LETTERS TO THE EDITOR

SYNTHESIS OF QUATERNARY SALTS OF 2-METHYLMERCAPTOTHIAZOLE DERIVATIVES

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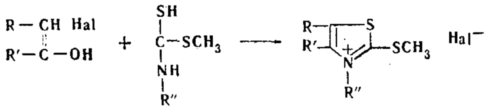
The quaternary salts of 2-methylmercaptothiazole derivatives, which are widely used in the synthesis of cyanine dyes, up to now have been obtained by the condensation of α-halo ketones or aldehydes with ammonium dithiocarbamate [1] with subsequent methylation of the thioketone obtained or by direct condensation with methyl dithiocarbamate [2]; in both cases it was necessary to subsequently quaternize the bases by heating with alkylating agents (for example, with dimethyl sulfate, ethyl p-toluenesulfonate, etc.).

We have worked out a method that makes it possible to carry out the process in one step, as a result of which a considerably purer product is obtained in higher yields. For this, we introduced an N-alkyl derivative of methyl dithiocarbamate into the reaction with the α-halo ketone. A quaternary thiazole salt is immediately formed in the process.



Using this method we obtained a number of quaternary salts of 2-methylmercaptothiazole derivatives, whose structures were confirmed by their analyses, analyses of the dyes obtained from them, and identification of the latter with dyes that are derivatives of the quaternary salts obtained by the method indicated above.

EXPERIMENTAL

2-Methylmercapto-4,5-dimethyl-3-ethylthiazolium Bromide. A mixture of 3 g (0.02 mole) of 3-bromo-2-butanone was heated with 2.7 g (0.02 mole) of N-ethyl-S-methyldithiocarbamate at 80° for 2.5 h. The thickened mass was triturated with acetone, and the solid was filtered and washed with acetone and ether to give 70% of a product with mp 168° (from alcohol). Found %: S 23.71; Br 30.20. $C_8H_{14}BrNS_2$. Calculated %: S 23.88; Br 29.85.

3-Allyl-5-(3-ethyl-4,5-dimethylthiazolinylidine-2-ethylidene)thiazolidine-2-thione-4-one. A mixture of 1.08 g (0.004 mole) of 2-methylmercapto-3-ethyl-4,5-dimethylthiazolium bromide, 0.7 g (0.004 mole) of N-allylrhodanine, 0.4 g (0.004 mole) of acetic anhydride, 0.6 g (0.006 mole) of triethylamine, and 6 ml of absolute alcohol was refluxed for 20 min. The mixture was cooled, and the precipitate was filtered and washed with alcohol to give 81% of a product with mp 194-195° and λ_{max} 437 nm. Found %: S 30.62; N 8.85. $C_{13}H_{16}N_2OS_3$. Calculated %: S 30.74; N 8.97.

2-Methylmercapto-4,5-tetramethylene-3-ethylthiazolium Chloride. A mixture of 4.4 g (0.0035 mole) of α-chlorocyclohexanone and 4.5 g (0.0035 mole) of N-ethyl-S-methyldithiocarbamate was heated at 90° for 3 h. The viscous melt was washed with dry acetone and ether to give 35% of product. Because of its high hygroscopicity, the preparation was used successfully without further purification in the ensuing operations. An analytically pure sample obtained by repeated washing with dry acetone had mp 115°. Found %: Cl 26.98. $C_{10}H_{16}ClNS_2$. Calculated %: Cl 27.21.

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3-Ethyl-5-(4,5-tetramethylenethiazolinylidene-2-ethylidene)thiazolidine-2-thione-4-one. A mixture of 2.46 g (0.001 mole) of 2-methylmercapto-3-ethyl-4,5-tetramethylenethiazolium chloride, 1.61 g (0.001 mole) of N-ethylrhodanine, 0.8 g of acetic anhydride, and 1 ml of triethylamine was heated on a water bath at 70° for 10 min. The dye that precipitated was triturated with alcohol and washed with ether to give 2.4 g (70%) of light-yellow plates. After crystallization from alcohol, a product with mp 204° was obtained in 60% yield. λ_{max} 434-436 nm. Found %: S 29.70. $C_{14}H_{18}N_2OS_3$. Calculated %: S 29.42.

N-Ethyl-5-methyldithiocarbamate. This was obtained from ethylamine, carbon disulfide, and methyl iodide by the method described for similar compounds [3]. The product was distilled to give 35% of a compound with mp 110° (5 mm) and n_D^{20} 1.626. Found %: S 47.31; N 10.40. $C_4H_9NS_2$. Calculated %: S 47.40; N 10.37.

LITERATURE CITED

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2. E. Knott, J. Chem. Soc., 1658 (1947).
3. J. Braun, Ber., 35, 3381 (1902).