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A. I. Ginak, K. A. V'yunov, and E. G. Sochilin

Thiazolidine-2-thione-4-one (rhodanine) and its 5-ylidene derivatives undergo hydrolysis in aqueous alkali to give mercapto acetic acid [1], but in nonaqueous solutions form disodium salts, the structures of which, however, have not been rigorously proved [2]. In this connection, it seemed of interest to isolate the monosubstituted salts of rhodanine and its 5-substituted derivatives, which are intermediates in alkylation reactions [3].

We have found that the salts can be obtained by mixing equimolecular amounts of rhodanine and alkaline agents such as alkali metal alkoxides, alkali metal hydroxides, and amines. The reaction is conveniently carried out in ether, in which the solubility of the salts formed is limited, in connection with which the losses from side reactions are insignificant.

Salts I-IV are quite soluble in water and polar organic solvents. The UV spectra of the salts (in water) coincide with the spectra of the corresponding anions. The  $\nu_{C=O}$  band (1665 cm<sup>-1</sup>) in the IR spectrum of I is shifted considerably to the low-frequency side in comparison with unsubstituted rhodanine (1710 cm<sup>-1</sup>), which is associated with charge delocalization in the anion.

Just as in [4], the formation of isomeric alkylation products with respect to the exocyclic sulfur atom and the nitrogen atom in the 3 position is observed on treatment of the salts with alkyl halides. Depending on the solvent, the isomer ratios remain practically constant in comparison with [4].

## EXPERIMENTAL

Triethylammonium Salt of Rhodanine (I). Triethylamine [1.01 g (0.01 mole)] was added to 1.33 g (0.01 mole) of rhodanine in 30 ml of dry ether, and the mixture was stirred for 1 h. The precipitate was filtered, washed, and dried to give 2.15 g (92%) of a product with mp 104° (from alcohol-ether). Found %: N 11.8; S 27.1.  $C_3H_3NOS_2 \cdot (C_2H_5)_3N$ . Calculated %: N 11.9; S 27.4.

Lithiorhodanine (II). This was similarly obtained from lithium hydride and had mp 158° (decomp., from alcohol-ether). Found %: N 9.9; S 46.0. C<sub>3</sub>H<sub>2</sub>NOS<sub>2</sub>Li. Calculated %: N 10.1; S 46.1.

<u>3-Sodio-5-benzylidenerhodanine (III)</u>. This was similarly obtained from 5-benzylidenerhodanine and sodium methoxide and had mp 241° (decomp., from alcohol-ether). Found %: N 5.7; S 26.0.  $C_{10}H_6NOS_2Na$ . Calculated %: N 5.8; S 26.4.

<u>3-Piperidinium Salt of Rhodanine (IV)</u>. This had mp 262° (with darkening, from alcohol). Found %: N 12.7; S 29.2.  $C_3H_3NOS_2 \cdot C_5H_{11}N$ . Calculated %: N 12.8; S 29.4.

2-Methylrhodanine (V) and 3-Methylrhodanine (VI). An equimolecular amount of methyl iodide was added to a solution of 2.34 g (0.01 mole) of I in 30 ml of alcohol. The disappearance of the starting salt was determined by means of thin-layer chromatography on aluminum oxide in an acetone-hexane-acetic acid system (800:300:1). The reaction mixture was separated with a chromatographic column packed with  $Al_2O_3$ . 3-Methylrhodanine was eluted with hexane-acetone, while 2-methylrhodanine was eluted with alcohol. 2-Methylrhodanine had mp 82°. Found %: N 9.5; S 43.5.  $C_4H_5NOS_2$ . Calculated %: N 9.5; S 43.6. 3-Methylrhodanine had mp 75°. Found %: N 9.6; S 43.4.  $C_4H_5NOS_2$ . Calculated %: N 9.5; S 43.6.

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## LITERATURE CITED

- 1. E.C. Brown, Chem. Rev., <u>61</u>, 463 (1961).
- 2. H. Beekurts, E. Dillanaer, H. Suter, and K. Kohl, Ber., <u>91</u>, 2773 (1958).
- 3. A. I. Ginak, K. A. V'yunov, and E. G. Sochilin, Zh. Organ. Khim., 6, 1744 (1970).
- 4. A. I. Ginak, V. V. Barmina, K. A. V'yunov, and E. G. Sochilin, Zh. Obshch. Khim., <u>40</u>, 941 (1970).