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Photolysis of α-Azidoacetophenones: Trapping of Triplet Alkyl Nitrenes in Solution

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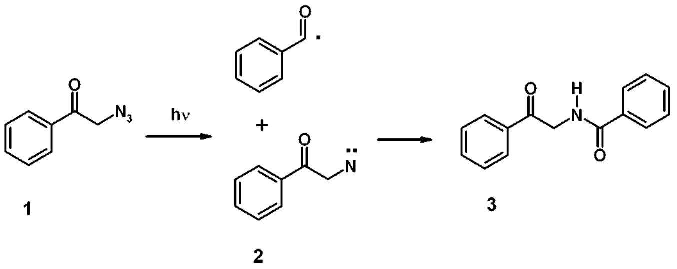
ABSTRACT



Selective excitation of the ketone chromophore in α-azidoacetophenones, 1, leads to intramolecular triplet energy transfer to the azido group, which forms the corresponding triplet alkyl nitrene, 2. Azides 1 also undergo α-cleavage to form benzoyl and methyl azido radicals in competition with nitrene formation. Thus the major photoproduct, 2-benzoylamino-1-phenylethanone, 3, comes from trapping of 2 with a benzoyl radical. This appears to be the first observation of bimolecular trapping of triplet alkyl nitrenes in solution.

Upon irradiation or thermal activation, alkyl azides rearrange with loss of nitrogen to form imine derivatives, possibly through nitrene intermediates. However, there are only a few examples where products have been isolated, which could be attributed to the decomposition of alkyl azides into alkyl nitrene intermediates.[1] This has led to the view that the rearrangement of the alkyl azide takes place not through a singlet nitrene intermediate but directly from the excited state of the azide.[2] More recently, physical measurements have been reported that support the existence of triplet alkyl nitrenes in the gas phase and in matrices.[3]

We set out to study the reactivity of triplet alkyl azides in solution, with the intention of intercepting triplet alkyl nitrenes in bimolecular reactions. Triplet alkyl nitrene is presumably the ground state, as triplet methyl nitrene is 38.6 kcal/mol lower in energy than singlet methyl nitrene.[4] Furthermore, a spin barrier prohibits the triplet nitrene from rearranging to a singlet imine product, whereas there is no such restriction on the singlet nitrene. Triplet alkyl nitrene can therefore be expected to be longer-lived than the singlet and thus easier to intercept by chemical reactions.

We selected α-azidoacetophenone derivatives for this study since they contain an intramolecular triplet sensitizer, which ensures efficient formation of the triplet alkyl nitrene by bypassing the singlet nitrene intermediate (Figure 1). The UV spectra of azides **1** trail out to 365 nm due to the

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

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

(3) (a) Ferrante, R. F. *J. Chem. Phys.* **1987**, *86*, 25. (b) Chapell, E. L.; Engelking, P. C. *J. Chem. Phys.* **1988**, *89*, 6007. (c) Carrick, P. G.; Brazier, C. R.; Bernath, P. F.; Engelking, P. C. *J. Am. Chem. Soc.* **1987**, *109*, 5100. (d) Carrick, P. G.; Engelking, P. C. *J. Chem. Phys.* **1984**, *81*, 1661. (e) Radziszewski, J. G.; Downing, J. W.; Jawdosiuk, M.; Kovacic, P.; Michl, J. *J. Am. Chem. Soc.* **1985**, *107*, 594. (f) Barash, L., Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1967**, *89*, 3931. (b) Wasserman, E.; Smolinsky, G.; Yager, W. A. *J. Am. Chem. Soc.* **1964**, *86*, 3166. (g) Smolinsky, G.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 3220.

(4) (a) Richards, C., Jr.; Meredith, C.; Kim, S.-J.; Quelch, G. E.; Schaefer, H. F., III. *J. Chem. Phys.* **1994**, *100*, 4819. (b) Demuynck, J.; Fox, D. J.; Yamaguchi, Y.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1980**, *102*, 6204. (c) Nguyen, M. T.; Sengupta, D.; Ha, T. K. *J. Phys. Chem.* **1996**, *100*, 6499. (d) Nguyen, M. T. *Chem. Phys. Lett.* **1985**, 290.

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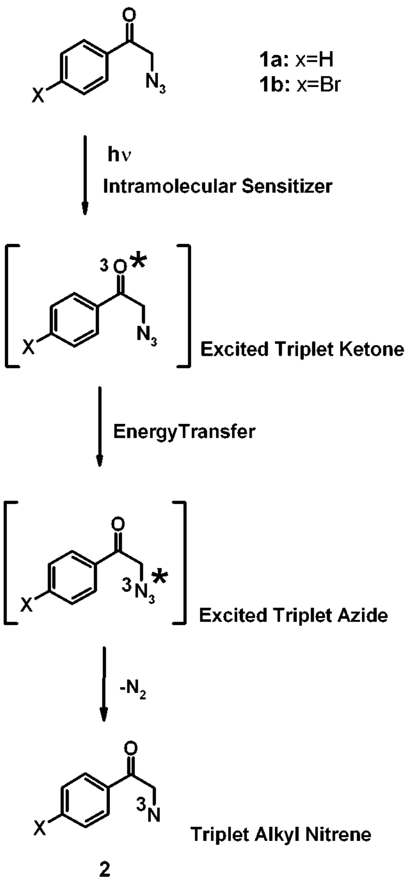
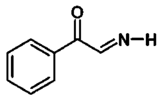


Figure 1. Intramolecular sensitization in azide **1**.

absorption of the aryl ketone chromophore, whereas the UV absorption spectra of simple nonconjugated alkyl azides exhibit only a weak band around 285 nm.[5] Thus, by irradiating azides **1** with a light source above 300 nm, it can be ensured that the ketone chromophore absorbs most of the light. We anticipate the intersystem crossing from the singlet manifold to the triplet state in azides **1** to be similar to the analogous acetophenone. The intersystem crossing from the singlet to the triplet excited state in acetophenone is of the order 10^{11} s^{-1}, and the quantum efficiency approximates unity.[6] Furthermore, we expect to observe reactivity mainly from the triplet manifold of the azido group since Wagner et al. have shown that phenyl ketones are efficiently quenched by intramolecular γ-azido groups.[7]



2-imino-1-phenyl-ethanone

The thermal decomposition of azide **1a** yields 2-imino-1-phenyl-ethanone, presumably via a singlet nitrene intermediate that undergoes a 1,2 H shift.[8] We do not expect to observe any 2-imino-1-phenyl-ethanone formation upon irradiation, since 1,2 H shifts are not allowed in the triplet manifold.

Azides **1** were photolyzed at ambient temperature in toluene under argon. Preparative photolysis of azide **1a** yielded one major product, 2-benzoylamino-1-phenylethanone (**3a**, 73%), and acetophenone (**9a**, 15%) plus small amounts of 2-benzylamino-1-phenylethanone (**4a**), *N*-benzyl-*N*-(2-oxo-2-phenylethyl)benzamide (**5a)**, benzaldehyde (**6a**), 1,2-diphenylethanone (**7a**), 1,2-diphenylethane-1,2-dione (**8a**), and 1,4-diphenyl-1,4-butadione (**10a**) (Figure 2). The major product, **3a**, was isolated and characterized using spectroscopy and crystallography.[9] All of the other products were characterized by injecting authentic samples in a GCMS. From the product study, it is apparent that azide **1a** undergoes α-cleavage to form a benzoyl radical in competition with nitrene formation. Benzoyl radicals do not readily abstract H atoms from appropriate solvents but are quenched rapidly by molecular oxygen.[10] Similarly, interception of a benzoyl radical by triplet nitrene **2a** yields radical **12a** (see Figure 3), which can abstract an H atom from toluene to form the major product **3a** and a benzyl radical. Product **5a** is formed when radical **12a** combines with a benzyl radical. The minor product **4a** comes from nitrene **2a** reacting with a benzyl radical. Products **6a**−**8a** result from the benzoyl radical

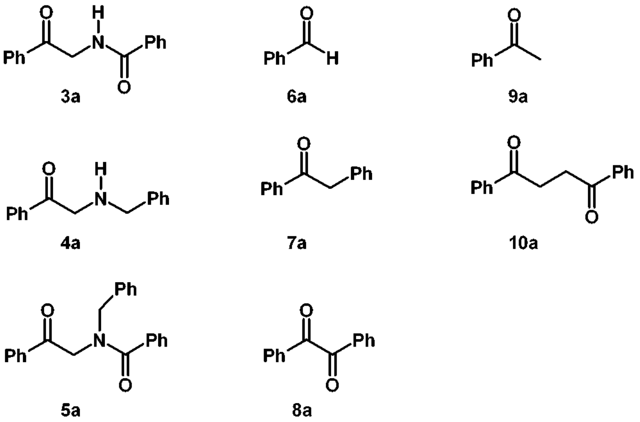


Figure 2. Products from photolysis of azide **1a**.

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[5] Reiser, A.; Wagner, H. M. *Chemistry of the Azido Group*; Patai, S., Ed.; John Wiley & Sons: London, 1971.

[6] (a) McGarry, P. F.; Doubleday, C. E., Jr.; Wu, C.-H.; Stabb, H. A.; Turro, N. J. *J. Photochem. Photobiol. A* **1994**, *77*, 109. (b) Lamola, A. A.; Hammond, G. S.; *J. Chem. Phys*. **1965**, *43*, 2129. (c) Borkman, R. F.; Kearns, D. R. *Chem. Commun*. **1966**, *14*, 446.

[7] Wagner, P. J.; Scheve, B. J. *J. Am. Chem. Soc*. **1979**, *101*, 378.

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

[9] (a) The ^{1}H NMR, IR, and MS spectra of **3a** are identical to those reported. Demeuov, N. B.; Akhmedzhanova, V. I.; Moldagulov, M. A.; Shakirov, R. S.; *Chem. Nat. Compd. (Engl. Transl.)* **1998**, *34*, 484. (b) Crystallographic data for the structure reported is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K. as supplementary publication no. CCDC-1557621.

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

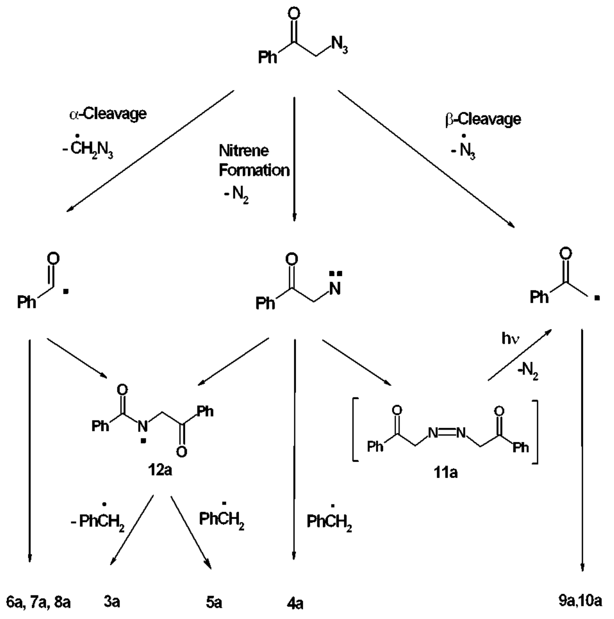

Figure 3. Possible reaction pathways for azide **1a** in toluene.

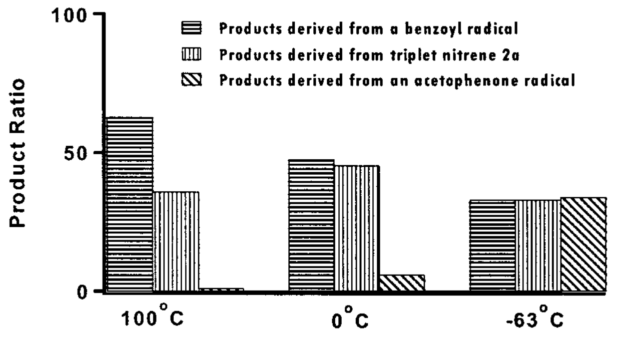

Figure 4. Product ratio from photolysis of azide **1a** at different temperature.

reacting with the solvent or itself. The product ratio indicates that nitrene **2a** does not abstract H atoms efficiently from the solvent and is therefore similar to triplet phenyl nitrenes that dimerize to form azo compounds rather than abstract H atoms from typical solvents or undergo rearrangement.[11] We did not isolate the corresponding azo dimer (**11a**, see Figure 3) of nitrene **2a**, but we speculate that **9a** and **10a** are secondary photoproducts from photolysis of **11a** and that under our experimental conditions **11a** is not photostable. It is, however, also possible that azide **1a** undergoes *β*-cleavage to form acetophenone and azide radicals, which can then yield compounds **9a** and **10a**.

We investigated how temperature affects the product ratio. As the temperature of the photolysis is lowered, **10a** becomes more predominant in the product mixture, as well as **9a**, whereas at higher temperatures **7a** and benzaldehyde are more prevalent. In Figure 4, the percent of products coming from triplet nitrene **2a**, benzoyl, and acetophenone radicals is plotted at 100, 0, and −63 °C. Since benzoyl radical-based products are favored at higher temperatures the α-cleavage must have a larger activation energy than the energy transfer leading to formation of nitrene **2a**. At lower temperatures when less benzoyl radical is formed to trap nitrene **2a**, more **9a** and **10a** are formed, which suggests that these products come from nitrene **2a**, unless the direct *β*-cleavage of **1a** has an even lower activation energy than either the α-cleavage or internal energy transfer.

We studied the photochemistry of azide **1b** to verify that α-azidoacetophenone derivatives generally undergo α-cleavage in competition with nitrene formation. Preparative photolysis of azide **1b** at ambient temperature yielded products **3b** and **9b** (see Figure 5) in the ratio of 9:1, indicating that the *p*-bromo group on the phenyl ring does not affect the photochemistry significantly.

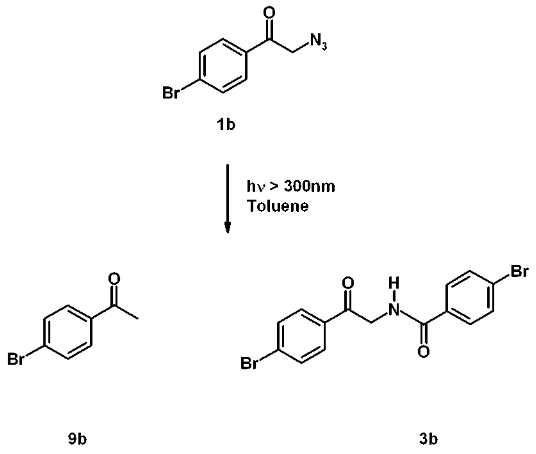

Figure 5. Products from photolysis of azide **1b**.

In conclusion, photolysis of α-azido acetophenone leads to intramolecular energy transfer to the azido group as well as α-cleavage to form benzoyl radicals. Presumably, the triplet excited azido group fragments to a triplet alkyl nitrene and a nitrogen molecule. Since neither the triplet alkyl nitrene nor the benzoyl radical efficiently abstracts H atoms from the solvent, the triplet alkyl nitrene is intercepted by the benzoyl radicals. To the best of our knowledge this is the first time that triplet alkyl nitrenes have been intercepted in bimolecular reactions in solution. We are further investigating the triplet reactivity of alkyl azides and are currently undertaking studies to detect the triplet nitrene intermediates directly with laser flash spectroscopy.

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[11] (a) Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 5228. (b) Marcinek, A.; Levya, E.; Whitt, D.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 8609. (c) Poe, R.; Schnapp, K.; Young, M. J. T.; Grayzar, J.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 5054.

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Supporting Information Available: Spectroscopic data for characterization of **1** and **3**, and the X-ray structure of **3a**. This material is available free of charge via the Internet at http://pubs.acs.org

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