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NEW PATHWAY TO THIA-2-CYCLANONES

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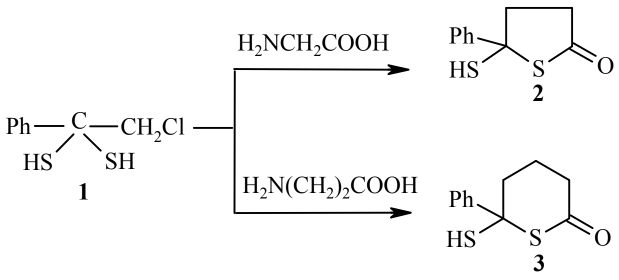
In a continuation of a study of the chemical transformations of recently synthesized α-halo *gem*-dithiols, R–C(SH)$_2$–CH$_2$X (R = CH$_3$, (CH$_3$)$_3$C, C$_6$H$_5$, 4-CH$_3$C$_6$H$_4$, 1-C$_{10}$H$_7$, 5-Cl-2-C$_4$H$_2$S, X = F, Cl, Br) [1], we investigated the reaction of 1-chloro-2-phenylethane-2,2-dithiol (**1**) with amino acids with the aim of obtaining new heterocyclic systems containing both endocyclic nitrogen and sulfur atoms.

However, the reaction of 0.2 g (1 mmol) of *gem*-dithiol **1** with a molar equivalent of glycine in moist ether over 72 h and subsequent separation of the mixture on a column packed with silica gel L 400/100 and 10:1 chloroform–hexane as the eluent gave 5-mercapto-5-phenyl-2-thiolanone (**2**), which lacks nitrogen. Under analogous conditions, the reaction of *gem*-dithiol **1** with β-alanine gave 6-mercapto-6-phenyl-2-tetrahydrothiopyranone (**3**).



The structures of **2** and **3** were supported by ^{1}H NMR and IR spectroscopy. The IR spectra of **2** and **3** in chloroform have bands typical for carbonyl groups in 1,2-thiolactones (1690-1710 cm^{-1}) [2, 3]. The band at 1410-1420 cm^{-1} corresponds to symmetric bending of the CH$_2$ fragment adjacent to the carbonyl group [4]. The C–S stretching vibrations appear at 710-720 cm^{-1}, which is in accord with the frequencies observed for endocyclic C–S bonds (these vibrations are noted at 690 cm^{-1} in the spectra of linear sulfides) [1, 5]. The series of bands at 1280, 1180, 1000, and 890 cm^{-1} are due to the skeletal vibrations of the saturated heterocycles in **2** and **3** [1]. The intensities of these bands and of $\nu_s(CH_2)$ at 2860-2840 cm^{-1} and $\nu_{as}(CH_2)$ at 2920-2940 cm^{-1} are quite enhanced as a consequence of the large number of methylene fragments in the six-membered heterocycle. The bands for the aromatic C–C bonds are found at 1600, 1580, and 1490 cm^{-1}, while the weak band at 2520 cm^{-1} corresponds to mercapto S–H stretching vibrations.

The study of this new reaction and the mechanism for the formation of **2** and **3** is presently underway.

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5-Mercapto-5-phenyl-2-thiolanone (2) was obtained in 78% yield (0.16 g) as a thick oil, R_f 0.87 on a Silufol UV-254 plate (10:1 chloroform–hexane). ^{1}H NMR spectrum at 400 MHz ($CDCl_3$), δ, ppm: 3.45 (1H, s, SH); 4.22 (2H, m, CH_2); 4.67 (2H, m, CH_2); 7.46-7.93 (5H, m, C_6H_5). Found, %: C 56.95; H 4.22; S 29.87. $C_{10}H_{10}OS_2$. Calculated, %: C 57.11; H 4.79; S 30.49.

6-Mercapto-6-phenyl-2-tetrahydrothiopyranone (3) was obtained in 68% yield (0.15 g); mp 112-113°C (chloroform), R_f 0.76 on Silufol UV-254 (10:1 chloroform–hexane). ^{1}H NMR spectrum at 400 MHz ($CDCl_3$), δ, ppm: 3.45 (1H, s, SH); 4.07 (2H, m, CH_2); 4.48 (2H, m, CH_2); 4.68 (2H, m, CH_2); 7.50-7.93 (5H, m, C_6H_5). Found, %: C 58.78; H 5.15; S 28.85. $C_{11}H_{12}OS_2$. Calculated, %: C 58.89; H 5.39; S 28.58%.

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