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# The novel 1-aza-di-π-methane rearrangement of 1-substituted-1-aza-1,4-dienes promoted by DCA-sensitization

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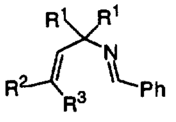
## Abstract

Irradiation of a series of *N*-substituted-1-aza-1,4-dienes, using DCA as an electron transfer sensitizer, leads to the formation of the corresponding cyclopropane derivatives, in the second example of a rearrangement of the di-π-methane type that takes place in the ground state of radical-cation intermediates. © 1999 Elsevier Science Ltd. All rights reserved.

Studies carried out on the photochemistry of 1,4-unsaturated systems for more than thirty years have shown that these compounds undergo unique and synthetically useful photoreactions. Examples of this are found in di-π-methane (DPM) rearrangements of 1,4-dienes [1a,2], oxa-di-π-methane (ODPM) photoreactions of β,γ-unsaturated ketones [1a,3,4] and aldehydes [1a], 1,3-acyl migration processes of β,γ-unsaturated ketones [3] and 1-aza-di-π-methane (1-ADPM) rearrangements of differently *N*-substituted 1-aza-1,4-dienes [1].



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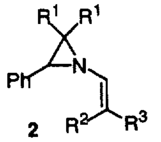
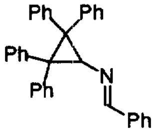


**2**

**1a, 2a**: $R^1 = R^2 = R^3 = Ph$
**1b, 2b**: $R^1 = Me, R^2 = Ph, R^3 = H$
**1c, 2c**: $R^1 = Me, R^2 = R^3 = $ 9-fluorenyl



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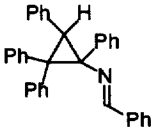

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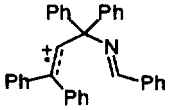

**5**

Within this area of research we recently reported [5] the discovery of a novel 2-aza-di-π-methane (2-ADPM) rearrangement promoted by triplet-sensitized irradiation of the 2-aza-1,4-diene **1a** that yields the vinylaziridine **2a** and the cyclopropylimine **3**. The formation of these two products was explained by a conventional biradical di-π-methane mechanism. This result is an important step forward in the study of the di-π-methane processes because it is the first example of a di-π-methane rearrangement that occurs *via* a three-membered ring heterocyclic biradical and brings about formation of a heterocyclic product. Perhaps the most surprising observation made in this study was that irradiation of compound **1a** using 9,10-dicyanoanthracene (DCA) as a SET-sensitizer leads to production of vinylaziridine **2a** and the cyclopropylimine **4** [5]. A

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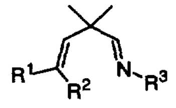
mechanism involving the initial generation of the radical-cation **5** was proposed to account for this transformation. This process represents the first example of a di-π-methane type rearrangement that takes place *via* radical-cation intermediates. The novel DCA-sensitized rearrangement reaction also occurs with the 2-aza-1,4-dienes **1b** and **1c** to afford the corresponding vinylaziridines **2b** and **2c**, respectively.

These observations suggested the possibility that other β,γ-unsaturated systems might also undergo novel SET-promoted rearrangements *via* radical-cation intermediates. Therefore, in an extension of this study aimed at probing the generality of this proposal, we have investigated the photochemical properties of other 1-aza-1,4-dienes, such as **6**. Preliminary results of this work which demonstrates that these substrates also undergo SET-sensitized rearrangement to form cyclopropane derivatives **7** are described below.

The syntheses of **6c-e** have been described previously [6,7,8]. Compounds **6a** and **6b** were prepared from 2,2-dimethyl-4-phenyl-3-butenal [9] by use of standard procedures. DCA-sensitized irradiation of **6a** for 7h leads to formation of the cyclopropylimine **7a** as shown by $^1$H NMR analysis of the crude photolysate.[1] Column chromatography (silica gel) of the reaction mixture yielded 2,2-dimethyl-4-phenyl-3-butenal (65%), *trans*-cyclopropanecarbaldehyde **8** (13%) [10], and unidentified highly polar material (15%).[2] The isolated aldehydes are formed by hydrolysis of the respective imines **6a** and **7a** during chromatography. This result demonstrates clearly that, like their 2-aza-1,4-dienes **1** analogs, 1-aza-1,4-dienes such as **6a** also undergo di-π-methane type radical-cation rearrangement reactions.



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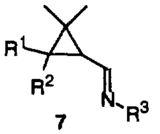
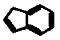
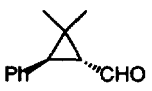


**7**

**6a, 7a**: R$^1$ = R$^3$ = Ph, R$^2$ = H
**6b, 7b**: R$^1$ = Ph, R$^2$ = H, R$^3$ = OMe
**6c, 7c**: R$^1$ = Ph, R$^2$ = H, R$^3$ = OAc
**6d, 7d**: R$^1$ = R$^2$ = Ph, R$^3$ = OAc
**6e, 7e**: R$^3$ = OAc, R$^1$ = R$^2$ = 



**8**

The mechanism shown in Scheme 1 accounts for the formation of **7a**. This involves the generation of the imine localized radical-cation intermediate **9** that bridges to give the cyclopropyl radical-cation **10**. Ring opening of bond (a) in **10** generates **11** which, by back electron transfer and biradical cyclization, yields **7a**. The alternative cleavage of bond (b) that would have yielded the vinylaziridine **13** is not observed probably because the resulting radical-cation **12** would be considerably less stable than intermediate **11** (Scheme 1).

Our attention was next directed at determining whether or not the reaction could be extended to other 1-aza-1,4-dienes in which the C=N bond would be less readily hydrolyzed thus facilitating the handling and isolation of starting materials and photoproducts. Our previous studies of the 1-ADPM rearrangement have demonstrated that β,γ-unsaturated oxime ethers [11] and oxime esters [1] rearrange efficiently on triplet sensitized irradiation and, furthermore, that the reactants and products of these processes are sufficiently stable to allow for their isolation by silica gel chromatography. Therefore, the study was extended to the oxime ether

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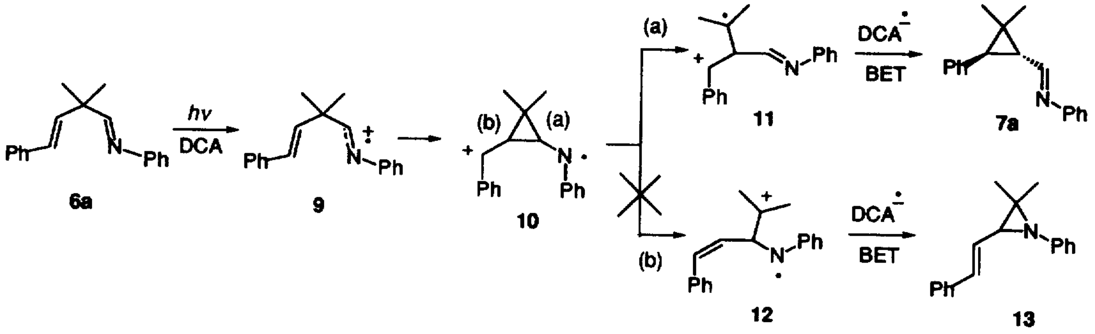
[1] The irradiations were carried out in acetonitrile in an immersion well apparatus with a Pyrex filter and a 400 W medium pressure Hg arc lamp using DCA as sensitizer. A vanadate filter was used to insure that all the light was absorbed by the DCA. Biphenyl was used as a co-sensitizer.

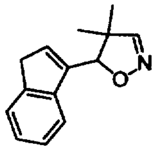
[2] The progress of the reactions was followed by thin-layer chromatography on silica gel and the irradiation was stopped when the formation of new products was observed. Attempts made at this preliminary stage to increase the yields of products resulted in a decrease in the percentage of recovered starting material without increasing the yields of products.

**6b** and the oxime acetate **6c**.



Scheme 1

DCA-sensitized irradiation of **6b** for 13 h afforded, after column chromatography on silica gel, recovered starting material (**6b**, 40%) and a new product that was identified by independent synthesis as the *trans*-cyclopropane derivative **7b** (10%) as a 1:1 mixture of C=N bond *E*/*Z*-isomers. Similarly, irradiation of the oxime acetate **6c** under these conditions for 2.5 h afforded, after chromatography, recovered starting material (**6c**, 65%) and the known [6] *trans*-cyclopropane derivative **7c** (12%). These results show that the novel 1-ADPM rearrangement promoted by electron-transfer sensitization can be extended to other imine derivatives.



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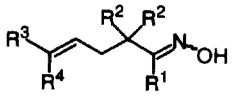

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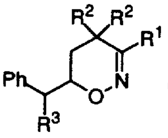

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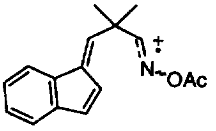

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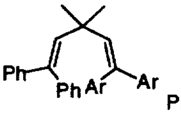

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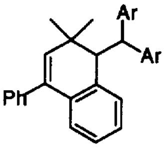

**19**

In qualitative terms the rearrangement reaction is considerably more efficient for the oxime acetate **6c** than for the oxime ether **6b**. As a result the photochemical reactivity of the oxime acetates was probed. Irradiation of **6d** [7] for 3 h under the same conditions used for **6a-c** afforded, after column chromatography on silica gel, recovered starting material (**6d**, 30%), the cyclopropane **7d** (25%) as a 1:2 mixture of *Z*:*E* isomers [7] and 30% of unidentified highly polar material. Likewise, DCA-sensitized irradiation of **6e** [8] for 1 h yields the cyclopropane derivative **7e** (16%) [8], the dihydroisoxazole **14** (18%) and recovered starting material (26%). The identity of **14** was established by comparison of its spectral data with those previously reported for similar compounds [12]. $^1$H NMR analyses of the crude photolysates show that the corresponding dihydroisoxazoles are not produced in the photoreactions of **6b-d**. It is still unclear at this point how **14** arises in SET-sensitized reaction of **6e** only. However, this cyclization process is similar to that observed by us in studies of the DCA-sensitized reaction of the γ,δ-unsaturated oximes **15** which afford the 5,6-dihydro-4*H*-1,2-oxazines **16** [13]. A possible mechanism to justify the formation of **14** could involve intramolecular electrophilic attack to the alkene unit in **17**, by the oxygen from the oxime localized radical-cation, followed by elimination of an acyl cation. This would be trapped by any of the radical anions present in the reaction medium.

The results obtained in this study show that the di-π-methane rearrangement of 1,4-unsaturated systems *via* radical-cations is not restricted to the 2-aza-1,4-dienes **1** but is extended to differently *N*-substituted 1-aza-

1,4-dienes **6**. This leads to the suggestion that other 1,4-unsaturated compounds, such as 1,4-dienes and β,γ-unsaturated ketones and aldehydes, that undergo di-π-methane rearrangements in the singlet and triplet excited state, might also rearrange in electron transfer sensitized reactions. In this regard it is worth mentioning that a study carried out by Zimmerman [14] on the photoreactivity of dienes **18** using electron acceptor sensitizers demonstrated that these compounds do not undergo radical-cation rearrangements of the di-π-methane type under these conditions but, instead, react to form benzhydryldihydronaphthalenes **19**. The operation of a cyclization pathway of this type has not been detected in our study with the azadienes **6**. However, the results reported by Zimmerman do not rule out the possibility that other 1,4-dienes with different types of substitution patterns could undergo rearrangement to form vinylcyclopropanes under SET-sensitized conditions.

We believe that the rearrangements of the di-π-methane type observed in the DCA-sensitized irradiations of 1-aza- and 2-aza-1,4-dienes are of importance because the di-π-methane process has been considered until now a paradigm of reactions that take place in the excited state manifold only. Our results show that rearrangements of this type can also occur in the ground-states of radical-cation intermediates. This opens the possibility of promoting di-π-methane type rearrangements by alternative thermal means.

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## References

[1] (a) Zimmerman HE, Armesto D. Chem. Rev. 1996; 96: 3065-3112. (b) Armesto D. CRC Handbook of Organic Photochemistry and Photobiology. New York: CRC Press, 1995: 915-930.
[2] Zimmerman HE. The Di-π-methane Rearrangement. In: Padwa A, editor. Organic Photochem. New York: Marcel Dekker, Inc., 1991; 11: 1-36.
[3] Schuster DI. Photochemical Rearrangements of β,γ-Enones. In: DeMayo P. editor. Rearrangements in Ground and Excited States. New York: Academic Press, 1980; 3: 167-279.
[4] Demuth M. Synthetic Aspects of the Oxadi-π-methane Rearrangement. In: Padwa A, editor. Organic Photochem. New York: Marcel Dekker, Inc., 1991; 11: 37-109.
[5] Armesto D, Caballero O, Amador U. J. Am. Chem. Soc. 1997; 119: 12659-12660.
[6] Armesto D, Horspool WM, Gallego MG, Agarrabeitia AR. J. Chem. Soc., Perkin Trans. 1 1992: 163-169.
[7] Armesto D, Horspool WM, Langa F, Ramos A. J. Chem. Soc., Perkin Trans. 1 1991: 223-228.
[8] Armesto D, Gallego MG, Horspool WM, Agarrabeitia AR. Tetrahedron 1995; 51: 9223-9240.
[9] van der Weerdt AJA, Cerfontain H. Tetrahedron 1981; 37: 2120-2130.
[10] (a) Armesto D, Ortiz MJ, Romano S. Tetrahedron Lett. 1995; 36: 965-968. (b) Armesto D., Ortiz MJ, Romano S, Agarrabeitia AR, Gallego MG, Ramos, A. J. Org. Chem. 1996; 61: 1459-1466.
[11] Armesto D, Ortiz MJ, Ramos A, Horspool WM, Mayoral EP. J. Org. Chem. 1994; 59: 8115-8124.
[12] Armesto D, Ramos A, Ortiz MJ, Mancheño MJ, Mayoral EP. Recl. Trav. Chim. Pays-Bas 1995; 114: 514.
[13] Armesto D, Austin MA, Griffiths OJ, Horspool WM, Carpintero M. Chem. Commun. 1996; 2715.
[14] Zimmerman HE, Hoffacker KD. J. Org. Chem. 1996; 61: 6526-6534.