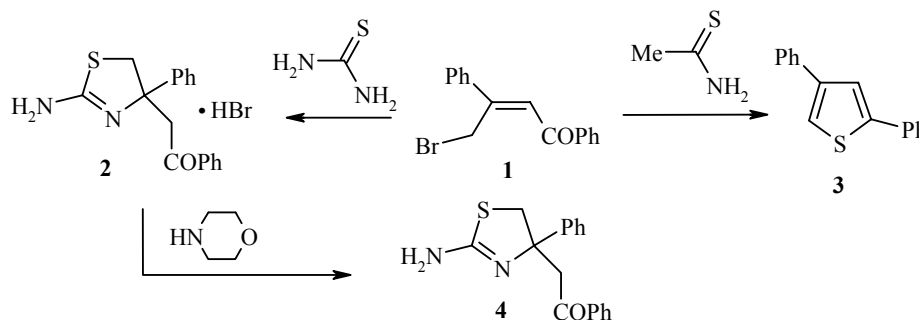


## REACTION OF $\gamma$ -BROMODIPNONE WITH THIOCARBAMIDES

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**Keywords:** 2-(2-amino-4-phenyl-4,5-dihydrothiazol-4-yl)-1-phenyl-1-ethanone,  $\gamma$ -bromodipnone, 2,4-diphenyl-thiophene.

One of the traditional methods for the synthesis of derivatives of thiazole is the reaction of  $\alpha$ -halo-carbonyl compounds with thiocarbamides [1]. A similar result is obtained if vinylogs of  $\alpha$ -halocarbonyl compounds are used in this reaction [2,3]. We have shown [4] that the reaction of 4-bromo-1,3-diphenyl-2-buten-1-one ( $\gamma$ -bromodipnone) with  $\alpha$ -aminoazines gives rise to products of nucleophilic substitution at position 4 and Michael addition at position 3 of the dipnone system – condensed imidazoles. We have presently established that the reaction of **1** with thiourea goes by such a scheme when the starting materials are heated in ethanol and gave rise to 2-(2-amino-4-phenyl-4,5-dihydrothiazol-4-yl)-1-phenyl-1-ethanone hydrobromide (**2**). The reaction of the same  $\gamma$ -bromodipnone with thioacetamide under the same conditions gave 2,4-diphenylthiophene (**3**) in high yield. 2-(2-Amino-4-phenyl-4,5-dihydrothiazol-4-yl)-1-phenyl-1-ethanone (**4**) was obtained as the free base when the salt **2** reacted with morpholine.



Characteristic of the  $^1\text{H}$  NMR spectra of thiazoles **2** and **4** is the presence of signals of two methylene groups with a splitting characteristic of AB systems, a pattern previously observed [4] for the products of 3,4-binucleophilic substitution of  $\gamma$ -bromodipnone. The structure of compound **4** was also confirmed by the presence of strong field shifts of the protons in its  $^1\text{H}$  NMR spectrum, most evident for the aliphatic part (in comparison of the spectrum of salt **2**).

$^1\text{H}$  NMR spectra of DMSO- $d_6$  solutions with TMS as internal standard were recorded on a Varian Mercury 400 (400 MHz).

**2-(2-Amino-4-phenyl-4,5-dihydrothiazol-4-yl)-1-phenyl-1-ethanone hydrobromide (2).** A mixture of  $\gamma$ -bromodipnone (1 g, 3.32 mmol) and thiourea (0.25 g, 3.32 mmol) in ethanol (50 ml) was boiled for 40 min. The solvent was evaporated and the residue was recrystallized from AcOH. Yield 0.65 g (52%); mp 194-196°C (from AcOH).  $^1\text{NMR}$  spectrum,  $\delta$ , ppm ( $J$ , Hz): 7.95 (2H, br. s,  $\text{NH}_2$ ); 7.95 (2H, d,  $^3J = 8.0$ , H-2",6");

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7.61 (1H, t,  $^3J = 8.0$ , H-4"); 7.49 (4H, m, H-2', 6', 3", 5"); 7.35 (2H, t,  $^3J = 8.0$ , H-3', 5'); 7.26 (1H, t,  $^3J = 8.0$ , H-4"); 4.10 (1H, d,  $^2J = 11.6$ , H<sub>A</sub>-5); 3.65 (1H, d,  $^2J = 11.6$ , H<sub>B</sub>-5); 4.60 (1H, d,  $^2J = 18.0$ , 4-CH<sub>A</sub>H<sub>B</sub>); 3.80 (1H, d,  $^2J = 18.0$ , 4-CH<sub>A</sub>CH<sub>B</sub>). Found, %: Br 21.24; N 7.46; S 13.49. C<sub>17</sub>H<sub>17</sub>BrN<sub>2</sub>OS. Calculated, %: Br 21.18; N 7.42; S 13.50.

**2,4-Diphenylthiophene (3).** Compound **3** was prepared by the method described above using thioacetamide (0.25 g, 3.32 mmol) in place of thiourea. Yield 0.49 g (62%); mp 122-123°C (from EtOH) (mp 123-5-124°C [5]).

**2-(2-Amino-4-phenyl-4,5-dihydrothiazol-4-yl)-1-phenyl-1-ethanone (4).** Morpholine (2 ml) was added to a suspension of salt **2** (0.5 g, 1.33 mmol) in 2-propanol (5 ml) and the mixture was heated until the salt had dissolved completely. The solvent and excess morpholine were evaporated and water (50 ml) was added to the residue. The solid was filtered off and recrystallized from 2-propanol. Yield 0.27 g (68%); mp 152-154°C (from 2-propanol). <sup>1</sup>NMR spectrum, δ, ppm (*J*, Hz): 7.77 (2H, d,  $^3J = 8.0$ , H-2", 6"); 7.50 (1H, t,  $^3J = 8.0$ , H-4"); 7.46 (2H, d,  $^3J = 8.0$ , H-2', 6'); 7.38 (2H, t,  $^3J = 8.0$ , H-3", 5"); 7.23 (2H, t,  $^3J = 8.0$ , H-3', 5'); 7.13 (1H, t,  $^3J = 8.0$ , H-4'); 6.42 (2H, br. s, NH<sub>2</sub>); 3.98 (1H, d,  $^2J = 11.6$ , H<sub>A</sub>-5); 3.61 (1H, d,  $^2J = 14.4$ , 4-CH<sub>A</sub>H<sub>B</sub>); 3.45 (1H, d,  $^2J = 10.8$ , H<sub>B</sub>-5); 3.41 (1H, d,  $^2J = 14.4$ , 4-CH<sub>A</sub>CH<sub>B</sub>). Found, %: N 9.43; S 10.85. C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>OS. Calculated, %: N 9.45; S 10.82.

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