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Competition Between Azido Cleavage and Triplet Nitrene Formation in Azidomethylacetophenones

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Photolysis of *p*- and *m*-azidomethylacetophenone (**1a**, **1b**) in argon-saturated solutions yields predominantly imine **2a**, **2b**, whereas irradiation of **1a**, **1b** in oxygen-saturated solutions results in heterocycles **3a**, **3b**, aldehydes **4a**, **4b** and nitriles **5a**, **5b**. Density functional theory calculations place the energy of the first and second excited state of the triplet ketones (T_{1K} and T_{2K}) in **1a**, **1b** in close proximity to each other. The triplet transition state for cleaving the C–N bond in **1a**, **1b** to form azido and benzyl radicals **1aB**, **1bB** is located only 3 kcal mol^{-1} (1 kcal = 4.184 kJ) above T_{1K}, indicating that azido cleavage is feasible. The calculations place the energy of the triplet azido group (T_A) in **1a**, **1b** ~25 kcal mol^{-1} below T_{1K}; thus, this process is also easily accessible via energy transfer. Further, the transition state barrier for T_A to expel N_2 and form triplet nitrenes is less than 1 kcal mol^{-1} above T_A in **1a**, **1b**. Laser flash photolysis of **1a**, **1b** reveals the formation of the triplet excited ketones of **1a**, **1b**, which decay to form benzyl radicals **1aB**, **1bB** and triplet alkylnitrenes. The triplet ketones and the benzyl radicals are quenched with molecular oxygen at rates close to diffusion, whereas the triplet nitrenes react more slowly with oxygen (~5×10^5 M^{-1} s^{-1}). We conclude that the triplet alkylnitrenes intercept the benzyl radicals to form **2** in argon-saturated solution, whereas the benzyl radicals are trapped to form **4** in oxygen-saturated solution; thus, the triplet nitrenes react with oxygen to form **3**.

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Introduction

Nitrenes are reactive intermediates that have a monovalent nitrogen atom.[1–3] The non-bonding electrons on the monovalent nitrogen atom can either be paired, denoting a singlet nitrene, or unpaired, representing a triplet nitrene. Singlet nitrenes are highly reactive intermediates that insert into surrounding chemical bonds and have therefore been used in various applications, such as photoaffinity labelling,[4,5] cross-linking of polymers,[6–9] and modification of surfaces.[10–12] In contrast, triplet nitrenes are generally less reactive, and owing to their high-spin characteristics, they have potential as building blocks for organic magnets.[13,14] Triplet alkylnitrenes have only been investigated sporadically because direct irradiation of alkyl azides does not yield triplet alkylnitrenes, but rather imine products from a concerted rearrangement of the singlet excited state of the alkylazides.[15] Formation of triplet alkylnitrenes from alkylazides requires triplet sensitization.[16,17] We have reported that the irradiation of simple α-azidopropiophenones, which have a built-in triplet sensitizer, results in selective formation of triplet alkylnitrene intermediates.[16] Intramolecular triplet sensitization of alkyl azides, however, does not always lead to formation of alkylnitrenes. For example, photolysis of α-azidoacetophenone derivatives results in both triplet energy transfer to form triplet alkylnitrenes and α-cleavage to form benzoyl radicals.[17] Furthermore, photolysis of β-azido propiophenone derivatives that have a β-phenyl substituent primarily results in photo-initiated cleavage to form azido and benzyl radicals.[18] Triplet alkylnitrenes are highly unreactive because they do not abstract an H atom from the solvent or react with their precursor; instead, they dimerize to form azodimers.[16,19–21] Triplet alkylnitrenes, however, react efficiently with benzoyl radicals to form amides,[17] and can be trapped with triplet oxygen to form nitro compounds.[16]

To investigate further the ability of triplet alkylnitrenes to act as radical scavengers, we investigated the photochemistry of *p*- and *m*-azidomethylacetophenones (**1a** and **1b**). These molecules can be expected to both undergo energy transfer to form triplet alkylnitrenes (**1aN**, **1bN**) and cleave to form azido and benzyl radicals (**1aB**, **1bB**). We used transient spectroscopy and density functional theory calculations to show that photolysis of **1a**, **1b** result in the formation of triplet alkylnitrenes and benzyl radicals. The major photoproducts in argon-saturated solutions are **2a**, **2b**, prompting us to conclude that triplet alkylnitrenes **1aN**, **1bN** trap benzyl radicals **1aB**, **1bB** to form **2a**, **2b**.

Results

Product Studies

Photolysis of **1a**, **1b** in argon-saturated methanol solutions resulted in the formation of imines **2a**, **2b** (Scheme 1). In comparison, photolysis of **1a**, **1b** in oxygen-saturated chloroform or methanol yields mainly heterocycles **3a**, **3b**, aldehydes **4a**, **4b**, and acetyl benzonitriles **5a**, **5b** (Scheme 2).

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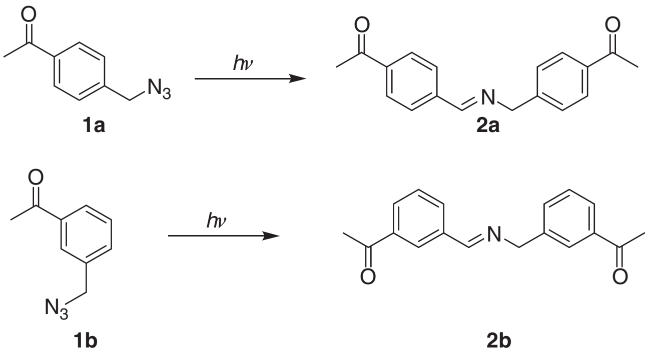
We studied the effect of concentration on the product ratio from photolyzing **1b** in oxygen-saturated methanol (Fig. 1). We found that more **3b** and less **5b** was formed as the concentration of **1b** was increased, whereas formation of **4b** was not significantly affected. Thus, we theorize that, on photolysis, **1b** forms the triplet state of the ketone, which undergoes energy transfer to form the triplet excited state of the azido moiety in **1b** and falls apart to yield triplet alkylnitrene **1bN** (Scheme 3). In competition with energy transfer, **1b** also undergoes cleavage of the azido group to form radicals **1bB**. We propose that triplet nitrene **1bN** reacts with radical **1bB** to form imine **2b** in argon-saturated solution. We did not observe products due to dimerization of **1aB**, **1bB** because triplet nitrenes **1aN**, **1bN** must trap **1aB**, **1bB** more efficiently than they dimerize. However, in oxygen-saturated methanol or chloroform, **1bB** is trapped with oxygen to form **4b**, allowing nitrene **1bN** to react with oxygen to form **3b** and **5b**. Corsaro et al. have shown that benzonitrile oxide and benzonitrile undergo cycloaddition to form 3,5-diphenyl-[1,2,4] oxadiazole.[22] Therefore, we propose that **1bN** reacts with oxygen to form the corresponding nitrile oxide and oxygen abstracts hydrogen atoms from **1bN** to yield **5b**, which adds to the acetylbenzonitrile oxide to form **3b**. We also theorize that the reactivity of **1a** is similar to **1b**.

We speculated whether **1aB**, **1bB** can react with **1a**, **1b** to form **2a**, **2b**. Because photolysis of 1,3-diphenylpropan-2-one has been reported to result in the formation of benzyl radicals,[23] we photolyzed 1,3-diphenylpropan-2-one and adamantyl azide in methanol. By irradiating through a Pyrex filter, we ensured that only 1,3-diphenylpropan-2-one absorbed the light and not adamantyl azide. The only product observed was 1,3-diphenylethane, and therefore we conclude that benzyl radicals do not react with the alkyl azides (Scheme 4). Furthermore, we photolyzed **1b** and 1,3-diphenypropan-2-one in methanol and GC-MS analysis of the reaction mixture showed formation of a product that corresponds to trapping **1bN** with benzyl radical to form **6** (Scheme 5).

Molecular Modelling

All structures were optimized using *Gaussian09*[24] at the B3LYP[25,26] level of theory and with the 6-31+G(d) basis set at the Ohio Super Computer Center. Time-dependent density functional theory (TD-DFT)[27–31] calculations of **1a** showed that the first and second excited states of the triplet ketone (T_{1K} and T_{2K} respectively) were located at 73 and 76 kcal mol^{-1} (1 kcal = 4.184 kJ) above its ground state (S_0). Inspection of the molecular orbitals shows that T_{1K} and T_{2K} have (n,π*) and (π,π*) configurations respectively (Table 1). The effect of solvation was calculated using the self-consistent reaction field (SCRF) method with the polarization continuum model (PCM) with acetonitrile as the solvent.[32–35] The calculated energies of



Scheme 1. Photolysis of **1a**, **1b** in argon-saturated methanol.

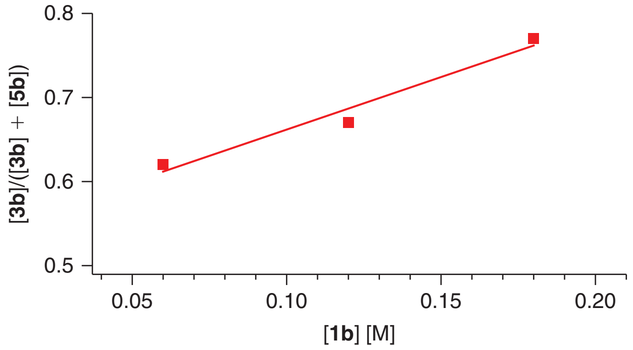
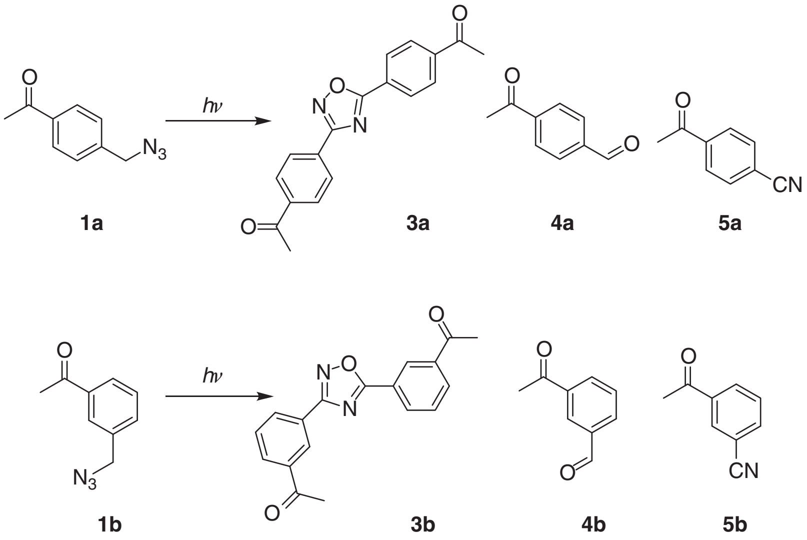
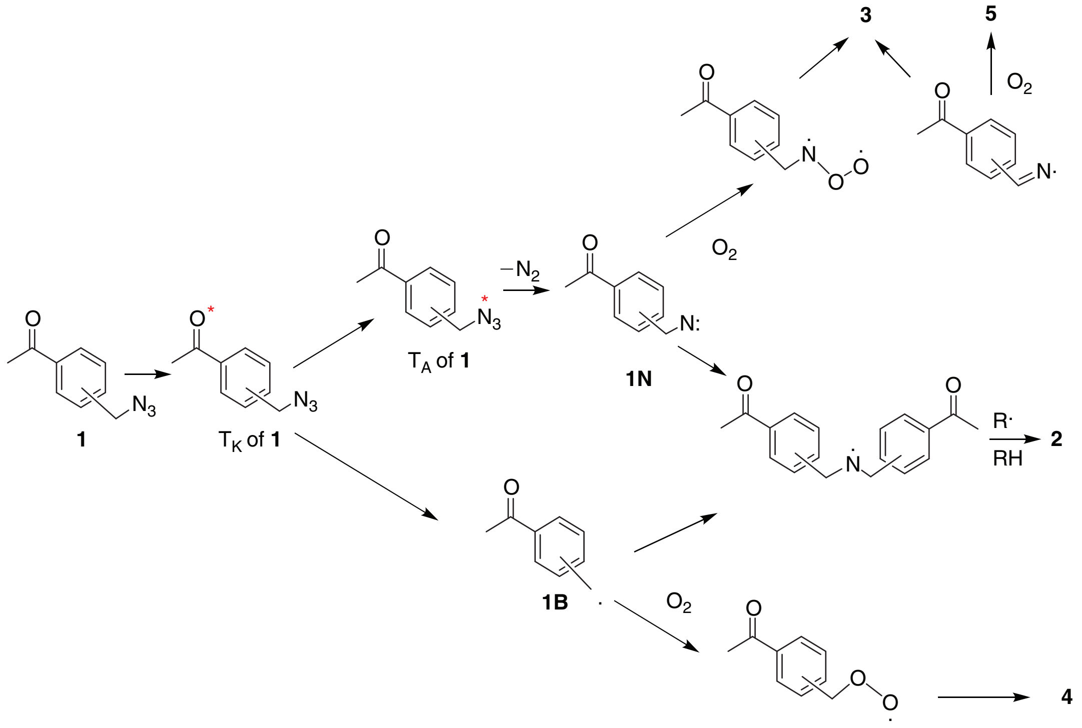


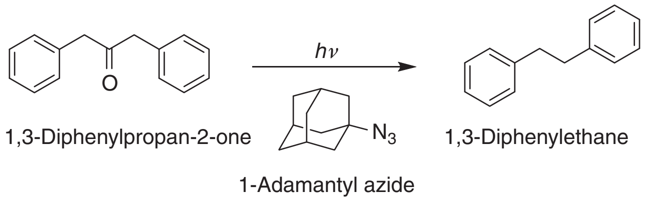
Fig. 1. The effect of the concentration of **1b** on the product ratio in oxygen-saturated methanol.



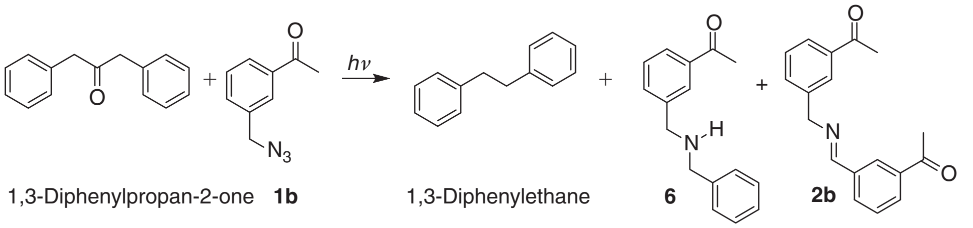
Scheme 2. Photolysis of **1a**, **1b** in oxygen-saturated methanol and chloroform.



Scheme 3. Proposed reaction mechanisms for **1a** and **1b**.



Scheme 4. Photolysis of 1,3-diphenylpropan-2-one and 1-adamantyl azide.



Scheme 5. Photolysis of 1,3-diphenylpropan-2-one and **1b**.

Table 1. Energies of T_{1K} and T_{2K} in 1a, 1b using time-dependent density functional theory (TD-DFT) and UB3LYP calculations

	1a				1b			
	TD-DFT		UB3LYP		TD-DFT		UB3LYP	
	Gas-phase	CH_3CN	Gas-phase	CH_3CN	Gas-phase	CH_3CN	Gas-phase	CH_3CN
(n,π*)	73	78	68	70	74	78	69	68
(π,π*)	76	75			77	77		

T_{1K} and T_{2K} in acetonitrile are 75 and 78 kcal mol^{-1}; thus, solvation does not change these values significantly. Similarly, TD-DFT calculations place T_{1K} and T_{2K} in **1b** 74 and 77 kcal mol^{-1} respectively in the gas phase and 77 and 78 kcal mol^{-1} respectively in acetonitrile above S_0. Thus, the energies of T_{1K} and T_{2K} in **1a**, **1b** in acetonitrile are comparable. Furthermore, the calculated energies for T_{1K} in **1a** and **1b** are similar to the measured triplet state energy for the analogous *m*-methylacetophenone and *p*-methylacetophenone.[36,37]

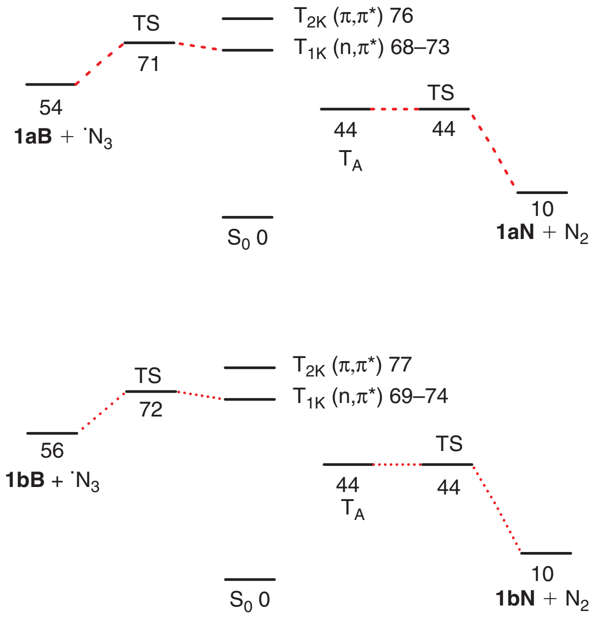


Fig. 2. Calculated stationary points on the energy surface of (a) **1a**, and (b) **1b** to form **1N** and **1B** at the UB3LYP and TD-B3 LYP levels of theory. The energies are in kcal mol^{-1}.

We also optimized T_{1K} of **1a**, **1b** at the UB3LYP level of theory in the gas phase. The optimized structure of T_{1K} of **1a**, **1b** has carbonyl groups with a bond length of 1.32 Å, which is consistent with the triplet ketones having an (n,π*) configuration;[38,39] visualization of the molecular orbitals of T_{1K} in **1a**, **1b** further support this assignment. The bond lengths and angles of the azido group of T_{1K} of **1a**, **1b** are similar to those observed for the S_0 of **1a**, **1b**, thus indicating that the triplet excited state is localized on the aryl ketone moiety. The calculated energies of the optimized T_{1K} in **1a**, **1b** are 68 and 69 kcal mol^{-1} above S_0, respectively, which is somewhat lower than those estimated from the TD-DFT calculations. However, we have previously shown that the B3LYP/6-31G+(d) calculation underestimates the energies of triplet ketones with the (n,π*) configuration.[21,40] In addition, solvation does not significantly change the energies of T_{1K} in **1a**, **1b**.

Optimization of the triplet configuration of the azido moieties (T_A) in **1a**, **1b** in the gas phase shows that the N1–N2 and N2–N3 bonds are lengthened to 1.45 and 1.18 Å respectively compared with 1.24 and 1.14 Å in S_0 of **1a**, **1b**. Furthermore, the azido groups are bent because the N1–N2–N3 bonds have an angle of 120° in the triplet state. The energies of T_A of **1a**, **1b** are 44 and 45 kcal mol^{-1} above S_0. Thus, the triplet energies and optimized structures of T_A in **1a**, **1b** are similar to those reported previously.[21] The bond length and angles of the carbonyl group in T_A of **1a**, **1b** are similar to those we observed for the S_0 of **1a**, **1b**, thus indicating that the triplet excited state is localized on the azido group.

We calculated the transition state for forming triplet alkylnitrene (**1aN**, **1bN**) from the T_A of **1a**, **1b** in the gas phase and found that it was located at less than 1 kcal mol^{-1} above the T_A of **1a**, **1b**. Intrinsic reaction coordinate (IRC)[41] calculations were performed to correlate these transition states with the T_A of **1** and **1N**.[42–44]

We calculated the triplet transition state for cleavage of the azido group in **1a**, **1b** in the gas phase. These triplet transitions states are located at 3 kcal mol^{-1} above T_{1K} in **1a**, **1b**. IRC

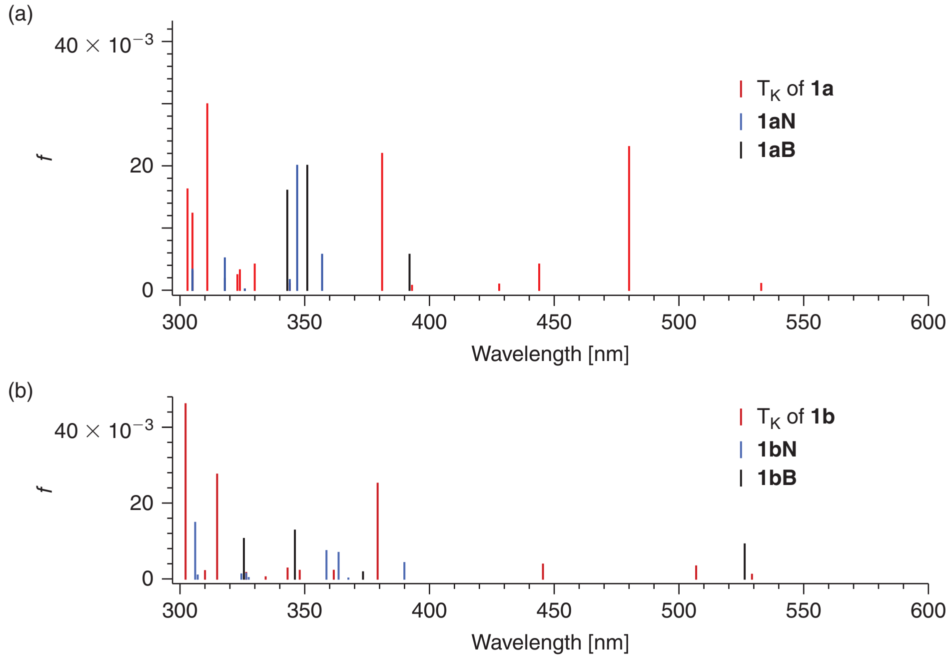


Fig. 3. Calculated major absorption spectral features (above 300 nm) for T_{1K} of **1a**, **1b**, **1aN**, **1bN** and **1aB**, **1bB** in acetonitrile. *f* is the calculated oscillator strength for the electronic transitions.

calculations correlate these transitions state with a triplet state that has elongated C–N–N bonds and the **1B** and azido radicals instead of with the T_{1K} of **1**. This process is similar to what has been reported for α-cleavage in triplet ketones, where the characteristic state for an α-cleavage has an (n,σ*) nature; in contrast, the excitation is into the triplet (n,π*) state of the ketone chromophore.[45–47]

In Fig. 2, stationary points on the triplet surface of **1a**, **1b** are plotted. The transition state barrier for breaking the C–N bond in **1a**, **1b** to form **1aB**, **1bB** is only 3 kcal mol^{-1} above T_{1K}, and therefore the azido cleavage should be easily accessible at ambient temperatures. Because the energies of T_{1K} and T_{2K} are similar, we expect them to be in equilibrium and thus energy transfer and azido cleavage to be competitive from these triplet excited states.

Finally, we used TD-DFT calculations to calculate the UV-absorption spectra of T_{1K} of **1a**, **1b**, benzyl radicals **1aB**, **1bB**, and triplet nitrenes **1aN**, **1bN**. The calculated spectra in acetonitrile are displayed in Fig. 3.

Laser Flash Photolysis

We used laser flash photolysis (LFP) to identify the intermediates formed on photolysis of **1a**, **1b**. LFP (excimer laser, $\lambda = 308$ nm, 17 ns) of **1a** in argon-saturated acetonitrile produces a broad transient absorption with λ_{max} between ~350 and 420 nm due to the absorption of T_{1K} of **1a**, which decays with a rate constant of 3.2×10^6 s^{-1} (Fig. 4). We assign this transient absorption to T_{1K} of **1a** because the triplet ketone in *p*-methylacetophenone has similar absorption. In oxygen-saturated acetonitrile, T_{1K} of **1a** becomes shorter-lived and decays with a rate constant of 1×10^7 s^{-1} due to quenching by oxygen. Simultaneously with the decay of T_{1K} of **1a**, a new transient absorption with λ_{max} at ~350 nm forms with the same

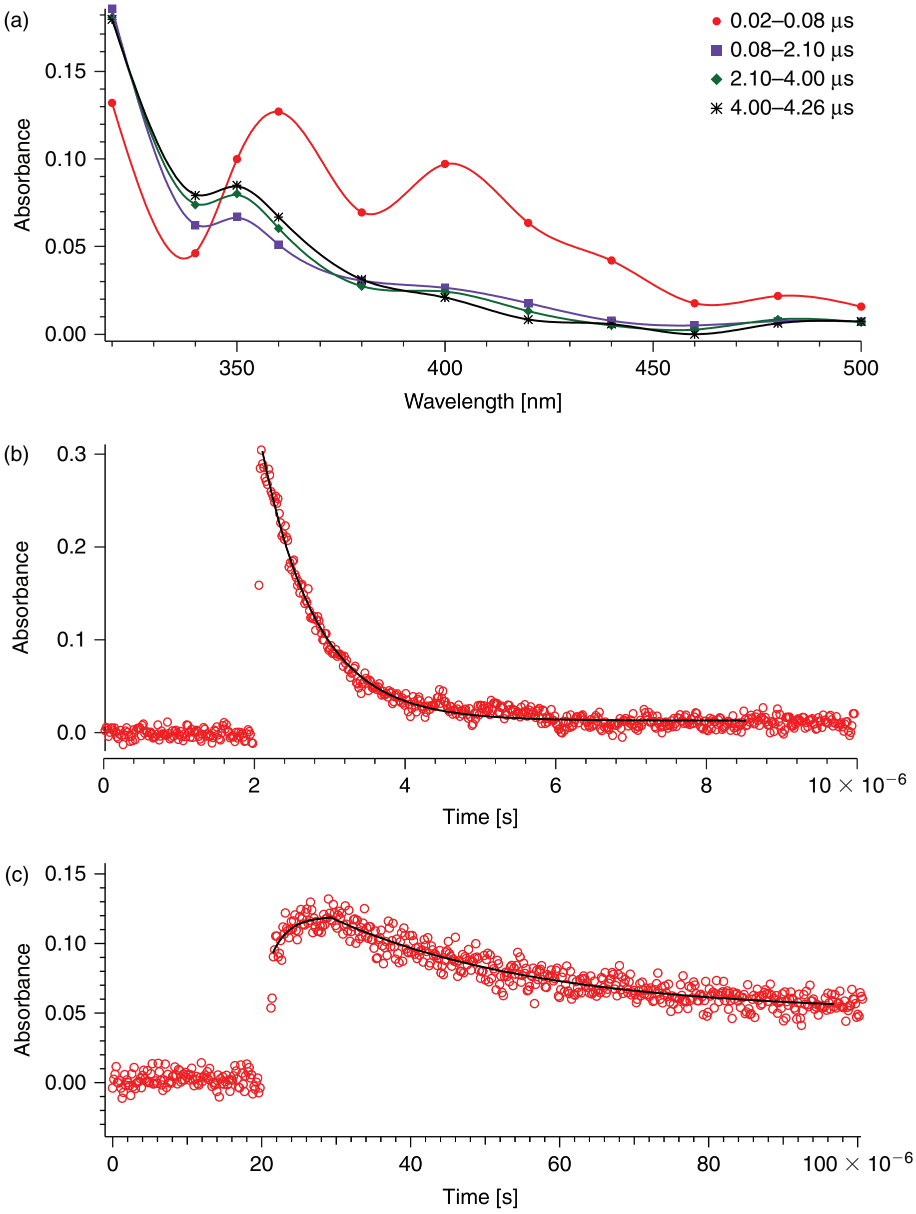


Fig. 4. (a) Transient spectra obtained by laser flash photolysis of **1a** in argon-saturated acetonitrile over 50 µs. (b) Kinetic trace obtained at 390 nm. (c) Kinetic trace obtained at 330 nm.

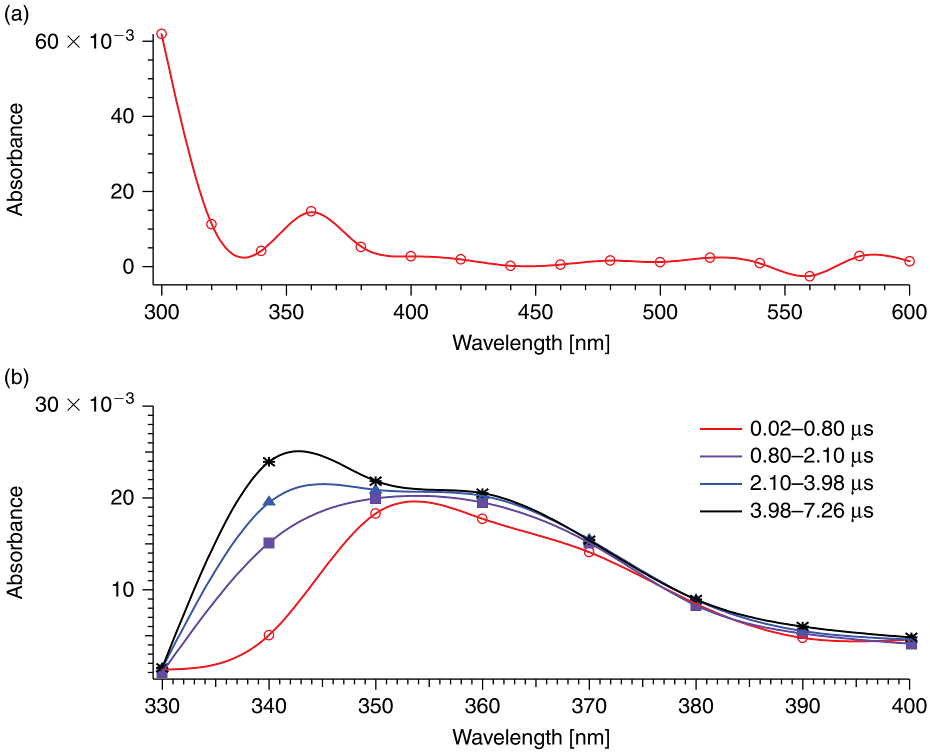


Fig. 5. Transient spectra obtained from laser flash photolysis of **1b** in argon-saturated acetonitrile over (a) 2.5 µs, and (b) 10 µs.

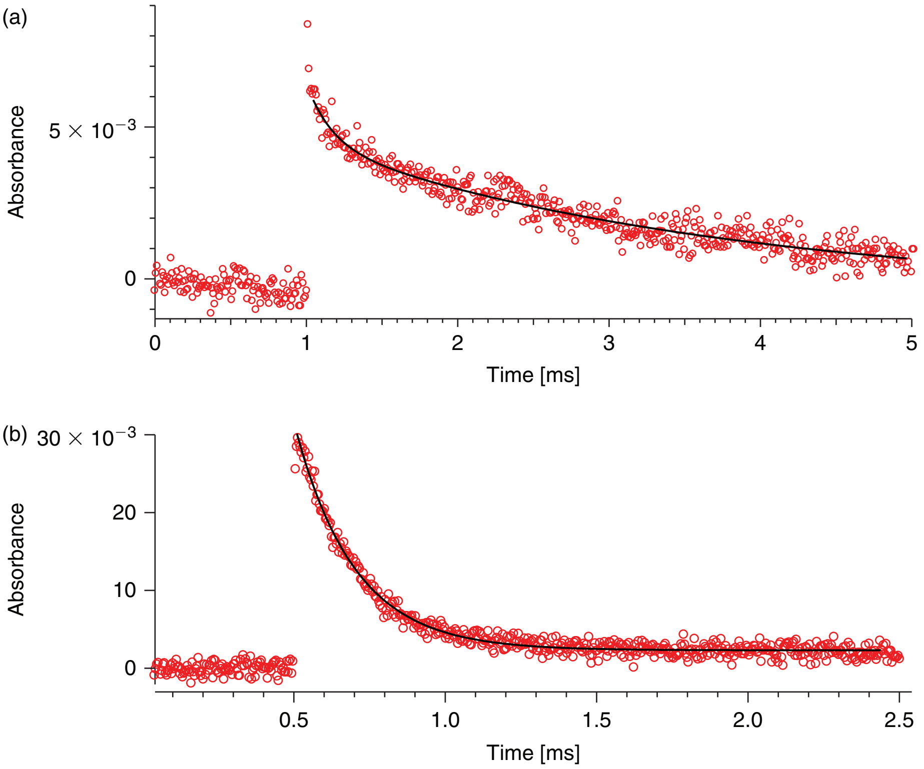
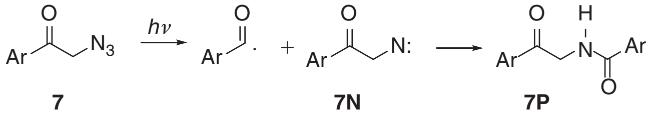
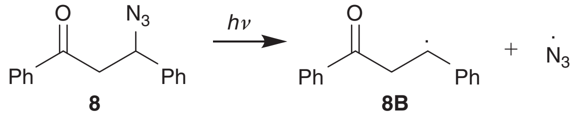


Fig. 6. Kinetic traces from laser flash photolysis of **1b** at 380 nm (a) in argon-saturated and (b) in oxygen-saturated acetonitrile.

rate constant; we assign this absorption to **1aB** and **1aN** (Fig. 4). We base this assignment on the similarity of this transient absorption to the calculated absorption spectra of **1aB** and **1aN** (see Fig. 3). On shorter timescales, we observe a decay that can be fitted with a mono-exponential function to yield a lifetime of ~30 µs and assign it to **1aB**. On a longer timescale or on a millisecond timescale, we observe a decay that cannot be fitted with a mono-exponential function. We assign this decay to **1aN**,



Scheme 6. Photolysis of **7**.



Scheme 7. Photolysis of **8**.

and because **1aN** decays by several different routes (Scheme 3), its decay cannot be fitted with a mono-exponential function. The assignment of the transient absorption of **1aB** and **1aN** is further supported by LFP of **1a** in oxygen-saturated acetonitrile. In oxygen-saturated acetonitrile, we did not observe transient absorption due to **1aB**, presumably because **1aB** reacts with a rate of the order of diffusion with oxygen. In comparison, the triplet nitrene **1aN** has a lifetime of ~200 μs in oxygen-saturated acetonitrile; by assuming the concentration of oxygen is 0.0091 M,[48] we can estimate that **1aN** reacts with oxygen with a rate of $5 \times 10^5\,M^{-1}\,s^{-1}$.

LFP of **1b** resulted in a transient absorption with λ_{max} at 355 nm, which decayed with a rate constant of $5 \times 10^6\,s^{-1}$; we assign this transient absorption to T_{1K} of **1b** (Fig. 5). As the transient absorption at 380 nm decays, a new transient is formed with the same rate constant at λ_{max} ~340 nm. We assign this transient absorption to **1bB** and **1bN** based on their calculated spectra (Fig. 3). Benzyl radical **1bB** decays at a rate constant of $\sim 3 \times 10^4\,s^{-1}$. In comparison, the decay of **1bN** is observed over a longer timescale and cannot be fitted as a mono-exponential function. In oxygen-saturated acetonitrile, the transients due to T_{1K} of **1b** and **1bB** are quenched, whereas the absorption due to **1bN** decays with a rate constant of $5.3 \times 10^3\,s^{-1}$ (Fig. 6). Because the concentration of O_2 in a saturated acetonitrile can be assumed to be $\sim 9 \times 10^{-3}$ M,[48] **1bN** can be estimated to react with oxygen at a rate of $6 \times 10^5\,M^{-1}\,s^{-1}$.

We have previously estimated that triplet β-nitrenopropiophenones react somewhat more slowly with oxygen or with a rate of $5 \times 10^4\,M^{-1}\,s^{-1}$. In comparison, Liang and Schuster reported that triplet *p*-nitrophenylnitrene reacts with oxygen at a rate of less than $2 \times 10^5\,M^{-1}\,s^{-1}$.[49] However, Gritsan and Pritchina estimated this same rate to be somewhat larger.[50,51] The rates for triplet alkyl- and arylnitrenes reacting with oxygen are, however, in agreement with computational work by Liu et al., who reported that triplet alkylnitrenes and triplet phenylnitrenes can be expected to react similarly with oxygen.[52]

Thus, LFP of **1a** and **1b** gives similar results; the main difference is that the T_{1K} of **1b** is somewhat longer-lived than the T_{1K} of **1a**, presumably because the energy of T_{1K} is lower for **1a** than **1b**. LFP supports the theory that **1a**, **1b** form long-lived triplet nitrenes (**1aN**, **1bN**) in competition with azido cleavage to form **1aB**, **1bB**.

Discussion

LFP demonstrated that **1a**, **1b** form both triplet nitrenes **1aN**, **1bN** and benzyl radicals **1aB**, **1bB** on irradiation. We propose that triplet alkylnitrenes **1aN**, **1bN** trap the benzyl radicals to form **2a**, **2b**, because in oxygen-saturated solution the benzyl radicals are trapped to form an aldehyde and in the absence of benzyl radicals, the triplet nitrenes decay by reacting with oxygen and form **3a**, **3b**. Thus, triplet alkylnitrenes **1aN**, **1bN** are inert or stable intermediates that have lifetimes on the order of milliseconds, as they do not react with the solvent or their precursor, but rather intercept radicals such as oxygen and **1aB**, **1bB**. Therefore, the reactivity of **1a**, **1b** is similarly to what we have previously reported for α-azidoacetophenone **7**, which undergoes α-cleavage to form benzoyl radicals and energy transfer to yield triplet alkylnitrenes **7N** (Scheme 6).[17,21b] Nitrene **7N** did not dimerize to form azo-dimers but rather reacted with benzoyl radicals to form **7P**. However, the reactivity of **7N** was further complicated because it was photolabile and underwent α-cleavage to form a benzoyl radical.

We have shown previously that photolysis of azide **8** (Scheme 7) in solution results mainly in azido cleavage to form azido radical and benzyl radical **8B**.[21b] The major difference between **8** and **1a**, **1b** is that the triplet ketone in **8** also undergoes deactivation via β-phenyl quenching in competition with product formation. In more detail, propiophenone derivatives with β-phenyl substituents undergo efficient deactivation of their triplet ketones. The mechanism for β-phenyl quenching has not yet been fully characterized;[53–55] however, it has been proposed that the deactivation is due to charge transfer from the β-phenyl ring to the electron-deficient triplet ketone.[56] However, more recently Bucher performed calculations to support that the β-phenyl quenching is due to addition of the carbonyl oxygen to the *ipso*- or *ortho*-carbon atoms of the β-phenyl ring, which is followed by intersystem crossing and relaxation to the ground state.[57] The β-phenyl quenching in **8** presumably limits the energy transfer to form the corresponding triplet alkylnitrene but does not yield azido cleavage.

Conclusion

LFP of **1a**, **1b** result in triplet nitrenes **1aN**, **1bN** and benzyl radicals **1aB**, **1bB**. DFT calculations further support the photoreactivity of **1a**, **1b**. The triplet nitrenes are stable intermediates that act as radical scavengers and trap the benzyl radicals to form **2a**, **2b**. In the absence of benzyl radicals, the triplet nitrenes react with oxygen and form **3a**, **3b**.

Experimental and Computational Methods

*Synthesis of **1a**, **1b***

Azides **1a** and **1b** were synthesized by brominating the corresponding methylacetophenone derivatives, followed by reaction with sodium azide, as described below.

1-(3-Bromomethylphenyl)ethanone

3-Methylacetophenone (1.02 mL, 7.5 mmol), *N*-bromosuccinimide (1.34 g, 7.5 mmol) and benzoyl peroxide (0.036 g, 0.15 mmol) were dissolved in CCl_4 (25 mL) and refluxed for 12 h. The reaction mixture was filtered and concentrated under vacuum to afford a yellow oil. Purification was performed on a silica column with a solvent system of hexane/ethyl acetate (9:1) to give 1-(3-bromomethylphenyl)ethanone (0.96 g, 4.5 mmol, 60% yield). ν_{max} (neat)/cm^{-1} 3003, 2965, 2921, 1685, 1601, 1586, 1440, 1357, 1277, 1217, 1191, 797, 691, 585. δ_H (400 MHz, $CDCl_3$) 2.62 (s, 3H), 4.53 (s, 2H), 7.46 (t, *J* 7.6, 1H), 7.61 (d, *J* 7.6, 1H), 7.90 (d, *J* 7.6, 1H), 7.98 (s, 1H). δ_C (100 MHz, $CDCl_3$) 26.70, 32.52, 128.35, 128.72, 129.19, 133.62, 137.64, 138.45, 197.55. *m/z* (EI) 214, 212 (M^+), 199 (10), 197 (10), 133 (100), 118 (19), 90 (26).

1-(3-Azidomethylphenyl)ethanone **1b**

1-(3-bromomethylphenyl)ethanone (0.96 g, 4.5 mmol) was dissolved in acetonitrile (25 mL), NaN_3 (2.93 g, 45 mmol) was subsequently added to the solution and the resulting solution was refluxed for 2 h. The reaction mixture was filtered and concentrated under vacuum to afford 1-(3-azidomethylphenyl) ethanone (0.79 g, 4.5 mmol, 99% yield). ν_{max} (neat)/cm^{-1} 3065, 3004, 2929, 2877, 2101, 1686, 1603, 1586, 1438, 1358, 1273, 1185, 796, 693. δ_H (400 MHz, $CDCl_3$) 2.62 (s, 3H), 4.43 (s, 2H), 7.48–7.55 (m, 2H), 7.91–7.94 (m, 2H). δ_C (100 MHz, $CDCl_3$) 26.68, 54.44, 127.82, 128.27, 129.19, 132.65, 136.12, 137.63, 197.66. *m/z* (EI) 175 (M$^+$, 10), 133 (76), 132 (90), 118 (10), 105 (13), 104 (67), 90 (13), 78 (21), 77 (100). *m/z* (HRMS) calc. for $C_9H_9N_3ONa$: 198.0640 $[M + Na]^+$. Found: 198.0643.

1-(4-Bromomethylphenyl)ethanone

4-Methylacetophenone (5.01 g, 37.4 mmol), *N*-bromosuccinimide (8.05 g, 45.2 mmol), and benzyl peroxide (0.071 g, 0.326 mmol) were dissolved in benzene (300 mL). The solution was degassed by bubbling argon through it for 20 min. This solution was photolyzed with a Honoiva Mercury lamp via a Pyrex sleeve. Once GC-MS spectroscopy indicated that 4-methylacetophenone was depleted, the reaction mixture was filtered through glass wool, and washed with distilled water and saturated aqueous sodium bicarbonate solution. The organic layer was dried with anhydrous magnesium sulfate and was concentrated under vacuum to yield an oil that was characterized as 1-(4-bromomethylphenyl)ethanone (6.72 g, 33.1 mmol, 88.5% yield). The characterization of the product was confirmed by obtaining IR and ^{1}H NMR spectra and the spectral data matched with those reported earlier.[58]

Mp 38–40°C (lit.[59] 40–42°C). ν_{max} (CH_2Cl_2)/cm^{-1} 1683. δ_H 2.60 (s, 3H), 4.50 (s, 2H), 7.48 (d, *J* 8.0, 2H), 7.92 (d, *J* 8.0, 2H). δ_C ($CDCl_3$, 100 MHz) 26.69, 32.14, 128.84, 129.25, 136.90 142.81, 197.39.

1-(4-Azidomethylphenyl)ethanone **1a**

1-(4-Bromomethylphenyl)ethanone (5.0 g, 24.6 mmol) was dissolved in a mixture of ethanol (150 mL) and acetic acid (1.5 mL) and cooled in an ice bath. To this solution was added dropwise sodium azide (10 g, 156 mmol), dissolved in a minimal amount of water. The resulting mixture was stirred in an ice bath for 2 h and stored at 4°C for 72 h. The reaction mixture was extracted with diethyl ether (100 mL) and the organic layer was washed with water, then dried with anhydrous magnesium sulfate and concentrated under vacuum. The resulting oil was purified via a silica column using an ethyl acetate and hexane mixture as the eluent to yield 1-(4-azidomethylphenyl)ethanone (505 mg, 2.89 mmol, 11.7% yield). The ^{1}H NMR spectrum of 1-(4-azidomethylphenyl)ethanone matched that found in the literature.[60]

ν_{max} ($CDCl_3$)/cm^{-1} 3005, 2102, 1684, 1609, 1574, 1412, 1359, 1267, 1182, 1116, 1075, 1017, 956, 847, 814, 694, 660, 595. δ_H ($CDCl_3$, 400 MHz) 2.63 (s, 3H), 4.44 (s, 2H), 7.43 (d, *J* 8.0, 2H), 7.99 (d, *J* 8.0, 2H). δ_C ($CDCl_3$, 100 MHz) 26.67, 54.24, 128.15, 128.88, 136.93, 140.58, 197.53.

Preparative Photolysis

Photolysis of **1b** *in Argon-saturated Methanol*

Azide **1b** (83 mg, 4.7 mmol) was dissolved in methanol (21 mL) in a Pyrex test tube. The solution was purged with argon for 20 min. The test tube was irradiated with a medium-pressure Hg arc lamp through a Pyrex filter for 21 h. GC-MS and NMR analysis of the reaction mixture showed the formation of imine **2b** as the only major photoproduct (86%) and some remaining **1b** (14%). The solvent was removed under vacuum and the crude product mixture was purified on an aluminium oxide column, eluting with dichloromethane, which was gradually increased to 5% methanol in dichloromethane. Imine **2b** hydrolyzed on the column to yield 3-acetylbenzaldehyde and 3-acetylbenzylamine. Thus, **2b** was characterized by spectroscopy prior to any purification.

2b: ν_{max} (neat)/cm^{-1} 3351, 3032, 3064, 3003, 2922, 2856, 1682, 1645, 1601, 1504, 1404, 1434, 1358, 1273, 1190, 1082, 1021, 958, 915, 799, 730, 692, 650, 588. δ_H (400 MHz, $CDCl_3$) 2.63 (s, 3H), 2.60 (s, 3H), 4.89 (s, 2H), 7.44–7.54 (m, 3H), 7.85–8.03 (m, 4H), 8.33 (s, 1H), 8. 49 (s, 1H). δ_C (100 MHz, $CDCl_3$) 26.73, 64.65, 127.22, 127.77, 128.22, 128.83, 129.01, 130.47, 132.50, 132.81, 136.41, 137.36, 137.47, 139.66, 161.40, 197.68, 198.17. *m/z* (EI) 279 (M$^+$, 38%), 278 (14), 236 (12), 133 (100), 118, 90 (26), 89 (29). *m/z* (HRMS) calc. for $C_{18}H_{17}NO_2$: 302.1157 $[M + Na^+]$. Found: 302.1164.

3-Acetylbenzylamine

ν_{max} (neat)/cm^{-1} 3608, 3583, 3354, 3062, 3002, 2923, 2854, 1682, 1602, 1584, 1359, 1275, 1189, 795. δ_H (400 MHz, $CDCl_3$) 2.62 (s, 1H), 3.95 (s, 2H), 7.44 (t, *J* 7.6, 1H), 7.54 (d, *J* 7.6, 1H), 7.84 (d, *J* 8.0, 1H), 7.93 (s, 1H). δ_C (100 MHz, $CDCl_3$) 26.73, 46.16, 126.850, 126.96, 128.80, 131.95, 137.42, 143.68, 198.27. *m/z* (EI) 149 (M$^+$, 14), 148 (27), 134 (24), 132 (19), 106 (100), 105 (14), 104 (24), 89 (14), 79 (22), 78 (15), 77. *m/z* (HRMS) calc. for $C_9H_{11}NO$: 150.0918 $[M + H^+]$. Found: 150.0919.

Photolysis of **1b** *in Oxygen-saturated Chloroform*

Azide **1b** (211.7 mg, 1.21 mmol) was dissolved in chloroform (62 mL) in a Pyrex test tube. Then the solution was purged with oxygen for 30 min. The test tube was photolyzed under a medium-pressure Hg arc lamp through a Pyrex filter for 10.5 h. GC-MS of the reaction mixture showed formation of **3b**, **4b** and **5b** in the ratio of 1.4:1:1.4. The solvent was removed under vacuum and the resulting yellow solid was dissolved in methanol, which precipitated **3b** (43.2 mg, 0.141 mmol, 23% yield). The mother liquor was separated on a silica column eluting with dichloromethane to yield **1b** (16.7 mg, 0.095 mol, 8% recovery), 3-acetylbenzaldehyde (7.3 mg, 0.049 mmol, 4.0% yield) and 3-acetylbenzonitrile (18.2 mg, 0.13 mmol, 11% yield).

1-{3[5-(3-Acetylphenyl)-[1,2,4]oxadiazol-3-yl]-phenyl} ethanone **3b**

ν_{max} (neat)/cm^{-1} 1678, 1603, 1411, 1353, 1246, 919, 799, 678, 586. δ_H (400 MHz, $CDCl_3$) 2.72 (s, 3H), 2.74 (s, 3H), 7.65 (t, *J* 7.6, 1H), 7.71 (t, *J* 7.6, 1H), 8.15 (d, *J* 7.6, 1H), 8.23 (d, *J* 8.0, 1H), 8.40 (d, *J* 7.6, 1H), 8.44 (d, *J* 8.0, 1H), 8.81 (s, 1H), 8.77 (s, 1H). δ_C (100 MHz, $CDCl_3$) 26.81, 124.77, 127.34, 127.59, 128.12, 129.44, 129.71, 130.88, 131.85, 132.30, 137.789, 137.97, 168.51, 175.21, 196.79, 197.44. *m/z* (EI) 306 (M$^+$), 291 (100), 221, 147, 138, 130, 118, 102, 91, 76, 65. *m/z* (HRMS) calc. for $C_{18}H_{14}N_2O_3$: 329.0917 $[M + Na^+]$. Found: 329.0902.

*Preparative Photolysis of **1a** in Oxygen-saturated Toluene*

1-(4-Azidomethylphenyl)ethanone (0.459 g, 2.6 mmol) was dissolved in dry, distilled toluene (100 mL). The solution was photolyzed for 15 h using a Honoiva Mercury lamp via a Pyrex sleeve. The reaction was monitored by HPLC and the irradiation was stopped when the HPLC showed formation of two new major products, **4a** (17%) and **3a** (24%) and remaining starting material (31%). HPLC yielded recovered starting material (25 mg, 0.14 mmol, 30% yield), 4-acetylbenzaldehyde (5 mg, 0.0368 mmol, 16% yield) and 1-{4[5-(4-acetylphenyl)-[1,2,4] oxadiazol-3-yl]phenyl}ethanone **3a** (10 mg, 0.0328 mmol, 44% yield).

*1-{4[5-(4-Acetylphenyl)-[1,2,4]oxadiazol-3-yl]phenyl} ethanone **3a***

$\nu_{\max}$ (CH_2Cl_2)/cm^{-1} 2924, 1693, 1589, 1526, 1406, 1357, 1267, 960, 845, 760, 714, 600, 474. δ_H ($CDCl_3$, 400 MHz) 2.17 (s, 6H), 8.29–8.10 (dd, 8.5 and 8.5, 4H), 8.36–8.34 (dd, 8.5 and 8.5, 4H). δ_C ($CDCl_3$, 100 MHz) 29.45, 127.53, 128.22, 128.58, 128.73, 139.28, 139.86, 196.85, 197.20. *m/z* (EI) 306 (M^+ 16%), 291 (100), 147 (30), 104 (30). *m/z* (HRMS) calc. for $C_{18}H_{14}N_2O_3$: 306.1004. Found: 306.1081.

*Photolysis of **1a** and **1b***

Methanol solutions of **1b** (0.06 and 0.18 M) were purged with argon for 10 min and irradiated. GC-MS analysis of the reaction mixture showed only formation of **2b** in significant amounts. Similarly, GC-MS analysis of 0.06 and 0.18 M methanol solutions of **1a** after irradiation showed only formation of **2a**. Similar results were obtained in argon-saturated acetonitrile and chloroform solutions.

Oxygen-saturated chloroform solutions of **1a** (0.06 M) and **1b** (0.06, 0.12, and 0.18 M) were photolyzed and the reaction mixture was analyzed by GC-MS. The conversion was kept below 30%. The major products observed were **3a**, **3b**, **4a**, **4b**, and **5a**, **5b**.

Photolysis of 1,3-Diphenylacetone in Argon-saturated Methanol

1,3-Diphenylacetone (60 mg, 0.3 mmol) was dissolved in methanol (3 mL) in a Pyrex test tube. The solution was purged with argon for 10 min and irradiated with a medium-pressure Hg arc lamp through a Pyrex filter for 13 h. GC-MS analysis of the reaction mixture showed the formation of 1,3-diphenylethane as the only photoproduct (100%).

1,3-Diphenylethane: *m/z* (EI) 182 (M^+), 176, 165, 152, 139, 128, 115, 104, 98, 91 (100%), 86, 77, 65.

Photolysis of 1-Adamantyl Azide and 1,3-Diphenylpropan-2-one

Adamantyl azide (60 mg, 0.3 mmol) and 1,3-diphenylpropan-2-one (60 mg, 0.3 mmol) were dissolved in methanol (3 mL) in a Pyrex test tube. The solution was purged with argon for 10 min and irradiated with a medium-pressure Hg arc lamp through a Pyrex filter for 4 h. GC-MS analysis of the reaction mixture showed formation of 1,2-diphenylethane as the only major photoproduct (27%) and remaining adamantyl azide (45%) and 1,3-diphenylpropan-2-one (28%).

1,3-Diphenylethane: *m/z* (EI) 182 (M^+), 165, 152, 139, 128, 115, 104, 91 (100%), 77, 65, 51.

1-Adamantyl azide: *m/z* (EI) 177 (M^+), 148, 135 (100%), 120, 115, 106, 93, 84, 79, 70, 65, 58, 53.

1,3-Diphenylpropan-2-one: *m/z* (EI) 210 (M^+), 178, 165, 152, 119, 103, 91 (100%), 77, 65, 51.

*Photolysis of **1b** and 1,3-Diphenylpropan-2-one in Argon-saturated Methanol*

Azide **1b** (40 mg, 0.2 mmol) and 1,3-diphenylpropan-2-one (60 mg, 0.3 mmol) were dissolved in methanol (3 mL) in a Pyrex test tube. The solution was purged with argon for 10 min and irradiated with a medium-pressure Hg arc lamp through a Pyrex filter for 13 h. GC-MS analysis of the reaction mixture showed formation of 1,3-diphenylethane as the only major photoproduct (41%), a smaller amount of **2b** (7%) and **6** (6%) and some remaining starting materials.

1,3-Diphenylethane: *m/z* (EI) 182 (M^+), 165, 152, 139, 128, 115, 104, 91 (100%), 77, 65, 51.

6: *m/z* (EI) 239 (M^+), 162, 148, 133, 118, 111, 106, 91 (100%), 77, 65.

2b: *m/z* (EI) 279 (M^+), 264, 246, 236, 165, 144, 133, 118, 104, 90, 77, 65.

Calculations

All geometries were optimized as implemented in the *Gaussian09* programs,[24] at the B3LYP level of theory and with the 6-31G+(d) basis set.[25,26] All transition states were located at the UB3LYP level of theory, and each transition state was confirmed to have one imaginary vibrational frequency by analytical determination of the second derivatives of the energy with respect to internal coordinates.[61] IRC calculations were used to verify that the located transition states corresponded to the attributed reactant and product.[41–44] Vertical UV absorption spectra were calculated at the TD-B3LYP level with the 6-31+G(d) basis set using the optimized B3LYP/6-31+G(d) geometry for the S_0 state. The effect of solvation was calculated using the SCRF method with the PCM with acetonitrile as the solvent.[32–35]

LFP

LFP was done with an excimer laser (308 nm, 17 ns). The system has been described elsewhere.[62] Stock solutions of azides **1a** and **1b** were prepared with spectroscopic-grade acetonitrile, such that the solutions had an absorption between 0.6 and 0.8 at 308 nm. Typically, ~1 mL of the stock solution was placed in a 10 × 10 mm wide, 48 mm long cm quartz cuvette and was purged with argon or oxygen for 5 min. The rates were obtained by fitting an average of three to eight kinetic traces.

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