Chemistry of Heterocyclic Compounds, Vol. 44, No. 1, 2008

CONDENSATION OF γ-BROMODYPNONE WITH THIOCARBAMIDES: SYNTHESIS OF 4,4-DISUBSTITUTED 4,5-DIHYDRO-1,3-THIAZOL-2-AMINES AND THIAZOLIDIN-2-ONES

L. M. Potikha, A. V. Turov, and V. A. Kovtunenko

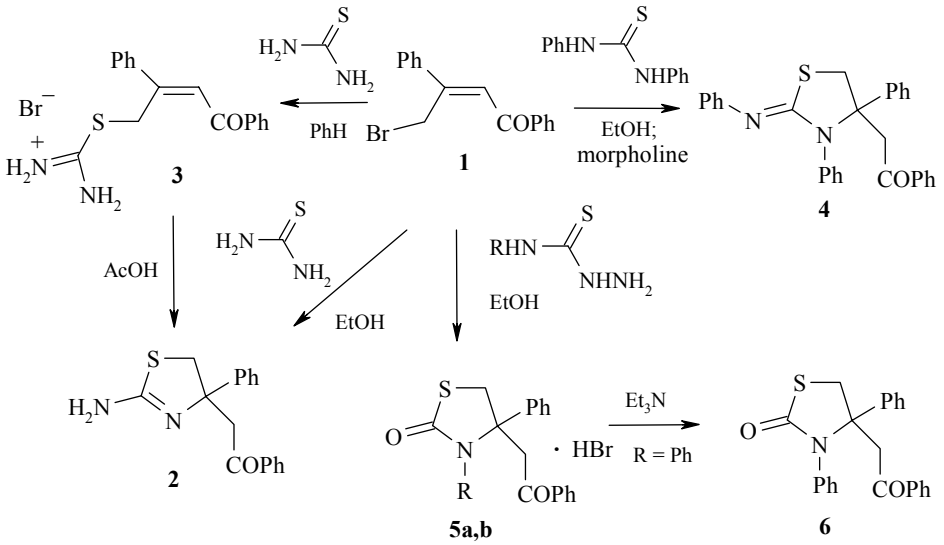
The reaction of 4-bromo-1,3-diphenyl-2-buten-1-one with thiourea or N,N'-diphenylthiourea gives 2-(2-amino-4-phenyl-4,5-dihydro-1,3-thiazol-4-yl)- and 2-[3,4-diphenyl-2-(phenylimino)-1,3-thiazolidin-4-yl]-1-phenyl-1-ethanone – the products of nucleophilic substitution of the halogen atom and Michael addition at position 3 of the 2-buten-1-one system. A similar reaction with thiosemicarbazide and 1-phenylthiosemicarbazide gives the 4-(2-oxo-2-phenylethyl)-4-phenyl- and 4-(2-oxo-2-phenylethyl)-3,4-diphenyl-1,3-thiazolidin-2-one hydrobromides respectively.

Keywords: 2-amino-4,5-dihydro-1,3-thiazole, γ-bromodypnone, 2,4-diphenylthiophene, 1,3-thiazolidin-2-one, thiourea, thiosemicarbazide.

Thiocarbamides are nucleophilic reagents with broad synthetic potential in the synthesis of hydrogenated azoles and azines [1, 2] which are of interest as biologically active substances with a wide spectrum of activity [3]. The reaction of α-halocarbonyl compounds with thioureas and thiosemicarbazides is a widely known method for the synthesis of 2-amino-1,3-thiazoles [2]. The use of certain activated allyl halides [4-9] or vinylogs of α-halocarbonyl compounds [7, 10] in this reaction also leads to the thiazoles. We have previously shown [11] that the reaction of 4-bromo-1,3-diphenyl-2-buten-1-one (γ-bromodypnone) (**1**) with thiourea gives the substituted 2-aminothiazole – 2-(2-amino-4-phenyl-4,5-dihydro-1,3-thiazol-4-yl)-1-phenylethanone (**2**). In this work we make a fuller study of the features of the synthesis and of the structure and properties of the reaction products of γ-bromodypnone **1** with thiocarbamides.

With the aim of developing an optimal method for the synthesis of the 2-aminothiazole **2** we have tried various conditions for the reaction of the γ-bromodypnone **1** with thiourea, *viz*. heating a mixture of the reagents in benzene, alcohol, or acetic acid and fusing them in the presence of sodium acetate. Carrying out the reaction in the presence of base gives a complex mixture of unidentified products but in acid medium (HOAc) to the formation of the 2-aminothiazole salt **2**·HBr but in lower yield (< 40%) than with the instance of alcohol used as solvent [11]. According to ^{1}H NMR data (DMSO-d_6) on the uncrystallized product, heating the reagents in benzene gave a mixture of products consisting of the S-(4-oxo-2,4-diphenyl-2-butenyl)isothiourea hydrobromide (**3**) and 2-aminothiazole hydrobromide **2**·HBr.

Taras Shevchenko National University, Kiev 01033, Ukraine; e-mail: potikha_l@mail.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 103-110, January, 2008. Original article submitted February 27, 2007.



a R = H, **b** R = Ph

The structure of the main reaction product (the thiouronium salt **3**) was established from its elemental analytical data and ^{1}H NMR spectroscopic parameters. The ^{1}H NMR spectrum showed two two-proton, broad signals for the NH_2 groups at 9.21 and 9.01 ppm as well as singlets for the protons of the $C_{(1)}H_2$ group and H-3 proton of the γ-substituted dypnone residue at 4.83 (2H) and 7.51 ppm (1H) respectively. Upon refluxing salt **3** in acetic acid for 10 min it cyclizes to the 2-aminothiazole hydrobromide **2**·HBr.

The 2-aminothiazole **2** free base was prepared by treating the **2**·HBr salt with morpholine [11] but the overall yield of this compound from the γ-bromodypnone was not high (35%). The main loss is evidently explained by the low hydrolytic stability of the 2-amino-4,5-dihydro-1,3-thiazoles in acid medium [2, 12]. We also could not exclude the possible removal of an acetophenone fragment in the presence of base [5, 6, 13] but the separation of 4-phenyl-1,3-thiazol-2-amine from the mixture was not achieved. The occurrence of hydrolytic processes is the main reason for the low yield of 2-[3,4-diphenyl-2-(phenylimino)-1,3-thiazolidin-4-yl]-1-phenylethanone (**4**) in the reaction of γ-bromodypnone with N,N'-diphenylthiourea. It only proved possible to separate the free base in a pure state. Attempts to purify the hydrobromide of compound **4** by recrystallization proved unsuccessful because of the ease of its degradation upon heating both in protic (alcohols, acetic acid) and in aprotic solvents (acetonitrile, nitromethane).

A feature of the ^{1}H NMR spectrum of the 2-(phenylimino)thiazole **4** (see Table 1) is, as in the case of compound **2** [11], the presence of signals for the protons of two methylene groups with splitting characteristic of AB spin systems at 4.30 (d, H_A-5) and 3.56 (d, H_B-5) with spin-spin coupling 11.0 Hz and at 4.21 (4-C$\underline{H}_A$H$_B$) and 4.02 ppm (d, 4-CH$_A$C$\underline{H}_B$) with coupling 16.0 Hz. Final confirmation of the structure of the product **4** came from the ^{13}C NMR spectra.

The assignments of signals in the complex aromatic proton system and of the carbon signals was made using homonuclear (COSY) and heteronuclear (HMBC and HMQC) two-dimensional correlation spectroscopy and clarification of the steric proximity of specific protons from their NOESY spectra (Table 2). Figure 1 shows the signal assignments and the arrows indicate the structurally significant HMBC correlations. Hence for compound **4** the protons with chemical shifts of 4.30 and 3.56 ppm are correlated with the two quaternary carbon atoms absorbing at 144.49 and 71.04 ppm which correspond to the C-1''' and C-4 atoms. The latter also has correlations with the signals for the protons of the 4-CH_2 methylene group and the aromatic H-2''' and H-6''' protons which are three chemical bonds distant. Correlation of H_B-5 with the quaternary carbon atom absorbing at 159.3 ppm and lack of a correlation with other protons allows the assignment of this signal to the C-2 atom.

TABLE 1. Spectroscopic Characteristics the 4,5-Dihydro-1,3-thiazoles*

Compound	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm (*J*, Hz)		
		ArH	$C_{(5)}H_2$	4-CH_2
4	1620 (br., C=O, C=N), 1580, 1230, 750 (C–S), 683	7.76 (2H, d, ^3J = 8.0, H-2"",6""); 7.59 (2H, d, ^3J = 8.0, H-2"',6"'); 7.56 (1H, t, ^3J = 8.0, H-4"'); 7.44 (2H, t, ^3J = 8.0, H-3"",5""); 7.42 (2H, t, ^3J = 8.0, H-3"',5"'); 7.34 (1H, t, ^3J = 8.0, H-4""); 7.27 (2H, t, ^3J = 8.0, H-3",5"); 7.15 (2H, t, ^3J = 8.0, H-3',5'); 7.01 (4H, m, H-2',6', H-4',4"); 6.88 (2H, d, ^3J = 8.0, H-2",6")	4.30 (d, H_A); 3.56 (d, ^2J = 11.0, H_B)	4.21 (d, H_A); 4.02 (d, ^2J = 16.0, H_B)
5a*[2]	1650 (br., C=O), 1585, 1420, 1280, 763 (C–S), 690	7.84 (2H, d, ^3J = 8.2, H-2",6"); 7.53-7.4 2 (7H, m, H-2',3',5',6', H-3"–5"); 7.38 (1H, td, ^3J = 6.0, ^4J = 2.4, H-4')	4.47 (d, H_A); 3.89 (d, ^2J = 11.2, H_B)	4.12 (d, H_A); 3.64 (d, ^2J = 17.6, H_B)
5b	1625 (br., C=O), 1590, 1220, 770 (C–S), 695	7.91 (2H, d, ^3J = 7.2, H-2"',6"'); 7.55-7.45 (11H, m, H-2',3',5',6',2",3",5",6", H-3"'–5"'); 7.39 (2H, m, H-4',4")	4.56 (d, H_A); 3.90 (d, ^2J = 10.8, H_B)	4.17 (d, H_A); 3.69 (d, ^2J = 17.6 H_B)
6	1625 (br., C=O), 1590, 1380, 1225, 940, 757 (C–S), 690	7.74 (2H, m, H-2"',6"'); 7.54 (2H, d, ^3J = 7.8, H-2",6"); 7.44-7.39 (5H, m, H-3",5", H-3"'–5"'); 7.32 (1H, t, ^3J = 7.5, H-4"); 7.28 (2H, t, ^3J = 8.0, H-3',5'); 7.02 (1H, t, ^3J = 8.0, H-4'); 6.90 (2H, d, ^3J = 8.0, H-2',6')	3.83 (d, H_A); 3.65 (d, ^2J = 10.8, H_B)	3.88 (d, H_A); 3.37 (d, ^2J = 17.6, H_B)

* Assignments of the aromatic proton and carbon atom signals are given in Figure 1.
*[2] ^{1}H NMR spectrum: 10.59 (1H, br., SH), 10.49 (1H, br., NH).

Assignment of the signal of the H-2"' and H-6"' signals was based on the NOESY spectroscopic data in which cross peaks point to the steric proximity of the indicated aromatic protons to the $C_{(5)}H_2$ and 4-CH_2 methylene group protons. From the data obtained we have also made the assignments in the ^{13}C NMR spectra of the 2-aminothiazole hydrobromide **2**·HBr.

TABLE 2. ^{13}C NMR Spectra of Compounds **4**, **5a**, and **6**

Compound	^{13}C NMR spectrum δ, ppm		
	C	CH	CH_2
4	197.43 (C=O), 159.4 (C-2), 152.2 (C-1"), 144.49 (C-1"'), 139.73 (C-1'), 137.62 (C-1"'), 71.04 (C-4)	133.81 (C-4"'), 129.49 (C-3",5"), 129.30 (C-2',6'), 129.16 (C-3"',5"'), 129.12 (C-3"", 5""), 128.85 (C-3',5'), 128.5 (C-4""), 128.21 (C-2"',6"'), 126.82 (C-4'), 126.77 (C-2"",6""), 123.45 (C-4"), 122.31 (C-2", 6")	43.79 (4-CH_2), 40.40 (C-5)
5a	169.27 (C=O), 164.52 (C-2), 140.80 (C-1'), 132.80 (C-1"), 77.49 (C-4)	130.29 (C-4"), 129.59 (C-3",5"), 129.57 (C-3',5'), 129.18 (C-4'), 128.34 (C-2",6"), 125.09 (C-2',6')	47.39 (4-CH_2), 44.55 (C-5)
6	158.4 (C=O), 153.4 (C-2), 151.6 (C-1'), 144.4 (C-1"), 132.05 (C-1"'), 74.6 (C-4)	130.9 (C-4"'), 129.68 (C-3',5'), 129.5 (C-3"',5"'), 129.35 (C-3",5"), 128.5 (C-4"), 127.2 (C-2"',6"'), 125.8 (C-2",6"), 123.9 (C-4'), 121.8 (C-2',6')	46.85 (4-CH_2), 41.95 (C-5)

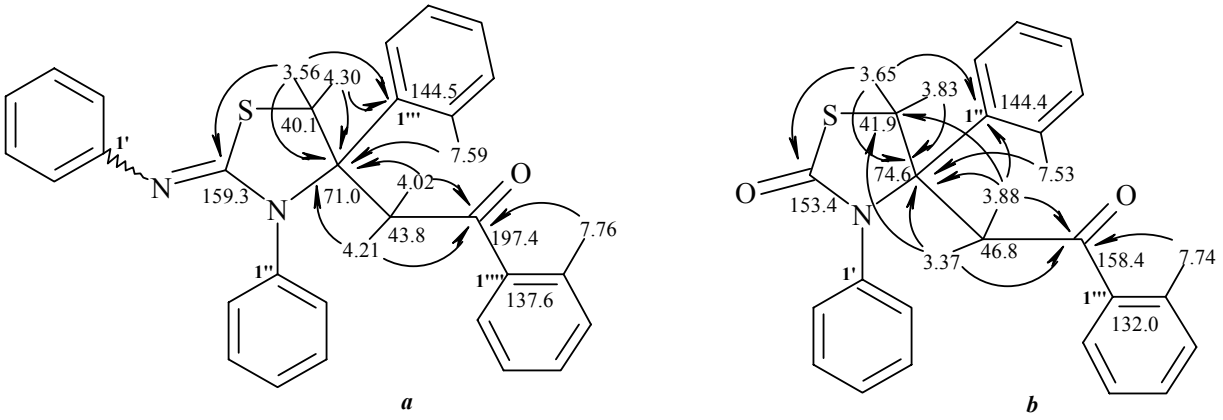


Fig. 1 Assignments of the aromatic proton and carbon atom signals.

It is known that treating α-halocarbonyl compounds with thiosemicarbazides gives 2-hydrazino-1,3-thiazoles [2]. Vinylogs of the α-halocarbonyl compounds have not previously been used in this reaction. We have found that heating a mixture of the γ-bromodypnone **1** with thiosemicarbazide or 1-phenyl-thiosemicarbazide in ethanol or acetic acid also gives 4,5-dihydro-1,3-thiazoles. However, according to

TABLE 3. Proton-Carbon and Proton-Proton Correlations for Compounds **4** and **6**

Com-pound	^{1}H NMR spectrum δ, ppm	Chemical shifts, δ, ppm		
		carbons with HMQC correlations	carbons with HMBC correlations	carbons with NOESY correlations
4	3.56	40.4	71.04, 144.5, 159.3	7.59, 4.30
	4.02	43.8	40.1, 71.04, 144.5, 197.43	4.22, 7.59, 7.76
	4.21	43.8	40.1, 71.04, 197.43	4.02, 7.59
	4.30	40.4	43.8, 71.04, 144.49	3.56
	6.88	122.3	122.3, 123.45	7.27
	7.01	129.3, 126.8, 123.45	122.3, 126.8, 129.3	7.15, 7.27
	7.15	128.85	128.85, 139.73	7.01
	7.27	129.5	122.3, 129.5, 152.2	7.00, 6.88
	7.37	128.5	126.7	7.44
	7.42	129.16	129.17, 137.6	7.56, 7.76
	7.44	129.12	129.16, 144.5	7.37, 7.59
	7.56	133.81	128.2	7.42
	7.59	126.77	71.04, 126.7, 128.5	3.56, 4.02, 4.21, 7.44
	7.76	128.2	128.2, 133.8, 197.43	4.02, 7.42
6	3.37	46.85	41.95, 74.6, 144.4, 158.4	3.88, 7.53, 7.74
	3.65	41.95	74.6, 144.4, 153.4	3.83, 7.53
	3.83	46.85	41.95, 74.6, 144.4	3.65
	3.88	41.95	46.8, 74.6, 144.4, 158.4	3.37
	6.90	121.8	121.8, 123.9	7.27
	7.02	123.9	121.8	7.27
	7.27	129.68	121.8, 129.7, 151.6	6.90, 7.02
	7.32	128.5	125.8	7.42
	7.42	129.35, 129.5	127.2, 129.5, 129.35, 132.0, 144.4	7.53, 7.74
	7.53	125.8	74.6, 125.8, 128.5	7.42
	7.74	127.2	130.9, 158.4	7.42

elemental analytical data and the NMR spectra, the reaction products do not contain a hydrazine residue in their structure but they are the products of the hydrolysis of 2-hydrazine-substituted thiazoles – 4-(2-oxo-2-phenyl-ethyl)-4-phenyl- (**5a**) and 4-(2-oxo-2-phenylethyl)-3,4-diphenyl-1,3-thiazolidin-2-one (**5b**) hydrobromides. It should be noted that the currently most favored methods for the synthesis of 1,3-thiazolidin-2-ones are based on the reaction of the difficult to obtain α-thiocyanoketones and amines [2] or oxidative thiocarboxylation of α-amino alcohols [14]. An alternative method for preparing 1,3-thiazol-2-ones is the hydrolysis of certain 2-amino-substituted 1,3-thiazoles [2].

By contrast with the thiazoles of structures **2** and **4** the thiazolidin-2-ones **5a,b** proved to be unstable towards hydrolysis both in acid [15, 16] and in basic media. The free base 4-(2-oxo-2-phenylethyl)-3,4-diphenyl-1,3-thiazolidin-2-one (**6**) could be separated and characterized by treatment of the 3-phenyl-substituted thiazolidin-2-one **5b** with triethylamine. The structure of the salts **5a,b** and base **6** was proved by analysis of the spectroscopic parameters (Tables 1 and 2). In order to assign the proton signals in the ^{1}H NMR spectrum and the carbon signals in the ^{13}C NMR spectrum in compound **6** we have used homonuclear (COSY) and heteronuclear (HMBC and HMQC) two-dimensional spectroscopy and the NOESY spectrum for identifying the spatial proximities for the individual protons.

Correlations for the base **6** are similar to those above for compound **4** (Table 3). Thus the protons with chemical shifts of 3.83 and 3.65 ppm have correlations with the two quaternary carbon atoms C-1" and C-4. The latter atom also has correlations with the proton signals for the 4-CH_2 methylene group and the aromatic H-2" and H-6" protons which are three chemical bonds distant. In addition, correlations of the proton H_B-5 with the C-2 atom at 153.4 ppm and the H_A-5 with the 4-CH_2 methylene group carbon at 46.85 ppm are observed as are the corresponding correlations of the 4-CH_2 group protons with the quaternary atoms C-1", C-4, and C-5 (41.95 ppm). Assignments in the NMR spectra of the 2-oxothiazoles hydrobromides **5a,b** were made on the basis of this data.

EXPERIMENTAL

Melting points were determined on a Boetius heating block apparatus and were not corrected. IR spectra (KBr tablets) were recorded on a Pye-Unicam SP3-300 instrument. ^{1}H NMR and ^{13}C NMR spectra and HMQC and HMBC heteronuclear correlation experiments were carried out on a Varian Mercury-400 spectrometer (400 and 100 MHz respectively). All of the two-dimensional experiments were carried out with gradient selection of useful signals. The mixing time in the pulse sequences was $^{1}J_{CH}$ = 8 Hz. The numbers of experiments were 128 for the HMQC and 400 for the HMBC spectra. In all cases DMSO-d_6 was used as solvent and TMS as internal standard. Mass spectra were taken on an AGILENT 1200 SL HPLC-MS instrument (CI, acetonitrile, 0.05% formic acid). Monitoring of the reaction course and purity of the compounds prepared was carried out by TLC on Silufol UV-254 plates.

S-(4-Oxo-2,4-diphenyl-2-butenyl)isothiourea Hydrobromide (3). A mixture of the γ-bromodypnone (1 g, 3.32 mmol) and thiourea (0.25 g, 3.32 mmol) in benzene (50 ml) was stirred for 8 h with heating on a water bath at 40ºC. It was held at this temperature for a further 8 h. The precipitate was filtered off, washed with alcohol, and twice recrystallized from acetic acid. Yield 0.41 g (33%); mp 162-164ºC ($MeCO_2H$). IR spectrum, ν, cm^{-1}: 3250 (br., NH_2), 3050, 1640 (C=O), 1450, 1223, 770 (C–S), 660. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.21 (2H, br. s, NH_2); 9.01 (2H, br. s, NH_2); 8.07 (2H, d, *J* = 8.0, H-2",6"); 7.74 (2H, d, *J* = 8.0, H-2',6'); 7.66 (1H, t, *J* = 8.0, H-4"); 7.54 (2H, t, *J* = 8.0, H-3",5"); 7.51 (1H, s, H-3); 7.50 (3H, m, H-3',5'); 4.83 (2H, s, $C_{(1)}H_2$). Mass spectrum, *m/z* (I_{rel}, %): 297 $[M-Br]^+$ (58), 192 (100). Found, %: Br 21.20; N 7.45; S 13.51. $C_{17}H_{17}BrN_2OS$. Calculated, %: Br 21.18; N 7.42; S 13.50.

2-(2-Amino-4-phenyl-4,5-dihydro-1,3-thiazol-4-yl)-1-phenylethanone (2·HBr). A solution of the thiosemicarbamide **3** (0.37 g, 1 mmol) in acetic acid (10 ml) was heated for 10 min. After cooling the precipitate

was filtered off and washed with acetone. Yield 0.25 g (67.5%); mp 194-196ºC (AcOH) (mp 196ºC [11]). IR spectrum, ν, cm^{-1}: 3150 (br., NH_2), 1647 (br., C=O, C=N), 1225, 995, 740 (C–S), 675. ^{13}C NMR spectrum, δ, ppm: 197.69 (C=O); 173.0 (C-2); 142.34 (C-1'); 136.76 (C-1"); 134.25 (C-4"); 129.25 (C-3",5"); 129.11 (C-3',5'); 128.77 (C-2",6"); 128.32 (C-4'); 125.61 (C-2',6'); 71.0 (C-4); 47.13 (4-CH_2); 44.12 (C-5). Mass spectrum, *m/z* (I_{rel}, %): 297 $[M-HBr]^+$ (100).

2-(2-Amino-4-phenyl-4,5-dihydro-1,3-thiazol-4-yl)-1-phenylethanone (2) was prepared by the method given in [11]. IR spectrum, ν, cm^{-1}: 3500 (NH_2), 3100, 1645 (br., C=O, C=N), 1220, 1000, 755 (C–S), 685.

2-[3,4-Diphenyl-2-(phenylimino)-1,3-thiazolidin-4-yl]-1-phenylethanone (4). A mixture of γ-bromodypnone (1 g, 3.32 mmol) and N,N'-diphenylthiourea (0.76 g, 3.32 mmol) in ethanol (50 ml) was refluxed for 1 h. Solvent was evaporated and the residue was dissolved in morpholine (2 ml) and then diluted with water (50 ml). The precipitate was filtered off, washed with water and 2-propanol, and recrystallized from 2-propanol. Yield 0.71 g (48%), mp 88-90ºC (i-PrOH). Mass spectrum, *m/z* (I_{rel}, %): 449 $[M+H]^+$ (100). Found, %: C 77.57; H 5.34; N 6.27, S 7.16. $C_{29}H_{26}N_2OS$. Calculated, %: C 77.65; H 5.39; N 6.24; S 7.15.

4-(2-Oxo-2-phenylethyl)-4-phenyl-1,3-thiazolidin-2-one Hydrobromide (5a). A mixture of γ-bromodypnone (1 g, 3.32 mmol) and thiosemicarbazide (0.3 g, 3.32 mmol) in ethanol (50 ml) was refluxed for 40 min. Solvent was evaporated and the residue was recrystallized from acetic acid. Yield 0.6 g (50%); mp 199-202ºC ($MeCO_2H$). Found, %: Br 21.13; N 3.74; S 8.50. $C_{17}H_{16}BrNO_2S$. Calculated, %: Br 21.12; N 3.70; S 8.48.

4-(2-Oxo-2-phenylethyl)-3,4-diphenyl-1,3-thiazolidin-2-one Hydrobromide (5b) was prepared as described above for the synthesis of the product **5a** using 1-phenylthiosemicarbazide (0.55 g, 3.32 mmol) in place of the thiosemicarbazide. Yield 0.87 g (58%); mp 208-211ºC (dec., $MeCO_2H$). Found, %: Br 17.61; N 3.10; S 7.10. $C_{23}H_{20}BrNO_2S$. Calculated, %: Br 17.59; N 3.08; S 7.06.

4-(2-Oxo-2-phenylethyl)-3,4-diphenyl-1,3-thiazolidin-2-one (6). Et_3N (2 ml) was added to a suspension of the salt **7b** (0.6 g, 1.33 mmol) in 2-propanol (5 ml) and heated to full solution of the salt. Solvent and excess Et_3N were evaporated off and the residue was treated with water (50 ml). The solid precipitate was filtered off, washed with 2-propanol, and recrystallized from 2-propanol. Yield 0.24 g (49%); mp 225-227ºC (*i*-PrOH). Found, %: C 73.91; H 5.08; N 3.76; S 8.60. $C_{23}H_{19}NO_2S$. Calculated, %: C 73.97; H 5.13; N 3.75; S 8.59.

REFERENCES

1. A. A. Bakibaev, A. Yu. Yagovkin, and S. N. Vostretsov, *Usp. Khim.*, **67**, 333 (1998).
2. J. V. Metzger (editor), *The Chemistry of Heterocyclic Compounds*, Vol. 34, Part 1, John Wiley and Sons Inc., New York (1979).
3. P. Catsoulacos and Ch. Camoutsis, *J. Heterocycl. Chem.*, **18**, 1485 (1981).
4. J. Liebscher and E. Mitzner, *Tetrahedron Lett.*, **26**, 4179 (1985).
5. J. Liebscher, M. Patzel, and U. Bechstein, *Synthesis*, 968 (1989).
6. J. Svetlik, F. Turecek, and I. Goljer, *J. Org. Chem.*, **55**, 4740 (1990).
7. T. P. Selby and B. K. Smith, *J. Heterocycl. Chem.*, **26**, 1237 (1989).
8. E. V. Krumkalns and D. L. Smiley, GB Patent 2121414*; Chem. Abstr.*, **100**, 191866 (1983).
9. R. Robiette, A. Dekoker-Malengreau, and J. Marchand-Brynaert, *Heterocycles*, **60**, 523 (2003).
10. M. M. Campbell, US Patent 4582907; *Chem. Abstr.*, **105**, 78924 (1986).
11. L. M. Potikha and V. A. Kovtunenko, *Khim. Geterotsikl. Soedin.* 625 (2007). [*Chem. Heterocycl. Comp.*, **43**, 521 (2007)].
12. Mitsui Toatsu Chemicals Inc. Jpn. Patent 57009758; *Chem. Abstr.*, **96**, 217230 (1982).
13. V. Kovtunenko, L. Potikha, and A. Turov, *Synth. Commun.*, **34**, 3609 (2004).
14. T. Mizuno, J. Takahashi, and A. Ogawa, *Tetrahedron*, **58**, 7805 (2002).
15. E. H. M. Abd Elall, M. I. Ashmawy, and J. M. Mellor, *J. Chem. Soc., Perkin Trans 1*, 2729 (1987).
16. Mitsui Toatsu Chemicals Inc. Japan, Jpn. Patent 60056951; *Chem. Abstr.*, **103**, 104540 (1985).