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Base-Induced Photocyclization of 1,2-Diaryl-1-tosylethenes. A Mechanistically Novel Approach to Phenanthrenes and Phenanthrenoids

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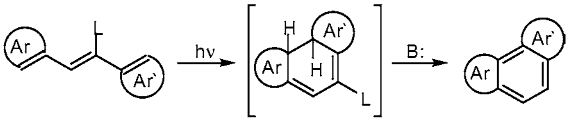
ABSTRACT



L= good-leaving group

The irradiation with UV light of a number of 1,2-diaryl-1-tosylstilbenes, in the presence of base, leads to the corresponding phenanthrenes and heterocyclic analogues. These results are consistent with a mechanism involving the base-induced elimination of *p*-toluenesulfinic acid from an intermediate 9-tosyl-4a,4b-dihydrophenanthrene, formed by photochemical cyclization of the starting 1,2-diaryl-1-tosylstilbenes.

On UV irradiation, stilbenes (**1a**, **2a**) undergo an initial equilibration to a photostationary mixture of *E* and *Z* isomers,[1] which is followed by a photochemically allowed ring closure of the *Z*-isomer (**2a**) to an unstable dihydrophenanthrene (**3a**) (Scheme 1). When an oxidant is present, the dihydrophenanthrene is transformed into a phenanthrene (**4**).[2] This is the most commonly used procedure for the preparation of phenanthrenes and related heterocyclic compounds.[3] An interesting variant of this reaction consists of the irradiation, in the presence of a base, of a stilbene containing a good leaving group—normally Cl or Br—at the ortho position of one of the phenyl rings (**1b**, **2b**). In this case, the unsubstituted phenanthrene **4** is produced by base-induced elimination of HL from the intermediate susbstituted dihydrophenathrene (**3b**).[4]

We speculated that irradiation of a stilbene containing a good leaving group (L) on the central double bond (**5**) would lead to the substituted dihydrophenanthrene **6**, which, in the

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(1) Lewis, G. N.; Magel, T. T.; Lipkin, D. *J. Am. Chem. Soc.* **1940**, *62*, 2973.

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(3) Mallory, F. B.; Mallory, C. W. *Organic Reactions*; Wiley: New York, 1984; Vol. 30, p 1. Ben, I.; Castedo, L.; Saá, J. M.; Seijas, J. A.; Suau, R.; Tojo, G. *J. Org. Chem.* **1985**, *50*, 2236. Rawal, V. H.; Jones, R. J.; Cava, M. P. *Tetrahedron Lett*. **1985**, *26*, 2423. Rawal, V. H.; Jones, R. J.; Cava, M. P. *J. Org.Chem.* **1987**, *52*, 19. Mirsadeghi, S.; Prasad, G. K. B.; Whittaker, N.; Thakker, D. R. *J. Org. Chem.* **1989**, *54*, 3091. Kaliakoudas, D.; Eugster, C. H.; Ruedi, P. *Helv. Chim. Acta* **1990**, *73*, 48. Yang, B.; Liu, L.; Katz, T. J.; Liberko, C. A.; Miller, L. L *J. Am. Chem. Soc*. **1991**, *113*, 8993. Karminski-Zamola, G.; Pavlicic, D.; Bajic, M.; Blazevic, N. *Heterocycles* **1991**, *12*, 2323. Dorst, K. J.; Cava, M. P. *J. Org. Chem.* **1991**, *56*, 2240. Beccalli, E. M.; Marchesini, A.; Pilati, T. *Tetrahedron* **1993**, *49*, 4741. Puls, C.; Stolle, A.; de Meijere, A. *Chem. Ber*. **1993**, *126*, 1635. Plater, M. *Tetrahedron Lett.* **1994**, *35*, 6147. Brooks, P.; Donati, D.; Pelter, A.; Poticelli, F. *Synthesis* **1999**, *8*, 1303. Ishikura, M.; Hino, A.; Yaginuma, T.; Agata, I.; Katagiri, N. *Tetrahedron* **2000**, *56*, 193. Piers, E.; Britton, R.; Andersen, R. J. *J. Org.Chem.* **2000**, *63*, 530. Castedo, L.; Delamano, J.; Enjo, J.; Fernández, J.; Grávalos, D. G.; Leis, R.; López, C.; Marcos, C. F.; Ríos, A.; Tojo, G. *J. Am. Chem. Soc.* **2001**, *123*, 5102. Enjo, J.; Castedo, L.; Tojo, G. *Org. Lett.* **2001**, *3*, 1343.

(4) Wood, C. S.; Mallory, F. B. *J. Org. Chem.* **1964**, 3373. Kupchan, S. M.; Wormser, H. C. *J. Org. Chem.* **1965**, *30*, 3792. Kanaoka, Y.; Itoh, K. *J. Chem. Soc., Chem.Commun.* **1973**, 647. Gellmann, K. H.; Kühle, W.; Weller, H.; Wolff, T. *J. Am. Chem. Soc.* **1981**, *103*, 6889. Mallory, F. B.; Rudolph, M. J.; Oh, S. M. *J. Org. Chem.* **1989**, *54*, 4619. Mallory, F. B.; Rudolph, M. J.; Oh, S. M. *J. Org. Chem.* **1989**, *54*, 4619. Jayalaban, L.; Shannugan, P. *Synthesis* **1990**, 789. Benedetti-Doctorovich, V.; Huang, F. Y.; Lambropoulos, J.; Burgess, E. M.; Zalkow, L. H. *Synth. Commun.* **1995**, *25*, 3701.

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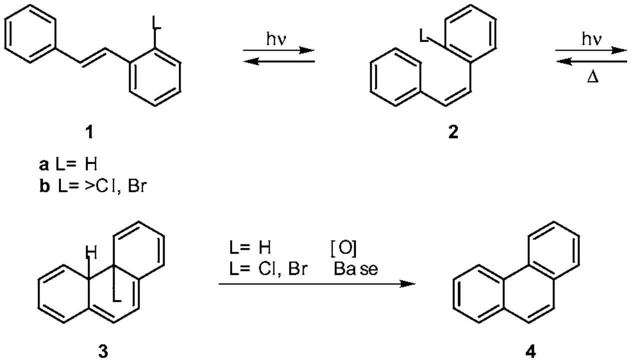
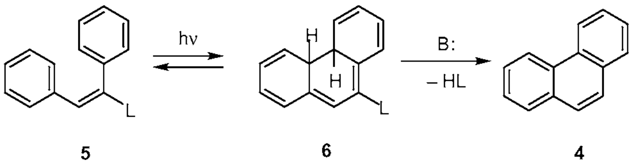
Scheme 1. Photochemical Preparation of Phenanthrenes an Phenanthrenoids



presence of base, might likewise lose HL to afford the unsubstituted phenanthrene (Scheme 2).[5]

Scheme 2. Irradiation of Stilbenes Containing a Leaving Group in the Central Double Bond

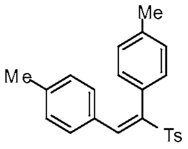
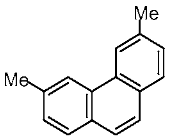
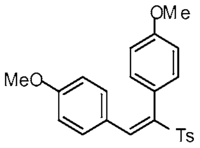
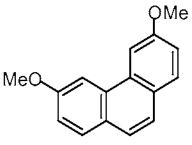
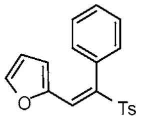
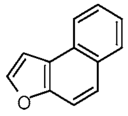
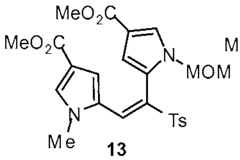
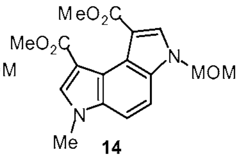
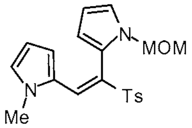
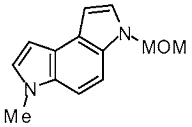
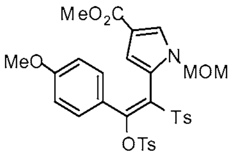
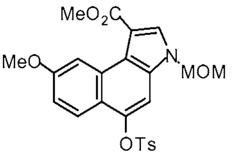
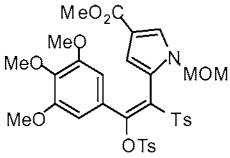
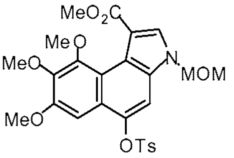


To check this hypothesis, we prepared 1,2-*p*-tolyl-1-tosylethene **7**, a 5:1 mixture of *E* and *Z* isomers, by condensation of the LDA-generated anion of *p*-methylbenzyl *p*-tolyl sulfone with *p*-tolualdehyde, followed by dehydration of the resulting *β*-hydroxysulfone with mesyl chloride and triethylamine.[6] The stereochemistry of these isomers was not determined, being irrelevant in view of the photochemical equilibration in the next step.

Irradiation of **7** in the presence of base leads to the desired phenanthrene (**8**) in yields which ranged from 30% to 95% depending on the base (DBU, Et_3N, or $CaCO_3$) and the solvent (THF, benzene, CH_2Cl_2, or MeOH).[7]

An optimum yield of 95% is obtained by irradiation of a 0.2 M solution of sulfone **7** in THF containing 5 equiv of DBU. The cyclization conditions were applied to other tosylstilbenes and stilbenoids leading to excellent yields of the corresponding phenanthrenes and phenanthrenoids (Table 1).

Table 1. Base-Induced Photocyclization of Tosylstilbenes to Phenanthrenes[a]

entry	substrates	products	time(h)	yield(%)
1	 **7**	 **8**	13	95
2	 **9**	 **10**	11	100
3	 **11**	 **12**	30	95
4	 **13**	 **14**	13	95
5	 **15**	 **16**	6.25	99
6	 **17**	 **18**	1.5	86
7	 **19**	 **20**	1.10	98

[a] A 0.2 M solution of starting stilbene or stilbenoid in THF containing 5 equiv of DBU was irradiated with a 450 W medium-pressure Hannovia mercury lamp until TLC showed consumption of most of the starting material.

In keeping with the proposed mechanism, irradiation of sulfone **7** in the absence of base led to a photostationary 1:1 mixture of *E* and *Z* isomers which fails to yield phenathrene **8** even after prolonged times. In the presence of I_2 as oxidant, the expected tosyl-substituted phenathrene **21** (Figure 1) is obtained in 80% yield.

A clue as to the mechanism of the based-induced conversion of the intermediate tosyl-substituted dihydrophenanthrenes into phenanthrenes is gained by the fact that

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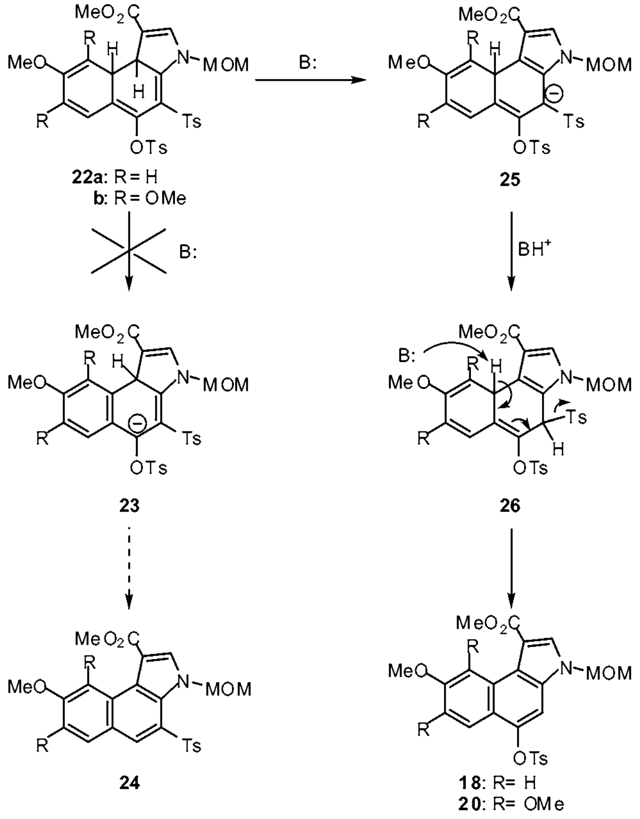
(5) For the photochemistry of stilbenes with a bromine on the central double bond, see: Kimatura, T.; Kobayashi, S.; Taniguchi, H. *J. Org. Chem.* **1990**, *55*, 1801. Kitamura, T.; Kabashima, T.; Taniguchi, H. *J. Org. Chem.* **1991**, *56*, 3739.

(6) Antelo, B.; Castedo, L.; Delamano, J.; Gómez, A.; López, C.; Tojo, G. *J. Org. Chem.* **1996**, *61*, 1188. Kondo, K.; Tunemoto, D. *Tetrahedron Lett.* **1975**, 1007. Cardillo, G.; Savoia, D.; Umani-Ronchi, A. *Synthesis* **1975**, 453.

(7) The following yields were obtained: Et_3N (40 equiv), benzene, 24 h (53%); Et_3N (40 equiv.), MeOH, 10 h (30%); Et_3N (40 equiv), CH_2Cl_2, 39 h (75%); Et_3N (40 equiv), THF, 11 h (75%); DBU (4 equiv), THF, 13 h (95%); DBU (4 equiv), benzene, 18 h (90%); $CaCO_3$ (10 equiv), THF, 15 h (62%); $CaCO_3$ (3 equiv), MeOH, 25 h (58%).

Scheme 3. Hypothetic Mechanism for the Photocyclization of Stilbenoids in the Presence of a Base



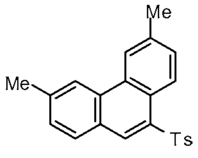


Figure 1.

compounds **17** and **19** both lose their tosyl groups rather than the tosyloxy substituent, which is a much better leaving group. This can be explained by the selective deprotonation of intermediate (**22a**, **22b)** to the sulfone-stabilized anion **25**. Protonation of this anion leads to intermediate **26**, which yields phenanthrenoids **18** and **20** by loosing *p*-toluenesulfinic acid. Phenanthrenoids **24** are not obtained, as the formation of anion **23** would be thermodynamically unfavorable (Scheme 3).[8]

This work shows a mechanistically novel photocyclization of stilbenes to phenanthrenes, which may prove useful for the preparation of biologically important phenanthrenes and phenanthrenoids. The starting tosylstilbenoids are easily obtained by condensation of arylmethyl sulfones with aromatic aldehydes[6] and the key photocyclization gives good yields in a range of different benzenic and heterocyclic compounds.

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Supporting Information Available: Experimental details and analytical data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[8] For precedents of base-induced tautomerization of 4a,4b-dihydrophenanthrenes, see: Somers, J. B. M.; Couture, A.; Lablache-Combier, A.; Laarhoven, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 1387.