REARRANGEMENT OF CYCLIC DITHIOCARBAMATES

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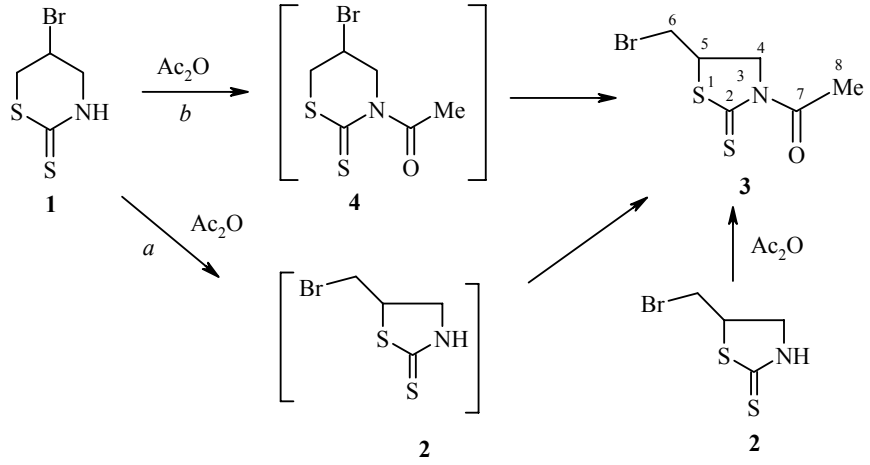
Continuing studies of the properties of cyclic dithiocarbamates [1, 2], we observed that acetylation of 5-bromo-3,4,5,6-tetrahydro-1,3-thiazine-2-thione (**1**) and 5-bromomethyl-1,3-thiazolidine-2-thione (**2)** by acetic anhydride leads to formation of the same compound: 3-acetyl-5-bromomethyl-1,3-thiazolidine-2-thione (**3**).

It has been hypothesized that thiazine **1** under the conditions of this reaction is rearranged with contraction of the ring to form compound **2**, followed by acetylation of the heterocycle obtained (route *a*), or from thiazine **1** its acetyl derivative is formed first: 3-acetyl-5-bromo-3,4,5,6-tetrahydrothiazine-2-thione (**4**) (route *b*), which then is rearranged with contraction of the ring to form compound **3**. The reaction possibly proceeds along these two directions simultaneously. Varying the acetylation conditions for thiazine **1** did not lead to isolation of tetrahydrothiazine-2-thione **4**.



We should note that 5-bromo-3-methyl-3,4,5,6-tetrahydro-1,3-thiazine-2-thione (**5**) when heated in acetic anhydride is also rearranged to form the five-membered isomer: 5-bromomethyl-3-methyl-1,3-thiazolidine-2-thione (**6**), which may be indirect evidence for the possibility that acetylation of thiazine **1** occurs along route *a*.

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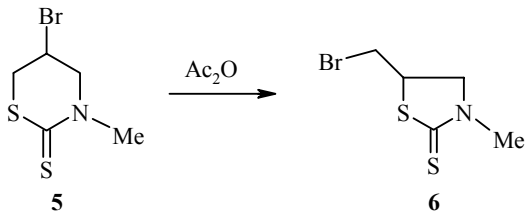

5 **6**

The structure of the obtained compound **3** was confirmed by comparative analysis of the ^{13}C NMR spectral data for the following compounds: compound **3**, 3-methyl-1,3-thiazine-2-thione **5**, 3-methyl-1,3-thiazolidine-2-thione **6**, and 3-acetyl-1,3-thiazolidine-2-thione (**7**) [3]. We established that for these compounds, the chemical shift of the $C_{(2)}$ atom is found in the ~200 ppm region, which is typical of substances containing the thione group [4]. Furthermore, in the proton-coupled ^{13}C NMR spectra for compounds **3**, **6**, and **7**, we observe a spin–spin coupling constant of $^{3}J(C_{(7)}–H\text{-}4) = 0.7±0.2$ Hz, which also suggests acetylation at the nitrogen atom.

The ^{13}C NMR spectra were recorded on a Burker CXP-200 spectrometer (50 MHz) in a 1:4 DMSO-d_6–CCl_4 mixture, internal standard TMS.

3-Acetyl-5-bromomethyl-1,3-thiazolidine-2-thione (3). A. 5-Bromomethylthiazolidine-2-thione **2** (0.2 g, 0.01 mol) was added to acetic anhydride (4 ml) and heated for 15 min at 80°C with vigorous stirring. The mixture was cooled down and the acetic anhydride was evaporated. The oil obtained was treated with water. Obtained 2.3 g (96%) of compound **3**; mp 76-77°C. Found, %: C 28.50; H 3.08; N 5.43. $C_6H_8BrNOS_2$. Calculated, %: C 28.35; H 3.17; N 5.51.

B. 5-Bromothiazine thione **1** (0.1 g, 0.005 mol) was added to acetic anhydride (10 ml) and heated with vigorous stirring for 6 h at 80°C. The mixture was cooled down and the acetic anhydride was evaporated. The oil obtained was treated with water. Obtained 1.1 g (92%) of compound **3**; mp 75-76°C. ^{13}C NMR spectrum, δ, ppm: 200.51 ($C_{(2)}$); 171.01 ($C_{(7)}$); 59.34 ($C_{(4)}$); 44.69 ($C_{(5)}$); 34.76 ($C_{(6)}$); 27.50 (CH_3). Found, %: C 28.33; H 3.13; N 5.58. $C_6H_8BrNOS_2$. Calculated, %: C 28.35, H 3.17; N 5.51.

5-Bromo-3-methyl-3,4,5,6-tetrahydro-1,3-thiazine-2-thione (5). A solution of NaOH (1.44 g, 0.036 mol) in water (30 ml) was added dropwise to N-methyl-2,3-dibromopropylamine hydrobromide (11.23 g, 0.036 mol) in a minimal amount of water with stirring. This was extracted with ether (4 × 60 ml). The ether extracts were combined, evaporated down to 150 ml, and then carbon disulfide (1.38 g, 1.1 ml, 0.038 mol) was added. The reaction mixture was held for 24 hours at room temperature. The white precipitate formed was filtered out and washed with water. Obtained 0.3 g (7%) of compound **5**; mp 140-142°C. ^{13}C NMR spectrum, δ, ppm: 188.27 ($C_{(2)}$); 58.69 ($C_{(4)}$); 44.30 (CH_3), 41.09 ($C_{(5)}$); 39.94 ($C_{(6)}$). Found, %: C 26.64; H 3.61; N 6.42. $C_5H_8BrNS_2$. Calculated, %: C 26.55; H 3.57; N 6.19.

5-Bromomethyl-3-methyl-1,3-thiazolidine-2-thione (6). The ether layer from the preceding experiment was held for 6 days at room temperature; the precipitating crystals were filtered out and washed with a small amount of water. Obtained 1.4 g of compound **6**. The ether filtrate was evaporated down, washed with water, and another 1.5 g of compound **6** was isolated. The precipitates were combined: yield 72%; mp 70-71°C. ^{13}C NMR spectrum, δ, ppm: 193.88 ($C_{(2)}$); 62.71 ($C_{(4)}$); 43.95 ($C_{(5)}$); 37.10 (CH_3); 35.99 ($C_{(6)}$). Found, %: C 26.72; H 3.40; N 6.38. $C_5H_8BrNS_2$. Calculated, %: C 26.55; H 3.57; N 6.19.

3-Acetyl-1,3-thiazolidine-2-thione (7) was obtained by acetylation of thiazolidine-2-thione by acetyl chloride; mp 112-114°C (mp 111-114°C [3]). ^{13}C NMR spectrum, δ, ppm: 202.64 ($C_{(2)}$); 170.78 ($C_{(7)}$); 56.08 ($C_{(4)}$); 28.22 ($C_{(5)}$); 26.74 (CH_3).

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