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

2.* 3-[R-(ALKYLTHIO)METHYLENE]AMINOTHIAZOLIDINE-2-THION-4-ONES

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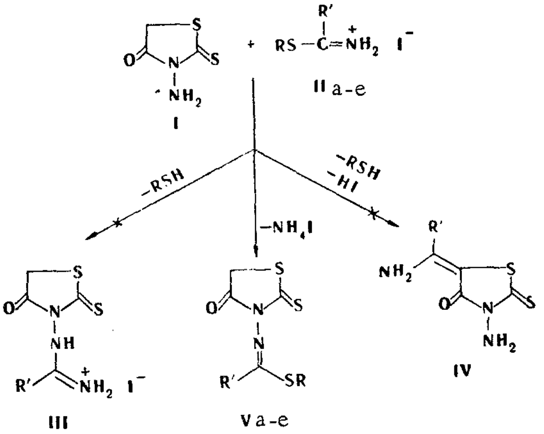
3-[R-(Alkylthio)methylene]aminothiazolidine-2-thion-4-ones were obtained by the reaction of 3-aminorhodanine with thioimino ester hydriodides.

Since some derivatives of 3-aminothiazolidine-2-thion-4-one (I) are starting compounds for the synthesis of cyanine dyes [2], it seemed of interest to obtain and investigate the properties of its new derivatives. In the present research we studied the reaction of I with thioimino ester salts IIa-e.



II, V a $R=R'=CH_3$; b $R=CH_3$, $R'=C_2H_5$; c $R=CH_2C_6H_5$, $R'=CH_3$; d $R=CH_3$, $R'=C_6H_5$; e $R=C_2H_5$, $R'=CH_3$

It is known that rhodanine I displays dual reactivity with respect to electrophilic agents. Derivatives involving either the amino or methylene group or both these groups simultaneously are formed, depending on the conditions [3]. Thioimino ester salts usually react with nucleophilic agents such as amines with splitting out of a mercaptan [4]. Let us also note that hemioxanols are formed in the reaction of 3-ethylthiazolidine-2-thion-4-one with salts with structure II [5]. On the basis of these data, one might have expected the formation of products with structure III or IV in our case.

However, we found that rhodanine I reacts in a different way with thioimino ester hydriodides IIa-e. Derivatives Va-e, the structure of which was established on the basis of data, from the IR, UV, and PMR spectra and chemical reactions, are formed. In fact, the absorption maxima of solutions of Va (295 nm) and I [6] coincide. The IR spectrum of rhodanine Va does not contain a band of stretching vibrations of the N–H bond of starting I at 3200-3350 cm^{-1} [7], while singlets of protons of two methyl and methylene groups with chemical shifts of 1.90 (3H), 2.45 (3H), and 3.95 ppm (2H) are observed in the PMR spectra. As in the case of ordinary rhodanines, the methylene group of Va-e is sufficiently active for cyanine condensations. Thus, for example, benzylidene derivative VI and dimethylidyne-

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*See [1] for Communication 1.

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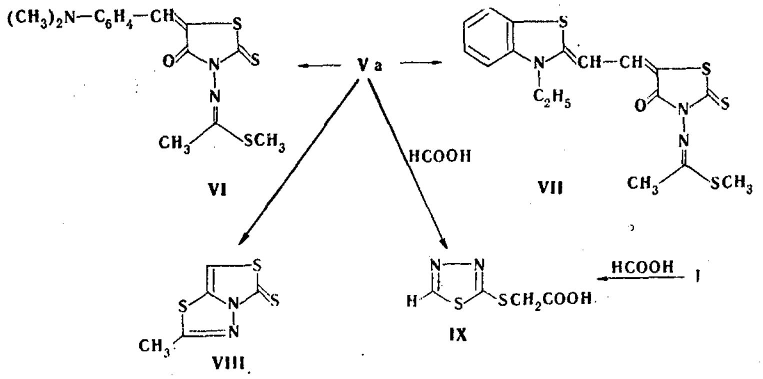
TABLE 1. 3-[R-(Alkylthio)methylene]aminothiazolidine-2-thion-4-one Derivatives (V-VII)

Compound	mp, °C (from alcohol)	Found, %		Empirical formula	Calc., %		Yield, %
		N	S		N	S	
Va	148—149	12,8	43,5	$C_6H_8N_2OS_3$	12,7	43,2	79
Vb	75—76	12,0	41,1	$C_7H_{10}N_2OS_3$	12,0	41,0	60
Vc	138—139	9,6	32,3	$C_{12}H_{12}N_2OS_3$	9,5	32,4	55
Vd	182—183	9,8	33,7	$C_{11}H_{10}N_2OS_3$	9,9	34,0	.30
Ve	82—83	12,1	40,7	$C_7H_{10}N_2OS_3$	12,0	41,0	48
VI	140—141	11,9	27,3	$C_{15}H_{17}N_3OS_3$	12,0	27,4	40
VII	232—233	10,3	31,4	$C_{17}H_{17}N_3OS_4$	10,3	31,4	75

merocyanine dye VII, respectively, were obtained in the reaction of 3-[N-(α-methylthio)-ethylidene]aminothiazolidine-2-thion-4-one (Va) with p-dimethylaminobenzaldehyde and 3-ethyl-2-(2-acetanilidovinyl)benzothiazolium iodide.



It is known that thiorhodanines are usually formed by the action of phosphorus pentasulfide on rhodanines [8]. However, in the case of Va this reaction leads to 5H-2-methylthiazolo[4,3-b][1,3,4]thiadiazole-5-thione (VIII), which is identical to a sample obtained by another method [9]. In the hydrolysis of Va in 50% formic acid the initially formed 3-aminopyridine is converted to 2-carboxymethylthio-1,3,4-thiadiazole (IX) as a result of formylation and subsequent isomerization, as in [1].

EXPERIMENTAL

The PMR spectra of solutions of the compounds in $CDCl_3$ were measured with a Tesla BS-467 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The UV spectra of solutions of the compounds in CH_3OH were recorded with an SF-8 spectrophotometer. The IR spectra of KBr pellets of the compounds were recorded with a UR-10 spectrometer.

3-[N-(α-Methylthio)ethylidene]aminothiazolidine-2-thion-4-one (Va). A mixture of 13.9 g (6.4 mmole) of iodide IIa and 9.5 g (6.5 mmole) of rhodanine I was fused at 80°C for 2 h, after which the crystallized melt was triturated with acetone. The precipitate was removed by filtration and washed with ether to give 11 g (Table 1) of a product with λ_{max} (log ε) 295 (3.50) and 240 nm (3.22).

Rhodanines Vb-e were similarly obtained from I and IIb-e.

5-(p-Dimethylaminobenzylidene)-3-[N-(α-methylthio)ethylidene]aminothiazolidine-2-thion-4-one (VI). A mixture of 0.44 g (2 mmole) of rhodanine Va, 0.3 g (2 mmole) of p-dimethylaminobenzaldehyde and 0.1 g (4 mmole) of sodium acetate was refluxed in 2 ml of acetic acid for 1 h, after which the dye was removed by filtration and washed with alcohol to give 0.25 g of a product with λ_{max} 488 nm. PMR spectrum (CF_3COOH): s, 2.45 (3H); s, 2.62 (3H); s, 3.05 (6H); m, 7.38 (4H); s, 7.55 ppm (1H).

3-[N-(α-Methylthio)ethylidene]amino-5-[(3-ethylbenzothiazolin-2-ylidene)ethylidene]-thiazolidin-2-thion-4-one (VII). A mixture of 0.43 g (1 mmole) of 3-ethyl-2-(2-acetanilidovinyl)benzothiazolium iodide and 0.22 g (1 mmole) of Va in 10 ml of absolute alcohol was heated to the boiling point, and 0.1 g (1 mmole) of triethylamine was added. The precipitated dye was removed by filtration to give 0.3 g of a product with λ_{max} 533 nm.

5H-2-Methylthiazolo[4,3-b]-1,3,4-thiadiazole-5-thione (VIII). A mixture of 0.22 g (1 mmole) of rhodanine Va, 0.22 g (1 mmole) of phosphorus pentasulfide, and 3 ml of dioxane was refluxed for 2 h, after which the dioxane was evaporated, and the residue was crystallized from alcohol to give 0.1 g (53%) of a product with mp 234-235°C (mp 235°C [9]). Found: N 14.7; S 50.9%. $C_3H_4N_2S_3$. Calculated: N 14.8; S 51.1%.

2-Carboxymethylthio-1,3,4-thiadiazole (IX). A solution of 0.22 g (1 mmole) of rhodanine Va in 5 ml of 50% formic acid was heated at 80°C for 2 h, after which it was evaporated to dryness, and the residue was triturated with acetonitrile to give 0.1 g (52%) of a product with mp 158-159°C (from acetonitrile) (mp 156-158°C [9]). Found: N 15.9; S 35.8%. $C_4H_4N_2O_2S_2$. Calculated: N 15.9; S 36.4%.

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REACTION OF A FISCHER BASE AND ITS DERIVATIVES WITH BENZOYLACETALDEHYDES

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The corresponding 2-(3-benzoyl-2-propen-1-ylidene)indolines, which exist in the form of merocyanines and do not display tendencies to undergo intramolecular cyclization to the spiro form, were obtained as a result of the reaction of 1,3,3-trimethyl-2-methyleneindoline and its analogs with p-substituted benzoylacetaldehydes.

Indolinespiropyrans presently constitute one of the most promising classes of photochromic substances [1]. The overwhelming majority of compounds of this type are synthesized by the reaction of a Fischer base and its derivatives with substituted salicylaldehydes and have indoline-2-spiro-2'-[2H]chromene structures. Recently performed quantum-chemical calculations have shown [2] that the photochromic properties of these compounds depend markedly on the electronic structure of the pyran fragment. Thus, for example, the transition from benzopyran derivatives to pyran derivatives sharply increases the stability of the open form, which leads to the loss of photochromic properties. In this connection, it seemed of interest to study the properties of indoline merocyanines in which one might have expected the formation of a closed form with a pyran fragment containing a phenyl substituent. We selected 2-(3-benzoyl-2-propenylidene)indolines as the subjects of this investigation.

It is known [3] that β-dicarbonyl compounds (primarily β-keto aldehydes) react smoothly with primary or secondary amines to give β-aminovinyl ketones. We have established that the reaction of β-keto aldehydes (IVa-g) with Fischer bases (I-III), which can be regarded

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