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Di-π-methane Reactions Promoted by SET from Electron-Donor Sensitizers

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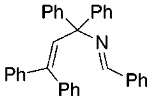
Studies of di-π-methane rearrangements of 1,4-unsaturated compounds have been the focus of several research efforts in organic photochemistry for many years. These reactions have proved to be very general for 1,4-dienes,[1,2] β,γ-unsaturated ketones,[1,3] and 1-aza-1,4-dienes.[1,4] We have reported recently the extension of the rearrangement to 2-aza-1,4-dienes.[5]

Investigations carried out for more than 30 years have established these rearrangements as the paradigm of processes that take place in the excited state, exclusively.[1−4] In all cases studied, biradical or concerted mechanisms have been proposed to account for the rearrangement processes. However, results from recent efforts in our laboratory have led to a drastic modification of these ideas. For example, irradiation of the 2-aza-1,4-diene **1**, using 9,10-dicyanoanthrathene (DCA) as an electron-acceptor sensitizer, yields the *N*-vinylaziridine **2** and the cyclopropylimine **3**.[5]



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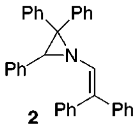

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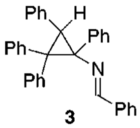

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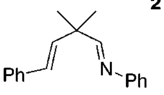
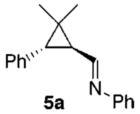


4a

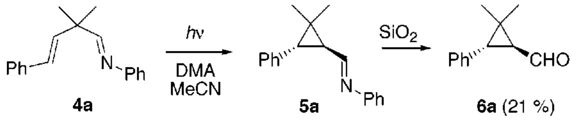


5a

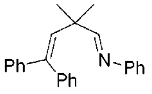
The formation of **2** and **3** represent the first examples of di-π-methane reactions (a 2-aza-di-π-methane reaction producing **2** and an aryl-di-π-methane process generating **3**) that take place via radical-cation intermediates. Furthermore, the formation of the heterocyclic product **2** is unprecedented in all of the studies carried out before on di-π-methane rearrangements. In addition, we found that 1-aza-1,4-dienes also undergo di-π-methane rearrangement promoted by excited-state electron transfer via radical-cation intermediates. Accordingly, **4a** affords the imine **5a** on irradiation using DCA as sensitizer.[6]

The aza-di-π-methane rearrangement (ADPM) of aza-1,4-dienes via radical-cations suggests the possibility that other radical-ion intermediates (e.g., radical-anions) could also be responsible for this rearrangement reaction. To test this proposal, the azadiene **4a**[6] was irradiated for 20 min, in acetonitrile, using *N*,*N*-dimethylaniline (DMA) as an electron-donor sensitizer.[7] The solvent and sensitizer were removed by vacuum distillation giving an oily residue, which was analyzed by ^{1}H NMR showing the presence of the cyclopropylimine **5a**. Separation of product mixture by column chromatography on silica gel afforded the aldehyde **6a**[8] (21%) resulting from hydrolysis of the imine **5a** (Scheme 1).

Scheme 1



The study was extended to 1-azadienes **4b**,[9] **4c**, and **4d**. Substrates **4c** and **4d** were synthesized by condensation of the corresponding aldehydes with aniline by using standard procedures. DMA-sensitized irradiation of these compounds under the conditions described above yielded, after silica gel column chromatography, the respective cyclopropane-carbaldehydes **6b**[10] (15%), **6c**[11] (15%), and **6d**[12] (11%). The isolated products are formed by hydrolysis of the primary cyclopropylimines photoproducts **5b**, **5c**, and **5d** (see Supporting Information for irradiation conditions).



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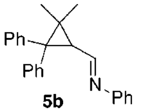
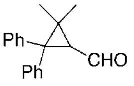
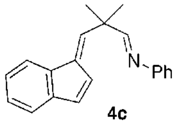


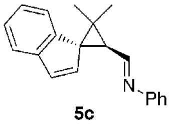
5b



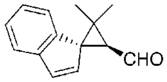
6b



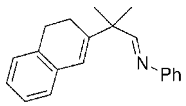
4c



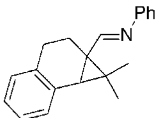
5c



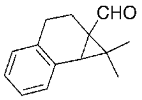
6c



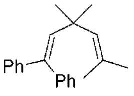
4d



5d



6d



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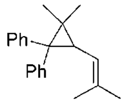

8

The results clearly show that 1-ADPM rearrangements of azadienes **4** occurs in DMA, a well-known electron-donor,[7] by single electron transfer (SET)-sensitized reactions. This interpretation is tentative since we previously observed triplet 1-ADPM reactivity of azadiene **4b** by using acetophenone as sensitizer.[9] Since the DMA has a triplet energy of 68.4 kcal/mol,[7] in these processes efficient energy transfer to the diphenylvinyl unit (triplet energy of ~53−62 kcal/mol)[13] is possible. The question that arises is whether the DMA-sensitized reactions take place via SET or

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[1] Zimmerman, H. E.; Armesto, D. *Chem. Rev.* **1996**, *96*, 3065−3112.

[2] (a) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 131−166. (b) Zimmerman, H. E. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1991; Vol. 11, pp 1−36.

[3] (a) Dauben, G. W.; Lodder, G.; Ipaktschi, J. *Top. Curr. Chem.* **1975**, *54*, 73−114. (b) Houk, K. N. *Chem. Rev.* **1976**, *76*, 1−74. (c) Schuster, D. I. In *Rearrangements in Ground and Excited States*; DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 232−279. (d) Demuth, M. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1991; Vol. 11, pp 37−109.

[4] (a) Armesto, D. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Soon, P.-S., Eds.; CRC Press: New York, 1995; pp 915−930. (b) Armesto, D. *EPA Newsl.* **1995**, *53*, 6−21.

[5] Armesto, D.; Caballero, O.; Amador, U. *J. Am. Chem. Soc.* **1997**, *119*, 12659−12660.

[6] Ortiz, M. J.; Agarrabeitia, A. R.; Aparicio-Lara, S.; Armesto, D. *Tetrahedron Lett.* **1999**, *40*, 1759−1762.

[7] Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401−449.

[8] Armesto, D.; Ortiz, M. J.; Romano, S. *Tetrahedron Lett.* **1995**, *36*, 965−968.

[9] Armesto, D.; Horspool, W. M.; Fernandez-Martin, J. A.; Perez-Ossorio, R. *J. Chem. Res. (S)* **1986**, 46−47.

[10] Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718−1727.

[11] Armesto, D.; Gallego, M. G.; Horspool, W. M.; Agarrabeitia, A. R. *Tetrahedron* **1995**, *51*, 9223−9240.

[12] Armesto, D.; Ortiz, M. J.; Romano, S.; Agarrabeitia, A. R.; Gallego, M. G.; Ramos, A. *J. Org. Chem.* **1996**, *61*, 1459−1466.

[13] Zimmerman, H. E.; Armesto, D.; Amezua, M. G.; Gannett, T. P.; Johnson, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 6367−6383.

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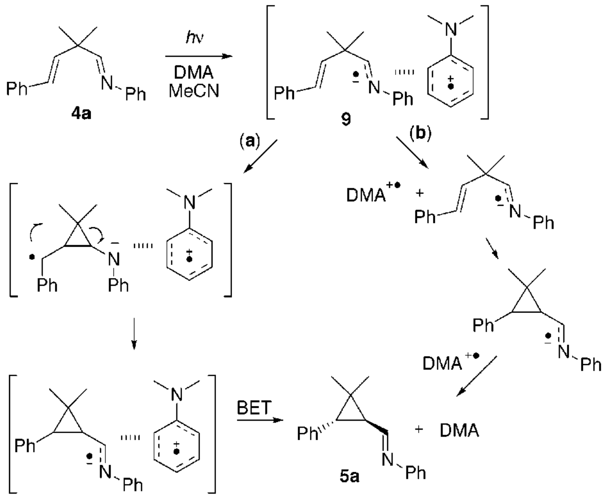
triplet energy-transfer mechanisms. To clarify this issue, azadienes **4** were irradiated for the same period of time, by using DMA in the nonpolar solvent hexane. Under this condition, radical-anion formation should not be favored. We observed that DMA-sensitized reactions of **4** occur in hexane to yield the corresponding cyclopropanecarbaldehydes **6a** (2%), **6b** (2%), and **6c** (4%). However, the yields of these processes are much lower than in the acetonitrile runs that afford 21% of **6a**, and 15% of **6b** and **6c**. These results support the proposal that radical-anions are involved as intermediates in photoreactions in acetonitrile. In the case of compound **4d**, the yields of aldehyde **6d** from the acetonitrile and hexane reactions were similar (ca. 11%), casting doubts again on whether this process occurs via SET or triplet energy sensitization.

In an attempt to obtain a more definite answer to this question, we searched for a substrate that would not undergo the di-π-methane rearrangement in the triplet excited-state manifold. With this goal in mind, the study was extended to the 1,4-diene **7**.[14] Numerous studies have demonstrated that triplets of acyclic 1,4-dienes do not undergo di-π-methane rearrangements.[1,2] The photochemical reactivity of **7** was studied earlier by Zimmerman and Pratt[14] who showed that it rearranges efficiently to yield the cyclopropane **8** on direct irradiation but that the process is very inefficient when benzophenone triplet sensitization is used. Therefore, compound **7** was considered to be a good candidate to test the possibility of promoting di-π-methane reactions by using electron-donor sensitizers. Irradiation of **7** in acetonitrile, for 3 h, by using DMA as a sensitizer, yielded cyclopropane **8** in 34% yield. Changing the solvent from acetonitrile to hexane does not modify significantly the efficiency (22%) of the process. However, when diene **7** was irradiated in hexane for 3 h, with benzophenone as sensitizer, the cyclopropane **8** was obtained in only 5% yield, in agreement with the earlier results.[14] Since the triplet energy of benzophenone (69.2 kcal/mol)[7] is comparable to the value reported for the DMA (68.4 kcal/mol),[7] both sensitizers should be able to transfer their triplet energy to the diphenylvinyl unit with the same efficiency. Therefore, the decrease in the yield of product observed in the reactions run in hexane, caused by changing the sensitizer from DMA to benzophenone, cannot be explained by less efficient triplet energy transfer from the benzophenone to the diene **7**. An alternative explanation could invoke the possible involvement of singlet energy transfer from the DMA to the diene **7**. However, this possibility seems unlikely since the energy of the diphenylvinyl singlet excited state (97.9 kcal/mol)[7] is considerably higher than the singlet excited state of DMA (88.8 kcal/mol).[7]

The above results lead to the conclusion that rearrangement of **7** to the cyclopropane **8** occurring in the reactions sensitized by DMA must take place via radical-anion intermediates. Considering that the C−N double bond in compounds **4** should be a better electron acceptor than the diphenylvinyl unit in **7** it is logical to assume that the rearrangement of **4** also occurs via similar ion-radical intermediates. A possible mechanism for these reactions is shown in Scheme 2 for compound **4a**. The absence of a solvent polarity effect on the efficiency of photoreactions of **4d** and **7** might be due to a very fast rearrangement of the radical-anion **9** within solvent cages (Scheme 2, path a). In cases in which this intermediate escapes from the cage before rearrangement occurs, a significant influence of the polarity of the solvent would have been observed. This is the situation in DMA-sensitized reactions of **4a**, **4b**, and **4c** (Scheme 2, path b).

Scheme 2



The results reported herein provide strong evidence in favor of the involvement of radical-anions in electron donor-sensitized 1-aza-di-π-methane rearrangements of azadienes **4** and also in the di-π-methane reaction of diene **7**. These observations open new lines of research in an area in which, due to the large number of studies carried out for more than 30 years, apparently there were very few things to uncover. Finally, photoreactions promoted by photoinduced electron transfer have became one of the main areas of research in organic photochemistry.[15] However, most of the studies in this field involve the generation of radical-cations using electron-acceptor sensitizers, while the photochemical production of radical-anions using electron-donor sensitizers has received less attention.[15] Our results, which demonstrate that these intermediates can participate in di-π-methane processes, could lead to an increased interest in these reactions. Further studies are in progress to determine the scope and synthetic applications of these reactions.

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Supporting Information Available: Experimental procedures for the synthesis of **4a**, **4c**, and **4d**, and for the irradiations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0164428

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[14] Pratt, A. C.; Zimmerman, H. E. *J. Am. Chem. Soc.* **1970**, *92*, 6259−6267.

[15] For a comprehensive review on electron-transfer processes, see: *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, 2001; five volumes.