SYNTHESIS OF ISOMERIC INDOLOBENZO[b]THIOPHENES

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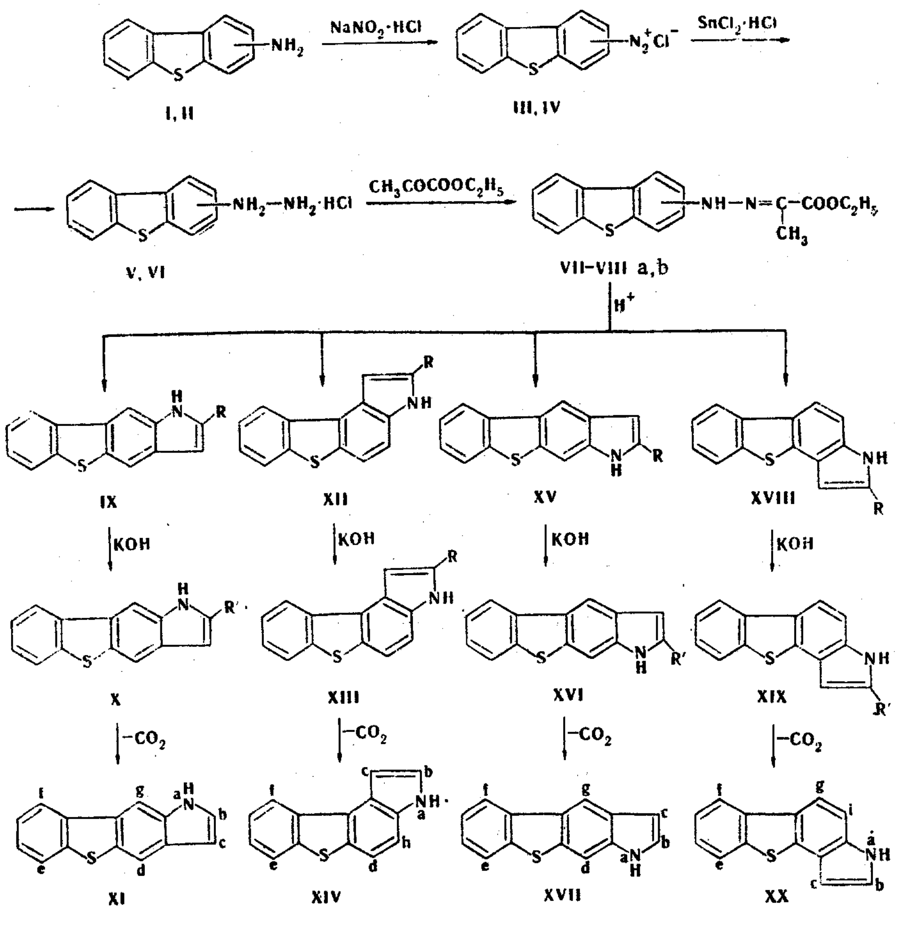
Indolo[6,5-d]benzo[b]thiophene, indolo[4,5-d]benzo[b]thiophene, indolo[5,6-d]benzo[b]thiophene, and indolo[5,4-d]benzo[b]thiophene were obtained from the 2- and 3-dibenzothienylhydrazones by means of the Fischer reaction. The structures of the compounds obtained were proved by their PMR, IR, UV, and mass spectra.

In a continuation of our research on condensed indole-containing systems we have developed a preparative method for the synthesis of the previously undescribed indolobenzo[b]thiophenes by means of the Fischer reaction via the scheme*



R = COOC$_2$H$_5$; R' = COOH

We selected 2- and 3-aminodibenzothiophenes as the starting compounds. 2-Aminodibenzothiophene (I) was synthesized by reduction of 2-nitrodibenzothiophene [1], which was obtained

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*The letter designations of the positions of the protons are presented for convenience in the comparison of the PMR shifts.

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TABLE 1. PMR Spectra of Hydrazones VII and VIII (in $CDCl_3$)

Compound	Chemical shifts, δ, ppm				J_{CH_2, CH_3}, Hz
	CH_3	CH_2—Et	CH_3—Et	NH	
VIIa	2,22	4,32	1,37	12,3	7,0
VIIb	2,16	4,35	1,42	—*	7,0
VIIIa	2,18	4,28	1,35	12,2	7,0
VIIIb	2,13	4,35	1,40	8,2	7,1

*The signal of this proton is located in the region of the shifts of the aromatic protons.

by direct nitration of dibenzothiophene [2]. In addition to 2-nitrodibenzothiophene, nitration also gives dibenzothiophene 5-oxide, the nitration and subsequent reduction of which lead to the formation of 3-aminodibenzothiophene (II) [3]. The 2- and 3-aminodibenzothiophenes were converted through their diazonium salts (III and IV) to the corresponding hydrazine hydrochlorides (V and VI), which react with ethyl pyruvate to give the hydrazones (VII and VIII) in the form of mixtures of two geometrical isomers. We were able to separate the latter by means of preparative column chromatography into the syn (VIIa and VIIIa) and anti (VIIb and VIIIb) forms, the structures of which were proved by a study of their PMR, IR, and UV spectra. A weak-field signal at 12.3 ppm, which indicates the presence of a rather strong intramolecular hydrogen bond between the NH proton and the carbonyl group, is observed in the PMR spectrum of isomer VIIa (Table 1). Corresponding changes due to the formation of a hydrogen bond are observed in the IR and UV spectra.

By cyclization of hydrazone VII with ethyl polyphosphate [4] under the conditions of the Fischer reaction we were able to obtain a mixture of ethyl indolo[6,5-d]- and indolo[4,5-d]benzo[b]thiophene-2-carboxylates (IX and XII). We were able to isolate IX and XII in 68 and 17% yields, respectively, by means of column chromatography. The corresponding carboxylic acids X and XIII were obtained by saponification of esters IX and XII. Decarboxylation of indolo[6,5-d]benzo[b]thiophene-2-carboxylic acid (X) leads to indolo[6,5-d]benzo[b]thiophene (XI) in 78% yield, while indolo[4,5-d]benzo[b]thiophene-2-carboxylic acid (XIII) gives indolo[4,5-d]benzo[b]thiophene (XIV).

Ethyl indolo[5,6-d]benzo[b]thiophene-2-carboxylate (XV) was obtained in a mixture with ethyl indolo[5,4-d]benzo[b]thiophene-2-carboxylate (XVIII) by cyclization of hydrazone VIII under the same conditions. The mixture of compounds was separated by means of column chromatography. Compounds XV and XVIII were obtained in 10 and 28% yields, respectively. Acids XVI and XIX were obtained by saponification of esters XV and XVIII. Indolo[5,6-d]benzo[b]thiophene (XVII) were synthesized in 42% yield by thermal decarboxylation of indolo[5,6-d]benzo[b]thiophene-2-carboxylic acid (XVI), while decarboxylation of indolo[5,4-d]benzo[b]thiophene-2-carboxylic acid (XIX) leads to indolo[5,4-d]benzo[b]thiophene (XX) in 61% yield.

The data from the PMR, IR, UV, and mass spectroscopy confirm the proposed structures of the synthesized compounds.

The assignment of the PMR signals of IX-XX was made on the basis of the change in the multiplicity of the signals of the indole part of the molecule: the observance of the spectrum of an AB system with a spin—spin coupling constant (SSCC) characteristic for ortho protons in the case of an angularly connected ring ($J_{ortho} \sim 8$ Hz) or two signals from weakly coupling para protons in the case of a linear molecule ($J_{para} < 1$ Hz). The possibility of the observation in the NMR spectrum of the indole of SSCC of the transoid type from remote protons (through five bonds, ^5J) and the change with time in the multiplicity of the signals of the protons that couple with the NM group due to deuteration of the latter in a deuterated solvent facilitated the unambiguous assignment of the lines (Table 2). The results are in good agreement with the published data for some 2-substituted dibenzothiophenes [5].

It follows from the data in Table 2 that the addition of a pyrrole ring to dibenzothiophene for angular rings XIV and XX and linear isomer XVII does not lead to substantial redistribution of the electron densities in the molecule. The chemical shifts of the same protons in the dibenzothiophene and pyrrole fragments of these compounds differ from one another by no more than 0.3 ppm. For the linear structure (XI), on the other hand, one observes a considerable change in the chemical shifts: the signal of the usually most shielded

TABLE 2. PMR Spectra of the Compounds Obtained

Compound	Solvent	Chemical shifts, δ, ppm									J, Hz
		a	b	c	d	e	f	g	h	i	
I*	$CDCl_3$		—	—	7,55	7,75	8,0	7,38	—	—	
IX	$CDCl_3$	—	4,47; 1,47 (Et)	7,84	7,68†	7,89	8,45	7,54†	—	—	$J_{CH_2, CH_3}=7,0$; $J_{a,c}=2,0$
XI	$CDCl_3$	8,5	7,50	7,23	7,67†	~7,9	8,46	7,56†	—	—	$J_{a,b}=2,4$; $J_{a,c}=2,0$; $J_{b,c}=3,0$; $J_{c,g}=0,7$
XI	$(CD_3)_2CO$	10,5	7,48	7,21	7,61	7,92	8,51	7,61	—	—	
XII	$(CD_3)_2CO$	11,6	4,39; 1,38 (Et)	7,36	8,04	8,00	8,30	—	7,77	—	$J_{CH_2, CH_3}=7,1$; $J_{a,c}=2,1$; $J_{c,h}=0,5$; $J_{d,h}=8,5$
XIV	$(CD_3)_2CO$	10,8	~7,4	6,63	7,91	7,92	8,22	—	7,66	—	$J_{a,c}=2,0$; $J_{b,c}=3,1$; $J_{c,h}\sim 0,5$; $J_{d,h}=8,4$
XV	$CDCl_3$	8,8	4,44; 1,42 (Et)	7,35	7,76	7,75	8,10	8,39	—	—	$J_{CH_2, CH_3}=7,1$; $J_{a,c}=2,3$; $J_{d,g}, J_{c,d}=0,7$
XVII	$(CD_3)_2CO$	10.4	7,46	6,66	7,93	7,84	8,23	8,49	—	—	$J_{a,b}=2,2$; $J_{a,c}=1,9$; $J_{d,g}=0,8$; $J_{b,c}=3,0$; $J_{c,d}=0,8$
XVIII	$CDCl_3$	9,2	4,44; 1,43 (Et)	7,45	—	7,88	8,08	8,02	—	7,45	$J_{CH_2, CH_3}=7,1$; $J_{a,c}=2,1$; $J_{c,i}=0,9$; $J_{g,i}=8,8$
XVIII	$(CD_3)_2CO$	11.2	4,36; 1,38 (Et)	7,39	—	8.00	8,22	8,16	—	7.67	$J_{CH_2, CH_3}=7,1$; $J_{a,c}=2,1$; $J_{c,i}=0,9$; $J_{g,i}=8,8$
XX	$(CD_3)_2CO$	10,7	7,47	6.70	—	7,95	8,26	8,00	—	7,59	$J_{a,b}=2,4$; $J_{a,c}=2,1$; $J_{b,c}=3,0$; $J_{c,i}=0,8$; $J_{g,i}=8,6$

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*From [5].

†The reverse assignment of the signals of the protons attached to the d and g atoms is possible.

c atom (the 3 position of indole) is shifted to weak field, while the least shielded g atom is shifted to strong field, approaching the shift that is characteristic for 2-aminobenzothiophene (I), i.e., the chemical shifts of the aromatic protons decrease. Compound XI is probably the most conjugated structure owing to p—π (and possibly d—π) interaction of the electrons of the sulfur and nitrogen atoms in the para position relative to one another with the aromatic system. However, in the case of XIV this para interaction does not lead to this sort of decrease in the interval of chemical shifts of the aromatic protons.

An estimate of the aromatic character of the XI, XIV, XVII, and XX molecules with respect to the observed interval of chemical shifts of the b-i protons (without allowance for the ring currents and steric interactions) leads to the following order [in $(CD_3)_2CO$]: 1.30 (XI), 1.56 (XX), 1.59 (XIV), and 1.83 (XVII). A decrease in the yields of the corresponding (to these rings) carbethoxy derivatives during the synthesis in the same order is also observed: 70 (IX), 28 (XVIII), 17 (XII), and 10% (XV), i.e., one observes a tendency for an increase in the stability of the isomer as the aromatic character of the molecule increases.*

We also analyzed the yields of IX separately from the syn and anti isomers of hydrazone VII. As expected, the yield of ethyl indolo[6,5-d]benzo[b]thiophene-2-carboxylate (IX) from anti isomer VIIb exceeds the yield obtained when syn isomer VIIa is used (47 and 29%, respectively); this is associated with an additional expenditure of energy in cleavage of the intramolecular hydrogen bond in VIIa.

An intense molecular ion (M^+) peak is observed in the mass spectra of the isomeric indolobenzo[b]thiophenes at m/e 223, and the character of the subsequent fragmentation of M^+, which was confirmed by metastable transitions, does not contradict the proposed structures. Because of the identical character of the mass spectra of the isomeric heterocycles we will

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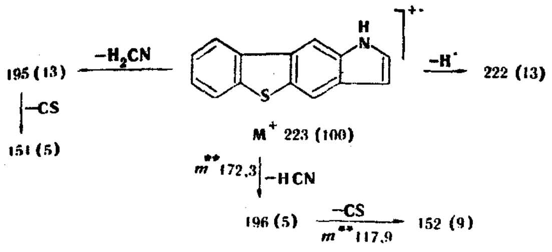
*Quantum-chemical calculations of the indicated indolobenzo[b]thiophenes were made.

present the fragmentation of indolo[6,5-d]benzo[b]thiophene*:



EXPERIMENTAL

The course of the reactions and the purity of the compounds were monitored by thin layer chromatography on plates with a fixed layer of Silufol UV-254 silica gel. The UV spectra of solutions of the compounds in ethanol were recorded with a Specord spectrophotometer. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer with NaCl and LiF prisms at a scanning rate of 160 and a spectral slit width of 4 cm^{-1}. The mass spectrum was recorded with an MKh-1303 spectrometer with direct introduction of the samples into the ion source at a cathode emission current of 1.5 μA and an ionizing voltage of 50 V. The PMR spectra were recorded with a Varian CFT-20 high-resolution spectrometer (80 MHz); the chemical shifts were measured relative to tetramethylsilane as the internal standard with an accuracy of 0.01 ppm, and the SSCC were measured with an accuracy of 0.1 Hz.

Ethyl Pyruvate 2-Dibenzothienylhydrazone (VII). A solution of 1.1 g (0.016 mole) of $NaNO_2$ in 5 ml of water was added dropwise with stirring at 0-5°C in the course of 15 min to a mixture of 3.18 g (0.016 mole) of 2-aminodibenzothiophene (I), 35 ml of water, and 15 ml of concentrated HCl, and the mixture was maintained at −5 to +5°C, after which stirring at 0°C was continued for 15 min. A solution of 6.05 g (0.032 mole) of stannous chloride in 30 ml of concentrated HCl was added slowly at 0 to 5°C, and the mixture was stirred at 2 h. The resulting precipitate of hydrazine hydrochloride V was removed by filtration and dissolved in 200 ml of hot water. The solution was filtered rapidly, the pH of the filtrate was adjusted to three with a saturated solution of sodium acetate, and 1.75 ml (0.016 mole) of ethyl pyruvate in 2 ml of ethanol was added gradually with stirring. The mixture was stirred for 30 min, and the yellow precipitate of hydrazone VII was removed by filtration, washed with water, and dried to give 2.35 g (47%) of VII.

To separate the stereoisomers, hydrazone VII was passed through a column filled with silica gel by means of elution with ether–petroleum ether (1:5). The first fraction consisted of 0.35 g (7%) of syn isomer VIIa with mp 110-112°C and R_f 0.55 [ether–petroleum ether (1:5)]. IR spectrum: 3240, 3265 (NH); 1680 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 243 (4.60), 266 (4.44), 300 (4.12), 344 (4.39), 371 nm (4.35). Found, %: C 65.18; H 5.54; N 8.67; S 10.64. $C_{17}H_{16}N_2O_2S$. Calculated, %: C 65.38; H 5.13; N 8.97; S 10.25. The second fraction consisted of 2 g (40%) of anti isomer VIIb with mp 170-172°C and R_f 0.16 [ether–petroleum ether (1:1)]. IR spectrum: 3265 (NH) and 1695 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 241 (4.59), 266 (4.38), 302 (4.36), 328 (4.51), 366 nm (4.14). Found, %: C 65.40; H 5.59; N 8.67; S 10.49. $C_{17}H_{16}N_2O_2S$. Calculated, %: C 65.38; H 5.13; N 8.97; S 10.25.

Ethyl Pyruvate 3-Dibenzothienylhydrazone (VIII). This compound was similarly obtained from 3-aminodibenzothiophene II. The yield was 1.28 g (26%). Stereoisomers VIIIa and VIIIb were separated by a procedure similar to that used to separate the isomers of VII. The yield of syn isomer VIIIa, with mp 136-138°C and R_f 0.58 [ether–petroleum ether (1:1)], was 0.29 g (6%). UV spectrum, λ_{max} (log ε): 206 (3.68), 236 (3.91), 281 nm (3.45). Found, %: C 65.20; H 5.25; N 8.80; S 10.11. $C_{27}H_{16}N_2O_2S$. Calculated, %: C 65.38; H 5.13; N 8.97; S 10.25. The yield of anti isomer VIIIb, with mp 190-192°C and R_f 0.3 [ether–petroleum ether (1:5)], was 0.99 g (20%). UV spectrum, λ_{max} (log ε): 205 (3.57), 239 (3.74), 267 (3.35), 347 nm (3.81). Found, %: C 65.50; H 5.85; N 8.90; S 10.30. $C_{17}H_{16}N_2O_2S$. Calculated, %: C 65.38; H 5.13; N 8.97; S 10.25.

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*The m/e values are given along with the relative intensities of the peaks of the ions in percent of the maximum peak (in parentheses); the metastable transitions are indicated in the scheme by means of two asterisks.

Ethyl Indolo[6,5-d]- and Indolo[4,5-d]benzo[b]thiophene-2-carboxylate (IX and XII). A mixture of 1.87 g (0.006 mole) of hydrazone VII and 18 g of ethyl polyphosphate was stirred at 75°C for 30 min, after which it was cooled and poured into water, and the resulting precipitate was removed by filtration, washed, and dried. Compounds IX and XII were separated with a column filled with silica gel by means of elution with ether–petroleum ether (1:5). The yield of ester IX, with mp 160-162°C and R_f 0.39 [ether–petroleum ether (1:1)], was 1.2 g (68%). IR spectrum: 3310 (NH) and 1695 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 204 (4.34), 232 (4.68), 282 (4.07), 292 (4.24), 327 (4.42), 342 nm (4.39). Found, %: C 69.45; H 4.19; N 4.60; S 10.63. $C_{17}H_{13}NO_2S$. Calculated, %: C 69.11; H 4.37; N 4.74; S 10.84. The yield of ester XII, with mp 218-220°C and R_f 0.52 [ether–petroleum ether (1:1)], was 0.3 g (17%). IR spectrum: 3305 (NH) and 1690 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 209 (4.27), 257 (4.52), 275 (4.49), 318 nm (4.43). Found, %: C 69.35; H 4.40; N 4.90; S 10.88. $C_{17}H_{13}NO_2S$. Calculated, %: C 69.11; H 4.37; N 4.74; S 10.84.

Ethyl Indolo[5,6-d]- and Indolo[5,4-d]benzo[b]thiophene-2-carboxylate (XV and XVIII). These compounds were similarly obtained from hydrazone VIII. The yield of ester XV, with mp 183-185°C and R_f 0.42 [ether–petroleum ether (1:1)], was 0.17 g (10%). IR spectrum: 3330 (NH) and 1685 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 213 (2.42), 225 (4.47), 266 (4.38), 276 (4.53), 298 (4.60), 339 (3.91), 354 nm (3.95). Found, %: C 69.62; H 4.68; N 4.24; S 10.44. $C_{17}H_{13}NO_2S$. Calculated, %: C 69.11; H 4.37; N 4.74; S 10.84. The yield of ester XVIII, with mp 210-212°C and R_f 0.38 [ether–petroleum ether (1:1)], was 0.5 g (28%). IR spectrum: 3350 (NH) and 1680 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 211 (4.36), 216 (4.28), 252 (4.66), 250 (4.68), 282 (4.69), 318 nm (4.21). Found, %: C 69.48; H 4.62; N 4.40; S 10.56. $C_{17}H_{13}NO_2S$. Calculated, %: C 69.11; H 4.37; N 4.74; S 10.84.

Indolo[6,5-d]benzo[b]thiophene-2-carboxylic Acid (X). A suspension of 1.7 g (0.006 mole) of ester IX, 80 ml of ethanol, 100 ml of water, and 1 g (0.018 mole) of KOH was refluxed with stirring for 2 h, after which the solution was cooled and filtered, and the filtrate was adjusted to pH 7-8 with dilute HCl. The filtrate was filtered, and the filtrate was acidified to pH ∿ 1. The precipitated X was washed with water and dried to give 1.24 g (80%) of a product with mp 270-272°C. IR spectrum: 3350 (NH) and 1700 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 205 (3.29), 232 (4.62), 281 (3.96) 392 (4.07), 322 (4.36), 339 nm (4.33). Found, %: C 67.45; H 3.40, N 5.14; S 11.88. $C_{15}H_9NO_2S$. Calculated, %: C 67.40; H 3.37; N 5.24; S 11.98.

Indolo[4,5-d]benzo[b]thiophene-2-carboxylic Acid (XIII). This compound was similarly obtained in quantitative yield and had mp 288-290°C. IR spectrum: 3340 (NH) and 1660 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 208 (4.32), 257 (4.66), 312 nm (4.49). Found, %: C 67.57; H 3.47; N 5.08; S 11.82. $C_{15}H_9NO_2S$. Calculated, %: C 67.40; H 3.37; N 5.24; S 11.98.

Indolo[5,6-d]benzo[b]thiophene-2-carboxylic Acid (XVI). This compound was obtained by the method used to prepare X. The yield of product with mp 258-260°C was 1.4 g (90%). IR spectrum: 3360 (NH) and 1710 cm^{-1} (C=O). UV spectrum, λ_{max}: 216, 253, 262, 274, 295, 388. Found, %: C 67.54; H 3.35; N 5.24; S 11.85. $C_{15}H_9NO_2S$. Calculated, %: C 67.40; H 3.37; N 5.24; S 11.98.

Indolo[5,4-d]benzo[b]thiophene-2-carboxylic Acid (XIX). This compound was similarly obtained. The yield of product with mp 302-304°C was 1.17 g (76%). IR spectrum: 3365 (NH) and 1715 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 212 (4.28), 259 (4.59), 277 (4.60), 317 nm (3.94). Found, %: C 67.54; H 3.30; N 5.18; S 11.89. $C_{15}H_9NO_2S$. Calculated, %: C 67.40; H 3.37; N 5.24; S 11.98.

Indolo[6,6-d]benzo[b]thiophene (XI). A 1-g (0.004 mole) sample of acid X was heated in a stream of argon at 260-280°C. Compound XI was purified with a column filled with silica gel by elution with ether–petroleum ether (1:5). Erlich's solution did not give a violet coloration with XI. The yield of product with mp 145-147°C was 0.65 g (78%). IR spectrum: 3415 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 224 (4.66), 236 (4.63), 266 (4.01), 311 nm (4.30). Found, %: C 75.80; H 4.24; N 6.70; S 14.42. $C_{14}H_9NS$. Calculated, %: C 75.33; H 4.03; N 6.27; S 14.34.

Indolo[4,5-d]benzo[b]thiophene (XIV). This compound was similarly obtained. The yield of product with mp 243-245°C was 0.5 g (60%). IR spectrum: 3440 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 213 (4.23), 248 (4.66), 255 (4.63), 286 (4.14), 303 (4.23), 321 nm (3.75). Found, %: C 75.11; H 4.50; N 6.26; S 14.36. $C_{14}H_9NS$. Calculated, %: C 75.33; H 4.03; N 6.27; S 14.34.

Indolo[5,6-d]benzo[b]thiophene (XVII). This compound was similarly obtained. The yield of product with mp 148-150°C was 0.35 g (42%). IR spectrum: 3395 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 217 (4.42), 247 (4.59), 264 (4.60), 303 (3.52), 316 (3.91), 345 nm (3.28). Found, %: C 75.26; H 4.57; N 6.25; S 14.65. $C_{14}H_9NS$. Calculated, %: C 75.33; H 4.03; N 6.27; S 14.34.

Indolo[5,4-d]benzo[b]thiophene (XX). This compound was similarly obtained. The yield of product with mp 130-132°C was 0.51 g (61%). IR spectrum: 3350 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 217 (4.39), 252 (4.77), 285 (4.24) 303 nm (3.36). Found, %: C 75.53; H 4.37; N 6.73; S 14.02. $C_{14}H_9NS$. Calculated, %: C 75.33; H 4.03; N 6.27; S 14.34.

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SYNTHESIS OF THIAZOLES AND THIADIAZOLES FROM 1,2-BIS(DIAZOACETYL)ETHANE

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The reaction of 1,2-bis(diazoacetyl)ethane (diazan) with phenyl isothiocyanate and urea leads to the formation of 1,4-diketo-1,4-bis(5-phenylamino-1,2,3-thiadiazolyl)-butane and 1,2-bis(2-amino-1,3-thiazolyl)ethane, respectively.

It was recently shown that 1,2-bis(diazoacetyl)ethane (diazan) (I) has a broad spectrum of antitumorigenic action and slows down or completely suppresses the growth of a number of experimental tumors [1]. Despite the numerous biochemical studies of this compound, virtually no research has been devoted to its chemical transformations up until now.

It is known [2] that primary diazo ketones react with mustard oils to give 5-amino-1,2,3-thiadiazoles. We have investigated the reaction of diazan with phenyl isothiocyanate. As a result of the reaction, we obtained two compounds (III and IV). Absorption bands of carbonyl groups (1630 and 1645 cm^{-1}), of a diazo group at 2135 cm^{-1}, and of an amino group (3083, 3180, and 3220 cm^{-1}) were observed in the spectrum of one of them (III). The absorption maxima in the UV spectrum corresponded to the maxima observed for 2-amino-1,2,3-thiadiazoles, which were previously obtained by Ried and Beck [2]. The mass spectrum of III provided evidence that it is formed by one molecule of diazan and one molecule of phenyl isothiocyanate. In addition to signals of a phenyl group at 7.0-7.4 ppm, signals of protons of two nonequivalent methylene groups, a singlet of a methylidyne proton at 5.3 ppm, and a broad signal of an NH proton at 11 ppm were observed in its PMR spectrum (in $CDCl_3$). The initial process is evidently 1,3-dipolar addition of one of the diazomethine groupings of diazan to the S=C bond of phenyl isothiocyanate to give intermediate II, which undergoes a sigmatropic shift of hydrogen and aromatization of the thiadiazole ring to give III. With respect to the spectral data and the results of elementary analysis (Table 1), the second compound isolated in the reaction corresponded to the product of symmetrical addition of two molecules of phenyl isothiocyanate to one molecule of diazan and had structure IV. 1,4-Diketo-1,4-bis(5-phenylamino-1,2,3-thiadiazolyl)butane (IV) was isolated in 38% yield in the reaction of III with phenyl isothiocyanate.

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