The purity and individuality of the compounds were monitored by TLC and data from the IR, UV, and PMR spectra.

The mass spectra were obtained with a Varian MAT-44S spectrometer at an ionizing-electron energy of 70 eV, an emission current of 450 μA, and a temperature range of 80-170°C. A system for direct introduction into the ion source was used.

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THIAZOLIDINE-2,4-DIONE DERIVATIVES WITH AN SO GROUP OUTSIDE THE RING

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The condensation of the potassium salt of thiazolidine-2,4-dione with bis(β-chloroethyl)sulfide leads to bis[β-(thiazolidine-2,4-dion-3-yl)ethyl]sulfide, which is readily oxidized by H_2O_2 to bis[β-(thiazolidine-2,4-dion-3-yl)ethyl]sulfoxide. Products of condensation of the latter with oxo compounds were obtained. The structures of the synthesized compounds were proved by their UV and IR spectra.

It is known [1, 2] that 3-substituted thiazolidine-2,4-diones are oxidized by potassium permanganate in acetic acid to the corresponding thiazolidine-2,4-dione 1-sulfones. The formation of 1-sulfoxides is observed only in the 2-iminothiazolid-4-one series; the properties of 2-iminothiazolid-4-one 1-sulfoxides, particularly the UV spectra, have been studied in detail [3]. Thiazolidine derivatives that contain a sulfoxide (S=O) group outside the ring have not yet been described.

We have obtained bis[β-(thiazolidine-2,4-dion-3-yl)ethyl]sulfide (I) in 58% yield by condensation of the potassium salt of thiazolidine-2,4-dione with bis(β-chloroethyl)sulfide in dimethylformamide (DMF). Oxidation of the product with hydrogen peroxide in dioxane at 16°C leads to bis[β-(thiazolidine-2,4-dion-3-yl)ethyl]sulfoxide (II) in 60% yield.

Compounds I and II are colorless crystalline substances and are characterized by two absorption maxima, viz., a high-intensity maximum at 225 nm and a low-intensity maximum at 323.5 nm. The spectra of these compounds differ only slightly in intensity. However, oxidation of thiazolidines at the sulfur atom in the 1 position leads to the development of new absorption bands [3].

As in the case of unsubstituted thiazolidine-2,4-dione [4], the first band with an absorption maximum at 225 nm corresponds to p–π conjugation in the thiocarbonate chromophore, while the second band with an absorption maximum at 323.5 nm corresponds to an $n \rightarrow \pi^*$ transition of a carbonyl group (compare with the data for cyclopentanone [5]).

The IR spectrum of II is characterized by a high intensity S=O band at 1038 cm^{-1}, which corresponds to I.

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TABLE 1. Thiazolidine Derivatives I-III

Compound	R	mp, °C	UV spectrum		Found, %		Empirical formula	Calc., %		Yield, %
			λ_{max}, nm	lg ε	N	S		N	S	
I	—	99—100	225, 323,5	4,48, 1,94	9,0	29,8	$C_{10}H_{12}N_2O_4S_3$	8,7	30,0	58
II	—	149—150	225, 323,5	3,95, 2,02	8,1	28,4	$C_{10}H_{12}N_2O_5S_3$	8,3	28,6	60
IIIa	C_6H_5CH	217—218	264,5 319	3,61, 4,08	5,7	18,8	$C_{24}H_{20}N_2O_5S_3$	5,5	18,8	22
IIIb	p-$O_2NC_6H_4CH$	230—231	266, 341	4,19, 4,61	9,1	15,7	$C_{24}H_{18}N_4O_9S_3$	9,3	16,0	66
IIIc	m-$O_2NC_6H_4CH$	198—200	269, 317	4,36, 4,54	9,5	15,7	$C_{24}H_{18}N_4O_9S_3$	9,3	16,0	66
IIId	p-ClC_6H_4CH	226—228	267, 325,5	3,96, 4,52	5,0	16,6	$C_{24}H_{18}Cl_2N_2O_5S_3$	4,8	16,6	29
IIIe	p-$CH_3OC_6H_4CH$	217—218	290*, 345,5	— 4,63	4,9	17,1	$C_{26}H_{24}N_2O_7S_3$	4,9	16,8	14
IIIf	p-$(CH_3)_2NC_6H_4CH$	160—162	255, 306, 323, 413	4,21, 3,25, 3,54, 4,68	9,5	16,2	$C_{28}H_{30}N_4O_5S_3$	9,4	16,1	32
IIIg	Furfurylidene	190—192	260, 340	3,67, 4,71	5,6	19,2	$C_{20}H_{16}N_2O_7S_3$	5,7	19,5	41
IIIh	3-Isatinylidene	265—266	261, 364	4,43, 4,42	9,7	16,2	$C_{26}H_{18}N_4O_7S_3$	9,4	16,2	20
IIIi	1-Ethyl-3-isatinylidene	267—269	260,5, 364	4,50, 4,48	8,9	14,8	$C_{30}H_{26}N_4O_7S_3$	8,6	14,8	31
IIIj	5-Bromo-3-isatinylidene	250—252	268, 364	4,35, 4,48	7,2	13,3	$C_{26}H_{16}Br_2N_4O_7S_3$	7,4	12,8	19

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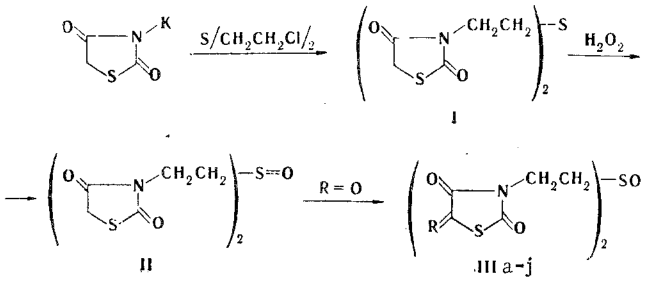
*Shoulder.

We investigated the condensation of II with six aromatic aldehydes, furfural, and isatin and two of its derivatives.



Compounds III are crystalline colorless or yellow, red, or brown substances. Two absorption bands with maxima at 255-268 nm and 317-413 nm are observed in the UV spectra of III in DMF, except for the p-dimethylaminobenzylidene derivative, which is characterized by two other absorption bands with maxima at 306 and 323 nm. The first band is of the benzene ^1L_b type, while the second corresponds to p → π conjugation in chromophores that contain residues of substituents in the 5 position.

EXPERIMENTAL

The UV spectra of $2 \cdot 10^{-3}$-$4 \cdot 10^{-3}$ mole/liter solutions of I and II in methanol and of III in DMF were recorded with an SF-16 spectrophotometer. The IR spectra were obtained from KBr pellets of the compounds.

Bis[β-(thiazolidine-2,4-dion-3-yl)ethyl]sulfide (I). A mixture of 31 g (0.2 mole) of the potassium salt of thiazolidine-2,4-dione and 15.9 g (0.1 mole) of bis(β-chloroethyl)-sulfide was heated at 75°C in 250 ml of DMF for 4 h, after which it was cooled, and the KCl was removed by filtration. The filtrate was evaporated to dryness in vacuo, and the residue was washed with water and ether, and recrystallized from propanol to give 18.6 g (0.058 mole) of I. IR spectrum: 1752 (C=O); 1688 (C=O); 1477 (CH_2); 1387, 1366, 1340, 1318 (C-N); 792, 672 cm^{-1} (C-S).

Bis[β-(thiazolidine-2,4-dion-3-yl)ethyl]sulfoxide (II). An 18.1-g (0.16 mole) sample of hydrogen peroxide was added at 16°C to a solution of 3.2 g (0.1 mole) of I in 30 ml of dioxane. After 15 h, the mixture was evaporated in vacuo, and the residue was washed with ether and recrystallized from butanol to give 2.02 g (6 mmole) of II. IR spectrum: 1752 (C=O); 1688 (C=O); 1440 (CH_2); 1394, 1357 (C-N); 1038 (S=O); 794, 667 cm^{-1} (C-S).

Condensation of II with Oxo Compounds. A mixture of 3.4 g (0.01 mole) of II, 0.03 mole of the oxo compound, and 2.5 g (0.03 mole) of CH_3COONa was refluxed in 40 ml of glacial CH_3COOH for 7 h, after which it was cooled, and the resulting precipitate was removed by filtration, washed with glacial CH_3COOH and water, and recrystallized from CH_3COOH (IIIa-c, e, g), butanol (IIId, f), or dilute (3:1) DMF (IIIh-j).

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SYNTHESIS AND REACTIONS OF 3-AMINOTHIAZOLIDINE-2-THION-4-ONE DERIVATIVES.

1. CONVERSION OF 3-AMINOTHIAZOLIDINE-2-THION-4-ONE DERIVATIVES TO SUBSTITUTED MERCAPTO-1,3,4-THIADIAZOLES

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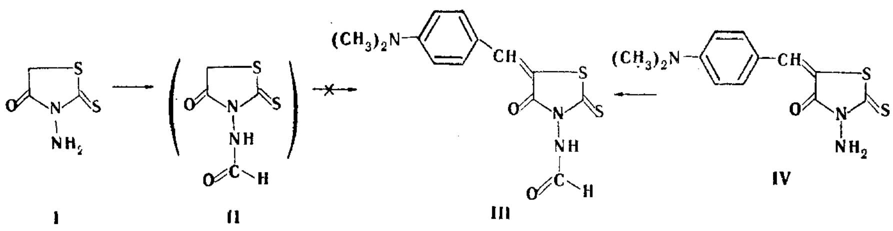
The corresponding carboxymethylthiothiadiazoles are formed by the action of formic acid on 3-aminorhodanine and 3-(3-phenylthioureido)rhodanine, and the action of rhodanineaniline on 3-(3-phenylthioureido)rhodanine leads to 2-anilino-5-carboxymethylthiothiadiazole anilide, whereas similar treatment of 3-ureidorhodanine leads to a semicarbazide derivative.

Continuing our investigation [1] of the reactions of derivatives of 3-aminothiazolidine-2-thion-4-one (I), we repeated its treatment with formic acid [2]. It has been proposed [3] that 3-formamidorhodanine (II) is formed in this case.



However, the properties of the compound that we obtained, the melting point of which was in agreement with the value presented in [2], were not in agreement with structure II. In contrast to ordinary 3-substituted rhodanines [4], this compound did not react with p-dimethylaminobenzaldehyde, although it did contain a methylene group according to the PMR spectral data (a signal at 4.0 ppm). The expected dye (III) was obtained by the action of formic acid on 3-amino-5-(p-dimethylamino)benzylidenethiazolidine-2-thion-4-one (IV). The structure of III was confirmed by data from the PMR spectrum, in which signals of protons of a phenyl ring and a dimethylamino group with chemical shifts of 7.45 and 3.08 ppm, as well as signals of C—H protons of methylidyne (7.58 ppm) and formamido (8.18 ppm) groups, are observed. The absorption maxima of solutions of dyes III and IV (470 and 472 nm) virtually coincide. One's attention is drawn to the fact that the chemical shifts of the C—H bond of the formamido group in III and of the C—H bond in the compound to which structure II was assigned (9.87 ppm) differ markedly, which indicates the absence of a formamido group in the latter. On the basis of the UV spectra it may be concluded that the product of the reaction of thiazolidine I with formic acid also does not contain a rhodanine ring, since the absorption maximum of its solution (265 nm) is considerably higher than in the case of the corresponding solution of aminorhodanine (295 nm) [5].

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