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Communications to the Editor

Reactions of Oxaziridines Initiated by n,π^* Triplet States of Photosensitizers[1]

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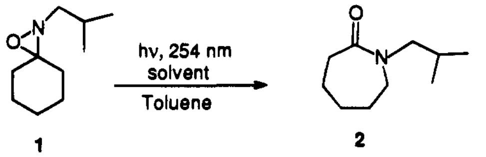
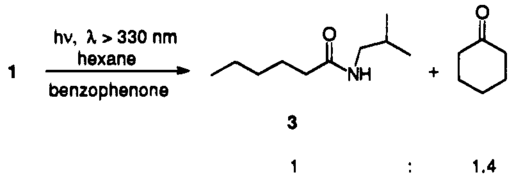
The photoinduced rearrangements of oxaziridines continue to command attention because of the successful utilization of this chemistry in synthesis.[2] We recently reported on the aryl-sensitized photoisomerization of *N*-alkyl spiro oxaziridines to lactams, as exemplified by the toluene-sensitized transformation of 2-isobutyl-1,2-oxazaspiro[2.5]octane (**1**) to the ring-expanded lactam, **2** (eq 1).[3] Because of the apparently endothermic nature of a vertical singlet−singlet energy transfer process involving the aryl π,π^* singlet state and the oxaziridine chromophore,[4] we proposed that "nonvertical" singlet energy transfer[6] was responsible for this chemistry. As part of this work, and in agreement with previous reports,[7] we observed that the oxaziridine could also be photosensitized with the classical triplet sensitizer, benzophenone. However, as had been noted by earlier workers, photosensitization with benzophenone did not afford the lactam but rather the ring-opened *N*-isobutylcaproamide, **3** (eq 2)[8] (in addition to cyclohexanone). Upon considering this observation, it seemed unlikely that the oxaziridine triplet would lie below that of benzophenone ($E_T = 69$ kcal/mol),[9] and we again found ourselves searching for a mechanism for photosensitization other than vertical (e.g., triplet−triplet) energy transfer. *We now report that the chemistry shown in eq 2 results from the involvement of ketyl radicals, formed during the photolysis of ketone n,π^* triplet sensitizers.*

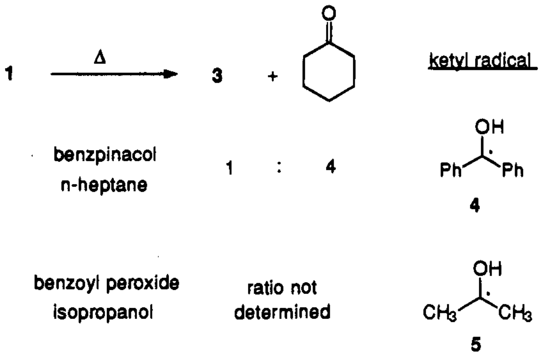


(1)



(2)

Scheme 1



To elucidate the mechanism of the benzophenone sensitization we first explored whether the carbonyl group of the sensitizer was a requirement by photolyzing a mixture of **1** and triphenylene[10] in hexane using light absorbed solely by the aromatic hydrocarbon ($\lambda = 300$ nm). No caproamide was formed though there was significant conversion to lactam resulting from singlet sensitization. With this observation in hand we next examined the importance of the sensitizer having a lowest lying n,π^* triplet excited state by taking advantage of the fact that acetophenone's lowest lying triplet state is known to be n,π^* in hexane and π,π^* in acetonitrile.[11] In fact, though photolysis of a mixture of **1** and acetophenone in hexane[12] did produce a mixture of **3** and cyclohexanone, no reaction was observed when the analogous photolysis was conducted in acetonitrile. Confirmation that this was not a solvent effect was provided by photolyzing **1** in hexane with *p*-methoxyacetophenone, a compound known to have a lowest lying π,π^* triplet excited state in both polar and nonpolar solvents.[11] Again there was no evidence for the formation of the amide and cyclohexanone, consistent with the requirement for an n,π^* ketone triplet for sensitization.

Since it has been shown that alkoxy radicals may be used as a model for the n,π^* triplet excited state of ketones,[13] we subjected **1** to conditions known to generate the *tert*-butoxy radical (refluxing an *n*-heptane solution of *tert*-butyl peroxide). There was no evidence for the formation of **3** or cyclohexanone. As an alternative we focused on the formation of ketyl radicals from the $^3n,\pi^*$ state by hydrogen atom abstraction since there is precedent for such species to be involved in "chemical sensitization" as the source of what has otherwise been thought to be photosensitization chemistry. Thus, it has been demonstrated that such radicals can reduce aryl *N*-alkylimines by hydrogen atom transfer.[14] Following the earlier work, a mixture of benzpinacol and **1** was refluxed in *n*-heptane so as to produce the diphenylketyl radical (**4**) in the presence of the oxaziridine (Scheme 1). Conversion to **3** and cyclohexanone was observed. In addition, we generated the ketyl radical **5** in the presence of **1**, by refluxing a 2-propanol solution of benzoyl peroxide, and

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[1] Organic Photochemistry. 109. Part 108: Morrison, H.; Agyin, K.; Xiao, C. *Pure Appl. Chem.* **1995**, *67*, 111−116. Part 107: Post, A. J.; Nash, J. J.; Love, D. E.; Jordan, K. D.; Morrison, H. *J. Am. Chem. Soc.* **1995**, *117*, 4930−4935. Presented, in part, at the 3rd International Conference on Solar Energy Storage and Applied Photochemistry, January 8−14, 1995, Cairo, Egypt.

[2] Aubé, J.; Hammond, M.; Gherardini, E.; Takusagawa, F. *J. Org. Chem.* **1991**, *56*, 499−508.

[3] Post, A. J.; Nwaukwa, S.; Morrison, H. *J. Am. Chem. Soc.* **1994**, *116*, 6439−6440.

[4] Oxaziridines show end absorption in the UV; the λ_{max} is reported as 210 nm.[5]

[5] Kobayashi, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3467−3470.

[6] Michl, J.; Bonačić-Koutecky, V. *Electronic Aspects of Organic Photochemistry*; John Wiley & Sons, Inc.: New York, 1990; p 83.

[7] Oliveros, E.; Rivière, M.; Lattes, A. *Nouv. J. Chim.* **1979**, *3*, 739−752

[8] Amide has also been previously produced as a minor product in the direct photolysis of *N*-alkyl spiro oxaziridines in hydrogen atom donating solvents.[7]

[9] Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker, Inc.: New York, 1973; p 31.

[10] The triphenylene triplet energy of 67 kcal/mol closely approximates that for benzophenone.[9]

[11] Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Mill Valley, CA, 1991; pp 380−381.

[12] Ketone-sensitized photolyses were done using a medium-pressure mercury lamp with a uranium yellow filter ($\lambda > 330$ nm) between 0−10 °C. The oxaziridine, **1**, is inert under these conditions.

[13] Padwa, A. *Tetrahedron Lett.* **1964**, 3465−3469.

[14] Padwa, A.; Bergmark, W.; Pashayan, D. *J. Am. Chem. Soc.* **1969**, *91*, 2653−2660.

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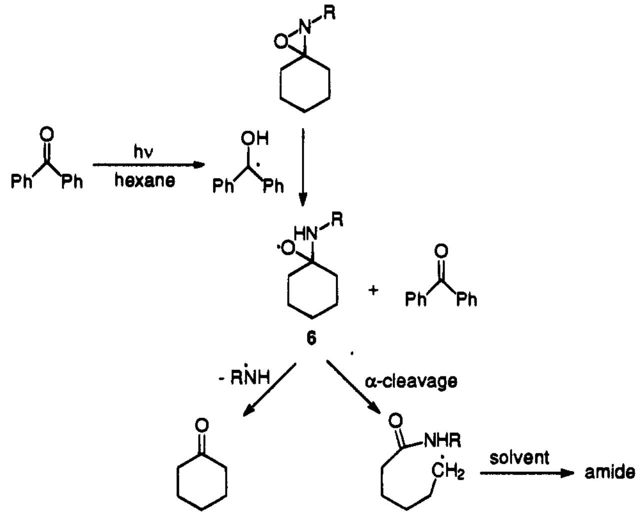
again observed the formation of **3** and cyclohexanone.[15] We conclude that ketyl radicals are indeed involved in the "triplet" sensitization chemistry of oxaziridines, with a proposed sequence for this photochemistry outlined in Scheme 2. *The novel step in this mechanism is the transfer of a hydrogen atom from a ketyl radical to the oxaziridine nitrogen with concomitant cleavage of the N−O bond to form an alkoxy radical* ***6***; we are unaware of an analogous hydrogen atom induced ring-opening reaction.[17,18] The radical **6** may then undergo β-scission by either losing an alkylamino radical to form cyclohexanone or undergoing ring cleavage, followed by hydrogen atom abstraction from the solvent, to give amide.

Scheme 2



We are exploring the potential extension of the hydrogen atom induced ring-opening reaction to other small ring heterocycles, while continuing our elaboration of the mechanisms involving the photoinduced rearrangements of oxaziridines.

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[15] Interestingly, cyclohexanone was formed in larger proportion by the independent generation of the ketyl radicals than in the aryl ketone sensitized photolyses. We attribute this to competitive thermal chemistry in the protic media. It is known that mild acid can degrade oxaziridines to the corresponding ketones,[16] and we have observed that refluxing 2-propanol or *n*-heptane/acetic acid solutions of **1** yields cyclohexanone, but with *no* evidence of amide formation. The amide (**3**) is stable in refluxing 2-propanol and is not decomposed by ketyl radicals.

[16] Davis, F. A.; Sheppard, A. C. *Tetrahedron* **1989**, *45*, 5703−5742.

[17] Radical **6** has also been suggested as an intermediate in the photolytic conversion of spiro oxaziridines to amides by direct photolysis.[7,8]

[18] There are interesting reports of the metal-catalyzed rearrangements of spiro oxaziridines to lactams[19] and metal-catalyzed homolysis of these substrates to amides.[16]

[19] Suda, K.; Sashima, M; Izutsu, M. Hino, F. *J. Chem Soc., Chem. Commun.* **1994**, 949−950.