretical calculations at several different levels of theory for azide **1a** and nitrene **2a**. Geometry optimization of azide **1a** at the B3LYP/6-311G level of theory resulted in two low-energy conformations with the azide group in either the syn or the gauche position (see Figure 6). The calculated energy difference between these two conformers is 0.4 kcal/mol. The geometries of the syn, gauche, and anti conformers of triplet nitrene **2a** were also optimized at the B3LYP/6-31G* level of theory (see Figure 7). The harmonic frequency calculations indicated that the syn and gauche conformers had all positive frequencies, demonstrating that these conformers correspond to local energy minima on the potential energy surfaces. In contrast, the anti conformer had one negative frequency for a vibration associated with the rotation of the $-CH_2-$ group. This indicates that the anti conformer corresponds to either a saddle point or maximum on the potential energy surface. As such, this conformer was not investigated any further. The calculated energy difference between the gauche and the syn conformers was 1.4 kcal/mol.

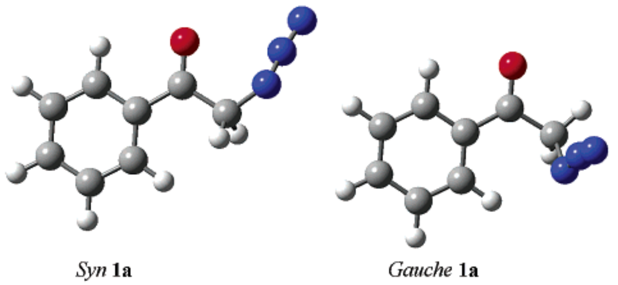

Syn **1a** *Gauche* **1a**

FIGURE 6. Syn and gauche conformers of **1a**.

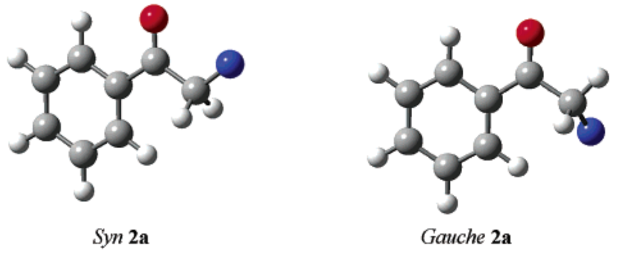
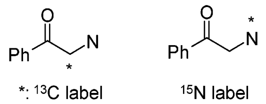

Syn **2a** *Gauche* **2a**

FIGURE 7. Syn and gauche conformers of **2a**.

SCHEME 8



Triplet nitrene **2a** was also investigated at the CASSCF-(6,6)/6-31G* level of theory. The active space consisted of six electrons and six molecular orbitals, which were the two half-filled p orbitals on the nitrogen, the lowest occupied π and σ orbitals, and the corresponding antibonding orbitals. At this level of theory, the syn and gauche conformers again were found to be local minima on the potential energy surfaces, with an energy difference of 0.8 kcal/mol. Infrared spectra, including those of compounds with ^{13}C (α position) and ^{15}N labels (see Scheme 8), were calculated for nitrene **2a** at both the B3LYP/6-31G* and CASSCF(6,6)/6-31G* levels of theory, and will be discussed below.

Matrix Isolation of Photolysis of 1a

We deposited azide **1a** into argon matrices in several different experiments, entraining the vapor pressure over a sample of the pure azide in flowing argon and depositing the resulting sample on a 14 K cryogenic surface. The infrared spectrum of such a sample showed a strong, broad azide band at 2111 cm^{-1} with a shoulder at 2104 cm^{-1} (see Figure 8). These frequencies fit reasonably well with the calculated frequencies for the syn and gauche conformers of **1a**, respectively, and thus we assign them accordingly. On the basis of the relative intensities of the 2104- and 2111-cm^{-1} features, we estimated the syn conformer to be approximately three times as abundant in the argon matrix as the gauche conformer.

Irradiation of azide **1a** in argon matrices led to complete destruction of bands due to the azide, and the

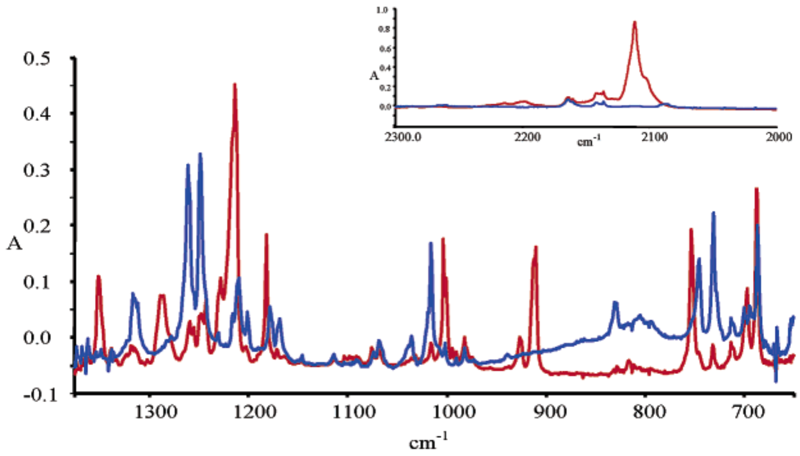


FIGURE 8. IR spectra of azide **1a** in argon matrices: before (red) and after irradiation (blue).

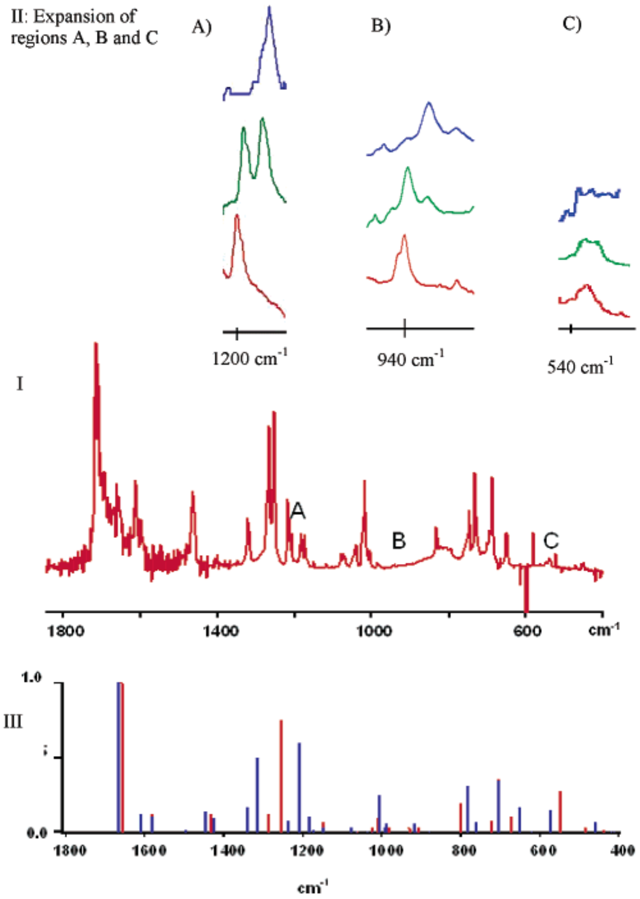


FIGURE 9. (I) IR spectra of **2a** in argon matrices. (II) Expansion of regions A, B, and C. Blue spectra are of **2a** with a ^{13}C isotope in the α-position. Green spectra are of **2a** with a 1:1 mixture of ^{15}N and ^{14}N isotopes. Red spectra are of **2a** with normal isotopes. (III) Simulated spectra (B3LYP, 631G*) of syn (blue) and gauche (red) conformers of **2a**.

growth of many new features attributable to photoproduct(s). Many of these occurred very near bands of the parent azide, which is expected since the acetophenone moiety should not be significantly affected by changes due to irradiation. This point is also validated by our calculations (see Figure 9). We observed several distinct new bands upon irradiation, at 536, 939, and 1201 cm^{-1} (see Figure 9). Of these, the band at 1201 cm^{-1} was the most intense and distinct. All three bands shifted to lower energy upon ^{13}C substitution, whereas the bands at 536 and 1201 cm^{-1} also shifted to lower energy with ^{15}N substitution, as shown in Table 1. In contrast, the remainding product bands did not shift upon isotopic substitution, confirming that they are associated with vibrations of the acetophenone moiety. This observation limits the number of possibilities of the absorbing species. Candidates include the triplet nitrene, the singlet nitrene, imine **17**, and the α-cleavage products. We can rule out imine **17** since we do not observe any N−H stretching mode between 3100 and 3500 cm^{-1}, despite the fact that the vibrational mode should absorb strongly in this region. This allows us to exclude the formation of singlet alkyl nitrene in matrices as well. Ellison et al. have shown that there is no barrier separating the rearrangement of singlet methyl nitrene into an imine and thus we would expect singlet nitrene to undergo a 1,2-H shift to form imine **17** or intersystem cross to the ground-state triplet nitrene **2a**.[11] Furthermore, we can also rule out α-cleavage in argon matrices since we do not observe any benzoyl radical formation, which has a strong absorption at 1828 cm^{-1} in fluid solutions.[12] We speculated, though, that if α-cleavage took place at low temperature then the methyl azide radical could expel a nitrogen molecule and rearrange into an imine radical. The argon matrices would hold the benzoyl and imine radicals in close approximation and allow them to recombine to form imine **16** (see Scheme 9). However, imine **16** is not formed in argon matrices, because our calculations show that the frequency of the carbonyl stretch would be shifted 27 and 18 cm^{-1} upon ^{13}C and ^{15}N substitution, respectively.

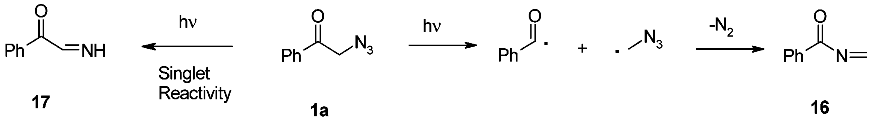
We calculated the infrared spectrum of the syn and the gauche conformers of triplet nitrene **2a** at several levels of theory, for comparison to these three bands. The C−N stretch and the C−C−N bending modes are expected to be very sensitive to ^{13}C and ^{15}N substitution, whereas the CH_2 wag should be sensitive to ^{13}C but not ^{15}N substitution. The C−N stretches of nitrenes have been observed between 1000 and 1075 cm^{-1}, for example, the C−N stretch of triplet methyl nitrene has been reported at 1040 cm^{-1} whereas the C−N stretch of tetrafluoropyridine-4-nitrene has been observed at 1272

TABLE 1. Comparison of Experimental and Theoretical Band Positions and Isotopic Shift for Nitrene 2a

band position			^{13}C shift			^{15}N shift		
B3LYP[a]	CASSCF	exptl	B3LYP	CASSCF	exptl	B3LYP	CASSCF	exptl
663	360	539	−5	−2	−2	−1	−5	−3
909	1002	939	−7	−8	−6	−1	−1	0
1067	1145	1201	−17	−16	−9	−15	−15	−6

[a] The calculated IR frequencies are not scaled. In the Supporting Information we have listed the calculated IR frequencies for B3LYP/6311++G*, which are generally not scaled. There is not a significant shift in the IR frequencies of these three bands with use of either one of these basis sets.

SCHEME 9



cm^{-1}.[6,24] Our calculations place this mode between 1067 (B3LYP/6-31G*) and 1145 cm^{-1} (CASSCF/6-31G*). On the basis of the location of the 1201-cm^{-1} band and its sensitivity to both ^{13}C and ^{15}N substitution, we assign it to the C−N stretch of the syn conformer of nitrene **2a**. Since azide **1a** is primarily trapped in the syn conformation we expect it to produce primarily the syn conformer of nitrene **2a**. We assigned the 939-cm^{-1} band to the CH$_2$ wagging motion of the −CH$_2$N group; the calculated position and isotopic shifts are in good agreement with the experimental values.

Less is known experimentally about the C−C−N bending mode, although it should occur at substantially lower frequency. For comparison, the C−C=O bending mode of acetone occurs near 535 cm^{-1}.[25] The bending mode is calculated at 663 cm^{-1} at the B3LYP/6-31G* level of theory. While this is higher than the 536-cm^{-1} experimental band, the calculated isotopic shifts are reasonable. On the other hand, calculations at the CASSCF/6-31G* level substantially underestimated this band position, but again the calculated isotopic shifts are in good agreement. Overall, while theoretical calculations have some difficulty calculating absolute band positions for the nitrene moiety, the calculated isotope shifts for these three modes are quite good, and confirm identification of nitrene **2a**.

The UV/vis spectrum obtained after photolysis of azide **1a** in argon matrices shows no absorption due to benzoyl radical formation (see Figure 10) and it does resemble the UV absorption spectrum of triplet methyl nitrene.[6] When comparing the transient spectra of nitrene **2a** obtained with the laser flash apparatus in fluid solutions and in matrices it must be kept in mind that the laser flash apparatus is limited to detection above 300 nm. Thus the laser flash photolysis catches the trail of the UV absorption of nitrene **2a**, whereas the transient spectrum of **2a** in argon matrices has λ_{max} at 280 nm.

Conclusion

We have shown that irradiation of azides **1** leads to the formation of benzoyl radicals and triplet alkyl nitrenes **2**. At higher temperatures α-cleavage to form benzoyl radicals is favored whereas at lower temperature more of the triplet alkyl nitrenes are formed. The triplet alkyl nitrenes **2** are intercepted with both molecular oxygen and benzoyl radicals. The triplet alkyl nitrenes can be detected directly with laser flash photolysis and they have a lifetime longer than microseconds in solution. The triplet alkyl nitrene intermediates were further characterized by obtaining their UV and IR spectrum in argon matrices. The UV absorption spectrum of triplet alkyl nitrene **2a** in argon matrices has maximum absorption at 280 nm. The IR spectrum of nitrene **2a** in argon matrices has a weak C−N stretch at 1201 cm^{-1}, which shifted on ^{15}N and ^{13}C isotope labeling.

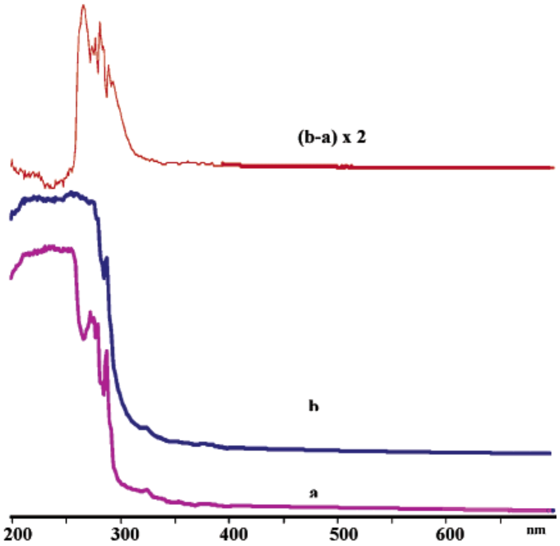


FIGURE 10. The UV absorbance spectra of azide **1a** in argon matrices: (a) before photolysis, (b) after photolysis, and (c) the difference of spectrum b − spectrum a.

Experimental Section

Calculations.: The geometries of azide **1a** were optimized by the B3LYP method as implemented in the Gaussian 98 programs, using the 6-311G basis set. The geometries and IR spectra of nitrene **2a** were optimized by the B3LYP and CASSCF theory, using the 6-31G* basis set. The calculated IR frequencies are not scaled. All the calculations were preformed with the Gaussian 98 software package.[32]

---

(23) Lewis, F. D.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 7033.

(24) Chapyshev, S. V.; Kuhn, A.; Wong, M. W.; Wentrup, C. *J. Am. Chem. Soc.* **2000**, *122*, 1572.

(25) Marcou, A.; Roche, D. *C. R. Acad. Sci. Ser. B* **1973**, *276*, 599.

(26) Ault, B. S. *J. Am. Chem. Soc.* **1978**, *100*, 2426.

Laser Flash Photolysis. Laser flash photolysis was carried out with an Excimer laser (308 nm, 17 ns). The system has been described in detail elsewhere.[27] The rate of the energy transfer for azides **1d**−**f** was measured directly. We did not detect the absorption of the triplet excited state of the ketone chromophore in azides **1a**−**c**. However, we succefully manged to reduce the nitrene absorption at 320 nm with isoprene, because the precursor or the triplet excited ketone is being quenched. Standard Stern−Volmer treatment of the quenching of the absorbance at 320 nm with isoprene gave a linear plot. By assuming that the energy transfer from the triplet excited state of the ketone to isoprene was diffusion controlled, or k_q is 5×10^9 M^{-1} s^{-1}, the lifetime of the triplet ketone could be estimated from the slope of the Stern−Volmer graph.[28]

Matrix Isolations. Matrix isolation studies were done on conventional equipment.[26]

General Procedures. Photolysis were carried out with a 450-W mercury lamp through Pyrex filters. Toluene was dried and distilled over sodium prior to use.

Preparation of Azides 1a−f. Azides **1** were synthesized as described.[28] In a typical reaction 2-bromoacetophenone (2.0 g, 0.010 mol) was dissolved in ethanol (50 mL) and glacial acetic acid (2 mL). To this mixture was added a solution of sodium azide (1.30 g, 0.204 mol) in water (5 mL) and the resulting mixture was refrigerated overnight. The reaction was neutralized with aqueous saturated sodium bicarbonate solution and extracted with ethyl acetate. The organic layer was washed with brine and dried over $MgSO_4$ and the solvent was removed under vacuum. The resulting solid was recrystallized from ethanol in an ice bath (1.32 g, 8.2 mmol, 82% yield). The ^{1}H NMR, IR spectra and the melting point of 2-azido-1-phenylethanone, **1a**, are identical with those in the literature.[10,28]

The labeled **1aC** was synthesized in the same manner from 2-bromo-1-^{13}C-acetophenone. The 1:1 mixture of **1aN1**:**1aN3** was prepared by the same method with ^{15}N-labeled sodium azide.

Azides **1b**−**f** were synthesized in approximately 80% yield by the same procedure as azide **1a**. The ^{1}H NMR, IR spectra, and melting points of 2-azido-(4′-bromophenyl)ethanone, **1b**,[33] 2-azido-(4′-chlorophenyl)ethanone, **1c**,[10,28] and 2-azido-1-benzo-[1,3]dioxol-5-ylethanone, **1e**,[34] are identical with those in the literature.

2-Azido-(4′-cyanophenyl)ethanone, 1d. Mp (ethyl acetate/hexanes) 127−130 °C. IR (KBr) 2232, 2107, 1693 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.57 (s, 2 H), 7.82 (d, 8 Hz, 2H), 7.99 (d, 8 Hz, 2H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$) δ 55.2, 117.5, 128.5, 132.5, 137.3, 192.2 ppm. MS (ESI) 159.1 ($M^+ - N_2$).

2-Azido-(4′-biphenyl-4-yl)ethanone, 1f. Mp (ethyl acetate/hexanes) 78−82 °C (lit.[28] mp 88−88.5 °C). IR (KBr) 2099, 1683 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.59 (s, 2H), 7.45 (m, 3H), 7.64 (d, 5 Hz, 2H), 7.71 (d, 8 Hz, 2H), 7.98 (d, 8 Hz, 2H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$) δ 54.59, 126.7, 126.9, 127.6, 128.1, 128.6, 132.6, 138.9, 146.2, 192.8 ppm.

Preparative Photolysis of 1. Formation of acetophenone **4** and benzaldehyde **5** was confirmed by authentic injection on GC and GC-MS and HPLC. Products **3a**−**f** were isolated and characterized.

Photolysis of 1a. A solution of azide **1a** (80 mg, 0.5 mmol) in toluene (2 mL) was degassed with argon and irradiated for 26 h. GC analysis of the reaction mixture showed no remaining **1a**. The solvent was removed under vacuum and the resulting oil purified on a silica column eluted with 10% ethyl acetate in hexane. The column yielded three fractions: benzaldehyde (15 mg, 0.14 mmol, 28%), acetophenone (11 mg, 0.09 mmol, 18%), and amide **3a** (26 mg, 0.11 mmol, 44%). The total isolated yield of photoproducts is 90%. The ^{1}H NMR, IR, and melting point of *N*-(2-oxo-2-phenyl-ethyl)benzamide, **3a**, were identical with those in the literature.[10]

Photolysis of 1b. A solution of **1b** (916 mg, 1.5 mmol) in toluene (80 mL) was photolyzed overnight. GC analysis of the reaction mixture showed no remaining starting material. The solvent was removed under vacuum and the resulting oil was purified on a silica column eluted with hexane in ethyl acetate. The major product isolated was 4-chloro-*N*-[2-(4-chlorophenyl)-2-oxoethyl]benzamide, **3b** (65 mg, 0.21 mmol, 30% yield). Mp (ethyl acetate/hexane) 172−174 °C. IR (KBr) 3367, 1691, 1635, 1094 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.92 (d, 6 Hz, 2H), 7.23 (s, 1H), 7.47 (m, 6 Hz, 5H), 7.80 (d, 8 Hz, 2H), 8.0 (d, 8 Hz, 2H) ppm.^{13}C NMR (60 MHz, $CDCl_3$) δ 47.0, 128.8, 129.1, 129.1, 129.2, 129.6, 129.7, 132.5, 133.0, 138.4, 141.1, 166.5, 193.3 ppm. GCMS 307/309 (M^+, 2%), 168/167 (5%), 139/141 (100%).

Photolysis of 1c. A solution of **1c** (200 mg, 0.84 mmol) was photolyzed until all the GC analyzis showed only 5% remaining starting material. The solvent was removed under vacuum and the resulting oil purified with silica column eluted with 5% ethanol in hexane. Three fractions were collected: **3c** (77 mg, 0.20 mmol, 47% yield), **4c** (12 mg, 0.06 mmol, 7% yields), and **5c** (3 mg, 0.017 mmol, 2% yields). The ^{1}H NMR, ^{13}C NMR, IR, and melting point of 4-bromo-*N*-[2-(4-bromophenyl)-2-oxoethyl]-benzamide, **3c**, were identical with those in the literature.[10]

Photolysis of 1d. A solution of **1d** (900 mg, 4.8 mmol) in toluene (20 mL) was bubbled with argon and irradiated overnight. Insoluble polymers formed upon photolysis which were filtered and discarded. HPLC showed formation of **3d** and **11d**. The solvent was removed under vacuum to yield oil that was purified on silica gel eluted with ethyl acetate in hexane.

4-Cyano-*N*-[2-(4-cyanophenyl)-2-oxyethyl]benzamide,, 3d, was isolated in 6% yield (39.2 mg, 0.14 mmol). IR ($CHCl_3$) 3407, 2230, 1704, 1641, 1607, 1404 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.14 (d, 8 Hz, 2H), 8.05 (d, 8 Hz, 2H), 7.9−7.6 (m, 4 H), 7.25 (s, 1H), 4.98 (d, 3 Hz, 2H) ppm. ^{13}C NMR (60 MHz, DMSO-d_6) δ 47.0, 118.2, 118.4, 128.2, 128.3, 132.6, 132.7, 138.2, 139.7, 165.5, 195.0 ppm. HRMS (ESI) calcd for $C_{17}H_{10}N_3O_2$ ($M^+ - 1$) 288.0773, found 288.0773.

4-(2-Benzylamino-acetyl)benzonitrile, **11d**, was isolated in 1% yield (13.5 mg, 0.054 mmol). IR ($CHCl_3$) 3406, 2233, 1667, 1607, 1521, 1422 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.65 (s, 2H), 4.84 (s, 2H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$) δ 38.7, 56.8, 115.6, 117.4, 127.7, 127.8, 128.7, 132.7, 132.8, 134.5, 137.7, 197.1 ppm.

Photolysis of 1e. A solution of **3e** (250 mg, 1.22 mmol) in toluene (50 mL) was photolyzed overnight. The solvent was removed under vacuum and the resulting oil purified on a silica column to yield four fractions: **1e** (40 mg, 0.20 mmol,

---

(27) Gritsan, N. P.; Zhai, H. B.; Yuzawa, T.; Karweik, D.; Brooke, J.; Platz, M. S. *J. Phys. Chem. A* **1997**, *101*, 2833.

(28) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Sausalito, CA, 1991; Chapter 8.

(29) (a) Boyer, J. H.; Straw, D. *J. Am. Chem. Soc.* **1952**, *74*, 4506. (b) Boyer, J. H.; Straw, D. *J. Am. Chem. Soc.* **1953**, *75*, 1642.

(30) (a) Hegarty, D.; Robb, M. A. *Mol. Phys.* **1979**, *38*, 1795. (b) Robb, M. A.; Niazi, U. *Rep. Mol. Theory* **1990**, *1*, 23. (c) Anderson, K.; Roos, B. O. In *Modern Electron Structure Theory*; World Scientific Publishing: Singapore, 1995; Part 1, Vol. 2, p 55.

(31) (a) Gross, E. K. U.; Kohn, W. *Adv. Quantum Chem.* **1990**, *21*, 255. (b) Casida, M. E. In *Recent Advances in Density Functional Methods*; World Scientific Publishing: Singapore, 1995; Vol. 1, 55. (c) Wiberg, K. B.; Stratmann, R. R.; Frisch, M. *J. Chem. Phys. Lett.* **1998**, *297*, 60.

(32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Cliford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rbuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stafanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Goperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 94*, Revision D.2; Gaussian, Inc.: Pittsburgh, PA, 1998.

(33) Nair, V.; Nair, L. G.; George, T. G.; Augustine, A. *Tetrahedron* **2000**, *56*, 7607.

(34) Ackrell, J.; Muchowski, J. M. *J. Org. Chem.* **1986**, *51*, 3374.

16%), **4e** (15 mg, 0.091 mmol, 7% yield), **5e** (35 mg, 0.23 mmol, 19% yield), and **3e** (60 mg, 0.18 mmol, 30% yield). The physical properties of (2-benzo[1,3]dioxol-5-yl-2-oxo-ethyl)amide benzo-[1,3]dioxole-5-carboxylic acid, **3e**, are as follows. IR ($CHCl_3$) 1677, 1657, 1604, 1254 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.84 (d, 4 Hz, 2H), 6.04 (s, 2H), 6.08 (s, 2H), 6.88 (m, 2H), 7.15 (s, 1H), 7.40 (m, 4H), 7.63 (d, 8 Hz, 2H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$) δ 192.3, 166.5, 152.7, 150.5, 148.5, 148.0, 129.2, 128.2, 124.4, 121.8, 108.3, 108.0, 107.9, 107.6, 102.1, 101.7, 46.6 ppm. HRMS calcd for $C_{17}H_{13}NO_6Na$, $[M + 23]^+$, 350.0641, found 350.0665.

Photolysis of 1f. A solution of **1f** (298 mg, 1.25 mmol) in toluene (60 mL) was photolyzed overnight. A TLC showed no remaining starting material. The solvent was removed under vacuum and the resulting oil purified on a silica column eluted with ethyl acetate in hexane. Three fractions were collected: **4f** (2.4 mg, 0.013 mmol, 1%), *p*-phenyl acetophenone **5f** (35 mg, 0.18 mmol, 14% yields), and **3f** (45 mg, 0.12 mmol, 20% yields). The spectroscopic characterization of biphenyl-4-carboxylic acid (2-biphenyl-4-yl-2-oxoethyl)amide, **3f**, is listed below. Mp 257−8 °C dec (lit.[34] mp 259 °C). IR (KBr) 3388, 1646, 1603 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.81 (d, 4 Hz, 2H), 7.39 (m, 10H), 7.72 (d, 8 Hz, 3H), 7.87 (d, 8 Hz, 3H) ppm.

Analytical Photolysis of Azides 1. Azides **1** were dissolved in toluene, degassed by bubbling argon through the solution, and photolyzed through Pyrex filter. The conversion of the starting material was kept below 20%. HPLC, GC analysis, and ^{1}H NMR of the reaction mixtures were used to estimate the product ratio for **3**, **4**, and **5**.

Photolysis of 1-Azidoadmantane and Methyl Benzoin, 8. A solution of **8** (17 mg, 0.1 mmol) and 1-azidoadmantane (22.6 mg, 0.1 mmol) in 2 mL of toluene was degassed with argon and photolyzed with a 450-W Mercury arc lamp through a 349-nm filter. A solution of **8** (0.1 M) in toluene was also prepared and photolyzed simultaneously. The major products coming from photolysis of **8** were characterized by GC/MS as **5a**, benzil (**9**), 1,2-diphenylethanone (**10**), 1-methoxy-1,2-diphenylethane (**12**), and 1,2-dimethoxy-1,2-diphenylethane (**11**).

Photolysis of 1a in Toluene at Low Temperature. A solution of **1a** (0.02 M) and hexadecane (0.005 M) in toluene was photolyzed at −63 and 100 °C. The reaction mixture was analyzed by GC and GC/MS. Formation of 1,2-diphenylethanone (**9**) and 1,4-diphenylbutane-1,4-dione (**12**) was verified with commercially available authentic samples. Formation of *N*-benzyl-*N*-(2-oxo-2-phenylethyl)benzamide (**13**) and 2-benzylamino-1-phenylethanone (**11**) was established by synthesizing these compounds following literature procedures.[36]

Photolysis of 1a in Toluene Saturated with Oxygen. An oxygen-saturated solution of **1a** (0.01 M) in toluene was photolyzed at 30 and −63 °C. GC analysis of the reaction mixture showed formation of benzoic acid, acetophenone, 2-nitrophenylethanone, and **3a** along with unreacted starting material. The formation of benzoic acid, acetophenone (**4a**), 2-nitrophenylethanone (**15**), and **3a** was verified by GC/MS and authentic samples.[36]

Acknowledgment. A.D.G. is grateful to the University of Cincinnati Research Council Faculty Research Support. We also acknowledge the finical support from the National Science Foundation (CHE No. 0093622) and the Petroleum Research Foundation (ACS-PRF No. #35809). S.M.M. thanks the University of Cincinnati Research Council for financial support. We thank Professor M. S. Platz at The Ohio State University for the use of his laser flash apparatus.

Supporting Information Available: Cartesian coordinates, number of imaginary frequencies, IR frequencies, and total energy of **1a**, **2a**, and **16**; the Stern Volmer graph for isoprene quenching of azides **1a**−**c** and ^{1}H NMR spectra of products **3**; the rate of intramolecular energy transfer in **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO034674E

---

(35) Balaban, A. T.; Bally, I.; Frangopol, P. T.; Bacescu, M.; Cioranescu, E.; Birladeanu, L. *Tetrahedron* **1963**, *19*, 169.

(36) Fuhrman, H.; Haber, H.; Haupt, M.; Henning, H.-G. *J. Prakt. Chem.* **1982**, *6*, 1055.