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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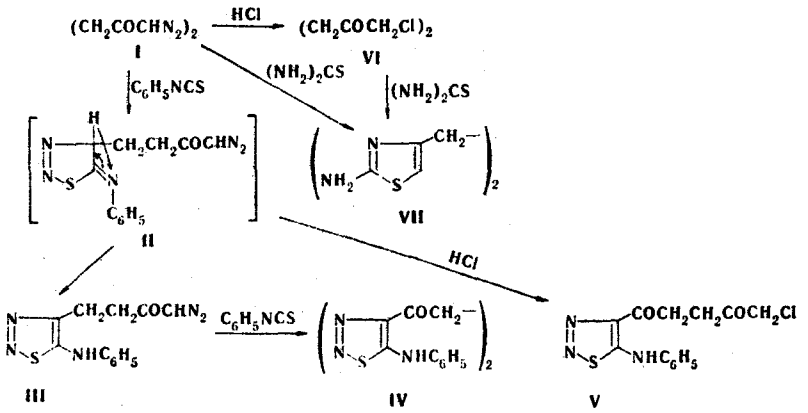
TABLE 1. Products of Conversion of Diazan

Compound	mp, °C	IR spectra, cm^{-1}	UV spectra, λ_{max} (log ε)	Mass spectra,† m/e (I/I_{max}, %)	Found, %			Empirical formula	Calc., %			Yield, %
					C	H	N		C	H	N	
III	83	1595 1630 1645 2130 3085 3200	 204 (4,40) 231 (4,19) 240* (4,14) 277 (4,09) 328 (4,24)	301 (6,0), 273 (7,8), 245 (12,8), 244 (11,7), 217 (6,8), 216 (7,3), 202 (7,3), 188 (8,3), 186 (6,0), 184 (8,3), 176 (6,3), 174 (6,3), 156 (8,3), 149 (9,4), 148 (19,3), 147 (10,9), 144 (19,3), 143 (18,2), 142 (54,2), 136 (34,4), 132 (6,3), 130 (9,9), 125 (16,1), 121 (13,5), 117 (20,3), 114 (8,9), 109 (13,5), 104 (58,3), 102 (19,8), 97 (14,6), 93 (17,7), 77 (100)	52,0	3,6	23,2	$C_{13}H_{11}N_5O_2S$	51,8	3,6	23,3	21
IV	215—216	1595 1630 3085 3220	 207 (4,25) 228 (4,01) 326 (4,27)	436 (3,9), 375 (2,4), 347 (4,9), 319 (2,8), 287 (2,1), 261 (2,8), 260 (4,7), 259 (2,6), 245 (3,7), 244 (6,4), 232 (8,2), 231 (4,7), 229 (2,3), 227 (3,8), 217 (3,0), 216 (5,8), 213 (2,4), 212 (4,0), 205 (2,2), 204 (29,7), 203 (8,2), 202 (16,3), 200 (18,7), 186 (11,0), 176 (38,7), [77 (100)]	55,3	3,7	19,1	$C_{20}H_{16}N_6O_2S_2$	55,1	3,7	19,3	34
V	130—132	1660 1660 1735 3185	 211 (4,03) 223 (3,90) 325 (4,11)	311 (2,4), 309 (6,3), 260 (2,6), 248 (2,1), 247 (3,8), 246 (22,9), 245 (2,1), 218 (2,9), 205 (2,3), 204 (11,9), 200 (2,2), 190 (6,3), 186 (3,2), 176 (14,7), 171 (4,5), 162 (5,4), 151 (2,9), 150 (7,2), 149 (50,2), 148 (25,8), 144 (8,1), 143 (7,4), 135 (26,3), 134 (5,2), 133 (83,7), 121 (13,0), 117 (24,1), 116 (8,5), 115 (17,6), [77 (100)]	—	—	13,6	$C_{13}H_{12}N_3O_2SCl$	—	—	13,6	80
VI	85	1735	206 (2,70)	185 (0,1), 183 (0,1), 167 (0,1), 165 (0,1), 149 (0,3), 147 (0,7), 136 (2,9), 135 (51,5), 134 (9,7), 133 (100), 132 (1,9), 117 (1,3), 116 (0,3), 115 (3,9), 111 (0,4), 107 (6,0), 106 (1,0), 105 (18,1), 104 (0,4), 98 (2,0), 97 (8,6), 91 (1,9), 89 (2,0), 79 (27,5), 78 (3,0)	39,4	4,5	—	$C_6H_8O_2Cl_2$	39,3	4,4	—	95
VII	227—228	1610 3170 3360	—	228 (8,8), 227 (10,6), 226 (83,4), 225 (9,4), 211 (13,1), 208 (4,9), 193 (21,5), 184 (11,0), 183 (7,4), 176 (5,1), 167 (10,0), 166 (39,5), 152 (9,4), 151 (34,4), 150 (49,1), 142 (7,9), 134 (9,2), 127 (17,6), 126 (9,0), 125 (17,0), 124 (6,7), 115 (8,0), 114 (51,5), 113 (100), 109 (5,5), 108 (11,0), 100 (5,3), 97 (7,8), 86 (13,9), 72 (10,0), 71 (30,3)	42,6	4,3	24,7	$C_8H_{10}N_4S_2$	42,5	4,4	24,8	8

*Inflection.

†The ions with intensities ≥6% for III, ≥2% for IV, ≥2% for V, ≥0.1% for VI, and ≥4% for VII are presented.

As expected, diazo ketone III forms chloro ketone V on reaction with dry hydrogen chloride, in conformity with the previously described conversion of diazo ketones to α-



bromomethyl ketones [3]. In contrast to phenyl isothiocyanate, thiourea reacts with diazan to give only one compound, viz., bis(2-amino-1,3-thiazolyl)ethane (VII). This reaction, like the addition of thiourea to benzoyldiazomethane [4], gives the product in low yield (∿ 8%). The structure of VII was confirmed by the set of spectral data (Table 1), as well as by alternative synthesis through 1,6-dichlorohexane-2,5-dione (VI).

Compounds III-V and VII are of interest as potential cancer-destroying agents and are currently being tested for their antitumorigenic activity.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The UV spectra were measured on a Pye–Unicam 8000 spectrophotometer, in methanol. The PMR spectra of solutions of the compounds in $CDCl_3$ were recorded with a Bruker-360 spectrometer with tetramethylsilane as the standard. The mass spectra were recorded with a Finnigan-4010 spectrometer at an ionizing-electron energy of 50 eV. Preparative chromatography was carried out on Brockmann activity II Al_2O_3 plates (with a layer thickness of 1.5 mm) in a benzene–methanol system (10:1).

1,4-Diketo-1,4-bis(5-phenylamino-1,2,3-thiadiazol-4-y)butane (IV). A solution of 0.664 g (4 mmole) of diazan (I) and 1.08 g (8 mmole) of phenyl isothiocyanate in 10 ml of chloroform was refluxed for 10 h, after which the solvent was evaporated, and the oily precipitate was extracted three times with boiling heptane. Compound IV precipitated in the form of beige crystals. The yield was 0.59 g (34%). The product was recrystallized from chloroform. The mother liquor was subsequently worked up to isolate III.

5-Diazo-1,4-diketo-1,4-bis(5-phenylamino-1,2,3-thiadiazol-4-yl)pentane (III). This compound was isolated preparatively from the mother liquor by collection of the band with R_f 0.6-0.7. The yield was 0.25 g (21%). The product was recrystallized from benzene.

5-Chloro-1,4-diketo-1-(5-phenylamino-1,2,3-thiadiazol-4-yl)pentane (V). A gentle stream of dry hydrogen chloride was passed through a solution of 60 mg (0.2 mmole) of III in 2 ml of benzene until the solution became colorless. The precipitate was recrystallized from benzene to give 49.5 mg (80%) of acicular crystals.

1,6-Dichlorohexane-2,5-dione (VI). A gentle stream of dry hydrogen chloride was passed through a solution of 0.83 g (5 mmole) of diazan I in 2 ml of chloroform until the solution became colorless, after which the chloroform was removed by evaporation, and the residue was recrystallized from heptane to give 0.87 g (95%) of colorless plates.

Bis(2-Amino-4-thiazolyl)ethane (VII). A) A solution of 0.83 g (5 mmole) of diazan (I) and 0.76 g (10 mmole) of thiourea in 5 ml of freshly distilled dimethylformamide (DMF) was heated on a boiling-water bath for 8 h, after which it was cooled and treated with 5 ml of water. The gray precipitate of VII was removed by filtration, dried, and recrystallized twice from methanol to give 0.113 g (8.5%) of fine colorless needles.

B) A solution of 0.915 g (5 mmole) of VI and 0.76 g (10 mmole) of thiourea in 10 ml of DMF was allowed to stand at room temperature for 5 h, after which the dihydrochloride of VII was removed by filtration, washed with methanol, dried, and dissolved in 10 ml of water. The

aqueous solution was made alkaline to pH 8 with concentrated K_2CO_3 solution, and the acicular precipitate was removed by filtration, dried, and recrystallized from methanol. The yield was 0.96 g (85%).

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NEW DATA ON DERIVATIVES OF 1-ALKOXYAZIRIDINE-2-CARBOXYLIC ACIDS*

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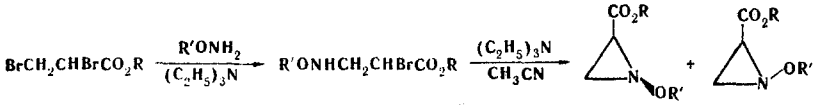
Esters of β-alkoxyamino-α-bromopropionic acids were obtained by reaction of α,β-dibromopropionic acid esters with alkoxyamines in the presence of triethylamine at 20°C for 1 month. When the products are refluxed in acetonitrile in the presence of triethylamine, they are converted to aziridines. Selective amidation of the alkoxyaziridines with excess dimethylamine in absolute methanol in the presence of sodium methoxide leads to enrichment with the cis isomer. The parameters of inversion of the nitrogen atom in the alkoxyaziridines were determined.

An increase in the fraction of the cis isomer as the volume of R is increased was observed in the preparation of methyl 1-alkoxyaziridine-2-carboxylates from methyl α,β-dibromopropionate and alkoxyamines ($RONH_2$) (in acetonitrile in the presence of triethylamine, at 20°C for 4 days, followed by refluxing for 5 h) [2]. The irreversible cis—trans isomerization that is possible under these conditions evidently does not affect the ratio of the isomers formed (see [2] and the information presented below).

To exclude postisomerization of the 1-alkoxyaziridines, the reaction was carried out at 20°C for 1 month (according to the data in [2], $\tau_{1/2} > 100$ yr at 20°C). However, only the corresponding β-alkoxyamino-α-bromopropionic acid esters I-VI (Table 1), which are stable at



I-VI VIII-XIII

I, VIII R=R'=CH_3; II, IX R=CH_3, R'=C_2H_5; III, X R=CH_3, R'=i-C_3H_7; IV, XI R=C_2H_5; R'=CH_3; V, XII R=i-C_3H_7, R'=CH_3; VI, XIII R=t-C_4H_9, R'=CH_3

20°C and when they are heated briefly to 100°C, are obtained in high yields in this case; refluxing in acetonitrile in the presence of triethylamine leads to the corresponding aziridines VIII-XIII (Table 2).

The yields of the alkoxyaziridines increase as the refluxing time is increased, while the trans/cis isomer ratio decreases as the volume of the alkyl substituent in the NOR and

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