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INDOLOBENZOTHIOPHENES.

2.* SOME ELECTROPHILIC SUBSTITUTION REACTIONS OF INDOLO[6,5-d]BENZO[b]THIOPHENE

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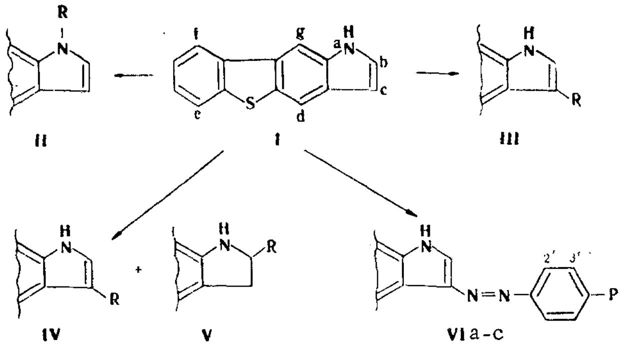
The behavior of indolo[6,5-d]benzo[b]thiophene in acylation, Mannich, Vilsmeier, and diazo coupling reactions was investigated. Acylation with acetic anhydride proceeds unambiguously at the pyrrole nitrogen atom to give 1-acetylindolo[6,5-d]benzo[b]thiophene. The products of formylation are 2- and 3-formylindolo[6,5-d]benzo[b]thiophenes. In the case of the Mannich reaction and diazo coupling substitution takes place in the 3 position of the indolobenzo[b]thiophene ring. The structures of the products obtained were proved by spectroscopic methods.

The present research was devoted to a study of the electrophilic substitution reactions of the previously synthesized indolo[6,5-d]benzo[b]thiophene (I) [1]. 1-Acetylindolo[6,5-d]benzo[b]thiophene (II) was obtained by the reaction of acetic anhydride with I. Data from PMR, IR, UV, and mass spectrometry show that the acetyl group is located in the 1 position.



II $R=COCH_3$; III $R=CH_2N(CH_3)_2$; IV,V $R=CHO$; VI a $R=H$; b $R=Cl$; c $R=NO_2$

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*See [1] for Communication 1.

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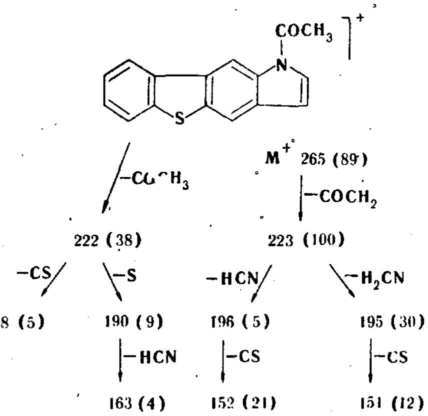
TABLE 1. Parameters of the PMR Spectra of II-VI in d_6-DMSO

Compound	a	b	c	d	e	f	g	CHO	$-CH_3$	$-CH_2$	Spin-spin coupling constants, J, Hz
IIa	—	—^{b}	6,50	—^{b}	—^{b}	~8,2	9,12	—	2,54	—	$J_{b,c}=3{,}9$
IIIa	~8,2	7,03	—	7,82	—^{b}	~8,1	8,07	—	2,24	3,59	$J_{a,b}=2{,}3$; $J_{b,c}=0{,}7$
IV	11,6	8,38	—	7,84	7,97	8,98	7,81	10,32	—	—	$J_{a,b}=3{,}3$; $J_{d,g}=2{,}5$
V^c	—^{d}	—	8,27	8,38	7,84	8,22	8,68	10,05	—	—	$J_{a,c}=3{,}2$; $J_{c,g}=0{,}3$; $J_{d,g}=1{,}0$
								2′	3′		
VIa	11,4	8,43	—	9,08	—^{b}	8,33	8,43	7,4—8,0			$J_{a,b}=3{,}1$
VIb	11,4	8,44	—	9,06	—^{b}	8,30	8,42	7,95	7,54		$J_{d,g}=0{,}8$; $J_{a,b}=3{,}0$; $J_{2',3'}=8{,}8$
VIc	11,8	8,54	—	9,04	—^{b}	~8,3	8,42	8,06	8,37		$J_{d,g}=0{,}6$; $J_{a,b}=3{,}2$; $J_{2',3'}=9{,}3$

[a] In CCl_4; at 60°C in the case of III. [b] In the region of the shifts of the aromatic protons. [c] At 50°C. [d] Not observed as a consequence of the low solubility and rapid deuterium exchange.

The IR spectrum of a Vaseline oil suspension contains an intense absorption band at 1660 cm^{-1} due to the stretching vibrations of the C=O group but does not contain an intense absorption band of an NH bond.

The mass spectrum of II contains an intense molecular-ion peak (M^+) with m/e 265, whereas the character of the subsequent fragmentation* and some of the fragmentation processes that were confirmed by metastable transitions do not contradict the proposed structure.



The data from the PMR spectra confirm that the acyl group replaces the hydrogen atom attached to the nitrogen atom of the pyrrole ring (Table 1).

The aminomethylation of I was carried out by the action of formaldehyde and an aqueous solution of dimethylamine. The structure of III was proved by the PMR, IR, UV, and mass spectra. The PMR spectrum of III confirms that the dimethylaminomethyl group is attached to the carbon atom in the 3 position (Table 1). A signal of an NH proton is observed in the spectrum at ∿8.2 ppm, whereas a signal of a proton attached to C_3 is absent. Signals at 3.59 and 2.24 ppm, which are related to CH_2 and $(CH_3)_2$ groups, respectively, are simultaneously observed. The absorption band of an NH group (3420 cm^{-1}) is retained in the IR spectrum of III, and an absorption band at 1380 cm^{-1}, which is probably due to vibrations of a C—N< bond, appears.

Two products with different R_f values and melting points were obtained in the formylation of I. The data from the PMR spectrum (Table 1) confirm that IV and V are isomers. An absorption band at 1615 cm^{-1}, which is due to stretching vibrations that are characteristic

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*The m/e values are presented along with the relative intensities of the ion peaks in percent of the maximum peak in parentheses.

for the C=O bond, is noted in the IR spectra of IV, in addition to an absorption band at 3230 cm^{-1} corresponding to an NH group. The spectrum of V contains a narrow intense absorption band at 1620 cm^{-1}, which is also due to stretching vibrations of a C=O group, as well as an intense band of an NH bond at 3220 cm^{-1}. The molecular weights of both compounds (250) were determined by mass spectrometry and correspond to mono compounds.

Diazo coupling was carried out in dioxane–water at pH 5-6. Over this pH range diazo coupling in the indole series takes place without substantial complications by side processes [2-4]. In our study of diazo coupling we selected benzenediazonium and p-chloro- and p-nitrobenzenediazonium chlorides as the diazo components. The reaction leads to the formation of primarily the corresponding 3-phenylazo derivatives, viz., 3-phenylazoindolo-[6,5-d]- (VIa), 3-(4'-chlorophenylazo)indolo[6,5-d]- (VIb), and 3-(4'-nitrophenylazo)-indolo[6,5-d]benzo[b]thiophene (VIc).

The structures of all of the compounds obtained were proven by a study of their PMR spectra (Table 1) and are confirmed by the results of elementary analysis and data from IR and UV spectroscopy and mass spectrometry.

The IR spectra of VI contain, in addition to an intense absorption band of an NH group (3200-3260 cm^{-1}), a narrow intense absorption band at 1465 cm^{-1}, which is evidently due to the stretching vibrations of an azo group.

The UV spectra of the compounds recorded in ethanol indicate the similarity in the structures of VI. They contain intense absorption maxima in the long-wave region (400, 395, and 448 nm for VIa-c, respectively).

EXPERIMENTAL

The course of the reaction and the purity of the compounds were monitored on Silufol UV-254 plates. The UV spectra of solutions of the compounds in ethanol were recorded with a Specord spectrophotometer. IR spectra were recorded on a UR-20 apparatus in the prisms from NaCl and LiF (in Vaseline oil.) The mass spectrum was recorded with an MKh-1303 spectrometer with direct introduction of the sample into the ion source; the cathode emission current was 1.5 mA, and the accelerating voltage was 50 eV. The PMR spectra were recorded with a Varian CFT-20 high-resolution spectrometer (80 MHz) with tetramethylsilane as the internal standard.

1-Acetylindolo[6,5-d]benzo[b]thiophene (II). A mixture of 0.45 g (2 mmole) of I, 1.5 ml (53 mmole) of freshly distilled acetic anhydride, and 0.5 ml (87 mmole) of acetic acid was refluxed for 30 h, after which it was cooled and poured into water. The aqueous mixture was extracted with ethyl acetate, and the extract was washed with a solution of $NaHCO_3$ and water and concentrated to 20 ml. The concentrate was passed through a column filled with silica gel (100/250 μ) by elution with benzene to give 0.31 g (58%) of a product with mp 125-127°C. IR spectrum: 1660 cm (C=O). UV spectrum, λ_{max} (log ε): 215 (4.10), 252 (4.01), 262 (4.08), 283 (3.80), 309 (3.95), 339-344 nm (3.30). Found: C 72.5; H 4.3; N 5.4; S 12.2%. $C_{16}H_{11}NOS$. Calculated: C 72.4; H 4.2; N 5.3; S 12.1%.

3-Dimethylaminomethylindolo[6,5-d]benzo[b]thiophene (III). A 6-ml (104 mmole) sample of glacial acetic acid was added slowly to 0.4 g (9 mmole) of dimethylamine in a cooled (to 0°C) solution in water, after which 0.23 g (8 mmole) of 40% formalin and 0.45 g (2 mmole) of I were added, and the mixture was stirred at 20°C for 3 h. It was then treated with 5 ml of water and filtered, and a 10% solution of NaOH was added dropwise with stirring to pH 9. The precipitate was removed by filtration, washed with water, and dried over potassium hydroxide to give 0.34 g (60%) of a product with mp 138-140°C. IR spectrum: 1380 (C–N<) and 3420 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 210 (4.48), 240 (4.73), 260-265 (4.29), 317 (4.27), 333-339 nm (3.95). Found: C 72.8; H 5.6; N 10.0; S 11.1%. $C_{17}H_{16}N_2S$. Calculated: C 72.9; H 5.7; N 10.0; S 11.4%.

3-Formylindolo[6,5-d]benzo[b]thiophene (IV) and 2-Formylindolo[6,5-d]benzo[b]thiophene (V). A 0.2-ml (2 mmole) sample of $POCl_3$ was added dropwise with stirring to 0.62 ml (8 mmole) of freshly distilled DMF cooled to 0°C. The resulting complex was stirred at 20°C for 1 h, after which it was cooled to 0°C and added dropwise to a solution of 0.45 g (2 mmole) of I in 2 ml of DMF. The reaction mixture was maintained at 40-45°C for 50 min, after which it was poured over ice (20 g). A 10% solution of NaOH was added dropwise to the solution to pH 7, and the mixture was stirred at 20°C for 1 h. The precipitate was removed by filtration, washed with water, and dried. The pulverized precipitate was mixed with 1 g of silica gel and 30 ml of acetone, the solvent was removed by vacuum distillation, and the residue was transferred to a column filled with silica gel (100/250 μ) and eluted with ether—hexane (2:9), as a result of which IV and V were isolated. The yield of IV, with R_f 0.5 (ether) and mp 203-205°C, was 0.23 g (46%). IR spectrum: 1615 (C=O) and 3230 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 220 (4.35), 240 (4.55), 296 nm (4.62). Found: C 71.8; H 3.5; N 5.6 S 12.9%. $C_{15}H_9NOS$. Calculated: C 71.7; H 3.6; N 5.6; S 12.8%.

The yield of V, with R_f 0.2 (ether) and mp 250-252°C, was 0.11 g (22%). IR spectrum: 1620 (C=O) and 3220 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 213 (4.66), 277 nm (4.42). Found: C 71.9; H 3.7; N 5.7; S 12.8%. $C_{15}H_9NOS$. Calculated: C 71.7; H 3.6; N 5.6; S 12.7%.

3-Phenylazoindolo[6,5-d]benzo[b]thiophene (VIa). A solution of 2 mmole of benzenediazonium chloride was added at 0°C to a solution of 0.45 g (2 mmole) of I in 30 ml of dioxane while maintaining the solution at pH 5-6 by the addition of sodium acetate. The mixture was stirred for 5 h, after which the azo compound was extracted with ether. The ether solution was washed with 10% NaOH solution and with water to neutrality, after which it was dried with $CaCl_2$ and evaporated to dryness. Compound VIa was purified by chromatography with a column filled with silica gel (100/250 μ) by elution with ether—petroleum ether (1:5) to give 0.3 g (47%) of a product with mp 160-162°C. IR spectrum: 1465 (—N=N—) and 3260 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 206 (4.50), 229 (4.66), 239 (4.65), 328 (4.25), 330 (4.28), 400 nm (4.17). Found: C 73.6; H 3.7; N 12.8; S 9.8%. $C_{20}H_{13}N_3S$. Calculated: C 73.6; H 3.7; N 12.8; S 9.8%.

3-(4'-Chlorophenylazo)indolo[6,5-d]benzo[b]thiophene (VIb). This compound was similarly obtained by the reaction of I with a solution of p-chlorobenzenediazonium chloride. Workup gave 0.48 g (66%) of a product with mp 257-259°C. IR spectrum: 1465 (—N=N—) and 3200 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 204 (4.25), 218 (4.30), 244 (4.33), 320 (4.27), 395 nm (4.22). Found: C 66.9; H 3.3; N 11.6%. $C_{20}H_{12}N_3ClS$. Calculated: C 66.5; H 3.3; N 11.6%.

3-(4'-Nitrophenylazo)indolo[6,5-d]benzo[b]thiophene (VIc). This compound was similarly obtained by the reaction of I with a solution of p-nitrobenzenediazonium chloride. Workup gave 0.49 g (70%) of a product with mp 160-162°C. IR spectrum: 1465 (—N=N—) and 3200 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 205 (4.27), 240 (4.32), 307 (4.13), 448 nm (4.16). Found: C 64.5; H 3.2; N 15.1; S 8.6%. $C_{20}H_{12}N_4O_2S$. Calculated: C 64.5; H 3.2; N 15.1; S 8.6%.

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