# 2-AMINO-6-MERCAPTO-6-PHENYL-5,6-DIHYDRO-1,3,4-THIADIAZINES

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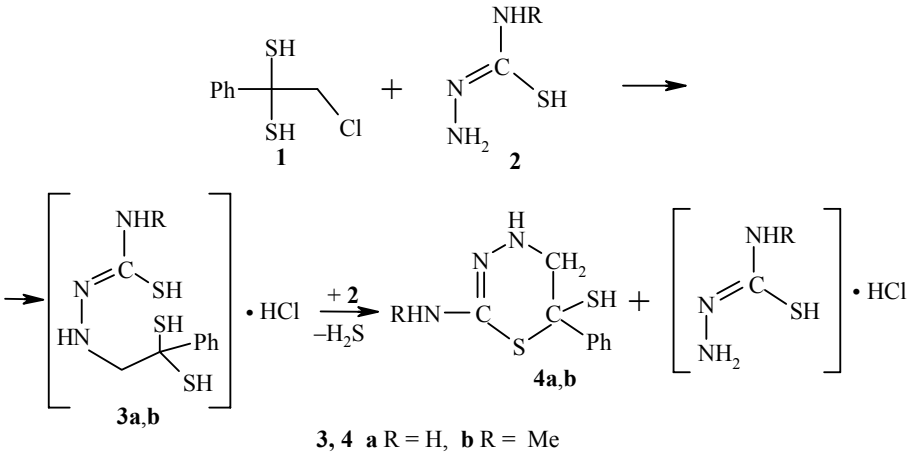
5,6-Dihydro derivatives of 1,3,4-thiadiazine have been insufficiently studied [1]. The progenitor compound of this class (5,6-dihydro-4H-1,3,4-thiadiazine) was synthesized by cyclodehydration of 2-(β-hydroxyalkyl)-1-thioacylhydrazide by means of treatment with concentrated HCl [2]. Its 2-amino derivatives were obtained by condensation of β-hydrazinoalkyl thiols with cyanogen bromide [3].

We have found that reaction of 2-chloro-1-phenylethane-1,1-dithiol (**1**) with thiosemicarbazide (**2**) in anhydrous methanol at -5°C leads to a previously unknown dihydro derivative of thiadiazine: 2-amino-6-mercapto-6-phenyl-5,6-dihydro-1,3,4-thiadiazine (**4a**), in 64% yield.

An intermediate in this reaction is the hydrochloride of the corresponding derivative of the enethiol form of thiosemicarbazide **3a,b**. The hydrochloride **3a** is isolated when the reaction is carried out with an equimolar ratio of dithiol **1** to thiosemicarbazide **2**. In the IR spectrum of the hydrochloride **3a**, there is a broad band for the moiety N–N=C–N at 1580 $cm^{-1}$ [4]. Furthermore, in the spectrum there are no bands for the $NH_2$ group at 3500-3400 $cm^{-1}$, and instead we see a characteristic broad, intense band for the hydrochloride, $\nu N^{+}H$, in the region 2000-3400 $cm^{-1}$ and bands for the associated $NH_2$ group in the 3250 $cm^{-1}$ region. In the IR spectrum of the cyclic end product **4**, we see a series of bands due to vibrations of the heterocycle: 1080, 1280, 1440, 1600-1630 $cm^{-1}$; for the mercapto group at 2560 $cm^{-1}$, and for the amino group in the 3360 $cm^{-1}$ region. The band at 3300 $cm^{-1}$ corresponds to absorption of the stretching vibrations (ν) of the NH group.

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6-Mercapto-2-methylamino-6-phenyl-5,6-dihydro-1,3,4-thiadiazine (**4b**) was synthesized in 59% yield by reaction of dithiol **1** and 4-methylthiosemicarbazide. This reaction is promising for synthesis of 6-substituted 5,6-dihydro-1,3,4-thiadiazine.

The $^1$H NMR spectra were taken on a Bruker DPX-400 (400 MHz) in $CDCl_3$, external standard HMDS (δ 0.05 ppm).

**2-Amino-6-mercapto-6-phenyl-5,6-dihydro-1,3,4-thiadiazine (4a).** A solution of *gem*-dithiol **1** (0.2 g, 1 mmol) in ethanol (5 ml) was slowly added dropwise to a solution of thiosemicarbazide (0.36 g, 4 mmol) in ethanol (10 ml), cooled down to -30°C. The reaction mixture was held at -5°C for 2 h until the starting dithiol **1** disappeared (according to TLC). After removal of the alcohol under vacuum, a pasty residue remained which was extracted with ether. The ether was removed under vacuum, obtaining 0.14 g (63.6%) thiadiazine **4a** as a light-yellow powder; mp 120-122°C. $^1$H NMR spectrum, δ, ppm: 1.89-1.99 (2H, q, $CH_2$); 2.3 (1H, s, SH); 4.10 (2H, s, $NH_2$); 7.2-7.4 (5H, m, $C_6H_5$); 8.65 (1H, s, NH). $^{13}$C NMR spectrum, δ, ppm: 25 ($CH_2$), 124-141 (CPh), 167.15 (C–SH); 182.87 (S–C=N). Found, %: C 47.30; H 4.92; N 18.97; S 28.76. $C_9H_{11}N_3S_2$. Calculated, %: C 48.00; H 4.88; N 18.66; S 28.44.

**6-Mercapto-2-methylamino-6-phenyl-5,6-dihydro-1,3,4-thiadiazine (4b)** was obtained as for **4a**, from methylthiosemicarbazide (0.42 g, 4 mmol) and *gem*-dithiol **1** (0.2 g, 1 mmol). Yield of thiadiazine **4b** 0.13 g (59%); mp 106-108°C. $^1$H NMR spectrum, δ, ppm: 1.7-1.9 (2H, q, $CH_2$); 2.27 (1H, s, SH); 3.15 (3H, s, $CH_3$); 4.25 (1H, s, NH–$CH_3$); 7.2-7.4 (5H, m, $C_6H_5$); 8.65 (1H, s, NH). $^{13}$C NMR spectrum, δ, ppm: 25 ($CH_2$), 45 ($CH_3$); 124-141 (CPh); 167.15 (C–SH); 182.87 (S–C=N). IR spectrum, ν, cm$^{-1}$: 2550 (SH). Found, %: C 50.49; H 5.80; N 16.87; S 26.70. $C_{10}H_{13}N_3S_2$. Calculated, %: C 50.20; H 5.43; N 17.57; S 27.10.

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