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BISINDOLES.
7.* SYNTHESIS OF DI(5-INDOLYL) SULFONE

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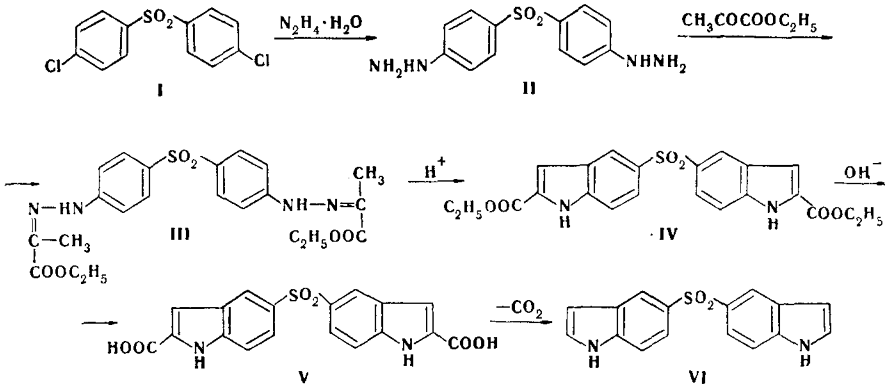
The parent compound of a new heterocyclic system, viz., di(5-indolyl) sulfone, was synthesized by the classical scheme of the Fischer reaction by means of polyphosphoric acid. The starting dihydrazine was obtained from 4,4'-dichlorodiphenyl sulfone.

We have accomplished the synthesis of the parent compound of a new heterocyclic system, viz., di(5-indolyl) sulfone, via the scheme



The presence of the electron-acceptor SO_2 group in I in the para position with respect to the halogens increases the lability of the chlorine atoms to nucleophilic substitution. Thus, in contrast to our earlier studies [2, 3], diazotization of the corresponding diamine with subsequent reduction of the diazonium salt is excluded in the step involving the formation of 4,4'-dihydrazinodiphenyl sulfone (II). Polyphosphoric acid was used as the cyclizing agent in the Fischer reaction. Saponification of ester IV gave acid V, decarboxylation of which leads to the formation of diindolyl compound VI.

The maximum peaks in the mass spectra of IV and VI are the molecular-ion peaks at 440 and 296,† respectively, while the character of the subsequent fragmentation confirms the

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*See [1] for Communication 6.

†Here and subsequently, the m/e values are given for the ion peaks.

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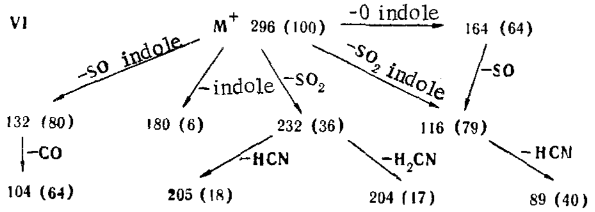
TABLE 1. Properties of the Synthesized Compounds

Compound	mp, °C	IR spectra, cm⁻¹ (in mineral oil)	UV spectra λ max, nm (log ε) (in mineral oil)	Found, %				Empirical formula	Calc., %				Yield, %
				C	H	N	S		C	H	N	S	
II	189—190[a]	3250, 3350 (NH); 1150, 1240 (SO_2)	205,5 (4,5); 216 (4,3) shoulder 266 (4,2); 303 (4,4)	52,3	5,0	20,2	11,5	$C_{12}H_{14}N_4O_2S$	51,8	5,0	20,1	11,5	90
III	178—179	3330 (NH); 1710 (C=O)	228 (4,3); 321 (4,7) shoulder 345 (4,8)	—	—	11,7	7,0	$C_{22}H_{26}N_4O_6S$	—	—	11,8	6,8	97
IV	235—236[a]	3450 (NH)[b], 1720 (C=O)	204 (4,3); 227 (4,1); 321 (4,5); 347 (4,7)	—	—	6,4	7,6	$C_{22}H_{20}N_2O_6S$	—	—	6,4	7,3	46
V	307—309	3305, 3360 (NH); 1725, 1750 (C=O)	241 (5,1) shoulder 258 (5,2); 305 (4,8)	55,9	3,3	7,4	8,4	$C_{18}H_{12}N_2O_6S$	56,2	3,1	7,3	8,3	80
VI	220—221	3410 (NH)	205 (3,7) shoulder 223 (4,0); 247 (4,1); 283 (3,6)	68,0	4,0	9,7	10,9	$C_{16}H_{22}N_2O_2S$	67,9	4,0	9,5	10,8	45

[a] From ethanol. [b] Spectrum of a solution in chloroform.

proposed structure. The ions with masses 164, 132, and 104 for VI can be formed only through a rearrangement process that originates in the molecular ion [4]; these peaks constitute ~60% of the total ion current.



The properties of the symthesized compounds are given in Table 1.

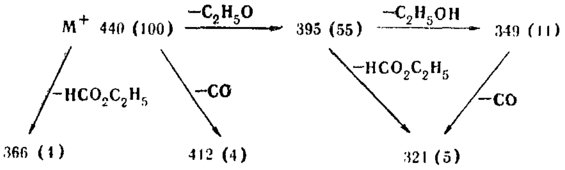
EXPERIMENTAL

The course of the reaction and the purity of the compounds were monitored on Silufol UV-254. Silicon dioxide (100-250µ) was used for chromatography. The IR spectra were recorded with a UR-20 spectrometer. The UV spectra were recorded with a Specord spectrophotometer. The PMR spectra of IV and VI were obtained with a Varian CFT-20 spectrometer (80 MHz) with tetramethylsilane as the internal standard. The accuracy in the measurement of the chemical shifts was 0.02 ppm, while the accuracy in the measurement of the spin–spin coupling constants was 0.1 Hz. The mass spectra were recorded with an MKh-1303 spectrometer with direct introduction of the samples into the ion source at an ionizing-electron energy of 50 eV, a cathode emission current of 1.5 mA, and an accelerating voltage of 2 kV.

4,4'-Dihydrazinodiphenyl Sulfone (II). Two to three drops of triethylamine were added to a suspension of 28.7 g (0.1 mole) of 4,4'-dichlorodiphenyl sulfone in 100 ml of hydrazine hydrate, and the mixture was refluxed for 20 h. The resulting solution was cooled and diluted with cold water, and the precipitate was removed by filtration, washed to neutrality with water, and dried over KOH. The yield was 25 g. Found: M^+ 278. Calculated: M 278.

Ethyl Pyruvate 4,4'-Dihydrazonodiphenyl Sulfone (III). Two to three drops of glacial acetic acid and 2.32 g (0.02 mole) of ethyl pyruvate were added to a suspension of 2.78 g (0.01 mole) of II in 50 ml of ethanol, and the mixture was stirred for 1 h. The precipitate was removed by filtration, washed with ether, and dried to give 3.1 g of product. The mother liquor was evaporated, and another 1.5 g of the hydrazone was precipitated from the residual viscous oil by means of ether. The overall yield was 4.6 g.

Bis(2-carbethoxy-5-indolyl) Sulfone (IV). A 4.74-g (0.01 mole) sample of hydrazone III was mixed with 50 g of polyphosphoric acid (PPA), and the mixture was heated slowly with stirring to 90°C. It was then stirred at 90-100°C for 1 h, after which it was cooled and poured into 500 ml of cold water. The precipitate was removed by filtration, washed to neutrality with water, dried over P_2O_5, and purified with a column (elution with chloroform) to give 2 g of white crystals with R_f 0.62 (ether). Yield 2 g. Found: M^+ 440. A diagram of its fragmentation is given below (m/e and relative intensity):



Calculated: M 440. PMR spectrum (in DMSO): 12.93 (NH, s), 7.98 (3-H, broad s), 9.05 (4-H, d), 8.4 (6-H, q), 8.25 (7-H, d), 5.02 (CH_2CH_3, q), and 2.02 ppm (CH_3CH_2, t); J_{46} = 1.9, J_{64} = 1.8, and J_{67} = J_{76} = 6.4 Hz.

Bis(2-carboxy-5-indolyl) Sulfone (V). A suspension of 4.4 g (0.01 mole) of IV in 100 ml of 6% aqueous NaOH was refluxed until a clear solution formed. The solution was filtered, the filtrate was acidified with 2 N HCl to pH 1, and the white precipitate was removed by filtration, washed to neutrality with water, and dried over P_2O_5. The yield was 3 g.

Di(5-indolyl) Sulfone (VI). A 3.84-g (0.01 mole) sample of V was heated to 320°C in a stream of CO_2 and stirred for 10 min. It was then cooled and dissolved in acetone, and the solution was purified with a column (elution with ether) to give 1.3 g of a product with R_f 0.45 (ether). Found: M^+ 296. Calculated: M 296. PMR spectrum (in d_6-acetone): 10.68 (NH,s), 7.47 (2-H, m), 6.65 (3-H, octet), 8.32 (4-H, q), 7.73 (6-H,]), and 7.53 ppm (7-H, m); J_{13} = 1.9, J_{23} = 3, J_{37} = J_{46} = J_{47} = 0.8, and J_{67} = J_{76} = 8.7 Hz.

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