## INVESTIGATION OF THE REACTIVITIES AND TAUTOMERISM OF AZOLIDINES.

49.\* SYNTHESIS OF 4-THIOXO-5-ARYLIDENESELENAZOLID-2-ONES

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I. B. Levshin, K. A. V'yunov, A. A. Tsurkan, A. I. Ginak, and N. L. Isaeva

A number of 5-benzylidene derivatives of 4-thioselenazolid-2-one with various substituents in the aromatic ring were synthesized as a result of the reaction of 4thioxoselenazolid-2-one with aromatic aldehydes in acetic acid with 25% aqueous methylamine solution as the catalyst. The structure of the compounds was confirmed by alternative synthesis from the corresponding 5-arylideneselenazolidine-2,4-diones.

It is known that many azolidine derivatives [2-6] have a broad spectrum of antimicrobial action, and this is why both pharmacologists and chemists are interested in these compounds.

It has been shown [3, 7-10] that replacement of the oxygen atom in the 4 position of the azolidine ring by sulfur leads to activation of the adjacent methylene group and makes it possible to obtain various 5-R-ylidene derivatives. However, further studies [11] showed that it was not possible to carry out the condensation of 4-thiorhodanine with several aromatic aldehydes (benzaldehyde, p-methylbenzaldehyde, anisaldehyde, and a number of other aldehydes) under any conditions. Our attempt to realize the condensation of 4-thioxoselenazolid-2-one (I) with these aldehydes under conditions that are typical for the Knoevenagel reaction [12], viz., in solution in glacial acetic acid or alcohol with sodium acetate or piperidine as the catalyst, was also unsuccessful. At the same time, the synthesis of 4-thioxo-5-(p-dialkyl-amino-, p-chloro-, p-nitrobenzylidene)selenazolid-2-ones in 50-70% yields on the basis of 4-thioxoselenazolid-2-one and the corresponding aldehydes in a 10% solution of sodium acetate in glacial acetic acid has been reported [13].

We were able to obtain these and other previously inaccessible 4-thioxo-5-arylideneselenazolid-2-ones in 60-95% yields as a result of the use of a 25% aqueous solution of methylamine as the catalyst in acetic acid:



The structure of II-X was proved by alternative synthesis by the reaction of 5-arylideneselenazolidine-2,4-diones [14] with phosphorus pentasulfide in dioxane. The compounds obtained are brightly colored crystalline substances that are readily soluble in alcohols, acetone, and chloroform but insoluble in water.

A characteristic feature of the UV spectra of 5-arylidene-4-thioxoselenazolid-2-ones as compared with the analogous 5-arylideneselenazolidine-2,4-diones is the appearance of a highintensity absorption band with maxima at 400-500 nm due to  $\pi \rightarrow \pi^*$  transitions of the electrons of the conjugated and arylidene substituents of the thioxo group. The UV spectrum of

\*See [1] for communication 48.

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Yield, %		668 802 755 60 755 755 755 755 755 755 755 755 755 75	
Calc., %	Se	255,3 256,1 256,1 256,1 256,1 256,1 257,25	ene.
	s	9,4 10,8 10,8 10,6 10,6 10,6 10,2 10,2	ed from tolue
	Z	80,44,04,488 80,77,530,000	
Empirical formula		C <sub>14</sub> H <sub>16</sub> N <sub>2</sub> OSSe C <sub>12</sub> H <sub>16</sub> N <sub>2</sub> OSSe C <sub>11</sub> H <sub>9</sub> NO <sub>2</sub> SSe C <sub>11</sub> H <sub>9</sub> NO <sub>2</sub> SSe C <sub>10</sub> H <sub>7</sub> NO <sub>2</sub> SSe C <sub>10</sub> H <sub>6</sub> NO <sub>2</sub> SSe C <sub>10</sub> H <sub>6</sub> N <sub>2</sub> O <sub>3</sub> SSe C <sub>10</sub> H <sub>6</sub> N <sub>2</sub> O <sub>3</sub> SSe	rere crystalliz
Found, $\sigma_{0}$	Se	22222222222222222222222222222222222222	V-VIII and X w
	s	9,5 10,7 10,7 10,7 10,7 10,1 10,1 10,1	
	z	8004404408 01-886017703	hile I
UV spectrum, $\lambda_{\max}$ , nm (log <b>s</b> )		$\begin{array}{cccccccccccccccccccccccccccccccccccc$	ere crystallized from ethanol, w
mp,* <sup>≜</sup> C		$\begin{array}{c} 212-213\\ 252-253\\ 250-211\\ 181-182\\ 196-197\\ 196-197\\ 201-202\\ 185-186\\ 185-186\\ 185-186\\ 189-190\\ 189-190 \end{array}$	, and IX we
2.		<i>p</i> -N(C <sub>2</sub> H <sub>6</sub> ) <sup>2</sup> <i>p</i> -N(CH <sub>3</sub> ) <sub>2</sub> <i>p</i> -OCH <sub>3</sub> <i>m</i> -OCH <sub>3</sub> <i>m</i> -OCH <sub>3</sub> <i>m</i> -OCH <sub>3</sub> <i>m</i> -NO <sub>2</sub> <i>m</i> -NO <sub>2</sub>	ds II, III,
Com- pound			*Compoun

TABLE 1. 4-Thioxo-5-arylideneselenazolid-2-ones (II-X)

4-thioxo-selenazolid-2-one (I), which is not substituted in the 5 position, is characterized by two intense absorption bands with maxima at 260 (4.18) and 315 nm (4.26) and one low-intensity long-wave band of an  $n \rightarrow \pi^*$  transition in the thiocarbonyl group with a maximum at 440 nm. Similar low-intensity bands have been observed for 2-thiohydantoins [15, 16] and rhodanines [17]. The disappearance of this absorption band in the spectra of aqueous and hydrochloric acid solutions of 4-thioxoselenazolid-2-one confirms the correctness of the assignment of the transition.

The IR spectra of the 4-thioxo-5-arylideneselenazolid-2-ones contain absorption bands at 1680-1720 (C=0), 1150-1200 (C=S), and 1580-1615 cm<sup>-1</sup>, which are related to the aromatic ring C=C vibrations [18].

## EXPERIMENTAL

The UV spectra of  $10^{-5}$  M solutions of the compounds were recorded with a Hitachi EPS-3T spectrophotometer. Solutions with maximum concentrations were prepared in order to record the low-intensity maxima in the long-wave region of the spectra. The IR spectra of mineral oil suspensions and KBr pellets of the compounds were recorded with a Perkin-Elmer 283 spectrometer. Compounds I-X were purified by recrystallization from toluene or alcohol. The purity of the substances and their individuality were verified by chromatography in a thin layer of aluminum oxide modified with oxalic acid in an acetone-hexane system (2:1).

4-Thioxoselenazolid-2-one (I) was obtained by the method in [3] by refluxing selenazolidine-2,4-dione with phosphorus pentasulfide in dioxane. The 5-arylideneselenazolidine-2,4diones were obtained by the method in [14]. The thionation of the 5-arylideneselenazolidine-2,4-diones was accomplished by the method in [11]. Compounds II-X were isolated by precipitation with water or hexane.

<u>4-Thioxo-5-(p-dimethylaminobenzylidene)selenazolid-2-one (III).</u> A 1.5-g (0.01 mole) sample of p-dimethylaminobenzaldehyde and two drops of a 25% aqueous solution of methylamine were added at 50°C to a solution of 1.8 g (0.01 mole) of 4-thioxoselenazolidin-2-one in 3 ml of acetic acid, and the reaction mixture was heated to the boiling point and refluxed for 1-2 min. The resulting crystalline mass was removed by filtration, washed on the filter with ether, dried, and crystallized from ethanol to give 2.9 g (92%) of product. IR spectrum: 3180 (NH); 1712 (C=0); 1610 (C=C); 1194 (C=S); 755, 740 cm<sup>-1</sup> (C-S). The results of elementary analysis and the UV spectrum of III are presented in Table 1.

The remaining 5-arylidene derivatives II-X were similarly obtained (Table 1).

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