

# 1,7-Dithioxo Systems. Reaction of Bis(5,5-dimethyl-3-thioxo-cyclohex-1-en-1-yl) Sulfide with Amines

L. V. Timokhina, O. V. Sokol'nikova, L. V. Kanitskaya,  
M. P. Yashchenko, and M. G. Voronkov

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences,  
ul. Favorskogo 1, Irkutsk, 664033 Russia  
e-mail: tim@irioch.irk.ru

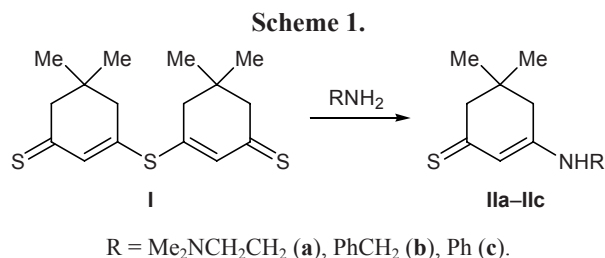
Received June 11, 2007

**Abstract**—Reactions of amines (*N,N*-dimethylethane-1,2-diamine, benzylamine, aniline) with bis(5,5-dimethyl-3-thioxocyclohex-1-en-1-yl) sulfide result in cleavage of the sulfide bond and formation of the corresponding 3-amino-5,5-dimethylcyclohex-2-ene-1-thiones. Aminolysis of bis(5,5-dimethyl-3-oxocyclohex-1-en-1-yl) sulfide occurs at the carbonyl groups with conservation of the divinyl sulfide fragment.

**DOI:** 10.1134/S1070428008040118

Studies on bis(chalcogenoxopropenyl) sulfide systems like (Se)S=CC=CSC=CC=S(Se) as possible solar energy transducers [1] requires knowledge of their chemical properties. Using bis(5,5-dimethyl-3-thioxocyclohex-1-en-1-yl) sulfide (**I**) as an example, we examined reactions of  $\alpha,\beta$ -unsaturated 1,7-dithioxo sulfides with amines. As a rule, thioketones readily react with amines to give Schiff bases [2]. We expected that aminolysis of dithioxo sulfide **I** will involve one or both thiocarbonyl groups to produce the corresponding mono- and diimino sulfides. Compounds having nitrogen-containing functional groups conjugated with a sulfide moiety could exhibit some biological activity.

However, contrary to the expectations, the products of reactions of sulfide **I** with *N,N*-dimethylethane-1,2-diamine, benzylamine, and aniline in benzene or chloroform at 20°C were mainly 3-[2-(dimethylamino)ethylamino]-5,5-dimethylcyclohex-2-ene-1-thione (**IIa**), 3-benzylamino-5,5-dimethylcyclohex-2-ene-1-thione (**IIb**), and 5,5-dimethyl-3-phenylaminocyclohex-2-ene-1-thione (**IIc**), respectively (Scheme 1).

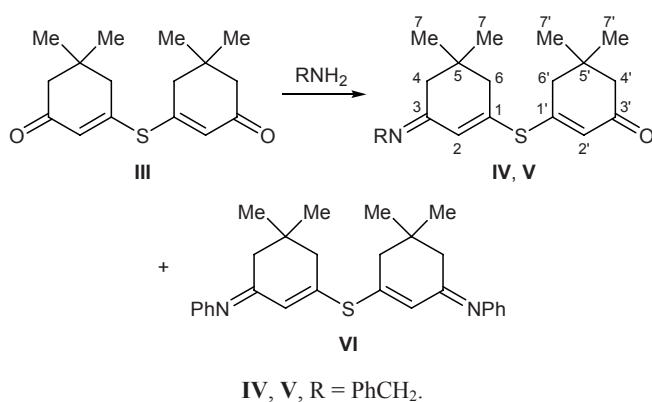


Obviously, enamino thiones **IIa–IIc** were formed as a result of cleavage of the sulfide bond in initial compound **I**.

Compounds **IIa–IIc** were synthesized by us previously by several methods, including sulfurization of 3-aminocyclohex-2-en-1-ones with diphosphorus decasulfide, hydrothiolysis of 3-iminocyclohex-1-en-1-amines, and aminolysis of 3-alkoxycyclohex-2-ene-1-thiones [3, 4]. In the present communication we present the <sup>13</sup>C NMR spectra of thioketones **IIb** and **IIc**.

An oxygen-containing analog of dithioxo sulfide **I**, bis(5,5-dimethyl-3-oxocyclohex-1-en-1-yl) sulfide (**III**), reacted with amines under more severe conditions (on heating for a longer time), but its conversion did not exceed 30%. Unlike compound **I**, in the reactions of diketone **III** with amines the divinyl sulfide fragment in molecule **III** remained intact. The reaction of **III** with benzylamine gave previously unknown 3-(3-benzylimino-5,5-dimethylcyclohex-1-en-1-yl-sulfanyl)-5,5-dimethylcyclohex-2-en-1-one (**IV**) (Scheme 2). The <sup>13</sup>C NMR spectrum of the isolated product mixture (see table) contained signals belonging to unreacted sulfide **III** and signals with different intensities at  $\delta_C$  165.1/167.5 and 160.1/162.2 ppm, which were assigned, respectively, to the C<sup>3</sup> (C=N) and C<sup>1</sup> atoms (S–C=C), the intensity ratio being ~1:2 in each couple. The C<sup>2</sup> and C<sup>2'</sup> nuclei gave rise to four signals in the  $\delta_C$  range from 118 to 124 ppm with the same intensity ratio. The =NCH<sub>2</sub> carbon nucleus

Scheme 2.



resonated at  $\delta_C$  53.2 and 55.0 ppm, and the signal at  $\delta_C$  195.3 ppm corresponded to the carbonyl carbon atom. In the aromatic region of the spectrum we observed two groups of partially overlapped signals at  $\delta_C$  125–128 and 135–140 ppm. This spectral pattern led us to presume formation of compound **IV** as a mixture of two stereoisomers.

Quantitative analysis of the  $^{13}\text{C}$  NMR spectrum [5] showed that the fractions of carbon atoms belonging to dioxo sulfide **III** and compound **IV** are 0.728 and 0.272, respectively, i.e., the molar ratio of compounds **III** and **IV** in the isolated mixture is 100:8.8. The elemental composition of the mixture, calculated from the  $^{13}\text{C}$  NMR spectrum was consistent with that determined by elemental analysis (see Experimental), which provides an additional proof for the assumed structure of compound **IV**.

By reaction of dioxo sulfide **III** with aniline we obtained previously unknown 3-(5,5-dimethyl-3-phenyliminocyclohex-1-en-1-ylsulfanyl)-5,5-dimethylcyclohex-2-en-1-one (**V**) and *N,N'*-[3,3'-thiobis(5,5-dimethylcyclohex-2-en-3-ylidene)]dibenzeneamine (**VI**) (Scheme 2). In the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the isolated product we observed signals from unreacted compound **III** and those with lower intensity, which were assigned to compounds **V** and **VI** (see Experimental and table). The aromatic region of the  $^1\text{H}$  NMR spectrum contained three groups of signals, indicating the presence of monosubstituted phenyl rings: overlapping doublets at  $\delta$  6.65–6.74 ppm were assigned to the *ortho*-protons, and two couples of partially overlapping triplets at  $\delta$  7.03–7.17 and 7.23–7.33 ppm corresponded to protons in the *meta* and *para* positions. Olefinic proton singlets at  $\delta$  5.90 and 6.40 ppm are likely to belong to 2-H (2'-H) in unsymmetrical sulfide **V**, and the signal at  $\delta$  6.00 ppm, to analogous protons in diimino derivative **VI**. Methyl protons resonated as

three singlets at  $\delta$  0.98, 1.00, and 1.11 ppm. According to the signal intensity, the ratio of compounds **III**, **V**, and **VI** is ~100:10:6.

It should be noted that structural analogs of compound **III**, bis(2-aryl-3-oxocyclohex-1-en-1-yl) sulfides, react with amines to give mixtures of the corresponding enamino ketones and enamino imines [6].

## EXPERIMENTAL

The IR spectra were recorded in KBr on a Bruker IFS 25 instrument. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Bruker DPX-400 spectrometer at 400.1 and 100.4 MHz, respectively, using HMDS as external reference. Quantitative  $^{13}\text{C}$  NMR analysis was performed using a pulse delay of 2.5 s and a pulse width of 90°; tris(acetylacetonato)chromium was added as relaxant to a concentration of 0.02 M. The relative error in the determination of fractions of components was 7.8%. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using chloroform–ethyl acetate (3:1) as eluent.

3,3'-Thiobis(5,5-dimethylcyclohex-2-ene-1-thione) (**I**) was synthesized according to the procedure reported in [7]. 3,3'-Thiobis(5,5-dimethylcyclohex-2-en-1-one) (**III**) was prepared as described in [8].

**3-[2-(Dimethylamino)ethylamino]-5,5-dimethylcyclohex-2-ene-1-thione (IIa)**. A solution of 0.31 g (1 mmol) of sulfide **I** in 10 ml of freshly distilled

$^{13}\text{C}$  NMR spectra ( $\delta_C$ , ppm) of compounds **III–VI**

Atom	<b>III</b>	<b>IV</b>	<b>V</b>	<b>VI</b>
C <sup>1</sup>	155.11	160.1, 162.2	141.15	149.90
C <sup>2</sup>	129.00	118–124	115.08	118.46
C <sup>3</sup>	196.21	165.1, 167.5	165.81	166.50
C <sup>4</sup>	50.69	50.3, 51.0	40.96	42.74
C <sup>5</sup>	34.01	32–34	34.02 <sup>a</sup>	33.12
C <sup>6</sup>	44.56		47.53 <sup>a</sup>	45.12
C <sup>1'</sup>	155.11		160.02	149.90
C <sup>2'</sup>	129.00	118–124	120.41	118.46
C <sup>3'</sup>	196.21	195.3	196.12	166.50
C <sup>4'</sup>	50.69		50.89	45.43
C <sup>5'</sup>	34.01	32–34	32.96 <sup>a</sup>	32.27
C <sup>6'</sup>	44.56		44.32 <sup>a</sup>	42.80
C <sup>7</sup>	27.77	28.0–29.2	27.97–27.80	27.97–27.80
C <sup>7'</sup>	27.77	28.0–29.2	27.97–27.80	27.97–27.80

<sup>a</sup> Alternative assignment is possible.

chloroform was cooled to 2–5°C, and a solution of 0.18 g (2 mmol) of *N,N*-dimethylethane-1,2-diamine in 3 ml of chloroform was added dropwise under stirring in an argon atmosphere. The mixture was stirred for 2 h at 2–5°C, vigorous evolution of hydrogen sulfide [identified by a test with a solution of Pb(OAc)<sub>2</sub>] was observed, and the original dark green color changed to dark orange. The mixture was then washed with water, the organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed, and the tarry residue was recrystallized from ethanol–hexane (1:1). Yield 0.15 g (68%), orange finely crystalline powder, mp 88–91°C; published data [4]: mp 90–92°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1049 (C=S), 1543 (C=C), 3238 (NH). Found, %: C 62.86; H 9.54; N 12.34; S 14.09. C<sub>12</sub>H<sub>22</sub>N<sub>2</sub>S. Calculated, %: C 63.72; H 9.73; N 12.39; S 14.45.

**3-Benzylamino-5,5-dimethylcyclohex-2-ene-1-thione (IIb).** A solution of 0.21 g (2 mmol) of benzylamine in 5 ml of benzene was added dropwise to a dark green solution of 0.31 g (1 mmol) of sulfide **I** in 10 ml of anhydrous benzene. The mixture was stirred for 4 h at 20°C in a continuous stream of argon, evolution of hydrogen sulfide was observed, and the mixture turned dark orange. The precipitate was filtered off, washed with benzene, and dissolved in chloroform–ethyl acetate (3:1), the solution was passed through a column charged with silica gel (100/400 mesh), and the column was eluted with chloroform–ethyl acetate (3:1). Yield 0.16 g (64%), bright yellow needles, mp 136–137°C. The melting point and IR spectrum of the product were consistent with those reported in [3]. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_C$ , ppm: 27.6 (CH<sub>3</sub>), 33.5 (C<sup>5</sup>), 43.4 (C<sup>4</sup>), 47.1 (CH<sub>2</sub>NH), 57.4 (C<sup>6</sup>), 111.9 (C<sup>2</sup>), 160.5 (C<sup>3</sup>), 219.2 (C=S), 127.4 (C<sup>p</sup>), 128.0 (C<sup>m</sup>), 128.9 (C<sup>o</sup>), 135.9 (C<sup>i</sup>). Found, %: C 73.95; H 7.81; N 5.57; S 13.02. C<sub>15</sub>H<sub>19</sub>NS. Calculated, %: C 73.47; H 7.76; N 5.71; S 13.06.

**5,5-Dimethyl-3-phenylaminocyclohex-2-ene-1-thione (IIc).** The reaction was carried out as described above using 0.31 g (1 mmol) of sulfide **I** in 10 ml of anhydrous benzene and 0.19 g (2 mmol) of aniline in 5 ml of anhydrous benzene. Yield 0.15 g (65%), orange crystals, mp 180–182°C. The melting point and IR spectrum of the product were consistent with those reported in [3]. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_C$ , ppm: 28.0, 29.7 (CH<sub>3</sub>), 33.6 (C<sup>5</sup>), 43.3 (C<sup>4</sup>), 57.7 (C<sup>6</sup>), 114.1 (C<sup>2</sup>), 158.5 (C<sup>3</sup>), 221.9 (C=S), 124.6 (C<sup>m</sup>), 126.8 (C<sup>p</sup>), 129.3 (C<sup>o</sup>), 137.1 (C<sup>i</sup>). Found, %: C 72.63; H 7.35; N 6.15; S 14.09. C<sub>14</sub>H<sub>17</sub>NS. Calculated, %: C 72.72; H 7.36; N 6.06; S 13.85.

#### Reaction of dioxo sulfide **III** with benzylamine.

A solution of 0.39 g (3.6 mmol) of benzylamine in 5 ml of benzene was added dropwise to a solution of 0.5 g (1.8 mmol) of sulfide **III** in 10 ml of benzene. The mixture was stirred for 22 h at 70–75°C, and it changed from colorless to red–orange. The mixture was then washed with water saturated with carbon dioxide, the organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The residue, 0.48 g, was a mixture of initial sulfide **III** and 3-(3-benzylimino-5,5-dimethylcyclohex-1-en-1-ylsulfanyl)-5,5-dimethylcyclohex-2-en-1-one (**IV**). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 698, 735 ( $\delta$ C–H<sub>arom</sub>), 1556 br (C=C, C=CS, C=N), 1654 (C=O). Found, %: C 70.36; H 7.40; N 2.67; S 10.74. Calculated (from the <sup>13</sup>C NMR spectrum), %: C 69.7; H 7.9; N 4.0; S 11.2.

**Reaction of dioxo sulfide **III** with aniline.** The reaction mixture obtained from 0.5 g (1.8 mmol) of sulfide **III** and 0.34 g (3.6 mmol) of aniline in 10 ml of benzene was stirred for 7 days at 20°C. The bright yellow mixture was washed with water saturated with carbon dioxide, the organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed under reduced pressure, and the tarry residue was treated with hexane. From the hexane solution we isolated 0.36 g (73%) of unreacted sulfide **III**. The undissolved material was ground with a small amount of diethyl ether to obtain 0.1 g of a mixture of compound **III**, 3-(5,5-dimethyl-3-phenyliminocyclohex-1-en-1-ylsulfanyl)-5,5-dimethylcyclohex-2-en-1-one (**V**), and *N,N'*-[3,3'-thiobis(5,5-dimethylcyclohex-2-en-3-ylidene)]dibenzeneamine (**VI**) as a light orange powder. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 696, 756 ( $\delta$ C–H<sub>arom</sub>); 1497, 1526 (C=C, C=C<sub>arom</sub>); 1582 (C=CS); 1603 (C=N); 1657 (C=O). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta_C$ , ppm: 0.98 s, 1.00 s, 1.11 s (CH<sub>3</sub>); 5.90 s, 6.00 s, 6.40 s (HC=); 6.65–6.74 d (*o*-H); 7.03–7.17 t (*m*-H); 7.23–7.33 (*p*-H). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_C$ , ppm: 119.38 (C<sup>o</sup>), 123.69 (C<sup>m</sup>), 126.41 (C<sup>p</sup>), 137.87 (C<sup>i</sup>) (**V**); 123.07 (C<sup>p</sup>), 123.80 (C<sup>o</sup>), 126.41 (C<sup>m</sup>), 139.44 (C<sup>i</sup>) (**VI**).

This study was performed under financial support by the Council for Grants at the President of the Russian Federation (project no. NSh-4575.2006.3) and by the Russian Foundation for Basic Research (project no. 05-03-32036).

#### REFERENCES

- Shagun, V.A., Timokhina, L.V., Panova, G.M., and Frolov, Yu.L., *Russ. J. Gen. Chem.*, 2003, vol. 73, p. 720.

2. *Poluchenie i svoistva organicheskikh soedinenii sery* (Synthesis and Properties of Organic Sulfur Compounds), Belen'kii, L.I., Ed., Moscow: Khimiya, 1998, p. 89.
3. Timokhina, L.V., Usov, V.A., Tsetlin, Ya.S., Tsetlina, E.O., and Voronkov, M.G., *Zh. Org. Khim.*, 1979, vol. 15, p. 82.
4. Usov, V.A., Timokhina, L.V., Shagun, V.A., Sidorkin, V.F., and Voronkov, M.G., *Zh. Org. Khim.*, 1981, vol. 17, p. 1816.
5. Kalabin, G.A., Kanitskaya, L.V., and Kushnarev, D.F., *Kolichestvennaya spektroskopiya YaMR prirodnogo organicheskogo syr'ya i produktov ego pererabotki* (Quantitative NMR Spectroscopy of Natural Organic Raw Materials and Products of Their Processing), Moscow: Khimiya, 2000.
6. Usov, V.A., Korchevin, N.A., Tsetlin, Ya.S., and Voronkov, M.G., *Zh. Org. Khim.*, 1973, vol. 9, p. 2149.
7. Timokhina, L.V., Panova, G.M., Toryashinova, D.-S.D., Albanov, A.I., Sokol'nikova, O.V., and Voronkov, M.G., *Russ. J. Org. Chem.*, 1999, vol. 35, p. 1408.
8. Timokhina, L.V., Panova, G.M., Kanitskaya, L.V., Toryashinova, D.-S.D., Sokol'nikova, O.V., Fedorov, S.V., and Voronkov, M.G., *Russ. J. Org. Chem.*, 2001, vol. 37, p. 1335.