## Communications

## Photochemical Ring Closure of 1-Tosyl-1,2-diarylethenes

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UV irradiation of 1,2-diarylethenes (**1a**, **2a**) leads to E-Z isomerization followed by conrotatory cyclization to the dihydroaromatic **3a**. When the irradiation is carried out in the presence of an oxidant, the dihydroaromatics **3** may produce good yields of the tricyclic aromatics **4**.<sup>1</sup>

This oxidative cyclization has been extensively used for the preparation of numerous compounds of type **4** in which Ar and Ar' are benzene rings (phenanthrenes). Nevertheless, its application to the synthesis of heterocycles has been rather limited.<sup>2</sup> This is probably due to either (1) the sensitivity of heterocycles, particulary electron-rich ones like pyrroles, to the oxidants necessary for the aromatization of the dihydro intermediates **3** or (2) the different  $\pi - \pi^*$  excited state distribution in heterocyclic diarylethenes relative to stilbenes.

Here we describe a novel strategy involving the introduction of an electron-withdrawing sulfonyl group in the starting diarylethenes **1** and **2**. The 1,2-diaryl-1-sulfonylethenes **1b** and **2b** are easily prepared stable crystalline solids which upon oxidative irradiation give good yields of sulfonyl tricyclic heterocycles **4b** without detectable desulfonylation. Unlike the sulfonyl compounds **1b** and **2b**, 1,2-diarylethenes with a pyrrole or thiophene ring and no stabilizing electron-withdrawing group are reported to be "very light sensitive, quickly becoming dark in room light".<sup>2a</sup> The tricyclic heterocycles **4a** may easily be obtained by reductive desulfonylation of the sulfonyl heterocycles **4b**.

Condensation of sulfone  $6a^3$  or benzyl tosyl sulfone  $(10)^4$  with *N*-(methoxymethylpyrrole)-2-carbaldehyde  $(5a)^3$  using NaOMe (50 equiv) in boiling MeOH gave the tosyl stilbenoids **7a** and **11** in 78% and 76% yield, respectively. (The stereochemistry about the central double bond of these stilbenoids, and all others prepared in this work, is unknown but is irrelevant for our purposes because UV irradiation induces rapid E-Z isomerization, affording the desired isomers for the photochemical cyclization.) Under the same conditions, condensation of sulfone **6b**<sup>3</sup> with pyrrolecarbaldehyde **5b**<sup>3</sup> led to a mixture of the

(4) Otto, R. B. Dtsch. Chem. Ges. 1880, 13, 1272.





desired tosylstilbenoid **7b** together with the acids resulting from partial hydrolysis of the esters by the equivalent of water released upon condensation. Reesterification was easily carried out by adding 23 equiv of thionyl chloride and refluxing for 1 h. This one-flask procedure allowed the isolation of an 89% yield of tosyl diester **7b**.

When these NaOMe-catalyzed condensations were tried on furan or thiophenecarbaldehydes, the tosyl stilbenoid yields were low or erratic. We believe that this was due to a Cannizzaro side reaction, to which less electron-rich aromatic aldehydes are prone. However, treatment of sulfones **6a** and **10** with BuLi (1.1 equiv) in THF at -78 °C, followed by sequential addition of thiophene-2-carbaldehyde or furan-2-carbaldehyde and HCl (10%) at -40 °C, allowed the isolation of alcohols **13** and **16** in 96 and 91% yield, respectively, as a mixture of diastereoisomers. Slow addition of 5 equiv of mesyl chloride over a cooled (-78 °C) solution of alcohols **13** or **16** and Et<sub>3</sub>N (10 equiv) in CH<sub>2</sub>Cl<sub>2</sub>, followed by stirring at room temperature, yielded the sulfonyl stilbenoids **14** (88%) and **17** (97%).

UV irradiation<sup>5</sup> of water-cooled solutions of tosylstilbenoids **7a,b**, **14**, and **17** in ethanol containing catalytic iodine led to the corresponding tosylphenanthrenoids in 46–89% yield. Alternatively, the cyclization conditions of Katz et al.,<sup>6</sup> involving the addition of 1 equiv of iodide and excess propylene oxide (CAUTION: propylene oxide is carcinogenic), gave consistently good yields (82–90%) of the corresponding tosylphenanthrenoids. While irradiation of stilbenoid **11** under Katz's conditions afforded a 90% yield of the desired phenanthrenoid **12a**, we were not able to isolate any sizeable amount of **12a** using O<sub>2</sub>/catalytic I<sub>2</sub> as oxidants.

Finally, the tosyl group was removed either simply with magnesium in methanol<sup>7</sup> or, generally with better, less erratic yields, with sodium dihydronaphthalenidyl at -78 °C.<sup>8</sup>

In conclusion, we have developed a simple, efficient, three- or four-step synthesis of heterocyclic phenanthrenoids. Its application to the preparation of biologi-

<sup>&</sup>lt;sup>†</sup> The authors wish to dedicate this paper to commemorate the 5th centenary of the University of Santiago de Compostela (1495–1995). (1) Mallory, F. B.; Mallory, C. W. *Org. Reac.* **1984**, *30*, 1.

<sup>(2)</sup> For some recent successful photochemical synthesis of heterocyclic phenanthrenoids see: (a) Rawal, V. H.; Jones, R. J.; Cava, M. P. Tetrahedron. Lett. 1985, 26, 2423. (b) Pascale, L.; Garbay-Jaureguiberry, C.; Le Pecq, J. B.; Roques, B. P. Tetrahedron Lett. 1985, 26, 4929. Beccalli, E. M.; Marchesini, A.; Pilati, T. Tetrahedron 1993, 49, 4741. Das, B. P.; Nuss, M. E.; Boykin, D. W. J. Med. Chem. 1974, 17, 516. Karminski-Zamola, G.; Pavlicic, D.; Bajic, M.; Blazevic, N. Heterocycles 1991, 12, 2323. Modi, S. P.; Zayed, A. H.; Archer, S. J. Org. Chem. 1989, 54, 3084. Pelaprat, D.; Oberlin, R.; Le Guen, I.; Roques, B. P. J. Med. Chem. 1980, 23, 1330.

<sup>(3)</sup> Castedo, L.; Delamano, J.; López, C.; López, M. B.; Tojo, G. *Heterocycles* **1994**, *38*, 495.

<sup>(5)</sup> A 450 W Hanovia medium-pressure UV lamp and Pyrex filter were used. A stream of air was passed through the solution. Batches of 0.1–1 g were irradiated during 3–18 h.
(6) Longin, L.; Bingwei, Y.; Katz, T. J.; Poindexter, M. K. J. Org.

<sup>(6)</sup> Longin, L.; Bingwei, Y.; Katz, T. J.; Poindexter, M. K. J. Org. Chem. **1991**, 56, 3769.

<sup>(7)</sup> Brown, A. C.; Carpino, L. A. J. Org. Chem. 1985, 50, 1749.
(8) Bank, S.; Platz, M. Tetrahedron Lett. 1973, 23, 2097.





<sup>*a*</sup> Key: (a) Pyrex filter, EtOH, I<sub>2</sub> (0.07 equiv), air; (b)  $h\nu$ , Pyren filter, benzene, I<sub>2</sub> (1 equiv), propylene oxide (153 equiv), Ar; (c) Mg (50 equiv), MeOH, rt; (d) Na (11 equiv), naphthalene (41 equiv), THF, -78 °C.

cally active compounds is currently being pursued in our laboratories.

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**Supporting Information Available:** Procedures and compound characterization data (5 pages).

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