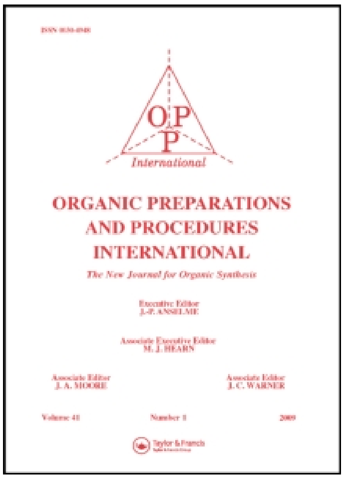

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PREPARATION OF *bis*-[SPIROFLUORENE-9,4'-(1-AZA-2-CYCLOPENTENE)[1,5-a]INDOLINE-8'-YL]SULFONE

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6. W. H. Pearson and M. J. Postich, *J. Org. Chem.*, **59**, 5662 (1994).

7. H. R. Snyder, A. J. Reedy and W. Lennarz, *J. Am. Chem. Soc.*, **80**, 835 (1968).

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PREPARATION OF *bis*-[SPIROFLUORENE-9,4'-(1-AZA-2-CYCLOPENTENE)[1,5-a]INDOLINE-8'-YL]SULFONE

Submitted by (10/26/99)

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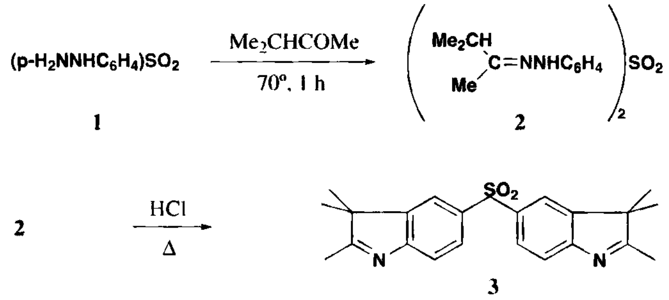
For many years, considerable attention has been directed toward the development of photochromic molecules. A large number of photochromic spiroindolines have been reported[1-4] and as a result, the preparation and study of their bichromophoric analogues are of great interest.[5] This communication describes the synthesis of symmetrical *bis*-(spiro[1,5-a]-indolines) **6a,b** containing isolated spiroindoline rings linked with a sulfone group.

The starting material, *bis*-[2,3,3-trimethylindolenin-5-yl]sulfone (**3**) was obtained by Fischer cyclization reaction of *bis*-[4-hydrazinophenyl]sulfone (**1**)[6] and methylisopropylketone in one step (*Scheme 1*), the *bis*-arylhydrazone **2** was not separated but used directly for further cyclization.



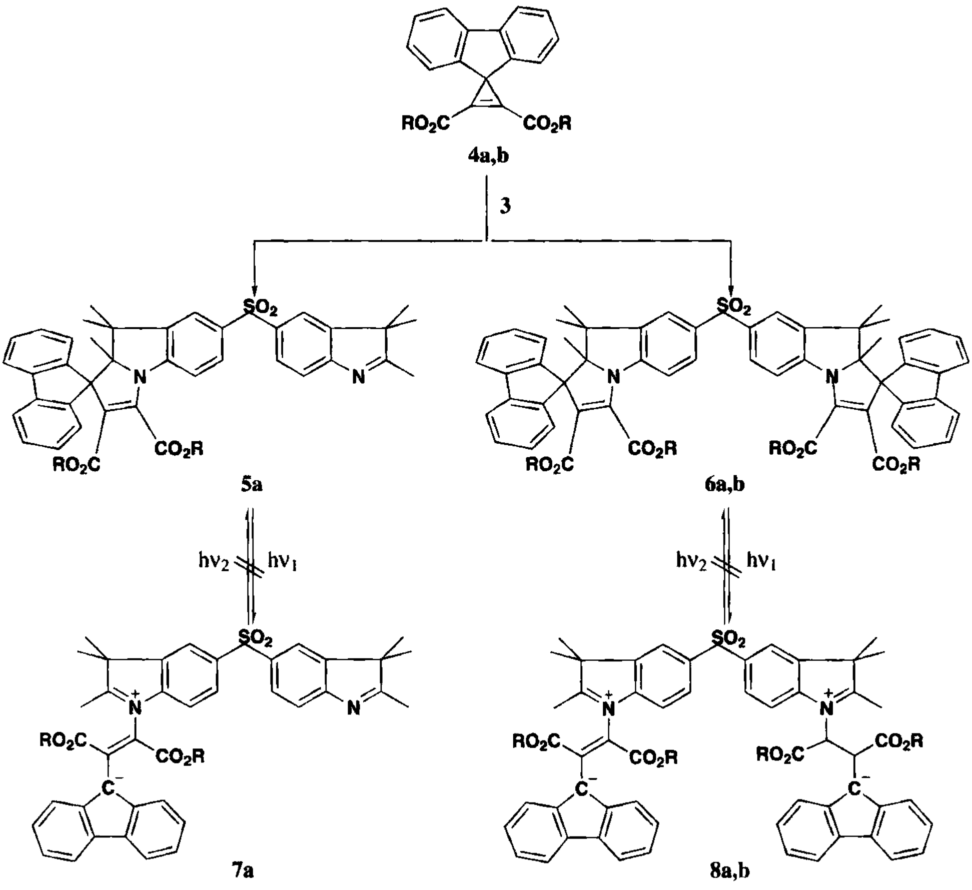
$$(p\text{-}H_2NNHC_6H_4)SO_2 \xrightarrow[70^\circ,\ 1\ h]{Me_2CHCOMe} \left(\begin{matrix} Me_2CH \\ Me \end{matrix}\!\!>C{=}NNHC_6H_4\right)_2 SO_2$$

Scheme 1

Compound **2** in principle can lead to the two products on Fischer cyclization.[7] In particular, each hydrazone fragment of compound **2** possesses two sites for ring closure: the primary carbon atom of methyl group, producing 2-isopropylindole ring and the tertiary carbon atom of isopropyl group, producing 2,3,3-trimethylindolenine ring. So it might be possible to predict the generation of *bis*-[2-substituted]indole and adjacent indole-indolenine system as well as of desired *bis*-indolenine 3.[8]. The reaction mixture was complex showing many spots on t.l.c.

The Fischer cyclization is reported[7,8] to be dependent to a large degree upon the choice of catalyst and reaction conditions. In order to obtain exclusively or predominantly one (namely compound **3**) of the possible cyclization products in a good overall yield, the cyclization step was carried out using a number of catalysts: glacial acetic acid, sulfuric acid, polyphosphoric acid and its esters, hydrochloric acid. The conc. hydrochloric acid was shown to be the highly regioselective catalyst giving predominantly *bis*-[2,3,3-trimethylindolenin-5-yl]sulfone (**3**). Thus, compound **3** was obtained in 69% yield, when cyclization of *bis*-arylhydrazone **2** was carried out in refluxing conc. hydrochloric acid. In other cases, the yields were significantly lower (21-33%).

Nucleophilic addition of *bis*-indolenine **3** to spirocyclopropene **4a,b** was performed according to literature procedure[1] in ether at for 48 h, to give *mono* and *bis* addition products (*Scheme 2*).



a) R = CH_3 b) R = CH_2CH_3

Scheme 2

Separation of the mixtures by chromatography afforded analytically pure **5a, 6a,b.** Some analytical results are presented in *Table 1*. The ^{1}H NMR spectral data are listed in *Table 2*. The reversible 1,5-electrocyclic photochromic transformation of compounds **5a, 6a,b** was expected,[9,10] but no betaines **7a, 8a,b** were detected under irradiation with UV light (OSRAM LF 78; 350-400 nm). Evidently due to the influence of the strong electron-withdrawing sulfone group, the stability of the betaine forms is decreased[11] and the photochromic ring opening does not occur.

EXPERIMENTAL SECTION

The melting points are uncorrected and were obtained on a Büchi spm-20 apparatus. The compounds were identified by ^{1}H NMR, IR, UV and mass spectroscopy (see *Tables* 1 and 2). The following instruments were used for the spectral and analytical analyses: IR: UR-20; UV: Konon UVIKON 860; ^{1}H NMR: Bruker AM-400 MHz using TMS as internal standard; MS: Varian Mat-31; C,H,N: LECO CHNS-932-Analysator. *bis*-[4-Hydrazinophenyl]sulfone (**1**)[6] and 2',3'-alkoxycarbonylspirofluorenylcyclopropene **4a,b** were prepared according to methods described.[1] The other reagents were commercially available (Aldrich).

***bis*-[2,3,3-Trimethylindolenin-5-yl]sulfone (3)**.- A mixture of *bis*-[4-hydrazinophenyl]sulfone (**1**) (8.34 g, 30 mmol) and methylisopropylketone (5.33 g, 62 mmol) was heated for 1 h at 70°. Then 60 mL of conc. HCl was added and the mixture refluxed for 2 h. The reaction mixture was cooled to room temperature and the resulting precipitation was filtered off. The filtrate was extracted with 100 mL of EtOAc. The aqueous layer was diluted with water (300 mL), treated with Na_2CO_3 until pH 10, and extracted with 300 mL of EtOAc (100 mL x 3). The extract was dried (K_2CO_3) and then concentrated to 60 mL *in vacuo*. The resulting colorless crystals were collected by filtration, washed with Et_2O and dried. Yield: 7.85 g (69%); mp 211-212°.

Anal. Calcd. for $C_{22}H_{24}N_2O_2S$: C, 69.47; H, 6.31; N, 7.37. Found: C, 69.22; H, 6.35; N, 7.30

[2,3,3-Trimethylindolenin-5-yl]-[2',3'-dimethoxycarbonyl-5',6',6'-trimethyl-spirofluorene -9,4'-(1-aza-2-cyclopentene)[1,5-a]indoline-8'-yl]sulfone (5a) and *bis*-[2',3'-Dimethoxycarbonyl-5',6',6'-trimethyl-spirofluorene-9,4'-(1-aza-2-cyclopentene)-[1,5-a]indoline-8'-yl]sulfone (6a).- To a solution of 2',3'-dimethoxycarbonylspirocyclopropene **4a** (0.62 g, 2 mmol) in 30 mL abs. Et_2O *bis*-[2,3,3-trimethylindolenin-5-yl]sulfone (**3**) (0.38 g, 1 mmol) was added. The reaction mixture became green. After stirring for 48 h at room temperature a pale yellow solid precipitated. The crude product was collected by filtration, washed with Et_2O and chromatographed (silica gel, petroleum ether 40-60°/ EtOAc, 1:1) to give compounds **5a** and **6a** as pale yellow powder.

Yield of **5a:** 0.12 g (7%); mp 174-175° (dec.).

Anal. Calcd. for $C_{41}H_{38}N_2O_6S$: C, 71.72; H, 5.54; N, 4.08. Found: C, 71.47; H, 5.72; N, 3.98

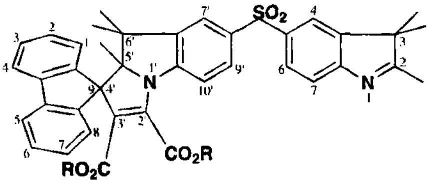
Yield of **6a:** 1.08 g (53%); mp 169-170° (dec.).

Anal. Calcd. for $C_{60}H_{52}N_2O_{10}S$: C, 72.58; H, 5.24; N, 2.82. Found: C, 72.30; H, 5.35; N, 2.94

***bis*-[2',3'-Diethoxycarbonyl-5',6',6'-trimethylspirofluorene-9,4'-(1-aza-2-cyclopentene)-[1,5 -a]indoline-8'-yl]sulfone (6b)**.- Compound **6b** was prepared in a similar way to **6a** except that 2',3'-

diethoxycarbonylspirocyclopropene **4b** was used. The pale yellow crude product was purified by chromatography (silica gel, CH_2Cl_2/MeOH, 95:9). Yield: 0.46 g (44%); mp 176-177°.

Anal. Calcd. for $C_{64}H_{60}N_2SO_{10}$: C, 73.28; H, 5.72; N, 2.67. Found: C, 73.51; H, 5.83; N, 2.57



5a

TABLE 1. Physical Data for Compounds **3, 5a, 6a,b**

Cmpd	Yield (%)	mp. (°C)	IR (Paraffin oil) (cm^{-1})	UV (CH_2Cl_2) ($C=10^{-4}$ mol l^{-1}) (nm)(log ε)	MS (EI) m/z (%)
3	69	211-212	1660, 1460, 1380, 1310, 1220, 1170, 1130, 1075, 1010	280 (4.483) 288 (4.488)	
5a	7	174-175 (dec.)	1710, 1625, 1585, 1460, 1380, 1310, 1260, 1215, 1170, 1130, 1080, 1040, 995	280 (4.122) 314 (4.255)	686 (30)
6a	53	169-170 (dec.)	1710, 1650, 1580, 1460, 1380, 1305, 1280, 1215, 1170, 1130 1080, 1040, 990, 960	288 (4.394) 321 (4.504)	992 (19)
6b	44	176-177 (dec.)	1710, 1650, 1590, 1465, 1380, 1310, 1265, 1205, 1165, 1130, 1075, 1050, 990, 960	297 (4.430) 318 (4.467)	1048 (8)

TABLE 2. ^1H NMR Data for Compounds **3, 5a, 6a,b**

Cmpd	^1H NMR (δ, $CDCl_3$)
3	1.32 (s, 6H, 3-CH_3), 2.31 (s, 3H, 2-CH_3), 7.60 (d, 1H, *J* = 8.0, 7-H), 7.87 (d, 1H, *J* = 2.2, 4-H), 7.90 (dd, 1H, *J* = 1.8, 6-H)
5a	1.33 (d, 6H, *J* = 0.9, 6'-CH_3), 1.36 (s, 3H, 3-CH_3), 1.45 (s, 3H, 3-CH_3), 2.05 (s, 3H, 5'-CH_3), 2.32 (s, 3H, 2-CH_3), 3.32 (s, 3H, 2'-$COOCH_3$), 3.69 (s, 3H, 3'-$COOCH_3$), 6.82 (d, 1H, *J* = 7.9, 7-H), 7.30 - 7.39 (m, 5H, Ar-H), 7.52 (d, 1H, *J* = 7.5, Ar-H), 7.60 (d, 2H, *J* = 8.0, Ar-H), 7.63 - 7.71 (m, 2H, Ar-H), 7.75-7.92 (m, 3H, Ar-H)
6a	1.37 (d, 3H, *J* = 1.4, 6'-CH_3), 1.46 (d, 3H, *J* = 1.4, 6'-CH_3), 1.57 (s, 3H, 5'-CH_3), 3.32 (s, 3H, 2'-$COOCH_3$), 3.67 (s, 3H, 3'-$COOCH_3$), 6.82 (d, 1H, *J* = 7.1, 10'-H), 7.31 - 7.39 (m, 5H, Ar-H), 7.52 (d, 1H, *J* = 7.1, 9'-H), 7.64 (m, 2H, Ar-H), 7.72 (d, 1H, *J* = 1.2, 7'-H), 7.79 (m, 1H, Ar-H)
6b	0.71 (t, 3H, 2'-$COOCH_2\underline{CH}_3$), 1.09 (t, 3H, 3'-$COOCH_2\underline{CH}_3$), 1.38 (d, 3H, *J* = 2.7, 6'-CH_3), 1.46 (d, 3H, *J* = 2.2, 6'-CH_3), 1.55 (s, 3H, 5'-CH_3), 3.75 (q, 2H, 2'-$COO\underline{CH}_2CH_3$), 4.13 (q, 2H, 3'-$COO\underline{CH}_2CH_3$), 6.85 (d, 1H, *J* = 7.2, 10'-H), 7.29-7.41 (m, 5H, Ar-H), 7.53 (d, 1H, *J* = 7.5, 9'-H), 7.65 (d, 2H, *J* = 7.6, Ar-H), 7.71 (d, 1H, *J* = 1.3, 7'-H), 7.77 (m, 1H, Ar-H)

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REFERENCES

1. H. Dürr, *Angew. Chem. Int. Ed. Engl.* **28**, 413 (1989).
2. H. Groß and H. Dürr, *Angew. Chem.*, **94**, 204 (1982).
3. H. Dürr andH. Bouas-Laurent, "*Photochromism, Molecules and Systems*", Chap 10, Elsevier, Amsterdam, 1990.
4. H. Dürr, *Naturwiss.* (Ch.), **4/40**, 22 (1991).
5. a) P. Spang and H. Dürr, *Angew. Chem.*, **96**, 227 (1984), (b) H. Bleisinger, P. Scheidhauer, H. Dürr, V. Wintgens, P. Valat, and J. Kossanyi, *J. Org. Chem.*, **63**, 990 (1998).
6. I. Sh. Chickvaidze, Sh. A. Samsoniya, T. A. Kozik and N. N. Suvorov, *Khim. Geterotsikl. Soedin.*, **11**, 1508 (1980); *Chem Abstr.*, 00, 000 (19??).
7. a) For a review see: B. Robinson, *Chem. Rev.*, **69**, 227 (1969), b) W. J. Houlihan, "*Indoles*", Part 1, Chap. 2, Wiley-Interscience, New York, 1972.
8. H. Illy and C. J. Funderburk, *J. Org. Chem.*, **33**, 4283 (1968).
9. R. Huisgen, *Angew. Chem.*, **92**, 979 (1980).
10. T. Bercovici, R. Heilgeman-Rim and E. Fisher, *Mol. Photochem.*, **1**, 23 (1969).
11. a) L. Schrader, *Chem. Ber.*, **104**, 941 (1971), b) H. Dürr, W. Schmidt, R. Sergio, *Ann.*, **7**, 1132 (1974).