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Preparation of Phenanthrenes by Photocyclization of Stilbenes Containing a Tosyl Group on the Central Double Bond. A Versatile Approach to the Synthesis of Phenanthrenes and Phenanthrenoids

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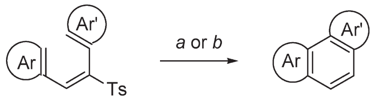


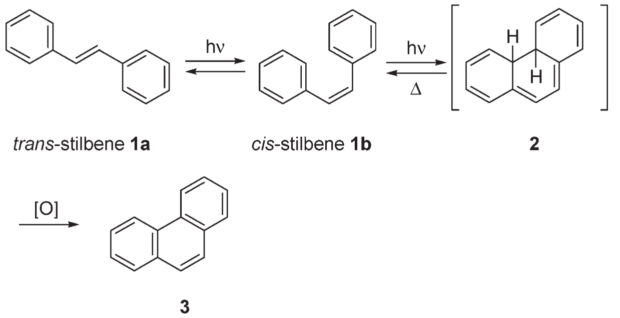
a: hν, [O] and [H]
b: hν in the presence of a base

We have developed a useful modification of the classical preparation of phenanthrenes by UV irradiation of stilbenes in the presence of an oxidant. This modification involves the irradiation, in the presence of base, of stilbenes possessing a sulfonyl group linked to the central double bond. We have proved that this protocol can be successfully applied for the synthesis of diverse phenanthrenes and phenanthrenoids.

Introduction

The irradiation with UV light of stilbenes (**1**) produces an inicial cis−trans isomerization (Scheme 1).[1] The cis isomer suffers a photochemically allowed conrotatory cyclization resulting in the formation of the unstable intermediate dihydrophenanthrene (**2**). This intermediate can be aromatized in situ by an oxidant, leading to a phenanthrene (**3**). This probably represents the most useful and versatile synthesis of phenanthrenes.[2] This reaction is equally useful for the preparation of the heterocyclic analogues of phenanthrenes, the so-called "phenanthrenoids", which are similarly prepared from "stilbenoids."[3]

SCHEME 1. Oxidative Photocyclization of Stilbenes



Many oxidants have been used for the transformation of dihydrophenanthrenes in phenanthrenes, including O_2,[4] I_2,[5] $I_2/CuCl_2$,[6] and TCNE.[7] The most commonly used oxidant is catalytic iodine in the presence of an excess of atmospheric

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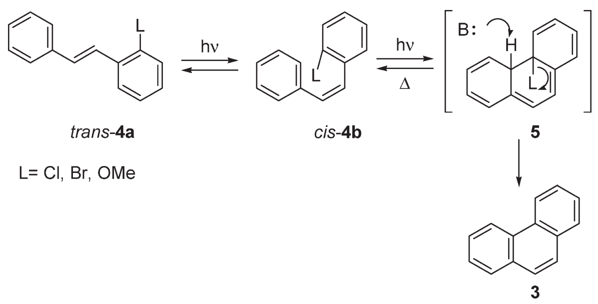
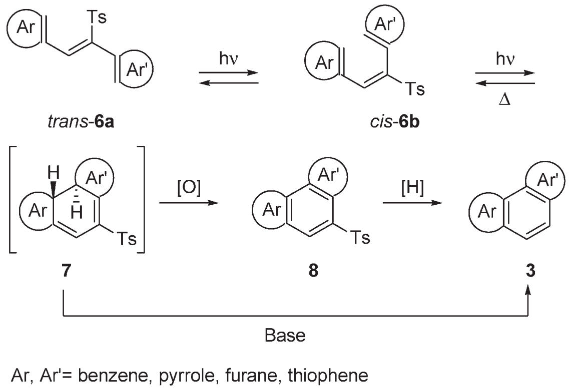
SCHEME 2. Photochemical Preparation of Phenanthrenes from Stilbenes Containing a Leaving Group at a Phenyl Ring



SCHEME 3. Irradiation of Stilbenes Containing a Leaving Group in the Central Double Bond



oxygen.[8] As this oxidizing system leads to the generation of hydroiodic acid, that can cause side reactions, a new very useful method was developed, in which an excess of iodine in the presence of propylene oxide—acting as a hydroiodic acid scavenger—is employed.[9]

The use of stilbenes containing a good leaving group at one of the ortho positions of the aryl substituents (**4**) allows the operation of an interesting variant of the photochemical preparation of phenanthrenes. Thus, the irradiation of stilbenes (**4**) (Scheme 2) leads to a dihydrophenathrene **5**, that can be aromatized by the action of a base.[10] Leaving groups commonly employed include Cl and Br. A methoxy group can also be used as a leaving group, being imperative in this case the addition of an acid. This results in the operation of a slightly different mechanism in which the methoxy group is protonated before the elimination of methanol from the intermediate dihydrophenanthrene.[11]

We described[12] the photocyclization in the presence of an oxidant of stilbenes containing a tosyl group linked to the central double bond (**6**) (Scheme 3). This leads to the formation—via intermediate dihydrotosylphenathrene **7**—of the tosylphenanthrene **8**. This compound can be purified and detosylated in a subsequent reaction by the action of a reducing agent, such as sodium naphthanelide[13] or magnesium in methanol.[14]

This procedure is very efficient in the preparation of both phenanthrenes and phenanthrenoids, being particularly useful for the synthesis of certain electron-rich phenanthrenoids that need to be prepared from electron-rich stilbenoids, which normally are easily destroyed by oxidants. Particularly, stilbenoids belonging to the bispyrrylethylene kind are very oxygen sensitive and their photochemical cyclization to the corresponding pyrroleindoles must be done under very exacting experimental conditions to succeed.[15]

The presence of a strongly electron-withdrawing sulfonyl group in stilbene **6**—as in the corresponding stilbenoids—renders such compounds much more resistant to oxidants, and therefore allows a much more convenient and higher yielding photochemical preparation of certain phenathrenoids.

Results an Discussion

We speculated that the intermediate dihydrotosylphenanthrenes **7** could be made to evolve directly to phenanthrenes **3** by the action of a base.[16] This would be facilitated by the gain in aromaticity accompanying the transformation of dihydrotosylphenanthrenes **7** into phenanthrenes **3**. It is important to note that this novel photochemical phenanthrene synthesis would allow the direct preparation of phenanthrenes (**3**) devoid of tosyl substituents, starting from tosylstilbenes, in a single operation involving the irradiation of tosylstilbenes **6** in the presence of a base.

Preparation of the Starting 1,2-Biaryl-1-tosylethylenes. 1,2-Biaryl-1-tosylethylenes (**9**) can be prepared by based-induced elimination of β-acetoxy[17]- and β-halosulfones,[18] Wittig–Horner condensation between diethyl sulfonylmethyl phosphonates and aldehydes,[19] Peterson reaction between α-silylsulfones and aldehydes,[20] and oxidation of 1,2-biaryl-1-arylthioethylenes.[21] Rather than employing some of these well-documented procedures, we opted for the direct—although less-precedented—method of condensing an aromatic aldehyde (**10**) with an arylmethyl aryl sulfone (**11**) followed by dehydration of the resulting β-hydroxysulfone (**12**) (Scheme 4).

SCHEME 4. Preparation of 1,2-Biaryl-1-tosylethylenes

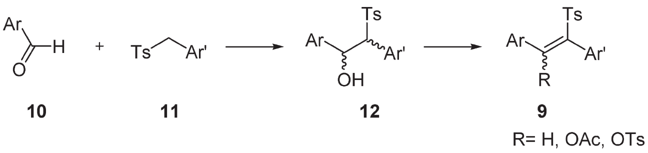


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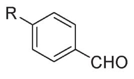
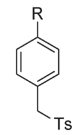
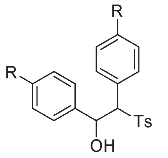
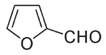
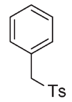
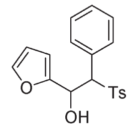
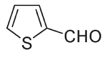
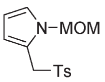
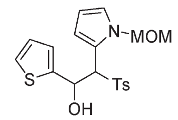
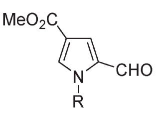
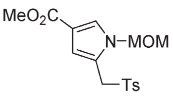
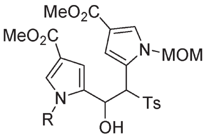
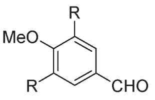
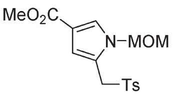
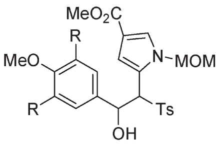
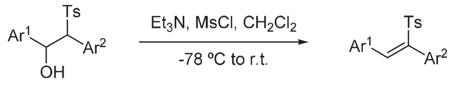
TABLE 1. Preparation of β-Hydroxysulfones[a]

Aldehyde	Sulfone	β-Hidroxysulfone
		
R= Me **10a** R= OMe **10b**	R= Me **11a** R= OMe **11b**	R= Me **12a** (68%) R= OMe **12b** (80%)
		
10c	**11c**	**12c** (91%)
		
10d	**11d**	**12d** (96%)
		
R= MOM **10e** R= Me **10f**	**11e** **11e**	R= MOM **12e** (97%) R= Me **12f** (82%)
		
R= H **10g** R= OMe **10h**	**11e** **11e**	R= H **12g** (63%) R= OMe **12h** (88%)

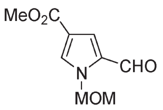
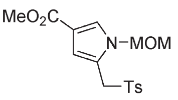
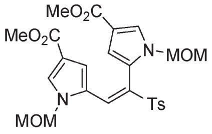
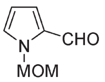
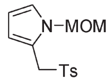
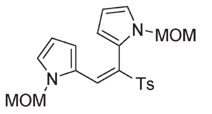
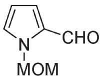
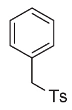
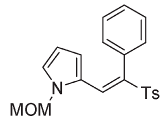
[a]The LDA-generated anions of the tosyl derivatives were condensed at ca. −50 °C with the corresponding aldehyde in THF. Quenching was carried out by addition of 10% HCl at low temperature.

SCHEME 5. Dehydration of β-Hydroxysulfones 12a−d



12a Ar^1= Ar^2= *p*-MePh — **9a** 87%
12b Ar^1=Ar^2= *p*-MeOPh — **9b** 94%
12c Ar^1= 2-furyl; Ar^2= Ph — **9c** 97%
12d Ar^1= 2-thienyl; Ar^2= *N*-MOM-2-pyrryl — **9d** 88%

TABLE 2. Condensation of Pyrrolecarbaldehydes with Arylmethylsulfones[a]

Aldehyde	Sulfone	1-Tosylethylene
		
10e	**11e**	**9e** (89%)
		
10i	**11d**	**9i** (78%)
		
10i	**11c**	**9l** (76%)

[a]Conditions of condensation: NaOMe, MeOH, Δ.

Aryl tosyl sulfones **11** are easely obtained by benzylation of commercially available sodium *p*-toluenesulfinate[22] with a benzyl halide.[23] As pyrrylmethyl halides tend to be very unstable compounds, the preparation of pyrrylmethyl tosyl sulfones is best done by reaction of pyrryl methyl alcohols with sodium *p*-toluenesulfinate in formic acid.[24]

After considerable experimentation, it was found that the LDA-generated anions of arylmethyl aryl sulfones (**11**) react efficiently in THF with aromatic aldehydes in a highly reliable manner, resulting in the formation of the desired β-hydroxysulfones, (**12**) (Table 1). This reaction has a tendency to partially revert during the elaboration, resulting in capricious yields, unless it is quenched at low temperature by the addition of 10% hydrochloric acid. The use of an elaboration protocol including the addition of mineral acid guarantees good yields of β-hydroxysulfones (**12**), which are obtained as a single diastereisomer or a mixture of two diastereoisomers in varying ratios depending in an unpredicted way on the substrates and the exacting reaction conditions.

It was found that good and reliable yields for the dehydration of β-hydroxysulfones **12** to tosylstilbenes (**9**) can be obtained by the use of mesylchloride and triethylamine in methylene chloride (Scheme 5). Other dehydrating conditions such as Ac$_2$O/Py, Et$_3$N/CH$_3$COCl, Ac$_2$O/NaOAc,[25] or *p*-TsOH/PhH[26] were less successful.

Interestingly, reaction of tosyl aryl sulfones with *N*-MOM-pyrrol-2-carbaldehydes (**10i**) failed to give a useful yield of the corresponding β-hydroxysulfone. We think that this is due to the instability of these β-hydroxysulfones which contain pyrrol rings. Compounds with alcohols located at the benzylic position of pyrrols are known to be unstable because they have a tendency to decompose by hydroxy detachment via highly stabilized carbocations.[27] However, pyrrole-containing β-hydroxysulfones **12e−f** are stable compounds and can be prepared in high yields, because the ester groups located in the pyrrol rings moderate its electron-richness.

It was observed that, in variance with other aromatic aldehydes, pyrrolcarbaldehydes **10e** and **10i** can be efficiently

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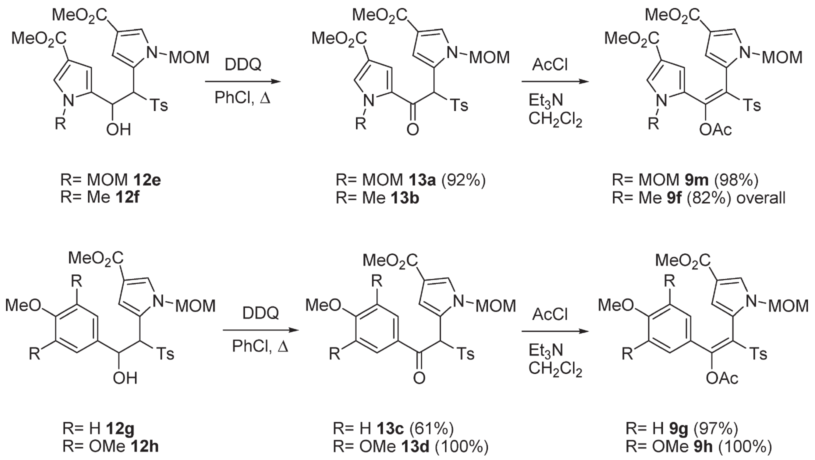
SCHEME 6. Preparation of Acetoxystilbenoids



condensed with aryl arylmethylsulfones by heating with sodium methoxyde in methanol (Table 2). This result is consistent with the operation of an $E_{1C}B$ dehydrating mechanism facilitated by the better leaving group ability of the hydroxy group in the intermediate β-hydroxysulfones.

Condensation with sodium methoxyde in methanol of sulfone **11e** with pyrrolecarbaldehyde **10e** results in partial hydrolysis of the esters in stilbenoid **9e**. We do not believe that this results from adventitious water, as consistent results are obtained in various runs. Most probably, the partial hydrolysis of the esters in **9e** results from the 1 equiv of water generated in the condensation. The methyl ester **9e** can be regenerated in situ by the subsequent addition of an excess of thionyl chloride after the condensation is complete. This allows the isolation of 89% of tosylstilbenoid **9e** in a one-pot reaction.

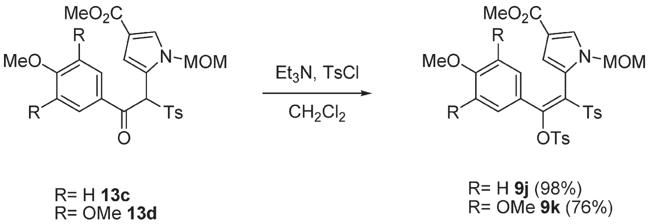
Thus, two complementary protocols were developed for the preparation of 1,2-diaryl-1-tosylethenes. The first one, which is useful for condensation with most aromatic aldehydes, involves the isolation of an intermediate β-hydroxysulfone, which is dehydrated with mesyl chloride and triethylamine (Table 1 and Scheme 5). The second one, which is useful in condensations with pyrrolecarbaldehydes, employs a direct condensation mediated by sodium methoxide (Table 2).

Stilbenoids containing an acetoxy group linked to the central double bond in addition to a tosyl group (**9f**-**h**,**m**) can be obtained by oxidation of β-hydroxysulfones **12e**-**h** by DDQ to the corresponding ketones, followed by treatment with acetyl chloride and triethylamine (Scheme 6).

Exploratory chemistry for the oxidation of alcohols **12** to ketones **13** was done on β-hydroxysulfone **12e**. It was found that some oxidants such as $KMnO_4$,[28] PCC,[29] or $BaMnO_4$[30] cause the reversion of the condensation leading to **12e**, resulting in the isolation of pyrrolecarbaldehyde **10e** and sulfone **11e**. Other oxidants, such as DMSO/TFAA/Et_3N[31] or $PPh_3{}^+BF_4{}^-$[32], cause the dehydration of β-hydroxysulfone **12e** to tosylstilbenoid **9e**. After substantial experimentation, it was found that treatment of β-hydroxysulfone **12e** with DDQ in boiling chlorobenzene leads to the efficient oxidation to ketone **13a** in 92%. This successful result is consistent with the intermediacy of a carbocation stabilized by the pyrrole ring. Mckittrick and Ganem supplied experimental data supporting the intermediacy of benzylic cations in the oxidation of benzyl alcohols to aldehydes or ketones with DDQ.[33] On the other hand, DDQ was shown to be a very good oxidant for other β-hydroxysulfones such as **12f**-**h**, leading to good yields of ketones **13b**-**d** (Scheme 6). Additionally, we found that ketone **13d** can be obtained by Jones oxidation[34] of alcohol **12h**, in a reaction with a much simpler elaboration than the oxidations with DDQ, in which removal the secondary product dihydro-1,2-dichoro-4,5-dicyanobenzoquinone can be very time consuming.

Treatment of ketones **13a**-**d** with acetyl chloride and triethylamine led uneventfully to acetoxytosylstilbenoids **9f**-**h** and **9m**. In all cases, a single isomer—of unknown but irrelevant stereochemistry due to the subsequent photochemical isomerization—was obtained.[35]

SCHEME 7. Preparation of Tosyloxystilbenoids 9j and 9k



Ketones **13c**-**d** can be transformed into stilbenoids, containing a tosyloxy group located at the central double bond in addition to a tosyl group, by treatment with tosyl chloride and triethylamine (Scheme 7).

As in acetoxytosylstilbenoids **9f**-**h**,**m**, tosyloxystilbenoids **9j**-**k** are obtained as a single isomer of unknown but irrelevant stereochemistry.

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[28] Dondoni, A.; Fantin, G.; Fogagnolo, M.; Pedrini, P. *J. Org. Chem.* **1990**, *55*, 1439.

[29] Nemoto, H.; Nagai, M.; Fukumoto, K.; Kametani, T. *J. Org. Chem.* **1985**, *50*, 2764.

[30] Shea, K. J.; Gilman, J. W.; Haffner, C. D.; Dougherty, T .K. *J. Am. Chem. Soc.* **1986**, *108*, 4953.

[31] Omura., K.; Sharma, A. K.; Swern, D. *J. Org. Chem.* **1976**, *41*, 957.

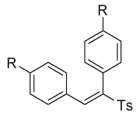
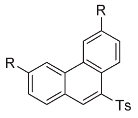
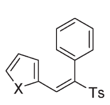
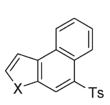
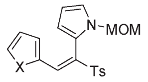
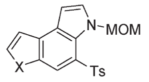
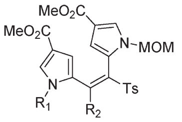
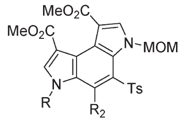
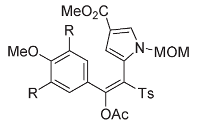
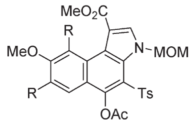
[32] Jung, M. E.; Brown, R. W. *Tetrahedron Lett.* **1978**, *31*, 2771.

[33] McKittrick, B. A.; Ganem, B. *J. Org. Chem.* **1985**, *50*, 5897.

[34] (a) Bowden, K.; Heilbron, I. M.; Jones, E. R. H.; Weedon, B. C. L. *J. Chem. Soc.* **1946**, 39. (b) Bowers, A.; Halsall, T. G.; Jones, E. R. H.; Lemin, A. J. *J. Chem. Soc.* **1953**, 2548.

[35] It is possible to obtain stilbenoids **9** directly from hydroxysulfones **12** in a one-pot reaction, involving DDQ in chlorobenzene, followed by addition of excess of AcCl and Et_3N. Although good yields of stilbenoids **9** can obtained, we do not recommend this procedure as it leads to a complex purification of stilbenoids **9**.

TABLE 3. Photochemical Cyclization of Tosylstilbenes and Stilbenoids in the Presence of Oxidant

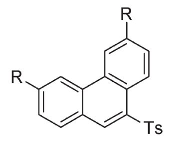
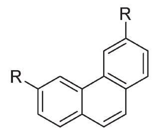
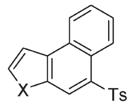
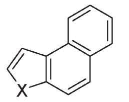
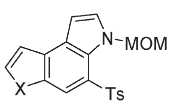
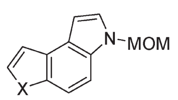
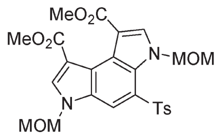
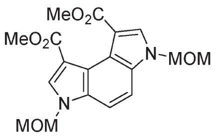
Tosylstilbene or Tosylstilbenoid	Tosylphenanthrene or Tosylphenanthrenoid	Time (h)	Yield (%)
 R= Me **9a** R= OMe **9b**	 R= Me **14a** R= OMe **14b**	(11)^a, (35)^b (8)^a, (30)^b	23^a, 85^b 32^a, 60^b
 X= O **9c** R= N-MOM **9l**	 X= O **14c** X= N-MOM **14l**	(6)^a, (3,5)^b 2	52^a, 89^b 90^a
 X= S **9d** X= N-MOM **9i**	 X= S **14d** x= N-MOM **14i**	(3)^a, (4)^b (5)^a, (8)^b	83^a, 90^b 46^a, 82^b
 R_1= MOM, R_2= H **9e** R_1= Me, R_2=OAc **9f** R_1= MOM, R_2= OAc **9m**	 R_1= MOM, R_2= H **14e** R_1= Me, R_2=OAc **14f** R_1= MOM, R_2=OAc **14m**	5 19 3,5	89^a 90^a 95^a
 R= H **9g** R= OMe **9h**	 R= H **14g** R= OMe **14h**	5,5 (8)^a, (4)^b	82^a 100^a, 94^b

^{a}Pyrex filter, EtOH, I_2 (0.10 equiv), air. ^{b}Pyrex filter, PhH, I_2 (1.1 equiv), propylene oxide (150 equiv), Ar.

Photochemical Cyclization of Tosylstilbenes in the Presence of an Oxidant. Irradiation of tosylstilbenes and stilbenoids **9a–i** and **9*l*,m** in benzene[36] in the presence of 1 equiv of iodine and an excess of propylene oxide, under Katz′s conditions,[38] leads to the corresponding tosylphenanthrenes and phenanthrenoids **14a–i** and **14*l*,m** (Table 3), a fact that proves that a tosyl group exerts no interference with the photochemical cyclization of stilbenes. The use of Katz′s conditions for the photochemical cyclization of stilbenes and stilbenoids, as opposed to the use of the more common protocole involving catalytic iodine and atmospheric oxygen, guarantees a consistent better yield in most cyclizations. In our experience, for the obtention of good yields of stilbenes under classical conditions, an excess of oxygen must be guaranteed by continuous liberal bubbling of air through the cooled reaction solution, this being particularly important in photocyclizations on a multigram scale.

Detosylation of phenanthrenes and phenanthrenoids **14a–e**,**i**,**m** can be done either with magnesium in methanol[14] or with sodium naphthanylide[13] (Table 4). Although the use of magnesium in methanol gives generally better yields and is more facile from the experimental point of view, as this reaction is highly irreproducible, it can be more convenient to use sodium naphthanylide in cool THF. The detosylation with magnesium in methanol requires an induction period of uncertain duration marked by the beginning of a conspicuous reaction of metallic magnesium with the solvent. Very low yields are obtained when a delay is observed for the outset of the reaction of magnesium with methanol, as witnessed by the evolution of bubbles of gaseous hydrogen from the metallic shavings.

TABLE 4. Detosylation of Tosylphenanthrenes and Tosylphenanthrenoids^a

Tosylphenanthrene or Tosylhenanthrenoid	Phenanthrene or Phenanthrenoid	Yield (%)
 R= Me **14a** R= OMe **14b**	 R= Me **15a** R= OMe **15b**	54^a, 85^b 20^a
 X= O **14c** R= N-MOM **14l**	 X= O **15c** X= N-MOM **15l**	83^a, 66^b 77^a
 X= S **14d** X= N-MOM **14i**	 X= S **15d** x= N-MOM **15i**	30^a, 23^b 69^a, 14^b
 **14e**	 **15e**	82^b

^{a}Reagents and conditions: Mg (50 equiv), MeOH, rt. ^{b}Reagents and conditions: Na (11 equiv), naphthalene (13 equiv), THF, −78 °C.

The photochemical cyclization in the presence of an oxidant of stilbenes and stilbenoids, as in Table 3, followed by detosylation, as shown in Table 4, represents a new and versatile method for the preparation of phenanthrenes and phenanthrenoids that have the great advantage of the ready availability of the starting tosylstilbenes and stilbenoids. This methodology can be further improved by subjecting the tosylstilbenes and stilbenoids to photocyclization in the presence of a base, whereby the final detosylated phenanthrene or phenanthrenoid can be directly obtained, as shown in the next section of this paper.

Photochemical Cyclization of Tosylstilbenes in the Presence of a Base. Stilbene **9a** and stilbenoid **9i** were singled out in order to check the empirical soundness of the putative transformation depicted in Scheme 3, in which the irradiation of tosylstilbenes in the presence of a base would lead directly to a desulfonated phenanthrene. Quite gratifyingly, it was found that regardless of the base or the solvent tried, in all essays some amount of the desired detosylated phenanthrene **15a** or phenanthrenoid **15i** was produced (Scheme 8).

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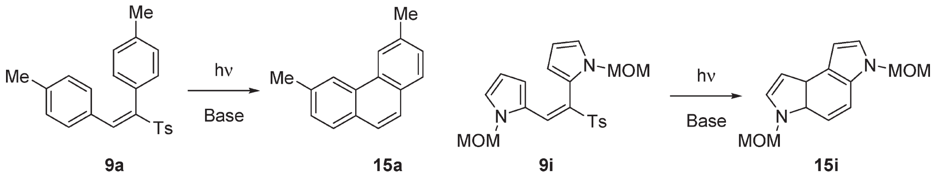
[36] Longbin, L.; Bingwei, Y.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, *56*, 3769.

SCHEME 8. **Photochemical Cyclization of Stilbene 9a and Stilbenoid 9i in the Presence of a Base**

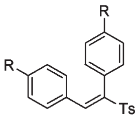
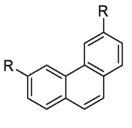
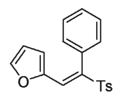
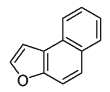
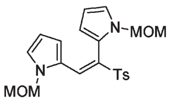
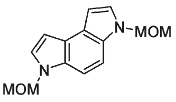
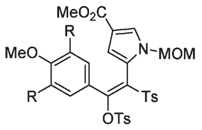
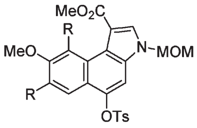
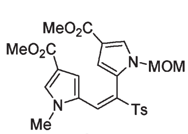
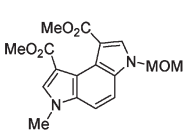


Base	Solvent	Time (h)	Yield
Et_3N (40 equiv)	PhH	24	53%
Et_3N (40 equiv)	MeOH	10	30%
Et_3N (40 equiv)	CH_2Cl_2	39	75%
Et_3N (40 equiv)	THF	11	75%
DBU (4 equiv)	THF	13	95%
DBU (4 equiv)	PhH	18	90%
$CaCO_3$ (10 equiv)	THF	15	62%
$CaCO_3$ (3 equiv)	MeOH	25	58%

Base	Solvent	Time (h)	Yield (%)
Et_3N (80 equiv)	PhH	6.25	40
Et_3N (40 equiv)	PhH	6.45	74
Et_3N (20 equiv)	THF	14	40
K*t*BuO^a (6 equiv)	THF	2	60
DBU (5 equiv)	THF	6.25	99

(a) Mixing of tosylstilbenoid **9i** with potassium *tert*-butoxide must be done at low temperature, otherwise a thermal elimination to the corresponding bisarylacetylene may occur

TABLE 5. **Photochemical Cyclization of Tosylstilbenes with DBU in THF**[a]

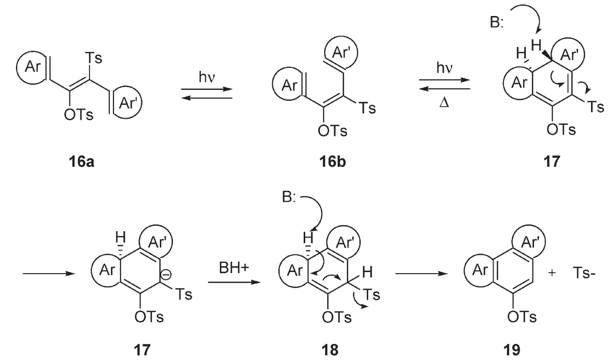
Stilbene or Stilbenoid	Phenanthrene or Phenanthrenoid	Time (h)	Yeld (%)
 R= Me **9a** R= OMe **9b**	 R= Me **15a** R= OMe **15b**	13 11	95 100
 **9c**	 **15c**	11	95
 **9i**	 **15i**	6	99
 R= H **9j** R= OMe **9k**	 R= H **15j** R= OMe **15k**	1.5 1.1	86 98
 **9n**	 **15n**	13	95

[a] The tosylstilbenes and stilbenoids were irradiated as a 0.2 M solution in dry THF containing 5 equiv of DBU.

Interestingly, best yields where obtained when DBU—which is the strongest base among amines—was used. This suggest that the slow step in these reactions is not the photochemical step, but the base-induced transformation of an intermediate tosyldihydrophenanthrene into the detosylated phenanthrene.

As the best yields were obtained with DBU in dry THF, these conditions were tried in a number of tosylstilbenes and stilbenoids, resulting in consistent good yields of the corresponding detosylated phenanthrenes and phenanthrenoids (Table 5).[16]

SCHEME 9. **Mechanism of the Photochemical Cyclization in the Presence of a Base**



This reaction was also carried out with triflylstilbenes, whose UV irradiation in the presence of base generates the corresponding phenanthrenes. This work is in preparation for publication.

Interestingly, stilbenoids **9j**–**k**, possessing both a tosyl (p-Me-Ph-S(O)$_2$–) and tosyloxy (p-Me-Ph-S(O)$_2$O–) group linked to the central double bond, suffer loss of the tosyl group. This happens regardless of the much better leaving group ability of the tosyloxy anion (TsO–) versus a Tosyl anion (Ts–). Scheme 9 shows a mechanism that is consistent with this fact. The key dihydrophenanthrene **17** suffers abstraction of a proton leading to the sulfone-stabilized anion **18**. This anion evolves by protonation followed by elimination of TsH. A parallel mechanism resulting in detachment of the tosyloxy group is not viable, because no sulfone-stabilized anion is possible.

Sulfones are known to suffer carbon–sulfur bond breakage on UV irradiation.[37] This poses the possibility of an alternative mechanism, in which a photocyclization in the presence of adventitious oxygen leads to a tosylphenathrene that is detosylated under the action of UV light. In fact, we

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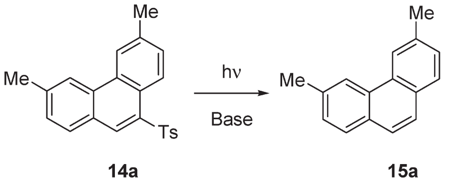
(37) (a) Laarhoven, W. H.; Cuppen, Th. J. H. M. *Tetrahedron Lett.* **1966**, *41*, 5003. (b) Zen, S.; Tashima, S.; Kotó, S. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 3025. (c) Nakai, M.; Furukawa, N.; Oae, S.; Nakabayashi, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1117. (d) Szarek, W. A.; Dmytraczenko, A. *Synthesis* **1974**, 579. (e) Chang, C.-D.; Hullar, T. J. *Carbohydr. Res.* **1977**, *54*, 217. (f) Givens, R. S.; Matuszewski, B. *Tetrahedron Lett.* **1978**, *19*, 861. (g) Berki, R. J.; Binkley, E. R.; Binkley, R. W.; Hehemann, D. G.; Koholic, D. J.; Masnovi, J. *Carbohydr. Chem.* **1996**, *15*, 33.

SCHEME 10. Detosylation of Tosylstilbene 14a



Base	Solvent	Time (h)	Yield (%)
DBU	THF	4	85
$CaCO_3$	THF	14	0
Aniline	THF	26	23
KOH	MeOH	20	43
LiBr	MeOH	20	44

found that tosylstilbene **16a** suffers detosylation by irradiation in the presence of several bases (Scheme 10).

Also, we found that irradiation of tosylphenanthrene **14a** in THF during 11 h in the presence of DBU yields quantitatively the detosylated phenanthrene **15a**. However, this photochemical detosylation procedure seems to be restricted to certain aryl sulfones, as we found no reaction in the case of *p*-tolyl *p*-tolylmethyl sulfone and allyl *p*-tolyl sulfone.

In our opinion, this mechanistically intriguing detosylation[38] is not operating in the photocyclization in the presence of a base for the following reasons:

(1) No adventitious oxygen was present in the experiments shown in Scheme 8 and Table 5. We checked the unaerobicity of the experimental settings by irradiating tosylstilbene **9a**, in the absence of oxidant or base, resulting only in a *E*−*Z* photoisomerization with no formation of phenanthrene at all.

(2) No photochemical detosylation of tosylphenanthrene was observed when $CaCO_3$ was used as base (Scheme 10) while this base is effective in the photocyclization of tosylstilbene **9a**, resulting in the formation of detosylated phenanthrene **15a** (Scheme 8).

We have proved that tosylstilbenes and stilbenoids are easily prepared compounds that can be transformed efficiently in phenanthrenes and phenanthrenoids by UV irradiation in the presence of base. This represents a novel preparation of phenanthrenes and phenanthrenoids that may find ample use for the synthesis of this important and broad type of compounds.

Experimental Section

Air- and moisture-sensitive reactions were performed in flame-dried round-bottomed flasks fitted with rubber septa under a positive pressure of argon. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. 2-Thiophenaldehyde, 2-furanaldehyde, *p*-anisaldehyde, 3,4,5-trimethoxybelzaldehyde, and *p*-tolualdehyde were purchased from commercial sources and used without purification.

Preparation of Key Compouds. Photochemical Cyclization of Tosylstilbenoids in the Presence of an Oxidant. Procedure A: A water-cooled solution of tosylstilbenoid (1 equiv) and I_2 (0.1 equiv) in ethanol was irradiated through a Pyrex filter with a 450 W Hannovia medium pressure mercury lamp, while it was being oxygenated by a stream of air. After 5−15 h, a saturated aqueous solution of $Na_2S_2O_5$ was added and most of the ethanol was removed in the rotatory evaporator. Extraction with CH_2Cl_2, drying (Na_2SO_4), and concentration gave a residue that was purified by flash chromatography (SiO_2, hexane: EtOAc gradient) giving the desired phenanthrenoid. **Procedure B:** A water-cooled solution of tosylstilbenoid (1 equiv), I_2 (1.1 equiv), and propylene oxide (150 equiv) in dry benzene was irradiated under Ar through a Pyrex filter with a 450 W Hannovia medium pressure mercury lamp. After 2−10 h, a workup similar to that of procedure A gave the phenantrenoid.

Methyl 5-Acetoxy-8-methoxy-3-metoxymethyl-4-tosyl-3*H*-benz[*d*]indole-1-carboxylate, 14g. 14g was obtained in 82% yield with procedure A. Mp 163−164 °C (hexane:EtOAc). ^1H NMR ($CDCl_3$, 250 MHz) δ 9.42 (d, J = 2.5 Hz, 1H), 8.24 (s, 1H), 7.60 (s, 1H), 7.59 (d, J = 8 Hz, 2H), 7.20 (d, J = 8 Hz, 2H), 7.13 (dd, J_1 = 2.5, J_2 = 9 Hz, 1H), 5.86 (s, 2H), 4.06 (s, 3H), 3.95 (s, 3H), 2.95 (s, 3H), 2.39 (s, 3H), 2.37 (s, 3H). UV (EtOH) 326, 272, 216 nm. MS (EI, 75 eV, *m*/*z*) 511 ($M^{+\bullet}$, 11), 469 (100), 437 (35), 315 (41), 139 (26). Anal. Calcd for $C_{26}H_{24}NO_8S$: C 61.17, H 4.74, N 2.74. Found: C 60.78, H 4.77, N 2.53.

Methyl 5-Acetoxy-3-metoxymethyl-4-tosyl-7,8,9-trimethoxy-3*H*-benz[*d*]indole-1-carboxylate, 14h. 14h was obtained in 100% employing procedure A and in 94% employing procedure B. Mp 165 −167 °C (hexane/EtOAc). ^1H NMR ($CDCl_3$, 250 MHz) δ 7.74 (s, 1H), 7.67 (d, J = 8 Hz, 2H), 7.25 (d, J = 8 Hz, 2H), 6.79 (s, 1H), 5.85 (s, 2H), 4.06 (s, 3H), 3.91 (s, 3H), 3.85 (s, 3H), 3.74 (s, 3H), 2.96 (s, 3H), 2.40 (s, 6H). ^{13}C NMR ($CDCl_3$, 62.83 MHz) δ 168.7, 167.5, 152.6, 148.6, 145.2, 144.9, 143.9, 141.4, 131.6, 129.5, 127.7, 126.3, 121.4, 120.8, 119.1, 118.8, 114.8, 98.8, 83.4, 61.2, 56.3, 55.9, 51.5, 21.4, 20.8. UV (EtOH) 334, 256, 212 nm. MS (EI, 75 eV, *m*/*z*) 571 ($M^{+\bullet}$, 12), 529 (45), 497 (16), 375 (100).

Photochemical Cyclization of Tosylstilbenoids in the Presence of a Base. A solution of stilbenoid (1 equiv) and DBU (5 equiv) in dry THF was irradiated with a 450 W medium pressure Hanovia mercury lamp until no substantial amount of starting compound was detected by TLC. The reaction mixture was poured onto H_2O, HCl (10%) was added, and the resulting mixture was extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and concentrated, leading to a residue that was purified by flash chromatography (SiO_2, EtOAc−hexane gradient), affording the corresponding phenanthrenoids.

Spectroscopic data of **15k**: Mp 129−131 °C (hexane/EtOAc). ^1H NMR ($CDCl_3$, 250 MHz) δ 7.75 (d, J = 8 Hz, 2H), 7,49 (s, 1H), 7.33 (s, 1H), 7.24 (d, J = 8 Hz, 2H), 6,97 (s, 1H), 5.37 (s, 2H), 3.97 (s, 3H), 3.83 (s, 3H), 3.77 (s, 3H), 3.72 (s, 3H), 3.20 (s, 3H), 2.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 62.83 MHz) δ 168.07 (C), 151.42 (C), 148.53 (C), 145.47 (C), 142.27 (C), 142.23 (C), 132.87 (C), 130.85 (C), 129.79 (CH), 128.51 (CH), 128.14 (CH), 121.16 (C), 118.45 (C), 116.18 (C), 113.72 (C), 104.748 (CH), 98.14 (CH), 77.98 (CH_2), 61.09 (CH_3), 61.01 (CH_3), 56.14 (CH_3), 55.65 (CH_3), 51.73 (CH_3), 21.62 (CH_3) ppm. UV (λ max, EtOH) 346, 310, 256, 228, 206 nm. MS (EI, 75 eV, *m*/*z*) 529 ($M^{+\bullet}$, 5), 374 (100), 44 (4). HMRS (EI, 75 eV) calcd 529.1046, found 529.1430. Anal. Calcd for $C_{26}H_{27}NO_9S$: C 58.97, H 5.13, N 2.64. Found: C 58.93, H 4.84, N 2.78.

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Supporting Information Available: General procedure to obtain all compounds, characterization for new products, and copies ^1H and ^{13}C MNR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(38) The mechanism does not seem to involve a carbon−sulfur bond breakage, resulting in a carbon radical that would abstract a proton from the solvent, as irradiation of *p*-tolyl *p*-tolylmethyl sulfone and allyl *p*-tolyl sulfone in the presense of DBU leads to recovery of the starting compounds. In both compounds a carbon−sulfur bond breakage would be particularly easy as it would produce very stabilized *p*-methylbenzyl or allyl radicals.