

Photoinduced C-N Bond Cleavage in 2-Azido-1,3-diphenyl-propan-1-one Derivatives: Photorelease of Hydrazoic Acid

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Photolysis of 3-azido-1,3-diphenyl-propan-1-one (1a) in toluene yields 1,3-diphenyl-propen-1-one (2), whereas irradiation of 3-azido-2,2-dimethyl-1,3-diphenyl-propan-1-one (1b) results in the formation of mainly 2,2-dimethyl-1,3-diphenyl-propan-1-one. Laser flash photolysis (308 nm) of 1a,b in acetonitrile reveals a transient absorption ($\lambda_{max} = \sim 310$ nm) due to the formation of radicals 4a and 4b, respectively, which have lifetimes of ~14 μ s at ambient temperature. TD–DFT calculations (B3LYP/6-31+G(d)) reveal that the first and second excited states of the triplet ketone (T_{1K} (n,π^*) and T_{2K} (π,π^*)) in azide 1a are almost degenerate, at ~74 and 76 kcal/mol above the ground state (S₀), respectively. Similarly, azide 1b has T_{1K} and T_{2K} 75 and 82 kcal/mol above S₀, respectively. The calculated transition state for cleaving the C–N bond is located 71 and 74 kcal/mol above S₀ in azides 1a and 1b, respectively. The calculated bond dissociation energies for breaking the C–N bond are 55 and 58 kcal/mol for azides 1a and 1b, respectively, making C–N bond breakage accessible from T_{1K} in azides 1 at ambient temperature. In comparison, the irradiation of azides 1 in argon matrices at 14 K lead to the formation of the corresponding triplet alkyl nitrenes (1-n), via intramolecular energy transfer from T_{2K}. The characterization of 1-n was supported by isotope labeling, IR spectroscopy, and molecular modeling.

1. Introduction

Photoprotecting or photocaging groups are used in a variety of applications, including the slow release of fragrances in household goods, synthesis of organic molecules, drug delivery, and as probes of biological processes.^{1,2} Since photoprotecting groups are so widely used, there is a need for new photoremovable protecting groups that can be tailored to specific applications.¹ We have designed the photoprotecting group 2-azido-1,3-diphenyl-propan-1-one **1a** and its derivative **1b**, which slowly release hydrazoic acid upon irradiation, making it possible to generate hydrazoic acid under benign conditions, without any heating. It should be noted that hydrazoic acid is toxic and explosive in high concentrations, making it a treacherous compound with which to work.³ Traditionally, hydrazoic acid is prepared by heating sodium azide in excess acid.⁴

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SCHEME 1



The photochemistry and spectroscopy of hydrazoic acid have been studied in detail.^{5,6} Recently, however, the atmospheric chemistry of hydrazoic acid has become a focus of attention.⁷ This renewed interest in hydrazoic acid stems from the fact that sodium azide is now heavily used in the automotive industry for air bag inflators, thus increasing the risk of release of hydrazoic acid into the environment.⁸ Hydrazoic acid has a pK_a of 4.7 and is therefore easily generated from aqueous sodium azide.⁹ Furthermore, hydrazoic acid is very volatile and evaporates effectively under normal atmospheric pressure. Effective studies of the reactivity of hydrazoic acid in the environment will require diverse methods for generating hydrazoic acid.

In this study, we used laser flash photolysis and product studies at ambient temperature to demonstrate that azides 1a,b undergo photoinduced C–N bond cleavage, forming azido radicals and the corresponding benzyl radical derivatives. The azido radical abstracts a H-atom to form hydrazoic acid, as shown by IR spectroscopy. Molecular modeling reveals that the bond dissociation energies of the C–N bonds in azides 1a,b are less than 59 kcal/mol, considerably lower than the energy of their triplet ketones (T_K), and thus, the cleavage is possible. In comparison, photolysis of azides 1 in argon matrices at 14 K yields the triplet alkyl nitrene intermediates, which we identified with the aid of IR spectroscopy and isotope labeling.

Azides 1 have a built-in acetophenone moiety as a triplet sensitizer, and acetophenone absorbs above 300 nm. More

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specifically, the first excited state of acetophenone, $S_1(n,\pi^*)$, has a maximum absorbance around 320 nm ($\epsilon = 50$).¹⁰ S₁ in acetophenone undergoes efficient intersystem crossing, 1011 s-1 to T_{1K} , with a quantum efficiency approximating unity.¹¹ In comparison, alkyl azides have maximum absorbance around 280 nm,⁵ and thus, by irradiating **1** above 300 nm, one can ensure that the ketone chromophore absorbs the light and that it will undergo intersystem crossing to form the first excited state of the singlet ketone, which intersystem crosses to form T_{1K} . On the basis of the similarity of azides 1 with the analogous 1,3-diphenyl-propanone derivatives, azides 1 are expected to have almost degenerate T_{1K} and T_{2K} , which are in thermal equilibrium with each other.¹² We propose that in azides **1a**,**b**, T_K with the (n,π^*) configuration results in cleavage of the C–N bond, whereas the (π,π^*) state undergoes intramolecular energy transfer to form nitrene intermediates.

2. Results

2.1. Product Studies. Photolyzing azide **1a** in an argonsaturated solution via a Pyrex filter yielded product **2** and a small amount of **3** (Scheme 1). We hypothesize that **2** is derived from breaking the C–N bond to form an azido radical and **4a**. The azido radical abstracts a H-atom from **4a** to form **2**. Dimers **3a** and **3b** are formed from secondary photolysis of **2**. The dimerization of the trans isomer of **2** in solution has been studied extensively and shown to yield mainly **3a**, which arises from head-to-head dimerization of *trans*-**2**.¹³ We established the stereochemistry of dimer **3b** by X-ray structure analysis, which showed that it must be formed by head-to-head dimerization of *cis*- and *trans*-**2**. Photolyzing azide **1a** in the presence of a good H-atom donor, (CH₃Si)₃SiH, makes it possible to trap **4a** to form **6**.



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SCHEME 2



To rule out the possibility that **2** is being formed by direct excitation of the azido chromophore in azide **1a**, we irradiated **1a** through a quartz filter, resulting in the formation of dimer **3a** and amine **5**. Direct irradiation of the azido chromophore in **1a** is expected to yield imine **5i**, either in a concerted pathway from the singlet excited azide or via singlet nitrene intermediates.¹⁴ Since amine **5** is a tautomer of imine **5i**, this verifies that photolysis of **1a** via a Pyrex filter must involve the triplet ketone in **1a**. Photolysis via quartz also produces **3a**, as expected, since the ketone chromophore in **1a** absorbs light in competition with the azido chromophore.



Photolysis of azide **1b** in an argon-saturated toluene solution at ambient temperature resulted in products **7–9** (Scheme 2). We propose that azide **1b** also undergoes β -cleavage to form radical **4b** and an azido radical. Radical **4b** can abstract a H-atom from the solvent to form **7**, whereas products **8** and **9** can be attributed to the formation of triplet alkyl nitrene **1b-n**, rather than to the azido radical reacting with **4b**. Since radical **4b** does not have any easily abstractable H-atom as does radical **4a**, we do not observe any product from **1b** corresponding to **2**.

2.2. Quantum Yields. We measured the quantum yield for the formation of **2** from **1a** using *p*-methoxy valerophenone as the actinometer and a 313 nm light source.¹⁵ The conversion was kept below 20%, and we did not observe a significant amount of dimers **3**. The quantum yield for forming **2** is 0.05. The quantum yields are low, presumably, because the azido radical and **4** can recombine to regenerate the starting material.

2.3. Molecular Modeling. All molecular modeling was performed using Gaussian 03^{16} at the B3LYP level of theory and using 6-31+G(d) as the basis set.¹⁷ We optimized the structures of azides **1** and radicals **4a,b** and calculated their IR spectra. Azides **1a,b** have several minimal energy conformations that are within a few kilocalories per mole of each other. The three lowest energy conformers of each azide are depicted in Figure 1.

Time-dependent density functional theory (TD–DFT) calculations¹⁸ of azide **1a-A** showed that the first and second excited states of the triplet ketone (T_{1K} and T_{2K}, respectively) were located 75 and 76 kcal/mol above its ground state (S₀). Inspection of the molecular orbitals shows that T_{1K} and T_{2K} have (n,π^*) and (π,π^*) configurations, respectively. Solvation¹⁹ of **1a** was calculated using the self-consistent reaction field (SCRF) method with the integral equation formalism polarization continuum model (IEFPCM). In methanol and acetonitrile, the configurations of the triplet ketone are interchangeable, such that T_{1K} has (π,π^*) and T_{2K} (n,π^*) configurations. The calculated energies of T_{1K} and T_{2K} in azide **1a-A** are listed in Table 1. Similar results were obtained for conformers **B** and **C** of azide **1a**.

In comparison, T_{1K} (n,π^*) and T_{2K} (π,π^*) in azide **1b** are located 75 and 82 kcal/mol, respectively, above S₀. Solvation calculations in methanol and acetonitrile do not affect the energies of T_{1K} and T_{2K} significantly for azide **1b**.

We also optimized the structure of T_{1K} for azides **1a,b** at the UB3LYP level of theory. The optimized structures of T_{1K} for azides **1a,b** have carbonyl groups with respective bond lengths of 1.32 and 1.33 Å, and the respective vibration stretches of the carbonyl bond are at 1149 and 1200 cm⁻¹ (Figure 2). The

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FIGURE 1. Optimized structures of azides 1a and 1b.

 TABLE 1. Comparison of Energies of Triplet Excited States of

 Azides 1 Using TD-DFT Calculations

	azide 1a			azide 1b		
	gas phase	CH ₃ CN	MeOH	gas phase	CH ₃ CN	MeOH
<i>(n,π*)</i>	74	77	78	75	76	76
(π,π^*)	76	76	76	82	83	83

band at 1200 cm⁻¹ in T_{1K} of azide **1b** is coupled with the bending of the methyl substituents. The bond length of the carbonyl bonds and their vibration stretches fit with the triplet ketones having an (n,π^*) configuration.^{20,21} Furthermore, visualization of the molecular orbitals of T_{1K} in **1a,b** further support this assignment (see Supporting Information). However, the calculated energies of the optimized T_{1K} are 69 and 67 kcal/ mol above S₀ in azides **1a,b**, 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.²²

Optimization of the triplet configuration of the azide moieties (T_{1A}) in **1a,b** shows that the N1–N2 and N2–N3 bonds are both lengthened to 1.42 and 1.188 Å, respectively, as compared to S_0 of **1** (Figure 2). The N1–N2–N3 bonds have an angle of 120°. The vibration stretches of the azide bands in triplet azides **1a,b** are observed at 1708 and 1724 cm⁻¹, respectively. The energies of T_{1A} of azides **1a,b** are 44 and 45 kcal/mol above S_0 . The triplet energies and optimized structures of the triplet azides are similar to what we have previously estimated for triplet alkyl azides.^{22,23}

We calculated the transition states for forming the triplet alkyl nitrenes (1-n) from $T_{1\rm A}$ and found that they were located

0.1 kcal/mol above the T_{1A} of azides **1**. Intrinsic reaction coordinate (IRC) calculations²⁴ were performed to correlate these transition states with T_{1A} and **1-n**. Thus, as expected, **1-n** can easily be formed from T_{1A} in azides **1**.

We calculated the triplet transition states for cleavage of the azido group in azides **1**. These transitions states are located 71 and 74 kcal/mol above S₀ in azides **1a,b**, respectively. IRC calculations correlate these transition states not with the T_{1K} of azide **1** but with a triplet excited state that has elongated C–N–N bonds (see Supporting Information) and the azido radical and **4**. This is similar to α -cleavage in triplet ketones, where the characteristic state for an α -cleavage has a (σ , σ^*) nature, whereas the excitation is into the triplet (n, π^*) state of the ketone chromophore.²⁵ More specifically, we theorize that the energy surface for T_{1K} in azides **1** has an avoided crossing with the energy surface of **4** and the azido radical. This is therefore comparable to what has been proposed for α -cleavage of triplet ketones.²⁶

In Figure 3, we have plotted the stationary points on the triplet surface of azides 1a,b. For comparison, we have added stationary points of the triplet surface of azide 1c, which does not have β -phenyl substituents (we have previously reported some of these calculations for azide 1c).²³ T_{1K} and T_{2K} in azides 1a,c have very similar energies, whereas the energy gap between T_{1K} and T_{2K} in azide **1b** is somewhat larger, due to the α -methyl substituents. The energy of T_{1A} for azides 1a-c is very similar, and the transition state for forming the corresponding triplet alkyl nitrenes is located less than 1 kcal/mol above T_{1A}. In comparison, the energies of the transition states for cleaving the C-N bond in azides 1 are different. In azides 1a,b, this transition state is less than 74 kcal/mol above S₀, whereas it is 82 kcal/mol above S_0 for azide **1c**. Thus, a radical-stabilizing substituent in the β -position facilitates cleavage of the C–N bond.

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FIGURE 2. Optimized structure of (A) T_{1K} and (B) T_{1A} of azide 1a. Bond lengths are in angstroms.



FIGURE 3. Stationary points on triplet energy surface of azides 1a-c. Calculated energies are in kilocalories per mole. The energies of T_{1K} and T_{2K} were obtained from their optimized structures and from TD–DFT calculations, respectively.

TD-DFT calculations were used to estimate the absorption spectra of 4a, b, as shown in Table 2. The effect of solvation was calculated with acetonitrile as the solvent.

We calculated the bond dissociation energy (BDE) for the cleavage of the C–N bond in azides **1**. BDE has been defined as the enthalpy change of a reaction where a bond is broken and each of the products retains one of the electrons from the broken bond.^{27,28}

$$X - Y \rightarrow X^{\bullet} + Y$$

The BDE can be calculated with eq 1, where $\Delta H_{\rm f}(XY)$ is the enthalpy change for the dissociation of X-Y, $\Sigma \Delta H_{\rm f(products)}$ is the sum of the heats of formation of all the products in the reaction, and $\Sigma \Delta H_{\rm f(reactant)}$ is the sum of the heat of formation of each reactant.

$$BDE(XY) = \Delta H_r(XY) = \Sigma \Delta H_{f(\text{products})} - \Sigma \Delta H_{f(\text{reactant})}$$
(1)

The calculated BDEs for azides 1a,b are 55 and 59 kcal/mol, respectively. Since the BDEs for breaking the C–N bond



TABLE 2. Major Absorption Spectral Features (nm, Oscillator Strength) for 4a and 4b^a

		electronic transition above 300 nm					
1a	gas phase	524 (0.0104)	369 (0.0016)	331 (0.0127)	326 (0.0324)		
	CH ₃ CN	525 (0.0159)	371 (0.0011)	368 (0.0025)	327 (0.0389)	323 (0.0040)	316 (0.0151)
1b	gas phase	506 (0.0087)	369 (0.009)	331 (0.0033)	330 (0.022)	326 (0.0184)	317 (0.011)
	CH_3CN	510 (0.0109)	368 (0.0013)	329 (0.0288)	321(0.0027)	316 (0.0021)	308 (0.0152)

^a Numbers in parentheses are the calculated oscillator strengths (f) for the electronic transition, in nanometers.



FIGURE 4. Laser flash photolysis of (A) azide 1a, (B) azide 1b, and (C) decay of radical 4a at 310 nm.

in azides **1** are considerably lower than the energies of their T_{1K} , it is feasible to break their C–N bond photochemically to form an azido radical and the corresponding alkyl radical. In comparison, the calculated BDE for the C–N bond in azide **1c** is 71 kcal/mol and thus comparable to the energy of its T_{1K} and T_{2K} , making cleavage of the C–N in azide **1c** less likely.

2.4. Laser Flash Photolysis. Laser flash photolysis (excimer laser 308 nm)²⁹ of azide **1a** in acetonitrile and in methanol produced transient spectra with λ_{max} at ~310 nm (Figure 4), which we assigned to **4a**. We based this assignment on the similarity of this transient to the calculated absorption spectrum of **4a**. TD-B3LYP calculations predicted that **4a** has absorption bands in acetonitrile at 316 and 327 nm. The band at 327 nm is mainly due to a mixed transition out of the lone pair on the oxygen atom into the half-full p orbital on the β -carbon atom and a π^* orbital, whereas the transition at 316 nm is mainly due to a transition out of the half-full p orbital on the β -carbon

into a π^* orbital. Furthermore, the transient spectra of radical **4a** is similar to the transient spectra of the benzyl radical, which has λ_{max} at ~320 nm and a lifetime of 20 μ s.³⁰ The rate of decay of the transient absorption of **4a** at 310 nm was 7 × 10⁴ s⁻¹, whereas in oxygen-saturated acetonitrile, the transient absorption was quenched.

Laser flash photolysis of azide **1b** resulted in the formation of a similar transient spectrum, with λ_{max} at 310 nm. As before, we used TD–DFT to assign this transient absorption to radical **4b** (Table 2). The rate of decay of radicals **4b** was 6.5 × 10⁴ s⁻¹.

2.5. Matrix Isolation. We deposited **1b** 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 a strong band at 2108 cm⁻¹ and a band at 1250 cm⁻¹ (Figure 5). We assign the band at 1250 cm⁻¹ to C–H bending that is coupled to the C–CO–C stretching, which is calculated to be at 1275 cm⁻¹ (Table 3). As expected, the bands at 2108 and 1250 cm⁻¹ were destroyed upon irradiation, and two new major bands were observed at

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FIGURE 5. IR Spectra of 1b in argon matrices (A) before irradiation (blue) and after irradiation (red) and (B) IR spectra after irradiation of 1b (red) and 1b-d (blue).

 TABLE 3.
 Calculated and Observed C-H Bands in Azides 1b and Nitrene 1b-n

	C-	-H	C-	-D
	calcd	obsd	calcd	obsd
1b	1275	1250	1280	1252
1b-n	1276 1251	1323 1275	1274	1286

1323 and 1274 cm⁻¹. In contrast, the remaining major bands were not shifted significantly upon irradiation. We assign this new photoproduct in matrices to nitrene 1b-n, based on the following observations. The calculated IR spectrum of nitrene **2b** has vibrational bands at 1276 and 1251 cm^{-1} , which are due to stretching of the C-CO-C bands coupled with the C-H bending. We assign the observed bands at 1323 and 1274 cm⁻¹ to those calculated bands. To support this assignment further, we prepared azide **1b** with a deuterium atom in the β -position. The calculated IR spectrum of nitrene **1b-n**-d has only one IR band for the stretching of the C-CO-C bonds at 1280 cm⁻¹ because the C-D band does not couple to the C-CO-C stretch as in 1b-n. Thus, if the assignment of the bands at 1276 and 1251 is correct, only one major band will be observed in this region of the spectrum of nitrene 1b-n-d. Deposition of azide 1b-d into argon matrices resulted in an IR spectrum that has an azido band at 2108 cm⁻¹ as before, whereas the C-H bend that is coupled with the stretching of the azide band is located at 1252 cm⁻¹, which fits reasonably well with the calculated isotope shift of 5 cm^{-1} . Upon irradiation of **1b**-d, we observed depletion of the azido band and the band at 1252 cm⁻¹. As expected, the photoproduct had only one major band at 1286 cm⁻¹, which fits well with the calculated band of the C-CO-C stretching for 1b-n-d.

The IR spectra of azide **1a** in argon matrices show a strong azido band at 2106 cm⁻¹ and two less intense bands at 2128 and 2136 cm⁻¹ (Figure 6). Upon irradiation, the bands at 2106 and 2136 cm⁻¹ were depleted, along with medium intensity bands at 1350, 1251, and 1211 cm⁻¹, which can all be assigned to coupled bending of the C–H bond on the β -carbon atom. The major new bands that were formed are at 1217 and 1207 cm⁻¹, and we assign them to the calculated C–H bending that is coupled with C–CO–C bending, at 1251 and 1210 cm⁻¹.

Thus, matrix photolysis of azide **1a**,**b** does not form azido radical and **4** since we do not observe the formation of either azido radical or hydrazoic acid; rather, photolysis of azides **1** at cryogenic temperatures results in the formation of nitrenes **1-n**.

2.6. Trapping of Hydrazoic Acid. To verify that the azido radical formed by irradiating azides **1** abstracts a H-atom to form hydrazoic acid, we placed crystals of **1a** in a Pyrex segment inserted into the argon deposition line. The glass segment of the line was irradiated for 24 h while argon flowed over the crystals. The flowing argon was condensed on the matrix cold window at 14 K and monitored by IR spectroscopy. After 24 h, IR bands were observed at 2135 and 1146 cm⁻¹, matching the two most intense bands reported for hydrazoic acid in argon matrices. Moreover, their relative intensities were consistent with the published spectrum.³¹ ¹H NMR spectra of the remaining yellow solid in the glass tube showed unreacted **1a** and the

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FIGURE 6. IR spectra of azide 1a before (black) and after (red) irradiation in argon matrices.





FIGURE 7. X-ray structure of azide 1a.

formation of mainly *trans-2* and dimer 3a. The X-ray structure of azide 1a shows that it crystallizes in a conformer that is similar to the calculated minimal energy structure, with the carbonyl and azide groups in a pseudo-syn alignment (Figure 7). The azide moiety in 1a forms non-traditional H-atom bonding with the β -hydrogen atom (H9 $_{\beta}$) on an adjacent molecule, and the N-H distance is 2.54 Å. The distances from the N1 to the H-atoms $H8_{\alpha 1}$ and $H8_{\alpha 2}$ are 2.64 and 3.35 Å, respectively (Figure 6). Solid state irradiation of 1a breaks the C-N bond to form 4a and an azido radical. The azido radical abstracts H₁ to form hydrazoic acid and 2. We observe mainly the trans isomers of 2, presumably because the azido radical abstracts $H_{\alpha 1}$. Examination of the crystal lattice shows that the shortest intermolecular distances between C α and C β atoms are 5.8 and 5.7 Å, respectively. These distances are considerably longer than the intermolecular distance observed for topochemically allowed dimerization in the solid state, which generally has an upper limit of 4.3 Å.32 However, it should be noted that the intermolecular distances between adjacent C α and C β will be different after the formation of 2.

3. Discussion

The TD–DFT calculations show that T_{1K} and T_{2K} in azide **1a** are almost degenerate. In comparison, the TD–DFT calcula-

tions place T_{2K} in azide **1b** ~6 kcal/mol higher in energy than T_{1K} . However, the energies obtained from the TD–DFT calculations are based on the assumption that the geometry of T_{1K} and T_{2K} are similar to that of S_0 (Frank–Condon excitation); thus, we cannot accurately determine the energy gap between these triplet excited states. Besides, they are close in energy and thus in equilibrium with each other. This is in agreement with what has been reported for valerophenone, α, α -dimethylacetophenone, which have their T_{1K} and T_{2K} values within a few kilocalories per mole of each other.³³

We propose that the cleavage of the azido group in azides **1a,b** comes from T_K with the (n,π^*) configuration, whereas the energy transfer to form triplet alkyl nitrenes **1a-n** and **1b-n** must take place from T_K with a (π,π^*) configuration. This is similar to what we have observed for α -azido acetophenone derivatives, where the T_K of the ketone with the (n,π^*) configuration cleaves to form an azido methyl and benzoyl radical pair, whereas T_K with the (π,π^*) configuration undergoes intramolecular energy transfer to form α -nitrenoacetophenone derivatives.^{22,34} In azide **1b**, only cleavage of the C–N bond is observed from T_{1K} with

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FIGURE 8. Transition state for C-N bond cleavage in azides 1.

the (n,π^*) configuration. In comparison, α -azidoacetophenone underwent both α -cleavage and energy transfer from $T_{1K}(n,\pi^*)$ and $T_{2K}(\pi,\pi^*)$, respectively. However, this is reasonable since the transition state for α -cleavage in azidoacetophenone is located 77 kcal/mol above its S_0 , whereas the transition state for C–N cleavage in azide **1b** is only 72 kcal/mol above its S_0 .²²

We reported previously that intramolecular triplet sensitization of β -azido-1-phenyl-propan-1-one, **1c**, yields mainly β -nitreno-1-phenyl-propan-1-one, 1c-n, via intramolecular energy transfer from the triplet ketone to the azido moiety, rather than cleavage of the azido group.²³ Since the calculated transition state for cleaving the C-N bond in azide 1c is 82 kcal/mol higher in energy than S_0 , it is reasonable that 1c does not undergo C-N bond cleavage efficiently. In comparison, the calculated transition states for cleaving the C-N bond in 1a,b are 71 and 74 kcal/mol above their S₀, respectively. Thus, C-N cleavage of azides 1a,b is facilitated by the resonance stabilization provided by the phenyl group. The calculated transition state for the cleavage of the C-N bond in azide 1b is approximately 3 kcal/mol higher in energy than for azide 1a, presumably because in the transition states the β -C radical is conjugated with the β -phenyl ring and there is more steric repulsion between the α -methyl groups and the β -phenyl group in azide **1b** than the α -H-atoms and the β -phenyl group in azide **1a** (Figure 8). This explains why products 8 and 9, which are attributable to the formation of triplet alkyl nitrene 1b-n, are observed in solution. The energy transfer from T_{2K} to form a nitrene can compete more efficiently with C-N cleavage from T1K in azide 1b than in azide 1a. However, we were not able to detect nitrene formation directly using laser flash photolysis, presumably because the quantum yields for forming the nitrene intermediates are low.

Propiophenone derivatives with phenyl substituents in the β -position undergo so-called β -quenching, which is an efficient deactivation of their triplet ketones with an (n,π^*) configuration.^{12,35} The mechanism of this process is not yet fully characterized, but it is thought to involve a charge transfer from the β -phenyl ring to the electronic-deficient triplet ketone.³⁶ It is possible that some of the T_{1K} (n,π^*) in azides **1** is quenched by the β -phenyl ring, which would also explain the low quantum yields for the cleavage of the C–N bond. Bohne and co-workers have shown that propiophenone derivatives with an α -methyl substituent undergo β -quenching less efficiently than propiophenone due to the steric demands of the methyl groups on the



geometry for β -quenching.¹² It is likely that β -quenching occurs when one of the lone pairs on the oxygen atom in the benzoyl moiety is oriented toward the center of the β -phenyl group. Thus, we theorize that β -quenching in azide **1b** is less efficient than in azide **1**, due to the α -methyl groups. Moreover, steric repulsion in azide **1b** makes both β -quenching and C–N bond cleavage less efficient and thus results in nitrene **1b-n** being formed from T_{2K}.

At cryogenic temperatures, irradiation of azides **1a**,**b** yields triplet alkyl nitrenes **1-n**, rather than the formation of azido radicals and **4**. Presumably, the thermal population of T_{2K} at low temperatures is more favorable than the thermal activation for cleaving the C–N bond from T_{1K} in matrices. Furthermore, the formation of the azido radical and **4** in matrices will only lead to the regeneration of **1** since the radical pair cannot diffuse apart.

Irradiation of azide **1a** selectively cleaves the C–N bond to form **4a** and the azido radical, and the latter abstracts an H-atom resulting in the release of hydrazoic acid. Interestingly, photolysis of azide **1a** both in solution and in the solid state at ambient temperature can be used to release hydrazoic acid. In comparison, photolysis of azide **1b** forms nitrene **1b-n** in competition with cleavage to form the azido radical.

Conclusion

We have shown that photolysis of β -azido-1,3 diphenylpropiophenone derivatives **1** results in C–N bond cleavage to form an azido radical and **4**. Irradiation of azides **1a**,**b** populates their T_{1K} (n,π^*), which results in cleavage of the C–N bond. The radical stabilization effect of the β -phenyl group makes the C–N bond cleavage in azides **1a**,**b** feasible at room temperature. Both solution and solid state irradiation of azide **1a** results in the formation of azido radicals that abstract a H-atom to form hydrazoic acid, and thus, azides **1** can be used as photoremoveable protecting groups of hydrazoic acid.

4. Experimental Section

4.1. Molecular Modeling. All geometries were optimized as implemented in the Gaussian 03 programs, at the B3LYP level of theory and with the 6-31+G(d) basis set.^{16,17} All transition states were located at the UB3LYP level of theory, and each transition state was confirmed to have one imaginary vibrational frequency. IRC calculations were used to verify that the located transition states corresponded to the attributed reactant and product.²⁴ UV absorption spectra were calculated at the TD-B3LYP level with the 6-31+G(d) basis set.¹⁸ The effect of solvation was calculated using the SCRF method with IEFPCM¹⁹ with toluene as the solvent.

4.2. Laser Flash Photolysis. Laser flash photolysis was performed with an excimer laser (308 nm, 17 ns). The system has been described in detail elsewhere.²⁹ A stock solution of azides **1a,b** in acetonitrile was prepared with spectroscopic grade acetonitrile, such that the solutions had an absorption between 0.6 and

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0.8 at 308 nm. Typically, $\sim 1 \text{ mL}$ of the stock solution was placed in a 10 mm \times 10 mm wide, 48 mm long quartz cuvette and was purged with nitrogen for 5 min. The rates were obtained by fitting an average of three to five kinetic traces.

4.3. Matrix Isolation. Matrix isolation studies were performed using conventional equipment.³⁷

4.4. Photolysis of Azide 1b. A solution of 1b (663.0 mg, 2.38 mmol) in toluene (125 mL) was purged with argon and photolyzed via a Pyrex filter for 18 h. GC analysis of the reaction mixture showed the formation of photoproducts **7–9** in the ratio 48:32:20 and no remaining starting material. Column chromatography (silica eluted with hexane/ethyl acetate) of the reaction mixture yielded photoproducts **8** (166 mg, 0.66 mmol, 28% yield) and **7** (189 mg, 0.85 mmol, 36%). Product **9** degraded on the column, so it was characterized by injection of authentic sample on the GC chromatography and ¹H NMR spectra of the reaction mixture.

4.5. 2,2-Dimethyl-1,3-diphenyl-propan-1-one (7). IR (CHCl₃) ν_{max} : 1675 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 7.02–7.52 (m, 12 H) 3.07 (s, 2 H), 1.30 (s, 6H), ppm; GC/MS (EI): *m/z* 238 (M⁺), 223, 131, 132, 117, 105, 91, 77.

4.6. 4,4-Dimethyl-3,5-diphenyl-isoxazolidine (8). IR (CHCl₃) ν_{max} : 2958, 2925, 2854, 1453, 909 cm⁻¹; ¹H NMR (250 MHz, CDCl₃): δ 1.58 (d, 6 H, 2.5 Hz), 5.94 (s, 1 H), 7.33–7.92 (m, 10 H) ppm; ¹³C NMR (60 MHz, CDCl₃): δ 178.2, 142.6, 133.6, 130.8, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.5, 127.3, 127.2, 86.8, 70.1, 27.8, 26.6 ppm; GC/MS (EI): m/z 252 (M⁺ + 1), 236, 194, 167, 146 (100), 131, 130, 119, 105, 104, 91, 77.

4.7. Synthesis of Azide 1a. 3-Bromo-1,3-diphenyl-propenone (1.7 g, 6 mmol) was dissolved in ethanol (60 mL) and placed in a 100 mL flask. To this solution was added sodium azides (1.5 g, 24 mmol) dissolved in a minimum amount of water. The resulting mixture was stirred for 12 h. The reaction mixture was extracted with diethyl ether, and the solvent was removed under vacuum to yield oil, which was crystallized from ethanol to yield white crystals of 3-azido-1,3-diphenyl-propenone, 1a (1.1 g, 4.5 mmol, 75% yield). The solid was recrystallized 3 times from ethanol to yield white crystals of 1a.

mp: 77–78 °C. IR (CHCl₃): 1680, 2094, 2123 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 7.95 (d, 6 Hz, 2H), 7.56–7.59 (m, 1H), 7.40–7.50 (m, 7H), 5.27 (m, 1H), 3.51–3.55 (m, 1H), 3.29–3.31 (m, 1H) ppm. ¹³C NMR (CDCl₃, 60 MHz): δ 196.4, 139.3, 136.5, 133.5, 128.9, 128.7, 128.4, 128.1, 126.8, 61.5, 45.2 ppm. GC/MS (EI): m/z 249 (M⁺), 221, 105.

4.8. Photolysis of Azide 1a. Azide 1a (153 mg, 0.61 mmol) was dissolved in toluene, argon was bubbled through the solution for 15 min, and the solution was irradiated via a Pyrex filter for 10 h. The progress of the reaction was followed with HPLC, which showed the formation of only 2 initially, but upon prolonged irradiation, more was formed of 3, at the expense of 2. The photolysis was stopped when HPLC showed the formation of *cis*-and *trans*-2 and 3 in a ratio of ~1:4 and ~20% remaining starting material. Dimers 3 were isolated using HPLC and yielded mainly 3a (54 mg, 0.12 mmol, 40% yield) and a small amount of 3b (6 mg, 0.015 mmol, 5% yield).

3a:³⁸ ¹H NMR (250 MHz, CDCl₃): δ 7.80 (d, 7 Hz, 4H), 7.5– 7.2 (m, 16H), 4.60 (d, 8.7 Hz, 2H), 3.98 (d, 8.7 Hz, 2H) ppm. ¹³C NMR (60 MHz, CDCl₃) 199.52, 141.9, 136.0, 133.9, 129.3, 129.2, 128.3, 127.8, 127.7, 48.4, 48.1 ppm. GC/MS (EI): *m*/*z* 416 (M⁺), 311, 207, 105.

3b:³⁹ ¹H NMR (250 MHz, CDCl₃): δ 8.68 (d, 7 Hz, 2H), 7.51 (d, 7 Hz, 2H), 7.3–6.8 (m, 16H), 5.76 (t, 9 Hz, 1H), 5.01 (t, 9 Hz, 1H), 4.51 (t, 9 Hz, 1H), 3.93 (t, 9 Hz, 1H) ppm. ¹³C NMR (60 MHz, CDCl₃): δ 197.2, 136.3, 135.9, 133.8, 133.1, 130.5, 129.9, 129.4, 128.7, 128.4, 128.4, 128.1, 127.0, 126.4, 48.5, 48.2, 43.6, 42.5 ppm. GC/MS (EI): m/z 416 (M⁺), 311, 296, 207, 105.

4.9. Quartz Photolysis of Azide 1a. Azide 1a (50 mg, 0.20 mmol) was placed in a quartz test tube, and toluene was added (1.5 mL) with a septum fixed by copper wire. The resulting solution was bubbled in argon for 15 min, sealed by Parafilm, and then photolyzed for 5 h via a quartz filter. Product **5** was isolated from the reaction mixture using HPLC (8 mg, 0.036 mmol, 18% yield). The progress of the reaction was followed by HPLC chromatography, which showed that **3** and **5** formed in the ratio of \sim 4:1, respectively. After 5 h of irradiation, HPLC showed some remaining starting material (10%) and that **3** and **5** (90%) formed in the ratio of 4:1

5: IR (CHCl₃): 3356, 1601, 1526 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 10.43 (b s, N–H), 7.94–7.97 (m, 2H), 7.63–7.66 (m, 2H), 7.43–7.50 (m, 6H), 6.12 (broad s, N–H) ppm. ¹³C NMR (250 MHz, CDCl₃): δ 190.2, 162.9, 140.3, 137.6, 131.1, 130.7, 129.1, 128.3, 127.2, 126.4, 91.9 ppm. HRMS: calcd for C₁₅H₁₃-ON (M + 1): 224.1075. Found: 224.1069.

4.10. Photolysis of 1a in the Presence of $(SiMe_3)_3SiH$. Azide 1a (0.01 g, 0.04 mmol) was placed in a Pyrex test tube, and toluene (1.5 mL) and $(SiMe_3)_3SiH$ (0.031 g, 0.08 mmol) were added. The resulting solution was bubbled in argon for 15 min and photolyzed for 6 h via a Pyrex filter. HPLC and GC-MS analyses of the reaction mixture showed the formation of **6** (95% yield), which was characterized by the injection of authentic samples on the GC and the HPLC with a commercially available standard.

4.11. Solid State Photolysis of 1a. Crystals of azide **1a** in a Pyrex glass tube were irradiated for 24 h while argon flowed over the crystals. ¹H NMR spectra of the irradiated crystals showed the remaining starting material and the formation of *trans*-**2** and dimer **3a** in the ratio of 4:1.

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Supporting Information Available: Cartesian coordinates, energies, vibrational frequencies, and X-ray structures of **1a** and **3b**. NMR spectra of **1b**-d, **5**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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