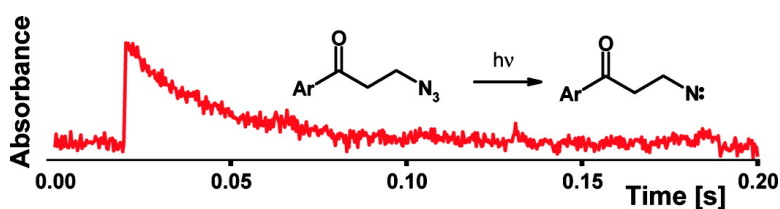


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Selective Formation of Triplet Alkyl Nitrenes from Photolysis of β -Azido-Propiophenone and Their Reactivity

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Abstract: Photolysis of β -azido propiophenone derivatives, **1**, with built-in sensitizer units, leads to selective formation of triplet alkyl nitrenes **2** that were detected directly with laser flash photolysis ($\lambda_{\text{max}} = 325$ nm, $\tau = 27$ ms) and ESR spectroscopy ($|D/hc| = 1.64$ cm⁻¹, $|E/hc| = 0.004$ cm⁻¹). Nitrenes **2** were further characterized with argon matrix isolation, isotope labeling, and molecular modeling. The triplet alkyl nitrenes are persistent intermediates that do not abstract H-atoms from the solvent but do decay by dimerizing with another triplet nitrene to form azo products, rather than reacting with an azide precursor. The azo dimer tautomerizes and rearranges to form heterocyclic compound **3**. Nitrene **2a**, with an n, π^* configuration as the lowest triplet excited state of the its ketone sensitizer moiety, undergoes intramolecular 1,4-H-atom abstraction to form biradical **6**, which was identified by argon matrix isolation, isotope labeling, and molecular modeling. β -Azido-*p*-methoxy-propiophenone, with a π, π^* lowest excited state of its triplet sensitizer moiety, does not undergo any secondary photoreactions but selectively yields only triplet alkyl nitrene intermediates that dimerize to form **3b**.

Introduction

The pursuit of organic magnetic materials has sparked renewed interest in triplet nitrene intermediates, which are readily studied models for exchange behavior because of their high spin properties.¹ A limitation, however, is that they are difficult to form selectively because they and their precursors are highly reactive.^{2,3} Thermal activation or direct photolysis of aryl, carboalkoxy, and phosphoryl azide precursors yields singlet nitrenes that are highly reactive and can insert into themselves and other molecules in competition with intersystem crossing to their triplet ground states. Direct photolysis of the azide precursors at low temperature favors intersystem crossing over other singlet reactivity. However, the triplet nitrenes themselves are sensitive to light. For example, Levya et al. have demonstrated that photolyzing phenyl azide at low temperature produces singlet phenyl nitrene that intersystem

crosses to the triplet, but the light used to decompose the phenyl azide precursor at low temperature is also absorbed by the phenyl nitrene to form ketenimine.⁴ Interestingly, Mahe et al. and Ichimura et al. have successfully formed stable triplet aryl nitrenes at low temperatures within crystal lattices.^{5,6}

In contrast to aryl nitrenes, triplet alkyl nitrenes have not been studied extensively, in part because direct irradiation of alkyl azides in solution leads to the formation of imine products via a concerted rearrangement of the singlet excited state of the alkyl azides rather than alkyl nitrenes.⁷ Some of us have shown that the photolysis of α -azidoacetophenone, having a built-in intramolecular triplet sensitizer, leads to intramolecular energy transfer and the formation of triplet alkyl nitrene intermediates.^{8,9} This process is complicated because, in competition with energy transfer to form triplet alkyl nitrenes, the α -azidoacetophenones undergo α -cleavage to form benzoyl and azido methyl radicals. The triplet alkyl nitrenes can then be intercepted by the benzoyl

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- (1) (a) Tomioka, H. Triplet Carbenes. In *Reactive Intermediates*; Moss, R. A., Platz, M. S., Jones, M., Jr., Eds.; Wiley-Interscience: 2004; Chapter 9, p 375. (b) Subhan, W.; Rempala, P.; Sheridan, R. S. *J. Am. Chem. Soc.* **1998**, *120*, 11528. (c) *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Dekker: New York, 1999. (d) Itoh, K.; Kinoshita, T. *Molecular Magnetism: New Magnetic Materials*; Godon and Breach: Amsterdam, 2000.
- (2) Platz, M. S. Nitrenes. In *Reactive Intermediates*; Moss, R. A., Platz, M. S., Jones, M., Jr., Eds.; Wiley-Interscience: 2004; Chapter 11, p 501.
- (3) Bucher G. Photochemical Reactivity of Azides. In *CRC Handbook of Organic Photochemistry and Photobiology*, 2nd ed.; Horspool, W., Lenci, F., Eds.; CRC Press: Boca Raton, FL, 2004; Chapter 44, pp 44–1.

(4) Levya, E.; Platz, M. S.; Persy, G.; Wirz, J. *J. Am. Chem. Soc.* **1986**, *108*, 3783.

(5) Mahe, L.; Izuoka, A.; Sugawara, T. *J. Am. Chem. Soc.* **1992**, *114*, 7904.

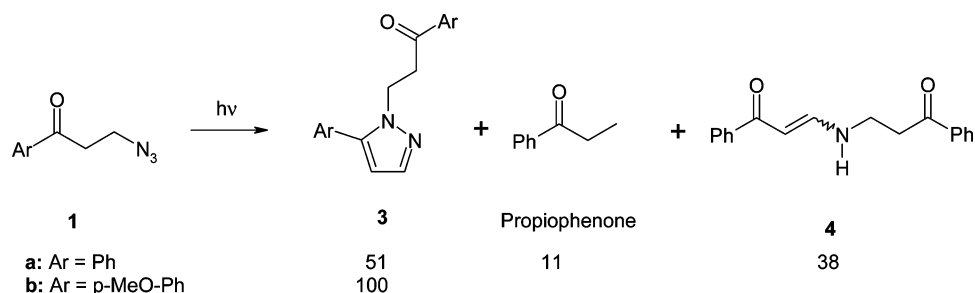
(6) Ichimura, A. S.; Sato, K.; Kinoshita, T.; Takui, T.; Itoh, K.; Lahti, P. M. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1995**, *272*, 57.

(7) (a) *Azides and Nitrenes. Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic Press, Inc.: New York, 1984. (b) Abramovitch, R. A.; Kyba, E. P. *J. Am. Chem. Soc.* **1971**, *93*, 1537.

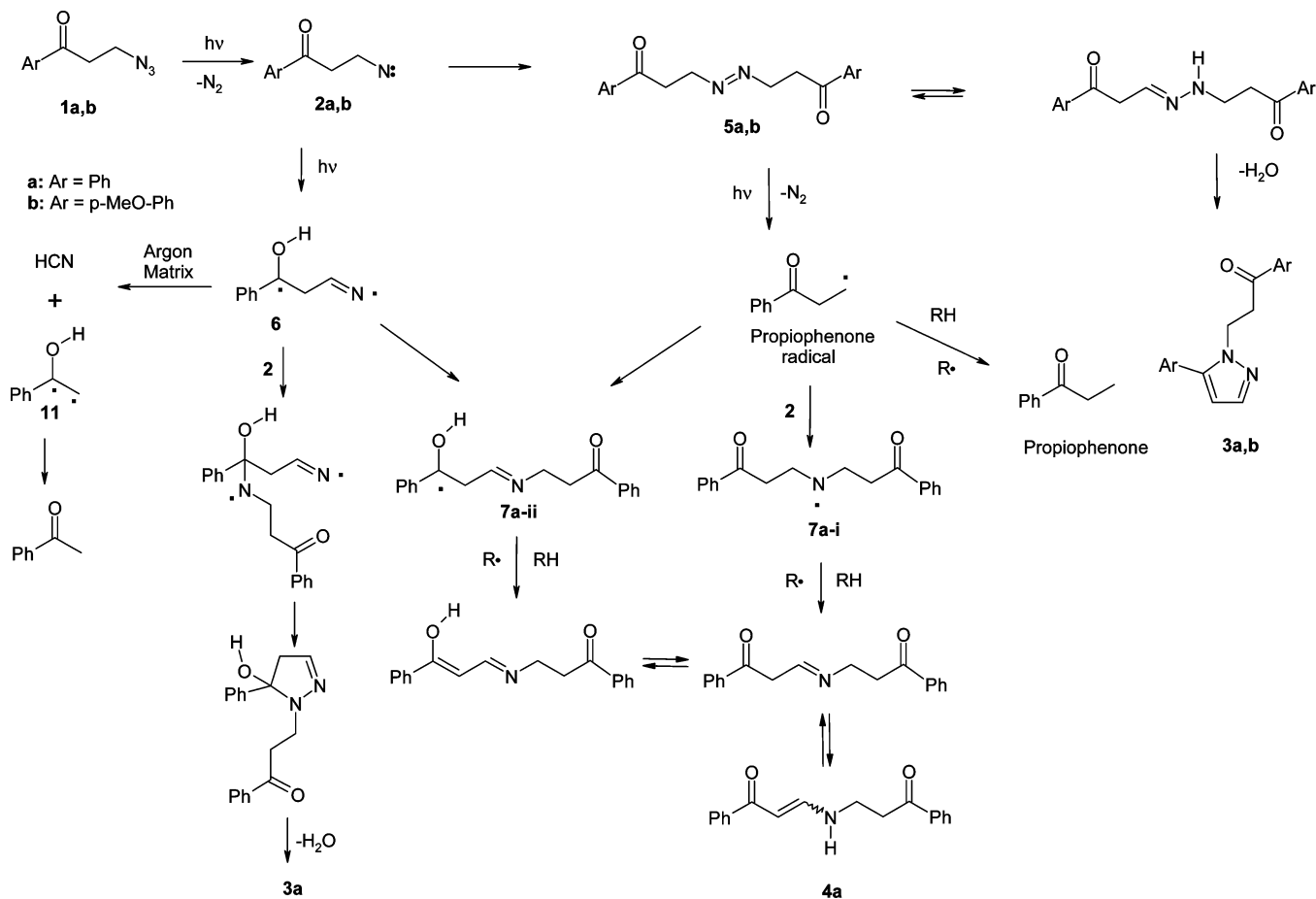
(8) (a) Singh, P. N. D.; Mandel, S. M.; Zhu, Z.; Franz, R.; Ault, B. S.; Gudmundsdóttir, A. D. *J. Org. Chem.* **2003**, *68*, 7951. (b) Mandel, S. M.; Krause Bauer, J. A.; Gudmundsdóttir, A. D. *Org. Lett.* **2001**, *3*, 523. (c) Muthukrishnan, S.; Mandel, S. M.; Hackett, J. C.; Singh, P. N. D.; Hadad, C. M.; Krause, J. A.; Gudmundsdóttir, A. D. *J. Org. Chem.* **2007**, *72*, 2757.

(9) Mandel, S. M.; Singh, P. N. D.; Muthukrishnan, S.; Chang, M.; Kraus, J. A.; Gudmundsdóttir, A. D. *Org. Lett.* **2006**, *8*, 4207.

Scheme 1



Scheme 2. Possible Mechanism for Formation of Photoproducts from Irradiation of Azide 1



radicals to form benzamide products. Thus, we investigated the photochemistry of azides **1**, with a built-in intramolecular sensitizer that is not able to undergo α -cleavage,¹⁰ to verify that triplet alkyl nitrenes can indeed be formed selectively, and to subsequently explore the reactivity of triplet alkyl nitrenes in the absence of radical traps. We prepared azide **1a** and **1b**, which have n,π^* and π,π^* configurations as the lowest triplet excited state of the ketone moiety, respectively. In this paper we demonstrate for the first time that triplet alkyl nitrenes can be formed selectively in solution and that triplet alkyl nitrenes are unreactive and long-lived intermediates, because they do not abstract H-atom from the solvent or react with their precursors. However, prolonged irradiation of the triplet alkyl nitrene formed from photolysis of azide **1a** leads to intramolecular β -H-atom abstraction to form an imine radical as a secondary photoproduct. In comparison, the nitrene formed from azide **1b**

is not photoreactive, since triplet ketones with π,π^* configuration do not undergo intramolecular H-atom abstraction efficiently.¹¹

Results and Discussion

Product Studies. Photolysis of azide **1a** yields **3a** as the major product and smaller amounts of **4a** and propiophenone (see Scheme 1). Pyrazole **3a** was characterized based on the similarity of its ¹³C and ¹H NMR spectra to those of the 1-methyl-5-phenylpyrazole and 1-(4-chloro-phenyl)-3-[3-(4-

(10) Klima, R. F.; Jadhav, A. V.; Singh, P. N. D.; Chang, M.; Vanos, C.; Sankaranarayanan, J.; Vu, M.; Ibrahim, N.; Ross, E.; McCloskey, S.; Murthy, R. S.; Krause, J. A.; Ault, B. S.; Gudmundsdottir, A. D. *J. Org. Chem.* **2007**, *72*, 6372.

(11) (a) Wagner, P. J. In *Rearrangements in Ground and Excited States*; De Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 42-3, p 381. (b) Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1.

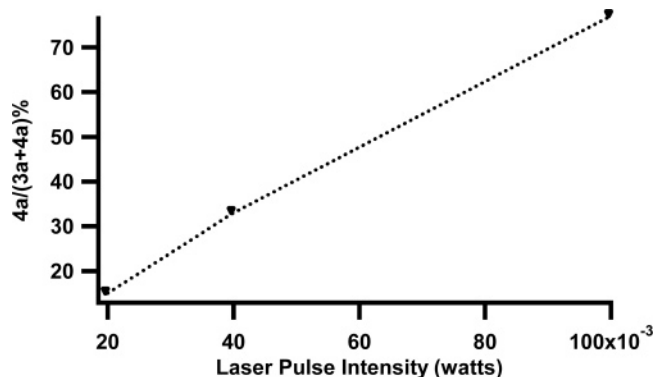


Figure 1. Product ratio from irradiation of **1a** vs laser intensity.

chlorophenyl)-pyrazol-1-yl]-propan-1-one analogues.^{12,13} Product **4a** was identified similarly based on a comparison of its ¹³C and ¹H NMR spectra with the NMR spectra of 3-alkyl-amino-1-phenyl-propenone derivatives.¹⁴

We propose that **3a** is formed by the dimerization of two triplet alkyl nitrene intermediates to form azo compound **5a**, which rearranges with loss of a water molecule as shown in Scheme 2. Similarly, triplet aryl nitrenes mainly dimerize to give diaryl diazenes, but triplet aryl nitrenes also abstract an H-atom from the solvent to form aniline derivatives and are therefore more reactive than triplet alkyl nitrenes.¹⁵ The formation of propiophenone can be explained by the secondary photolysis of the azo dimer **5a** to give a propiophenone radical that abstracts a H-atom from the solvent. Similarly, formation of **4a** can be attributed to the propiophenone radical that is intercepted by nitrene **2a**, and abstraction of a H-atom from the resulting radical **7a-i** would lead to the formation of oxoimino **4a**. Zhou et al. have shown that even though enaminones can exist in the tautomeric iminoenol, oxoimino, and ketoamino forms, in solution they are mainly present in the ketoamino form.¹⁴ Since, the present studies of nitrene **2a** support that it undergoes intramolecular H-atom abstraction to form biradical **6**, we speculated what products will arise from biradical **6**. Interestingly, trapping of **6** with nitrene **2a** might also yield product **3a**, whereas propiophenone radical and biradical **6** can combine to form **7a-ii** which results in formation of **4a**.

In order to verify that propiophenone and **4a** are formed upon secondary photolysis, we photolyzed azide **1a** with a high intensity argon laser jet at three different laser pulse powers, but keeping the conversion below 10%. Under these experimental conditions we did not observe any propiophenone formation. As the intensity of the laser pulse was increased, higher yields of **4a** were observed at the expense of **3a** (see Figure 1), demonstrating that **4a** must come from secondary photolysis, presumably of **5a** or **2a**. It can be speculated that a higher excited state of the azide **1a** is attainable upon irradiation with the high-intensity laser. However, the second excited triplet state of the ketone chromophore in azide **1a** has a π, π^* configuration which would not undergo efficient intramolecular β -H-atom abstraction.¹¹

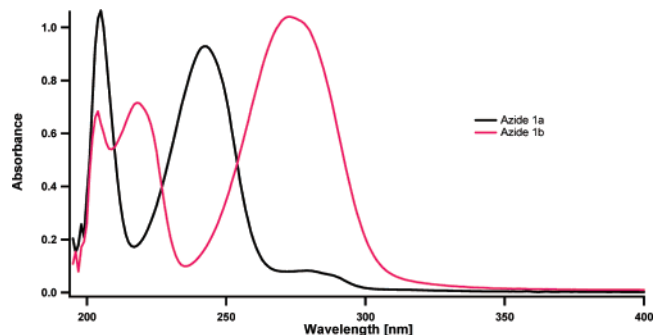
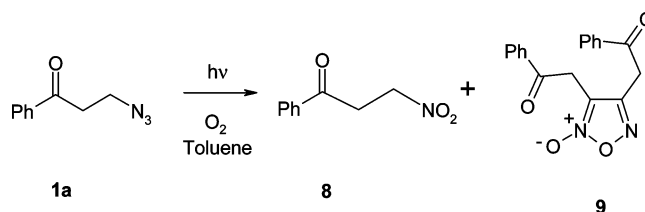


Figure 2. UV-vis absorbance spectra of azides **1**.

Scheme 3. Products from Photolysis of **1a** in Oxygen-Saturated Toluene



In contrast, photolysis of azide **1b** is much more selective than azide **1a**. Azide **1b** yields only one major compound, **3b**, which comes from the formation of the azo dimer **5b**. No formation of *p*-methoxy propiophenone from photolysis of azide **1b** was observed. Presumably, the major difference in the UV-vis spectra of the azo dimers **5a** and **5b** is that **5b** must have a stronger absorption in the visible region due to the methoxy substituent. The absorption spectra of azides **1a** and **1b** demonstrate this difference as well (see Figure 2). It is known that the azo chromophore in azomethane has a maximum absorption at $\lambda_{\text{max}} = 347 \text{ nm}$ ($\epsilon = 4.5$);¹⁶ thus direct absorption by the azo chromophore in **5a** is possible whereas in **5b** the methoxy-acetophenone chromophore absorbs much more strongly above 300 nm than the azo chromophore. Therefore it stands to reason that the azo chromophore in **5a** can absorb light directly to form a propiophenone radical and a nitrogen molecule. Since we do not observe the formation of methoxy propiophenone from **5b**, it can be surmised that the ketone chromophore in both **5a** and **5b** can absorb light and transfer its energy to the azo chromophore which most likely only results in *cis-trans* isomerization, whereas direct absorption by the azo chromophore cleaves the carbon nitrogen bond. Generally, the dominant reaction from triplet sensitization of simple acyclic azo compounds is *cis-trans* isomerization rather than decomposition to nitrogen and radicals.¹⁷ Furthermore, we do not expect nitrene **2b** to undergo intramolecular H-atom abstraction since triplet ketones with π, π^* electron configurations do not abstract H-atoms efficiently.¹¹

Oxygen Trapping of the Reactive Intermediates. We photolyzed azide **1a** in oxygen-saturated toluene solutions and observed the formation of compounds **8** and **9** (see Scheme 3). We characterized compound **9** based on its spectroscopic data. The ¹³C NMR and the IR spectra of **9** match precisely with the

(12) Pavlik, J. W.; Kebede, N. *J. Org. Chem.* **1997**, *62*, 8325.
 (13) Sankaranarayanan, J.; Mandel, S. M.; Krause, J. A.; Gudmundsdottir, A. D. *Acta Crystallogr., Sect. E* **2007**, *E63*, 6721.
 (14) Zhuo, J.-C. *Magn. Reson. Chem.* **1997**, *35*, 21.
 (15) (a) Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 5228.
 (b) Reiser, A.; Leyshon, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 4051.

(16) Gillam, A. E.; Stern, E. S. *An Introduction of Electronic Absorption Spectroscopy in Organic Chemistry*, 2nd ed.; Edward Arnold: London, 1957.

(17) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.

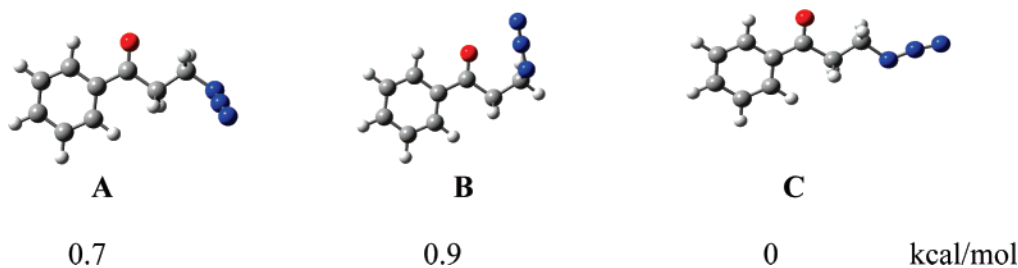
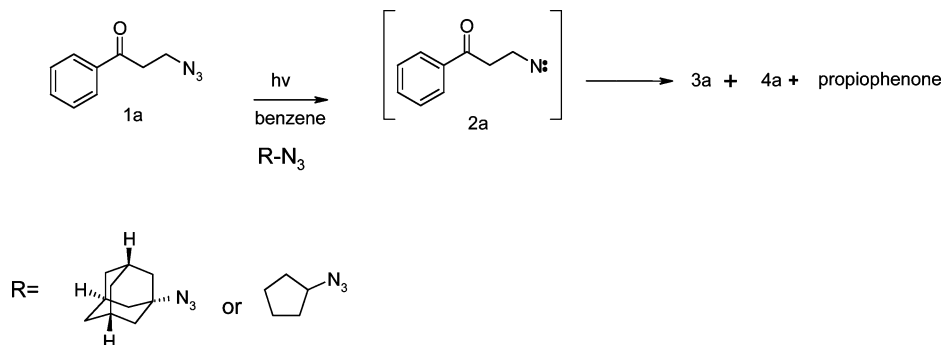


Figure 3. Minimal energy conformer of azide **1a** and their calculated relative energies.

Scheme 4. Photolysis of **1a** in the Presence of Alkyl Azides



characteristic spectra of other furazan 2-oxide derivatives.¹⁸ The nitro compound **8** comes from trapping nitrene **2a** with oxygen just as triplet aryl nitrenes are trapped with molecular oxygen to form nitroaryls.¹⁹ Compound **9**, however, must come from nitrene **2a** reacting with the precursors to **8**.

Formation of Azo Dimers. A point of curiosity to us was how the triplet alkyl nitrene decays. The product studies demonstrate that nitrene **2a** decays either by dimerization or by reaction with azide **1a**. In order to investigate this, we followed the photolysis of azide **1a** in the presence of an alkyl azide without a built-in sensitizer, which does not absorb light above 300 nm. If nitrene **2a** decays by reacting with an alkyl azide molecule we should observe cross-products between the nitrene and the alkyl azide. Photolysis of **1a** in the presence of adamantanyl azide or cyclopentyl azide (Scheme 4) did not yield any new products. Thus triplet alkyl nitrene **2a** must be a long-lived intermediate specifically reactive only toward other radicals such as **6** and propiophenone radicals.

Molecular Modeling. Molecular modeling studies of the target azides were done using Gaussian03²⁰ at a B3LYP²¹ level of theory and 6-31+G(d) as the basis set. We optimized the structure of azide **1a** and found several conformers and calculated their IR spectra (see Supporting Information). The minimal energy conformers of azide **1a** that are within 1 kcal/mol (Figure 3) were used for the calculations described below.

Time dependent calculation (TD-DFT)²² of azide **1a** showed that the lowest triplet state of the ketone moiety (T_1) is located ~ 75 kcal/mol above its ground state. T_1 and the second excited triplet ketone (T_2) are located within a kcal/mol of each other. The calculated energies of T_1 and T_2 in azide **1a** are similar to

those observed for butyrophenone.²³ We optimized the triplet azide configuration (T_{1A}) of azide **1a** and found it is ~ 44 kcal/mol above its ground state. The $N_1-N_2-N_3$ bond in T_{1A} has a bond angle of $\sim 120.6^\circ$ (Figure 4), and the N_1-N_2 bond is 1.43 Å, whereas in the ground state of azides **1** the N_1-N_2 bond length is 1.23 Å. As a reflection of the increased bond length of the N_1-N_2 bond, the calculated IR spectra of T_{1A} does not have an azide stretching vibration at ~ 2200 cm^{-1} as is seen for azide **1a**, but rather, the N–N stretch is calculated to be ~ 1748 cm^{-1} .

The calculated transition state for forming nitrene **2a** and a nitrogen molecule is approximately 0.1 kcal/mol above the energy of the triplet azide moiety in azide **1a**. Intrinsic reaction coordinate (IRC) calculation connected the triplet azide and nitrene **2** with this transition state.²⁴ Thus, the calculations support that nitrenes **2** can easily be formed via intramolecular energy transfer from the triplet ketone in azides **1** to the azide moiety which falls apart to form a nitrogen molecule and a triplet nitrene.

We optimized the minimal energy conformers of nitrene **2** and obtained their predicted IR spectra (see Figure 5). TD-DFT calculations were done to calculate the absorption spectra of nitrene **2a**, and in the gas phase the major bands above 290 nm are listed in Table 1. We used the self-consistent reaction field (SCRf) method with the integral equation formalism polarizable continuum model (IEFPCM)²⁵ to calculate the absorption spectra of nitrene **2a** in methanol above 290 nm (Table 1). The calculated absorption spectrum of nitrene **2b** is similar (see Supporting Information).

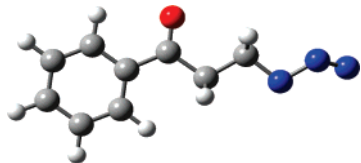
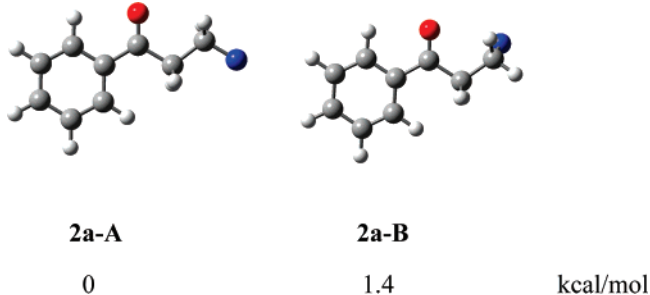
- (18) (a) Osawa, T.; Kito, Y.; Namiki, M. *Tetrahedron Lett.* **1979**, *45*, 4399. (b) Sitkowski, J.; Stefaniak, L.; Webb, G. A. *J. Crystallogr. Spectrosc. Res.* **1989**, *19*, 1003. (c) Curini, M.; Epifano, F.; Marcotullio, M. C.; Rosati, O.; Ballini, R.; Bosica, G. *Tetrahedron Lett.* **2000**, *41*, 8817. (19) Abramovitch, R. A.; Challand, S. R. *J. Chem. Soc., Chem. Comm.* **1972**, 964. (20) Frisch et al. *Gaussian03*, revision A.1. (21) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

- (22) (a) *Density Functional Methods in Chemistry*; Labanowski, J., Ed.; Springer-Verlag: Heidelberg, 1991. (b) Parr, R. G.; Weitao, Y. *Density-Functional Theory in Atoms and Molecules*; Oxford University Press: New York, 1989. (c) Bauerschmitt, R. *Chem. Phys. Lett.* **1996**, *256*, 454. (d) Stratmann, R. *J. Chem. Phys.* **1998**, *109*, 8218. (e) Foresman, J. *J. Phys. Chem.* **1992**, *96*, 135. (23) (a) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1968**, *90*, 5898–5899. (b) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604–5614. (24) (a) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154. (b) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

Table 1. TD-DFT Computed Major Absorption Spectral Features (nm, Oscillator Strength) for **2a**^{a,b}

		electronic transition above 290 nm				
2a	gas phase	305 (0.0071)	298 (0.0051)	292 (0.0493)		
	MeOH	313 (0.0458)	310 (0.0005)	303 (0.0010)	296 (0.0196)	

^a Number in parentheses is the calculated oscillator strength (*f*) for the electronic transition in nm. ^b Calculated absorption spectrum for vertical excitation using TD-B3LYP/6-31+G(d).

**Figure 4.** T_{1A} of **1a**.**Figure 5.** Minimal energy conformers of nitrene **2a**, showing relative energies.

We also optimized the structure of biradical **6**: several conformers were found and their IR spectra calculated (see Supporting Information). One of the lowest energy conformers, **6A**, has a hydrogen bond between the hydroxyl moiety and the imine radical, whereas the others are twisted such that hydrogen bonding cannot occur (see Figure 6). We calculated the transition state for the intramolecular H-atom abstraction in nitrene **2a** and found it was located 32 kcal/mol above its ground state. Thus, H-atom abstraction is feasible since TD-DFT calculation indicated that the triplet ketone moiety is located ~ 75 kcal/mol above the ground state in nitrene **2a**. IRC calculation connected nitrene **2a** and the biradical **6** to this transition state. We also calculated the transition state for acetophenone forming 1-phenylethenol, **10**, which is located 69 kcal/mol above the ground state of acetophenone. Finally, we calculated the transition state for biradical **6A** falling apart to yield hydrocyanic acid and triplet 1-phenylethenol, **11**. This transition state was 28 kcal/mol above the ground state of **6A**. IRC calculation verified that this transition state correlates **6A** with hydrocyanic acid and **11**.

Laser Flash Photolysis. We studied azides **1** by laser flash photolysis in methanol (Lambda Physik, excimer laser, 17 ns, 150 mJ, 308 nm), recording the spectra immediately after the laser pulse during a 200 ns window. The transient spectrum has a maximum absorbance at ~ 325 nm (see Figure 7) that we assign this absorbance to nitrenes **2** based on the predictions in Table 2. The calculated electronic transition for nitrene **2a** in methanol (see Figure 8) fits well with the observed transient

spectra of nitrenes **2**. We have previously shown that laser flash photolysis of α -azidoacetophenone results in transient spectra with broader absorption bands because benzoyl radicals, which have an absorption band further to the red ($\lambda_{\text{max}} \sim 370$ nm), are formed concurrently with the triplet alkyl nitrene.^{8a} Thus the transient spectra of nitrenes **2** are similar to the absorption spectra obtained for triplet phenyl nitrene and NH radicals that have an intense absorption band near 300 nm, which is attributable mainly to the $n_z \rightarrow n_y$ transition on the nitrogen atom.^{26,27} However, triplet methyl nitrene has a maximum absorption at ~ 280 nm in matrices, whereas the maximum absorption of triplet trifluoromethylnitrene is shifted to 354 nm.^{28,29}

We measured the decay for nitrene **2a** at 330 nm. The nitrene transient decays on the milliseconds time scale and can be fitted with first-order expression to have a lifetime of 27 ms in methanol (see Figure 9). The transient absorbance is quenched with isoprene, which quenches the triplet excited state of the ketone precursor. A Stern–Volmer plot of isoprene quenching is linear with a slope of 0.15. Thus the lifetime of the triplet excited state of the ketone is between 1.5 and 0.15 ns, assuming quenching is a diffusion-controlled process with k_q between 10^9 and $10^{10} \text{ M}^{-1} \text{ s}^{-1}$. The triplet ketone in azide **1a** is efficiently quenched by energy transfer to the azido group. The rate of the energy transfer in azide **1a** is similar to what we observed for intramolecular energy transfer in α -azido acetophenones^{8a} and much faster than intermolecular energy transfer in alkyl azides.³⁰ In oxygen saturated methanol solution the lifetime of the triplet nitrene **2** becomes approximately 2 ms. By assuming that the concentration of the molecular oxygen in methanol at room temperature is around 0.01 M,³¹ we can estimate the rate of quenching triplet nitrenes **2** is around $5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. In comparison, Liang and Schuster reported that triplet *p*-nitrophenyl nitrene reacts with oxygen at rate of less than $2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, whereas Gritsan and Pritchina estimate this same rate constant to be somewhat larger.^{32,33} These results are, however, in agreement with molecular modeling by Liu et al., who demonstrated that triplet alkyl nitrene can be expected to react similarly with oxygen as triplet phenyl nitrenes.³⁴ Furthermore, the lifetimes of nitrenes **2** in nitrogen-saturated solutions must be limited by residual oxygen as well as dimerization.

ESR Spectroscopy. Electron spin resonance (ESR) spectroscopy was used to characterize nitrene **2** further. Azide **1a** was dissolved in ethanol, and the resulting solution was frozen to form a glassy matrix at 4 K in a LHe cryostat in an X-band ESR spectrometer and then irradiated in situ through a Pyrex filter. The ESR spectrum was then recorded between 500 and 11 500 G. The spectrum showed a line at 8400 G (Figure 10), consistent with triplet state nitrene **2a** and similar to spectra of

(25) (a) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999. (b) Mennucci, B.; Cancès, E.; Tomasi, J. *J. Phys. Chem. B* **1997**, *101*, 10506. (c) Cancès, E.; Mennucci, B. *J. Chem. Phys.* **2001**, *114*, 4744. (d) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027. (e) Cramer, C. J.; Truhlar, D. J. *Chem. Rev.* **1999**, *99*, 2161.

(26) Gritsan, N. P.; Zhu, Z.; Hadad, C. M.; Platz, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 1202.

(27) Fairchild, P. W.; Smith, G. P.; Crosley, D. R.; Jeffries, J. B. *Chem. Phys. Lett.* **1984**, *107*, 181.

(28) Ferrante, R. F. *J. Chem. Phys.* **1987**, *86*, 25.

(29) Gritsan, N. P.; Likhovorik, I.; Zhu, Z.; Platz, M. S. *J. Phys. Chem. A* **2001**, *105*, 3039.

(30) Klima, R.; Gudmundsdottir, A. D. *J. Photochem. Photobiol. A* **2003**, *162*, 239.

(31) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker, Inc.: New York, 1993.

(32) Liang, T.-Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1987**, *109*, 7803.

(33) (a) Gritsan, N. P.; Pritchina, E. S. *J. Inf. Rec. Mater.* **1989**, *17*, 391. (b) Pritchina, E. A.; Gritsan, N. P. *J. Photochem. Photobiol. A* **1988**, *43*, 165.

(34) Liu, J.; Hadad, C. M.; Platz, M. S. *Org. Lett.* **2005**, *7*, 549.

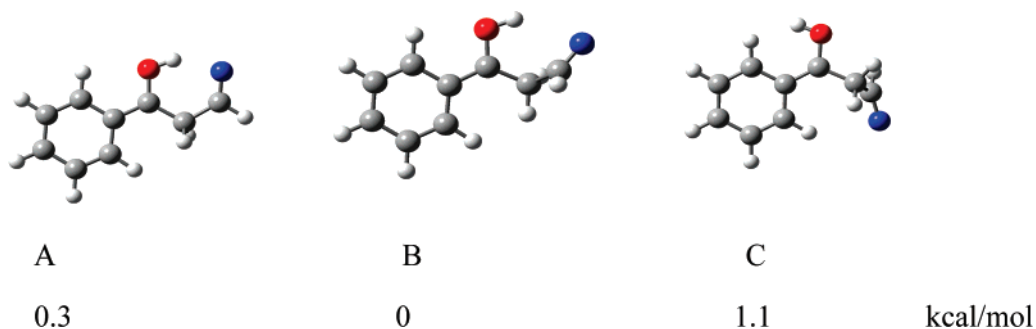


Figure 6. Minimal energy conformers of **6**, showing relative energies.

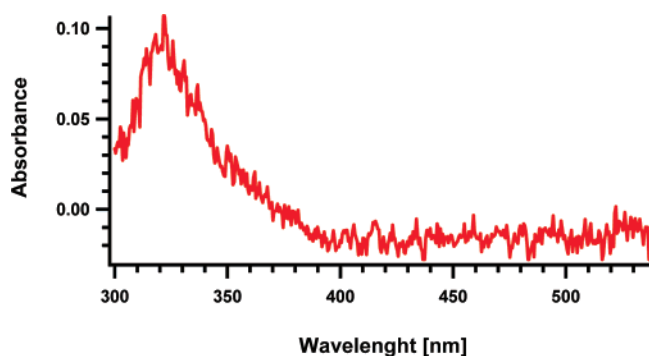


Figure 7. Transient spectrum of nitrene **1b** in methanol at ambient temperature.

Table 2. Calculated C–N Stretches (cm^{-1}) of Nitrene **2a**

conformer	relative energy (kcal/mol)	^{12}C – ^{14}N IR band, cm^{-1} (intensity, km/mol)	^{15}N substituted band, cm^{-1}	$^{13}\text{C} \times 3$ substituted band, cm^{-1}
2a-A	0	1071 (8)	1060	1058
2a-B	1.4	1068 (3)	1061	1047
		1033 (25)	1030	1011
		894 (3)	891	877

other triplet nitrene intermediates.^{28,29,35} The signal at 8400 G grew more intense with continued irradiation and did not decay for hours once irradiation ceased. Cycling the temperature to 40 K and recooling to low temperature did not significantly reduce the original signal intensity. The signal was readily observed upon further increase in temperature, until the solvent matrix became plastic above 77 K. Similar ESR spectra of nitrene **2a** were obtained in toluene and methanol glasses with only small changes in line position or shape. The spectral zero-field splitting parameters were estimated by line shape analysis to be $|D/hc| = 1.64 \text{ cm}^{-1}$ and $|E/hc| = 0.004 \text{ cm}^{-1}$ which is similar to those measured for *n*-propyl and *n*-octyl nitrenes, reported to be 1.607 and 1.616 cm^{-1} , respectively.^{35a,b}

In addition to the 8400 G peak, the ESR spectra obtained from photolysis of azide **1a** showed formation of lines around 3300 G (Supporting Information), possibly due to intramolecular H-atom abstraction in nitrene **2a**. However, we cannot rule out that they are due to direct photolytic cleavage of the solvent.

The intensity of the lines around 3300 G did not increase after irradiation and therefore was not due to dark reactions of **2a**. Thus, ESR spectroscopy further supports the conclusion that photolysis of azide **1a** results in formation of nitrene **2a** as a relatively persistent intermediate, since it does not react with the solvent.

Matrix Isolation: We studied the photochemistry of azide **1a** in argon matrices at 14 K to confirm the formation of the triplet alkyl nitrene intermediate and to determine whether nitrene **2a** undergoes secondary photolysis. We deposited **1a** into argon matrices in several different experiments, entraining the vapor pressure over a sample of pure azide in flowing argon, and depositing the resulting sample on a 14 K cryogenic surface. The infrared spectrum of such a sample showed strong azide bands at 2136, 2118, 2120, and 2108 cm^{-1} (Figure 11), which are all destroyed upon irradiation except the 2136 cm^{-1} band. The various azides bands are presumably due to different conformers of azide **1a**, which are also entrapped in different matrix sites.

Irradiation of **1a** in argon matrices led to the growth of new absorption bands, mostly occurring very near those of the parent azide, which is expected since the propiophenone moiety is not significantly affected by irradiation and the majority of the observed vibrational bands belong to it. Theoretical calculations suggest that nitrene **2a** is a likely candidate for the new absorptions. The calculated IR spectra of nitrene conformers **2a-A** and **B** have a weak C–N stretching mode at 1071 and 1068 cm^{-1} , respectively, with calculated intensities of less than 10 km/mol (Table 2). One notes that, in conformer **2a-B**, the C–N stretch is strongly coupled to the C–C stretching modes calculated at 1033 and 894 cm^{-1} . To aid in identifying these modes in the experimental spectra, ^{15}N and ^{13}C labeling experiments were done by synthesizing azide **1a** with the appropriate isotopes as shown in Scheme 5. In experiments with the natural isotopes, weak bands were observed at 1030 and 913 cm^{-1} ; these shifted to 1017 and 912 cm^{-1} upon ^{15}N labeling while ^{13}C labeling led to absorptions at 1017 and 906 cm^{-1} (see Table 3, Figure 12).

We assign the band at 1030 cm^{-1} to the C–N stretch of conformers **2a-A** and **2a-B**, although the C–N stretch is not as intense as was observed for the nitrene formed upon photolysis of α -azidoacetophenone.^{8a} Possibly, the C–N stretch in the α -nitrene is coupled with the adjacent C–O group which gives the C–N band a higher intensity and a higher vibrational frequency. The bands at 913 cm^{-1} is assigned to the calculated C–C stretch at 898 cm^{-1} that is coupled to the C–N stretch in conformer **2a-B**. While none of these bands is very intense, their positions and isotopic shifts fit reasonably with those

(35) (a) Wasserman, W.; Smolineksy, G.; Yager, W. A. *J. Am. Chem. Soc.* **1964**, *86*, 3166. (b) Carrick, P. G.; Brazier, C. R.; Bernath, P. F.; Engelking, P. C. *J. Am. Chem. Soc.* **1987**, *109*, 5101. (c) Radziszewski, J. G.; Downing, J. W.; Wentrup, C.; Kaszynski, P.; Jawdosiuk, M.; Kovacic, P.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 7996. (d) Radziszewski, J. G.; Downing, J. W.; Wentrup, C.; Kaszynski, P.; Jawdosiuk, M.; Kovacic, P.; Michl, J. *J. Am. Chem. Soc.* **1985**, *107*, 594. (e) Radziszewski, J. G.; Downing, J. W.; Wentrup, C.; Kaszynski, P.; Jawdosiuk, M.; Kovacic, P.; Michl, J. *J. Am. Chem. Soc.* **1985**, *107*, 2799.

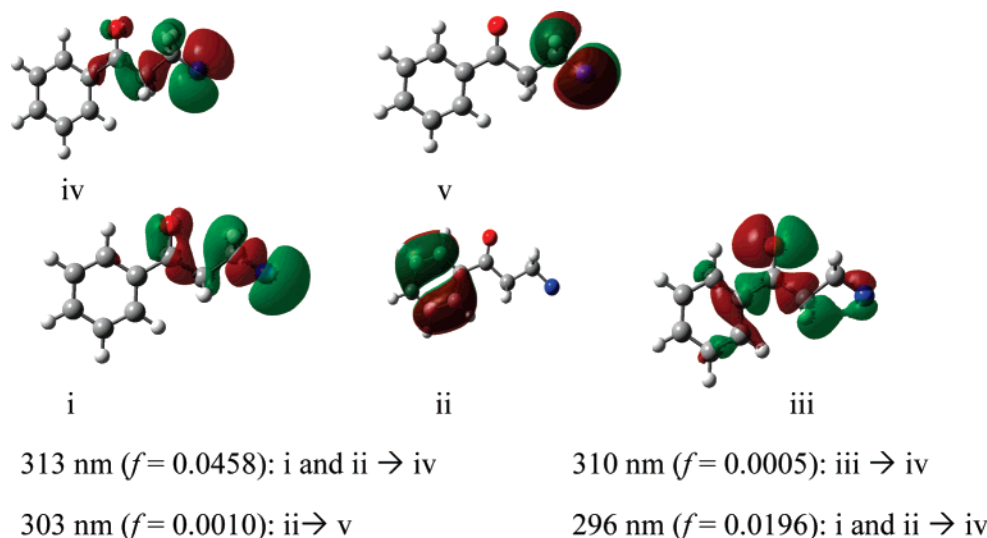


Figure 8. Orbitals involved in electron transition in nitrene **2a** in methanol.

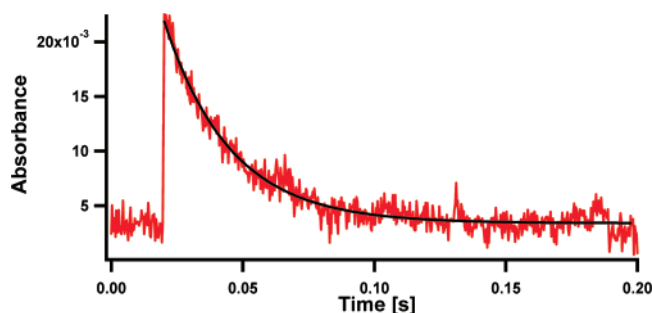


Figure 9. Decay of nitrene **2a** at 330 nm in methanol at ambient temperature.

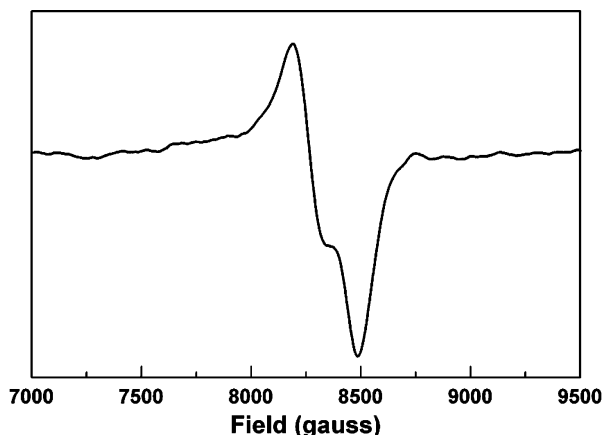


Figure 10. ESR spectrum of nitrene **2a** in ethanol at 10.4 K.

calculated for nitrene **2a**. In contrast, the remaining product bands did not shift upon ^{15}N isotopic substitution, confirming that they are associated with vibrations of the propiophenone moiety. These experiments further support the formation of triplet alkyl nitrenes in cryogenic matrices.

Secondary Photolysis in Matrices: Prolonged irradiation of the above matrices led to the growth of several new bands. The most significant of these were at 3526, 3508, 3302, 1721, 1713, and 725 cm^{-1} (see Figures 13 and 14, and Table 4). Integration of these IR bands shows that, within experimental errors, they are all formed with the same rate. The bands at 3526 and 3508 cm^{-1} are not shifted by ^{15}N or ^{13}C substitution. This isotopic behavior, coupled with the location, requires that the bands are

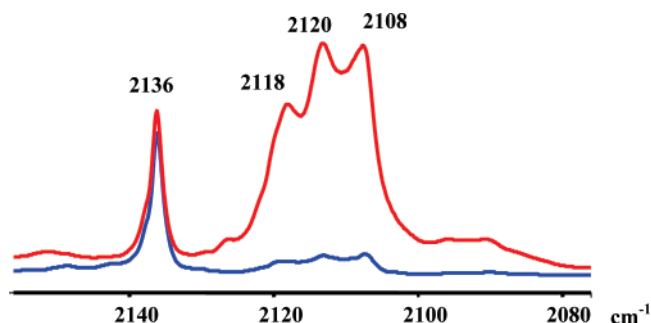


Figure 11. IR Spectrum of azide **1a** in an argon matrix.

Scheme 5. Isotope Substitution of Nitrene **2a**

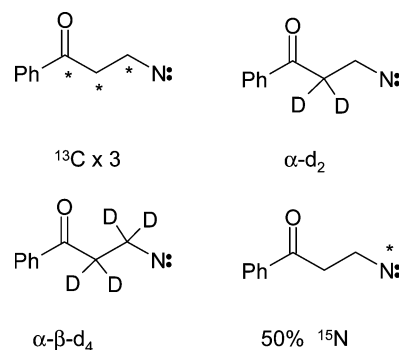


Table 3. Observed IR Bands (cm^{-1}) in **2a** That Are Affected by Isotope Substitution

assignment	intensity	natural isotopes	^{15}N	$^{13}\text{C} \times 3$
C–N	weak	1030	1017	1017
C–N coupled with C–C	weak	913	912	906

due to an O–H stretching mode. Our conclusion is supported by deuteration experiments, namely that when the α position was deuterated ($\alpha\text{-}d_2$ see Scheme 5), the band at 3526 and 3508 cm^{-1} did not shift. However, when both the α - and β -positions were deuterated ($\alpha,\beta\text{-}d_4$), these bands shifted to 2631 and 2594 cm^{-1} , respectively. Additionally, the band at 3302 cm^{-1} was not affected by ^{15}N substitution, whereas ^{13}C substitution shifted it to 3285 cm^{-1} . The 3302 cm^{-1} band was also not affected

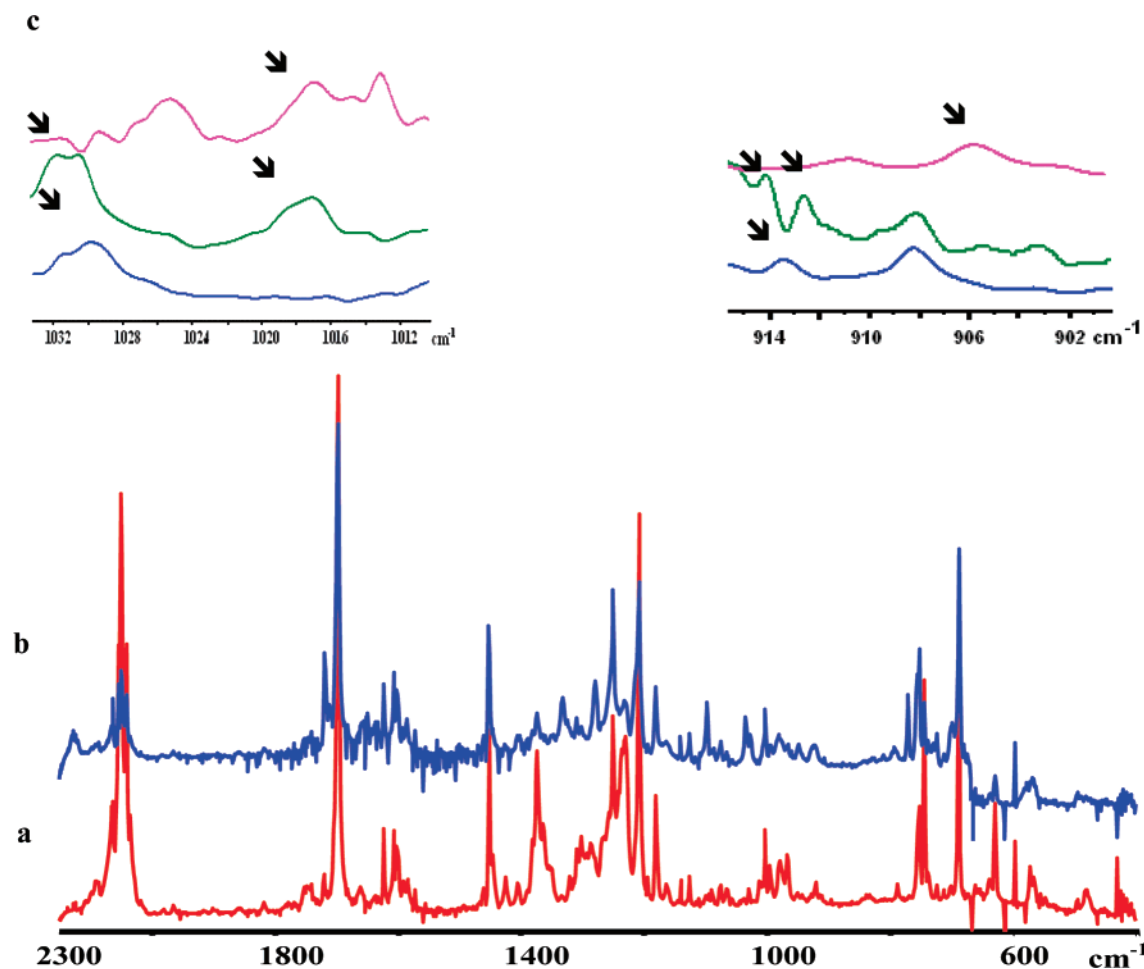


Figure 12. Argon matrix spectra of **1a** (a) before and (b) after irradiation. (c) IR bands that were affected by isotope labeling. Blue shows the photolyzed spectrum for natural abundances **1a**, and green and pink show the spectra ^{15}N and ^{13}C labeled **1a**, respectively (see Scheme 5). Arrows indicate peaks that are assigned to the same vibration.

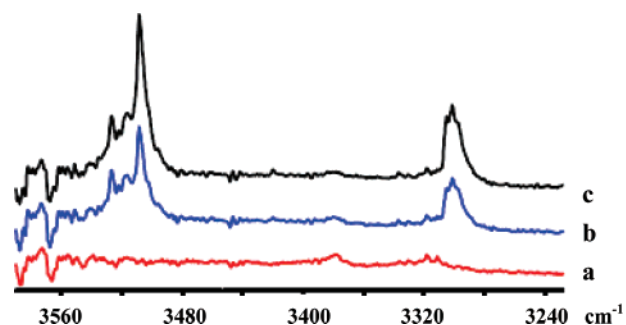


Figure 13. Part of the IR spectrum of **1a** in Ar matrix at 14 K before irradiation (a), after 5 h of irradiation (b), and after 11 h of irradiation (c). when the α position was deuterated, whereas deuteration of both the α - and the β -position caused a shift to 2626 cm^{-1} .

Consequently, we assign the secondary photoproducts to be biradical **6** and hydrocyanic acid based on these observations as well as comparison to calculations. Hydrocyanic acid has previously been isolated in argon matrices and exhibits major bands at 3306 and 721 cm^{-1} .³⁶ The vibrational bands at 3302 and 725 cm^{-1} (see Table 4) are affected by isotope substitution in exactly the same way as has been reported for hydrocyanic acid.

Conformer **6A** has a hydrogen bond between the hydroxyl moiety and the imine radical, whereas the others, **6B** and **6C**,

(36) Pacansky, J.; Calder, G. V. *J. Mol. Struct.* **1972**, *14*, 363.

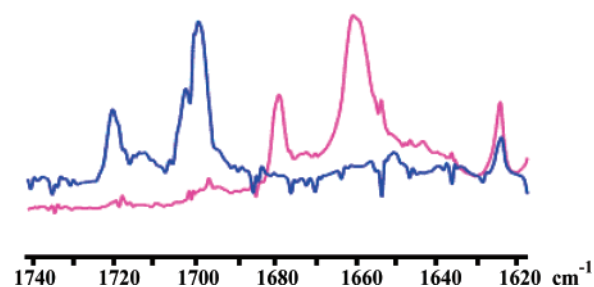


Figure 14. Part of the IR spectra of azide **1a** after 3.5 h of irradiation. Blue and pink traces show spectra from natural abundance and ^{13}C -enriched **1a**, respectively.

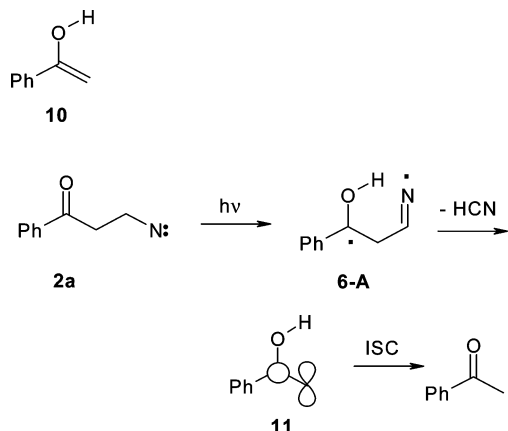
Table 4. IR Bands (cm^{-1}) in **6** and HCN That Are Affected upon Isotope Substitution

assignment	intensity	natural isotopes	^{15}N	$^{13}\text{C} \times 3$	$\alpha\text{-}d_2$	$\alpha\text{-}d_2, \beta\text{-}d_2$
6 (OH)	moderate	3526	3526	3526	3526	2605
6 (OH)	strong	3508	3508	3508	3508	2594
6 (C=N)	moderate	1721	n/a	1680	1721	1718
6 (C=N)	moderate	1713	n/a	1670	1713	1709
HCN	strong	3302	3302	3285	3302	2626
HCN	moderate	725	724	719	724	579

have a structure rotated such that hydrogen bonding cannot occur (Figure 5). The calculated deuterium shifts of an O–H stretch in **6B** and **6C** are 1024 and 1002 cm^{-1} (Table 5), which is in

Table 5. Calculated IR Bands (cm^{-1}) in **6**

conformer		$^{12}\text{C}-^{14}\text{N}$	^{15}N	$^{13}\text{C} \times 3$	$\alpha\text{-d}_2$	$\alpha\text{-d}_2, \beta\text{-d}_2$
6-B	O—H	3688	3688	3688	3688	2686
	C=N	1708	1686	1671	1704	1691
6-C	O—H	3744	3744	3744	3744	2724
	C=N	1718	1695	1680	1714	1703

Scheme 6

reasonable agreement with the experimental shifts of 921 and 914 cm^{-1} , respectively, once anharmonicity is taken into consideration.³⁷ We therefore assign the 3526 and 3508 cm^{-1} band to the O—H stretch of biradical **6** in the conformers lacking hydrogen bonding.

The bands at 1721 and 1713 cm^{-1} , having a shift of 41 cm^{-1} to lower energy upon ^{13}C substitution, are assigned to the C=N stretching modes of biradical **6**. The observed shifts are in very good agreement with calculated shifts of approximately 37 cm^{-1} . The ^{15}N shift was calculated as 22 cm^{-1} , placing them directly under the broad, intense C=O stretching band at 1700 cm^{-1} where they are obscured. Deuteration of the α -position does not affect these bands significantly. On the other hand, deuteration of both the α and β position causes a shift in the bands to 1718 and 1709 cm^{-1} , respectively. The calculated shifts of these bands are 19 and 16 cm^{-1} , considerably larger than observed experimentally. However, the coupling of the C—H band with the C=N band will be strongly affected by the angle between the two bonds, and thus small geometric changes will have large effects on the actual C=N vibrational band.

The matrix spectra support that nitrene **2a** undergoes secondary photolysis forming biradical **6**. It is reasonable to assume that conformers of biradical **6** that do not have intramolecular H-atom bonding are not the precursors to hydrocyanic acid in matrices since the vibrational bands due to biradical **6** and hydrocyanic acid grow in simultaneously and that hydrocyanic acid and biradical **6** come from the same precursor. We do not observe conformer **6A** in matrices, since no OH bands were detected at low frequency as is typical for OH bonds that are involved in hydrogen bonding. Conformer **6A** is best aligned to cleave, because the $\alpha\text{-C}-\beta\text{-C}$ bond-breaking will result in formation of biradical **11**, in which the p orbital on the α -carbon atom is orthogonal to the ketyl radical, thus allowing for the best separation of the triplet radical centers (Scheme 6). Unfortunately, the vibrational band for the carbonyl group of

(37) Del Bene, J. E.; Person, W. B.; Szczepaniak, K. *J. Phys. Chem.* **1995**, *99*, 10705.

Scheme 7. Ideal Parameters for Intramolecular γ -H-Atom Transfer

d : is distance between O and H.

Ideal value > 2.7 Å

θ : is the O—H—C angle

Ideal value 180°

Δ : is the C=O—H angle

Ideal value 90–120°

α : is the dihedral angle between the O—H vector and the nodal plane of the carbonyl π system

Ideal value 0°

the acetophenone that would result from **11** is obscured by the carbonyl groups of azide **1a** and nitrene **2a** and remains undetected in these experiments. However, isotope labeling rules out that biradical **6** forms secondary photoproducts 1-phenylethanol, **10**, and hydrocyanic acid, since the calculations show that the C=C in **10** would be expected to be shifted $\sim 56 \text{ cm}^{-1}$ upon ^{13}C labeling, and no bands exhibit this behavior. The large expected shift is further supported by Hawkins and Andrews who demonstrated that the C=C bond in ethenol shifts $\sim 55 \text{ cm}^{-1}$ with ^{13}C substitution.³⁸ We therefore concluded that conformer **6A** cleaves to yield hydrocyanic acid and acetophenone in matrices.

As mentioned before, molecular modeling shows that the transition state for nitrene **2a** to form biradical **6** is located 32 kcal/mol above its ground state. Thus, the ketone chromophore in nitrene **2a** could reasonably absorb another photon and undergo intramolecular H-atom abstraction to form biradical **6**. The calculated transition state for the cleavage of biradical **6A** is 28 kcal/mol above the ground state of **6A**. The calculated transition state for **10** to form acetophenone is ~ 4 kcal/mol below the energy of triplet biradical **11**. Thus, in matrix a vibrationally hot biradical **6A** cleaves to give hydrocyanic acid and triplet ketyl radical **11**, which intersystem crosses to the singlet surface and forms acetophenone rather than the less stable **10**. In solution the vibrationally hot imine biradical **6** would give up its excess energy to the surrounding solvent, so formation of acetophenone is not observed under these conditions.

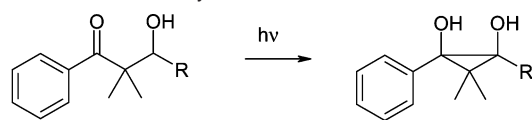
There are very few examples of intramolecular β -H-atom abstraction^{11,39–41} for which the geometric requirement must be similar to that for intramolecular γ -hydrogen abstraction, since it relies on a favorable orbital alignment between the carbonyl oxygen and the C—H bond that is being cleaved.¹¹ In Scheme 7 are shown the ideal ground state geometric parameters for intramolecular γ -H-atom abstraction.^{11a,40} For example, Scheffer et al. have reported intramolecular singlet state β -H-atom abstraction of enediones in crystals and that the β -H-atom abstraction occurs from a nearly perfect geometry.^{40a} Also, when

(38) Hawkins, M.; Andrews, L. *J. Am. Chem. Soc.* **1983**, *105*, 2523.

(39) Wagner, P. J. Yang photocyclization: coupling of biradicals formed by intramolecular hydrogen abstraction of ketones. In *CRC Handbook of Organic Photochemistry and Photobiology*, 2nd ed.; Horspool, W., Lenci, F., Eds.; CRC Press: Boca Raton, FL, 2004.

(40) (a) Scheffer, J. R. *Org. Photochem.* **1987**, *8*, 247. (b) Gudmundsdóttir, A. D.; Lewis, T. J.; Randall, L. H.; Scheffer, J. R.; Rettig, S. J.; Trotter, J.; Wu, C.-H. *J. Am. Chem. Soc.* **1996**, *118*, 6167.

(41) Yoshioka, M.; Miazoe, S.; Hasegawa, T. *J. Chem. Soc., Perkin Trans 1* **1993**, 2781.

Scheme 8. Photoreactivity of **12****12**R = CH(CH₃)₂, C(CH₃)₃, Ph

R is a bulky substituent, ketone **12** has been shown to undergo intramolecular β -hydrogen abstraction from the triplet excited state (Scheme 8).⁴¹

Our molecular modeling shows that conformers **A** and **B** of nitrene **2a** are geometrically aligned for intramolecular β -H-atom abstraction since the distances between the β -H-atom and the oxygen molecule, *d*, are 2.49 and 2.67 Å in **2a-A** and **2a-B**, respectively. The O–H–C angles (θ) are 82° and 92°, and the C=O–H angles (Δ) are 82° and 86° for nitrene conformers **2a-A** and **2a-B**, respectively. The distance for intramolecular H-atom abstraction is ideal for the **2a-A** and **2a-B** conformers, whereas the angles are not ideal, so this is reflected in a higher calculated activation energy for this β -H-atom transfer compared to intramolecular γ -H-atom abstraction.^{43,44} The calculated transition state for nitrene **2a** forming **6** is located ~37 kcal/mol above the ground state of **2a**, which is, however, below the energy of the triplet ketone in nitrene **2a** and thus the intramolecular H-atom abstraction should be feasible.

(42) Wagner, P. J.; Wiegel W. *J. Am. Chem. Soc.* **1996**, *118*, 12858.

(43) (a) Severance, D.; Pandey, B.; Morrison, H. *J. Am. Chem. Soc.* **1987**, *109*, 3231. (b) Dorigo, A. E.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 2195. (c) Dorigo, A. E.; McCarrick, M. A.; Loncharich, R. J.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 7508.

(44) Barton, D. H. R.; Beaton, J. M.; Geller, L. E.; Pechet, M. M. *J. Am. Chem. Soc.* **1960**, *82*, 2640.

Summary

Photolysis of azides **1** selectively yields triplet alkyl nitrene intermediates **2**, which preferentially react with another nitrene molecule to form azo dimers **5**. The azo dimers tautomerize and cyclize to form products **3**. Dimer **5a** also undergoes secondary photolysis to form propiophenone radicals, which are intercepted by nitrene **2a** to form **4a**. Triplet alkyl nitrenes **2** can be detected directly by laser flash photolysis of azides **1**, which confirms that nitrenes **2** are long-lived intermediates ($\tau = 27$ ms), because they do not abstract a H-atom from the solvent and selectively react with other radicals such as other nitrene molecules or molecular oxygen. ESR spectroscopy further supports the characterization of nitrene **2a** with zero-field splitting parameters $|D/hc| = 1.64$ cm⁻¹, $|E/hc| = 0.004$ cm⁻¹. Argon matrix isolation made it possible to further characterize nitrene **2a** and demonstrates that it undergoes a unique intramolecular β -H-atom abstraction to form biradical **6**, which was further characterized with isotope labeling.

Acknowledgment. We thank the National Science Foundation, Petroleum Research Foundation, and the Ohio Supercomputer Center for supporting this work. We also thank Professor M. S. Platz at The Ohio State University, Professor J. C. Scaiano at the University of Ottawa, and Professor R. M. Wilson at the University of Cincinnati for access to laser instrumentation.

Supporting Information Available: Preparation of **1**, isolation and characterization of **3** and **4a**. Cartesian coordinates, no. of imaginary frequencies, IR frequencies and total energy of azide **1a**, nitrene **2a**, **6**, **10**, **11** and the calculated transition states for nitrene **2a**, **16**, and **10**. The full IR matrix spectra of nitrene **2a**. Complete ref 20. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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