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Generation of Carbenes via the Photosensitization of Spirodiaziridines with Ketones[1]

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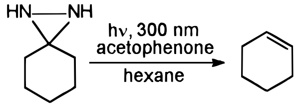
We recently reported on the aryl-sensitized isomerization[2] and the ketyl radical-initiated fragmentation[3] of *N*-alkylspirooxaziridines. As part of our continuing interest in the photosensitization of small ring heterocycles, we have extended these studies to an examination of the photosensitized chemistry of spirodiaziridines. We now report that the irradiation of these diaza heterocycles with ketone sensitizers leads to the formation of carbenes.

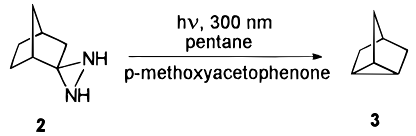
1,2-Diazaspiro[2.5]octane (**1**) was initially chosen as a prototypical diaziridine because its ring system is similar to that of the previously studied oxaziridines. The UV spectrum of **1** in acetonitrile indicates a high singlet energy with only end absorption past 200 nm and an extinction coefficient of 12 M^{-1} cm^{-1} at 254 nm (similar to oxaziridines). As anticipated, direct irradiation[4] of **1** in acetonitrile with 254 nm light for extended periods did not produce photoproducts in any significant quantities. Nor did photosensitization with several potential aromatic sensitizers, such as toluene, *N*,*N*-dimethylaniline, *p*-dicyanobenzene, and triphenylene.

This was not the case, however, when a ketone sensitizer was employed. Here, facile photochemistry was observed. Thus, photolysis of **1** with acetophenone in hexane yielded cyclohexene as the major photoproduct (eq 1). Since we had observed earlier that the carbonyl photosensitized cleavage of *N*-alkyl spirooxaziridines was restricted to sensitizers with lowest lying $^3n,\pi^*$ states (such as acetophenone in hexane)[5] we also explored the efficacy of sensitizers with lowest lying $^3\pi,\pi^*$ states, such as acetophenone in acetonitrile and *p*-methoxyacetophenone in hexane.[5] Both were also able to efficiently produce cyclohexene upon photolysis.

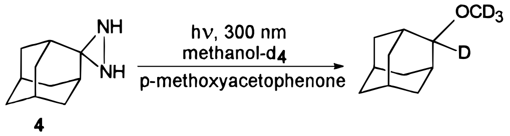


(1)

Given the facile photochemical fragmentation of *diazirines* to carbenes,[6] we considered a carbene to be the most likely intermediate in the spirodiaziridine reaction. Confirmation was provided by the photosensitization of spiro(bicyclo[2.2.1]heptane-2,3′-diaziridine) (**2**) and spiro(adamantane-2,3′-diaziridine) (**4**). When **2** was irradiated with *p*-methoxyacetophenone in hexane, nortricyclene (**3**) was formed as the only photoproduct (eq 2). It is known[7] that a carbene at C2 of norbornane preferentially inserts into C6 to form **3** as opposed to undergoing a 1,2 H shift to give norbornene. Likewise, analogous photolyses of **4** in either methanol or methanol-d_4 produced the carbene O−H insertion product, 2-methoxyadamantane (cf. eq 3),[8] in agreement with previous reports.[9]

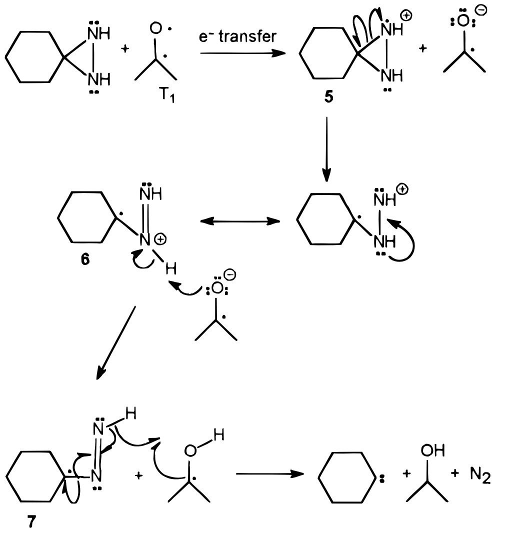


(2)



(3)

Scheme 1. Proposed Mechanism for the Formation of Carbenes by the Ketone-Photosensitized Fragmentation of Spirodiaziridines



A possible mechanism for the formation of carbenes from the spiro diaziridines by ketone photosensitization is outlined in Scheme 1. The initial step in this mechanism is electron transfer from the diaziridine to the carbonyl triplet excited state to form the diaziridine radical cation **5** and a ketyl. This step is well precedented in the extensive studies of the photoreduction of ketones by amines.[10] In the nonpolar hydrocarbon solvent one would expect these species to be closely associated as a tight ion pair. Homolysis within **5** would give a ring-opened radical cation **6** which might then be deprotonated by the ketyl to give **7**. Hydrogen atom abstraction by the hydroxycarbinyl radical, and loss of molecular nitrogen, would afford the carbene and the reduced ketone. In fact, reduced *p*-methoxyacetophenone was

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[1] Organic Photochemistry. 111. Part 110: Mohammad, T.; Morrison, H. *J. Am. Chem. Soc.*, in press.

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

[3] Post, A. J.; Morrison, H. *J. Am. Chem. Soc.* **1995**, *117*, 7812−7813

[4] All photolyses were carried out using a Rayonet Reactor (New England Ultraviolet Co.) equipped with a rotating turntable. The reactor was fitted with 16 254 or 300 nm lamps. Argon-degassed solutions were irradiated in quartz (254 nm) or Pyrex (300 nm) photolysis tubes.

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

[6] For reviews, see: (a) Baron, W. J.; DeCamp, M. R.; Hendrick, M. E.; Jones, J., Jr.; Levin, R. H.; Sohn, M. B. In *Carbenes*; Moss, R. A., Jones, J., Jr., Eds.; Wiley: New York, 1973; Vol. 1. (b) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1968.

[7] Freeman, P. K.; George, D. E.; Rao, V. N. M. *J. Org. Chem.* **1964**, *29*, 1682−1684.

[8] Specific deuteration at C2 was readily determined by the absence of the characteristic proton resonance in the NMR spectrum.

[9] Morgan, S.; Jackson, J. E.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 2782−2783 and references therein.

[10] For a review, see: Cohen, S. G.; Parola, A.; Parsons, G. H., Jr. *Chem. Rev.* **1973**, *73*, 141−161.

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detected by GC−MS upon photosensitization of **1**; this ketone is *not* photoreduced in hexane upon direct irradiation in the absence of the diaziridine.[5] In addition, the evolution of a gas, presumed to be elemental nitrogen, was evident in this photolysis.

The lack of any available data in the literature for the oxidation potential of diazirines prevents a computation of the thermodynamics of the proposed electron transfer step. It should be noted that an alternative to the electron transfer mechanism would be hydrogen abstraction by the ketones which, after ring opening, would produce species **7** directly. The success of sensitizers having lowest lying π,π^* triplets, which are not normally effective as hydrogen abstracting reagents, leads us to favor the electron transfer mechanism at this time.[11]

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Supporting Information Available: Preparative procedures for **1**, **2**, and **4** and experimental details for the photochemical studies (12 pages).

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(11) It is interesting that *p*-dicyanobenzene is ineffective as a sensitizer. Using readily available reduction potentials in *acetonitrile* (−1.60 and −1.85 eV for *p*-dicyanobenzene and acetophenone, respectively),[12] and the appropriate excited state energies (99 kcal (*p*-dicyanobenzene singlet) and 74 kcal (acetophenone triplet)),[13] one can determine that electron transfer should be appreciably more favorable to the *p*-dicyanobenzene. Both potential mechanisms discussed within the text ultimately invoke hydrogen abstraction by the sensitizer to create **7**, either by homolytic or heterolytic pathways; the failure of the cyanoaromatic may lie in its relative inability to carry out this step.

(12) Meites, L.; Zuman, P. *CRC Handbook Series in Organic Electrochemistry*; CRC Press: Cleveland, OH, 1976; Vol. I, pp 314, 338.

(13) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker, Inc.: New York, 1973; pp 8, 11.