

Photoinduced α -Cleavage of 2-Azido-2-phenyl-1,3-indandione at Cryogenic Temperatures

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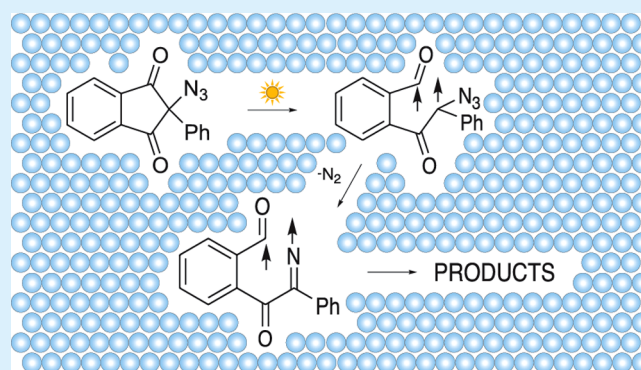


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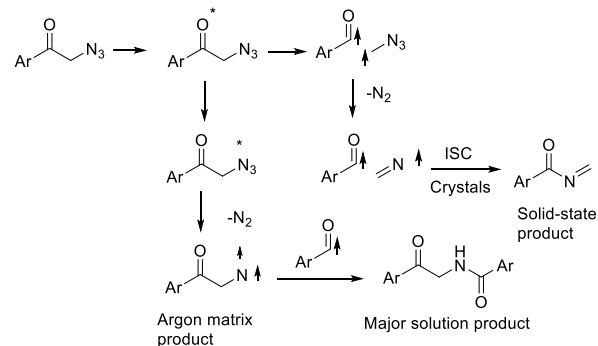
ABSTRACT: To expand the utility of α -cleavage at cryogenic temperatures, we investigated the photoreactivity of 2-azido-2-phenyl-1,3-indandione (**1**). EPR spectroscopy revealed that irradiating **1** in 2-methyltetrahydrofuran (mTHF) matrices forms alkylnitrene **3**², which has zero-field splitting parameters ($D/hc = 1.5837\text{ cm}^{-1}$; $E/hc = 0.0039\text{ cm}^{-1}$) typical of an alkylnitrene. IR spectroscopy demonstrated that irradiating **1** in argon matrices results in the concurrent formation of **3**², imine **3**, benzocyclobutenedione **4**, and benzonitrile **5**.



The well-established Norrish type I photoreaction, involving α -cleavage of a C–C bond adjacent to a carbonyl group, allows the convenient formation of radical pairs in solution.¹ Due to the ease of forming radicals via the photoinduced α -cleavage of ketones, this reaction is used in various applications including polymerization, photoinitiation, and photocuring.² However, the utility of α -cleavage to form radical pairs in confined media (e.g., cryogenic matrices or crystals) is limited because initial radical pairs generally recombine to regenerate the starting material because they cannot diffuse apart.³ However, α -cleavage of aliphatic ketones in the solid state can be rendered nonreversible if the cleavage of the second C–C bond to extrude CO is faster than the recombination of the initial radical pair.⁴ Using this approach, Garcia-Garibay and co-workers produced radical pairs in crystals that, due to the rigid confinement of the crystal lattice, formed new C–C bonds stereoselectively, allowing the elegant synthesis of natural products.⁵

Nonreversible α -cleavage of ketones can also be achieved by placing an azido group at the α -position because a carbon-centered radical adjacent to an azido moiety can undergo effective nitrogen molecule extrusion to form an imine radical (Scheme 1).⁶ We have shown that irradiating α -azidoacetophenone derivatives in solution yields the corresponding triplet excited ketones, which undergo α -cleavage to form benzoyl and azido methyl radicals.^{6a,c} However, in competition with α -cleavage, the triplet ketones also decay by energy transfer to their azido chromophores, which yields triplet alkylnitrenes. In solution, the benzoyl radicals are efficiently trapped by the triplet alkylnitrenes to form the major product. We theorized

Scheme 1. Nonreversible α -Cleavage of α -Azido-substituted Ketones

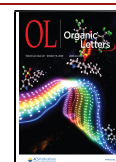


that the fate of the azido methyl radicals involves nitrogen molecule extrusion to form imine radicals. Irradiating α -azidoacetophenone derivatives in the solid state allows trapping of these imine radicals to form products.⁷

In contrast, irradiating α -azidoacetophenone in cryogenic matrices yields only the corresponding triplet alkylnitrene through intramolecular triplet sensitization of the azido group,

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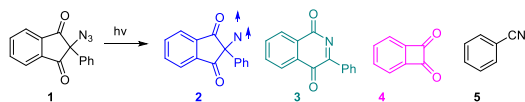
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with no products attributable to α -cleavage.⁷ Thus, it is unknown whether α -cleavage of azido alkyl derivatives can be achieved at cryogenic temperatures or if the recombination of the initial radical pair is more efficient than nitrogen molecule extrusion to form an imine radical.

Herein, we report the photoreactivity of azide **1** (CCDC 1970115) in cryogenic matrices. Using EPR, absorption, and IR spectroscopies, we determined that alkylnitrene **3**², imine **3**, benzocyclobutenedione **4**, and benzonitrile **5** form via α -cleavage of **1** in cryogenic matrices (Scheme 2), thus

Scheme 2. Photoreactivity of **1** in Cryogenic Matrices



expanding the scope of α -cleavage for forming desirable products or intermediates at cryogenic temperatures. However, we cannot exclude the possibility that **3**² forms through energy transfer from the triplet excited state of the ketone (T_1) of **1** to the triplet excited state of the azido moiety (T_{1A}).

EPR spectroscopy demonstrated that irradiation ($\lambda = 300$ – 400 nm) of **1** in an mTHF matrix at 80 K yields **3**² (Figure 1).

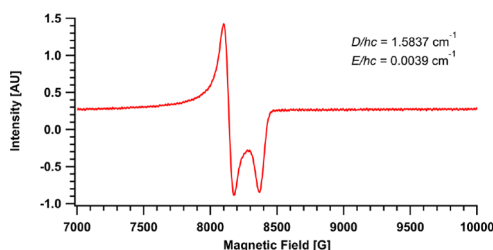


Figure 1. EPR spectrum obtained by irradiating **1** in an mTHF matrix (80 K).

The spectrum showed H_x and H_y lines at 8138 and 8363 G, respectively, at 9.40 GHz. The calculated zero-field splitting

parameters D/hc and E/hc were 1.5837 and 0.0039 cm^{-1} , respectively.⁸ The D/hc value of **3**² is similar to those of triplet 2-(λ^1 -nitreno)-1,3-dioxo-2,3-dihydro-1H-indene-2-carbonitrile (1.57 cm^{-1})⁹ and triplet methylnitrene (1.595 cm^{-1}) and its derivatives.¹⁰

Furthermore, Wentrup and co-workers have demonstrated a linear correlation between the calculated spin densities of triplet nitrenes and measured D/hc values, and **3**² follows the same trend, with a calculated spin density of 1.81 on the N atom (Supporting Information (SI)).¹¹

Because the formation of stable photoproducts or short-lived diradicals cannot be determined by EPR spectroscopy, the photoreactivity of **1** was studied in argon matrices using IR spectroscopy. Irradiation ($\lambda = 300$ – 400 nm) of **1** in an argon matrix resulted in the complete depletion of the IR bands for **1** at 2113, 1776, 1758, 1744, 1725, and 1268 cm^{-1} . Concurrently, new bands formed at 2238, 1817, 1788, 1754, 1708, 1697, 1692, 1600, 1595, 1566, 1250, 1187, 1135, 1070, 1059, 1021, 1002, 862, 764, 722, and 575 cm^{-1} (Figure 2), which were assigned to **3**², **3**, **4**, and **5** based on comparisons with their calculated (B3LYP/6-311++G(3df,3pd)¹²) and scaled (0.9604)¹³ IR spectra. The bands at 1754, 1708, 1187, and 722 cm^{-1} were assigned to **3**², as they match well with its calculated and scaled IR bands at 1755, 1719, 1197, and 736 cm^{-1} . The bands at 1697, 1692, 1600, 1595, 1566, 1250, 1135, 1070, 1059, 1021, 1002, 862, and 764 cm^{-1} were assigned to **3** based on a comparison with its computed spectrum, which has major bands at 1681, 1670, 1566, 1560, 1533, 1205, 1163, 1086, 1039, 1032, 993, 837, and 752 cm^{-1} . The bands at 1817 and 1788 cm^{-1} were assigned to the carbonyl stretches in **4** based on its reported IR bands at 1818 and 1787 cm^{-1} ,¹⁴ with the additional band at 1768 cm^{-1} presumably resulting from matrix splitting. The carbonyl bands for **4** were calculated to be at 1802 and 1778 cm^{-1} , which corresponds well to the observed bands. Finally, we assigned the weak band at 2238 cm^{-1} to the CN stretching of **5**, which has been reported to be at 2236 cm^{-1} in argon matrices.¹⁵

To determine whether **3**², **3**, **4**, and **5** form concurrently from the same precursor or if **3**² serves as the precursor to **3**, **4**,

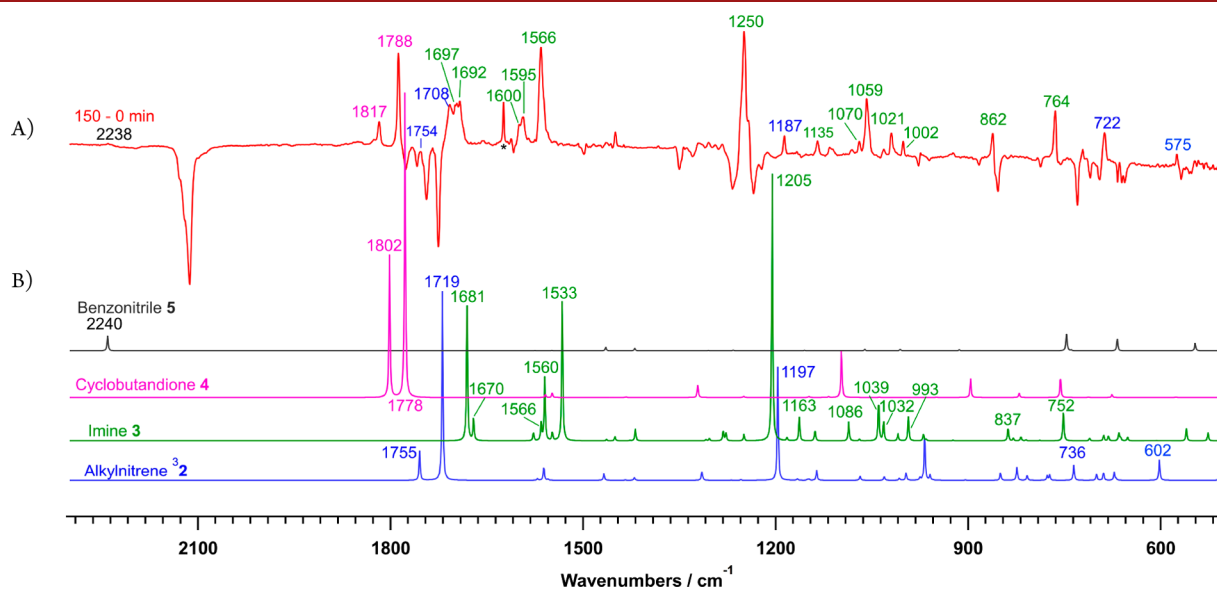


Figure 2. (A) Difference IR spectrum obtained by subtracting the spectrum of **1** before irradiation from the spectrum after 150 min irradiation. (B) Calculated (B3LYP/6-311++G(3df,3pd)) and scaled IR spectra of **3**², **3**, **4**, and **5**. *The band at 1624 cm^{-1} was attributed to matrix-isolated water.

and **5**, we compared the time profiles of the IR bands. Difference spectra were obtained by subtracting the IR spectrum obtained before irradiation from those collected after 15, 20, 30, and 40 min irradiation (Figure 3). As the IR

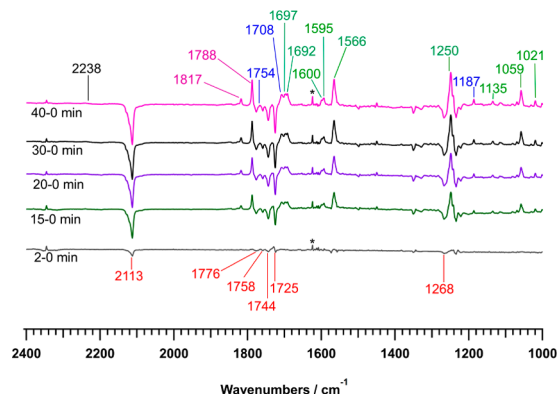


Figure 3. Difference IR spectra obtained by subtracting the IR spectrum of **1** from those obtained after 2, 15, 20, 30, and 40 min irradiation.

bands for **3**², **3**, **4**, and **5** formed concurrently at the same rate (Figure S14), we theorized that these photoproducts have a common precursor. Further, we employed absorption spectroscopy to support the formation of **3**², **3**, and **4** in mTHF matrices using a conventional setup.¹⁶ Using the absorption spectrum of **1** in an mTHF matrix before irradiation as the baseline, absorption spectra were recorded at regular time intervals following irradiation (LED, 400 ± 9 nm).

Upon irradiation, negative absorption was observed below 275 nm due to the depletion of **1** (Figure 4). However, a new

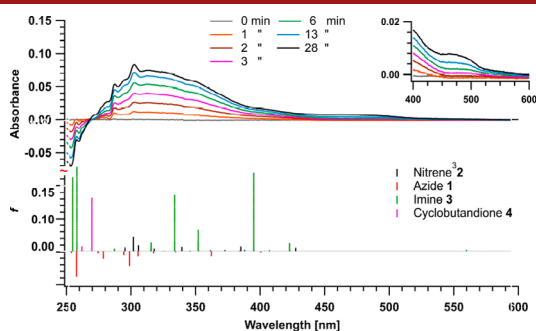


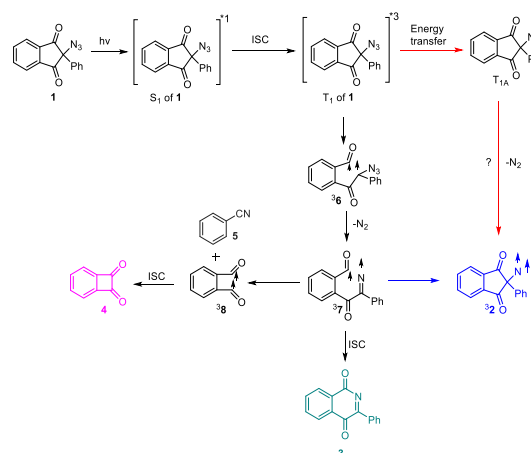
Figure 4. UV-vis difference spectra of **1** in mTHF (77 K) before and after irradiation, and calculated absorption spectra of **1**, **3**², **3**, and **4**.

broad absorption band was observed between 275 and 520 nm, which resembles the TD-DFT calculated spectra of **3**² and **3**. Because all the significant absorption bands of **4** overlap those of **1** and because **5** does not absorb above 250 nm, it is difficult to detect the absorption of these products in mTHF matrices. Therefore, the formation of **3**, **4**, and **5** was verified by HRMS and GC-MS. Similar results were obtained when the mTHF matrix of **1** was irradiated at 254 nm, indicating that the photochemistry is not wavelength dependent.

The EPR and absorption spectra demonstrate that irradiating **1** yields **3**², whereas the IR spectra verify that **3**, **4**, and **5** form concurrently with **3**². Thus, we propose that **3**², **3**, **4**, and **5** form simultaneously following α -cleavage of **1** to yield **3**⁶ (Scheme 3). However, we cannot exclude the

possibility that **3**² is formed through energy transfer at the exact same rate as **3**, **4**, and **5** are formed from **3**⁶ via α -cleavage of **1**.

Scheme 3. Proposed Mechanism for Forming **3**², **3**, **4**, and **5**



To support the proposed mechanism, DFT calculations were performed using Gaussian16 at the B3LYP level of theory with the 6-31+G(d) basis set.^{12,17} The ground state (S_0) of **1** was optimized, and TD-DFT calculations gave the vertical excitation energy of the first singlet excited state (S_1) and T_1 of **1**, which were located 70 and 62 kcal/mol, respectively, above S_0 . The optimized T_1 of **1** was located 55 kcal/mol above its S_0 , which is somewhat lower than the TD-DFT-calculated energy (Figure 5). Furthermore, spin density calculations on the T_1 of **1** showed that the spin densities are concentrated on the oxygen atoms of the C=O groups (0.42 each).

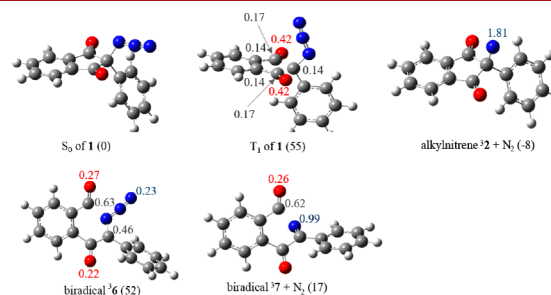


Figure 5. DFT (B3LYP/6-31+G(d)) optimized structures of **1**, T_1 of **1**, **3**², **3**⁶, and **3**⁷. Numbers in parentheses are the energies (kcal/mol) relative to the S_0 of **1**. Numbers near atoms are computed spin densities (red: on O; gray: on C; blue: on N).

Spin density calculations on the optimized structure of **3**² revealed spin localization on the N atom. The geometry of the open-shell singlet configuration ($^1\mathbf{2}$) was optimized using DFT calculation with the broken-symmetry method.¹⁹ The total spin $\langle S^2 \rangle$ value of 1.0061 suggested significant spin contamination, so we performed CASPT2 calculations on a similar alkylnitrene to better estimate the singlet–triplet gap (SI). The estimated singlet–triplet gap of ~32 kcal/mol strongly suggested that **3**² is unlikely to decay by intersystem crossing (ISC). Optimization of **3**⁶ demonstrated that it contains benzoyl and benzyl carbon-centered radicals, which was verified by the spin density calculations, as the unpaired

spins were mainly localized on the C atoms adjacent to the phenyl rings. Similarly, optimization of 37 revealed that both the imine and benzoyl radical moieties are conjugated to the adjacent phenyl rings. Furthermore, spin density calculations revealed that the unpaired spins are mainly located on the imine nitrogen and benzoyl carbon atoms (Figure 6). The

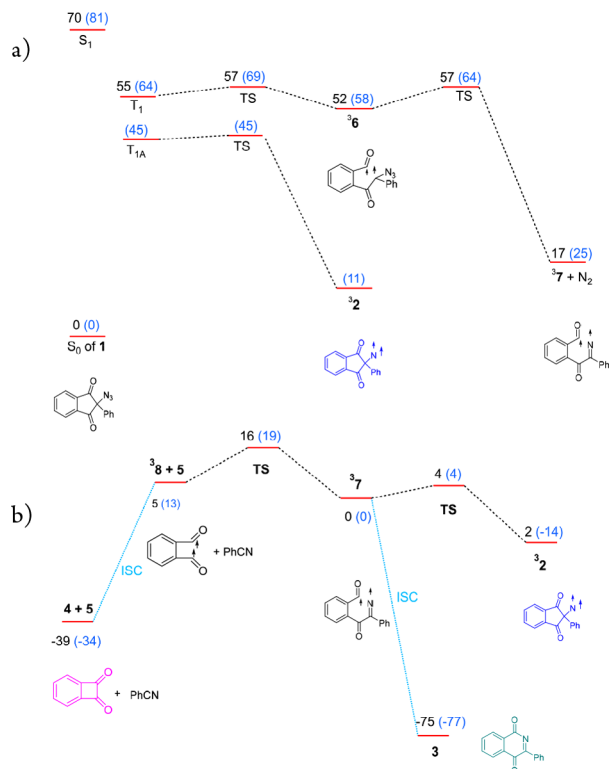


Figure 6. Calculated stationary points on the triplet energy surface of 1 forming (a) 37 and (b) 32 , 3, 4, and 5. Energy values (kcal/mol) calculated using B3LYP/6-31+G(d) and ω B97XD/6-31+G(d) are represented in black and blue, respectively.

energy of the optimized structure of 17 was similar to that of 37 , with a total spin (S^2) value of 0.9729. Despite this large spin contamination, it is reasonable to expect efficient ISC from 37 , as the singlet–triplet gap is small.

Figure 6 displays the calculated stationary points (B3LYP/6-31+G(d)) on the triplet surface of 1 for the formation of 32 , 3, 4, and 5. The calculated barrier for α -cleavage of the T_1 of 1 to form 36 is 2 kcal/mol. Similarly, the computed barrier for nitrogen molecule extrusion from 36 is small (5 kcal/mol). The calculated barrier for 37 to form 32 is only 4 kcal/mol, whereas that for 37 to cleave to form 5 and 38 is somewhat larger (16 kcal/mol). Therefore, it can be theorized that 37 undergoes ISC to form 3, 4, and 5 and that the ISC rate is comparable to the formation rate of 32 . As we were unable to optimize the T_{1A} of 1 using B3LYP, we used a long-range-corrected functional ω B97XD¹⁸ with the 6-31+G(d) basis set. The T_{1A} of 1 was located 45 kcal/mol above its S_0 , and the calculated barrier for forming 32 was less than 1 kcal/mol. The stationary points on the triplet surface of 1 showed similar trends using this theory and B3LYP (Figure 6), except for the energy of the T_1 of 1; however, B3LYP tends to underestimate the energies of triplet ketones with (n,π^*) configuration.^{6c} The ω B97XD-computed IR and absorption spectra of 32 , 3, 4, and 5 are similar to those obtained with B3LYP (Figures S26–S29).

Thus, we have demonstrated that α -cleavage of ketones with α -azido substituents is feasible in cryogenic matrices. This method can serve as a tool for forming heterocyclic compounds and potentially triplet alkylnitrenes. Forming triplet alkylnitrenes is challenging because the direct photolysis of alkyl azides does not produce the corresponding triplet alkylnitrenes but rather imine products, either through concerted reactions on the singlet excited state surface of the alkyl azides or through the formation of singlet alkylnitrenes.²⁰ If singlet alkylnitrenes are formed, they generate products faster than ISC to their triplet configuration occurs. Therefore, triplet alkylnitrene formation is generally limited to the triplet sensitization of alkyl azides. In our previous work on α -azidoacetophenone in argon matrices, α -cleavage could not compete with energy transfer to form triplet alkylnitrenes.^{6a} We theorize that energy transfer in 1 is less efficient than that in α -azidoacetophenone because the sensitizer moiety in 1 has a significantly lower triplet energy than the ketone chromophore in α -azidoacetophenone (74 kcal/mol), allowing α -cleavage to occur effectively at cryogenic temperatures.^{6a,c}

In conclusion, 1 undergoes α -cleavage in argon matrices because the rearrangement of 36 into 37 is sufficiently efficient to compete with the reformation of the initial radical pair of 1. Thus, α -cleavage at cryogenic temperatures can potentially be used for the formation of intermediates including triplet alkylnitrenes and heterocyclic products.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.0c02794>.

Experimental procedures, characterization of azide 1, theoretical calculations, argon and mTHF matrices (PDF)

Accession Codes

CCDC 1970115 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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