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# 1,7-Dithioxo Systems. Synthetic Routes to Bis(5,5-dimethyl-3-thioxo-1-cyclohexenyl) Sulfide*

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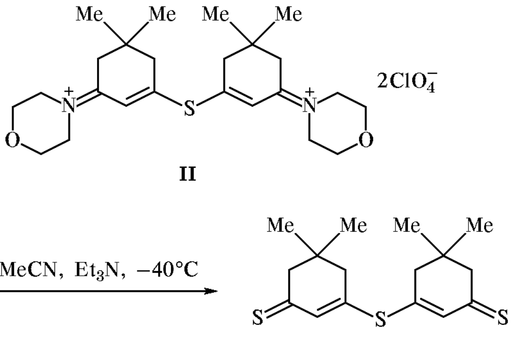
**Abstract**—Synthetic routes to bis(5,5-dimethyl-3-thioxo-1-cyclohexenyl) sulfide have been studied. The title compound can be obtained by reaction of 3-chloro-5,5-dimethyl-2-cyclohexenethione with sodium thiosulfate and by condensation of 3-mercapto-5,5-dimethyl-2-cyclohexenethione. The reaction of bis(5,5-dimethyl-3-oxo-1-cyclohexenyl) sulfide with hydrogen sulfide and hydrogen chloride yields 3-oxo-3′-thioxobis(5,5-dimethyl-1-cyclohexenyl) sulfide.

The first representative of unsaturated 1,7-dithiones, bis(5,5-dimethyl-3-thioxo-1-cyclohexenyl) sulfide (**I**), was synthesized by us by low-temperature reaction of bis[5,5-dimethyl-3-(4-oxa-1-azoniacyclohexylidene)-1-cyclohexenyl] sulfide diperchlorate (**II**) with hydrogen sulfide [1] (Scheme 1).

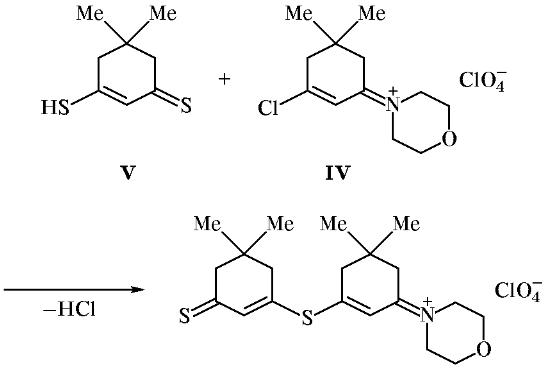
**Scheme 1.**



In continuation of our studies in the field of 1,7-dithioxo systems having an S=C–C=C–S–C=C–C=S fragment, in the present work we tried to develop alternative synthetic routes to dithione **I**, which could be useful for preparation of new representatives of 1,7-dithiocarbonyl compounds. The molecule of dithioxo sulfide **I** can be built up in two ways. The first way includes introduction of thioxo groups into molecules with already completed divinyl sulfide framework. According to the second route, the divinyl sulfide moiety is obtained from two fragments each containing a thioxo group.

In the reaction of diperchlorate **II** with hydrogen sulfide, apart from the major product, dithioxo sulfide **I**, we isolated 20% of 3-(4-oxa-1-azoniacyclohexylidene)-3′-thioxobis(5,5-dimethyl-1-cyclohexenyl) sulfide (**III**) which was formed by thionation of only one $C{=}\overset{+}{N}$ group in salt **II** [1]. In the present work we have synthesized perchlorate **III** by another method and studied its reaction with hydrogen sulfide. We previously found that halogen-substituted iminium

**Scheme 2.**



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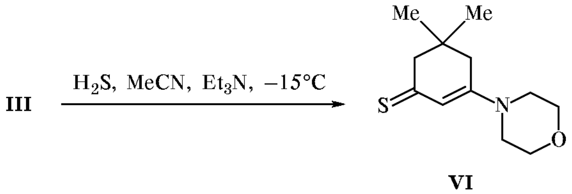
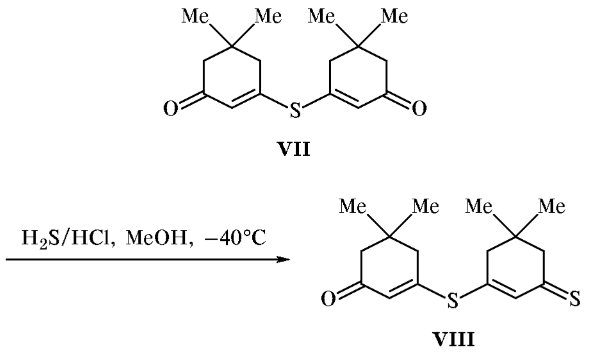
salts react with enaminothioketones under mild conditions to give bisiminio derivatives of α,β-unsaturated sulfides [2]. We have synthesized perchlorate **III** from 1-(3-chloro-5,5-dimethyl-2-cyclohexenylidene)morpholinium perchlorate (**IV**) [3] and 3-mercapto-5,5-dimethyl-2-cyclohexenethione (**V**) [4] (Scheme 2). The reaction was carried out in acetonitrile at 10°C in a continuous stream of argon. However, we failed to obtain the desired sulfide **I** by treatment of salt **III** with hydrogen sulfide under the same conditions as in the synthesis of dithione **I** from diperchlorate **II** (acetonitrile, triethylamine, –40°C, argon atmosphere). Raising the temperature to –15°C resulted in cleavage of the C–S bond in the initial sulfide and formation of 5,5-dimethyl-3-morpholino-2-cyclohexenethione (**VI**) [5] (Scheme 3).

**Scheme 3.**



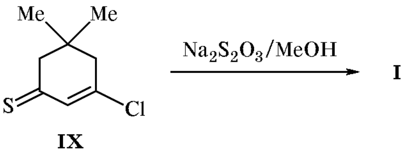
The most widely used procedure for preparation of dithiocarbonyl compounds is thionation of the corresponding oxygen analogs with common sulfurization agents [6]. By reaction of bis(5,5-dimethyl-3-oxo-1-cyclohexenyl) sulfide (**VII**) [7] with hydrogen sulfide in the presence of hydrogen chloride (methanol, –40°C) gave a complex mixture of unstable sulfur-containing products. Analysis of the reaction mixture by $^{1}H$, $^{13}C$, and two-dimensional (HETCOR) NMR spectroscopy using quantitation techniques [8] revealed formation of hitherto unknown 3-oxo-3′-thioxobis(5,5-dimethyl-1-cyclohexenyl)sulfide (**VIII**) in 26% yield (Scheme 4).

**Scheme 4.**



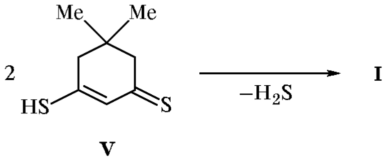
Traditional methods of synthesis of sulfides are based on alkylation or arylation of inorganic sulfur compounds [9]. In order to obtain dithioxo sulfide **I** we used as “alkylating” agent 3-chloro-5,5-dimethyl-2-cyclohexenethione (**IX**) which was synthesized by us previously [10]. The formation of dithione **I** was detected by TLC and IR spectroscopy when thione **IX** was treated with anhydrous sodium thiosulfate in methanol at –20 to –30°C (Scheme 5).

**Scheme 5.**



Another procedure for preparation of sulfides includes intermolecular condensation of thiols. This reaction usually requires elevated temperature or the presence of a catalyst [11]. We tried to synthesize bis(5,5-dimethyl-3-thioxo-1-cyclohexenyl) sulfide (**I**) from dithio analog of dimedone, which is known to exist mainly in the form of mercaptoenethione **V** [4]. Compound **V** is fairly stable at –70 to –40°C in an inert atmosphere. On keeping thione **V** at –10°C without a solvent or in chloroform we observed evolution of hydrogen sulfide and formation of sulfide **I** (Scheme 6).

**Scheme 6.**



Thus, our study of alternative methods for the synthesis of dithioxo sulfide **I** showed that the most convenient procedure is the low-temperature reaction of diperchlorate **II** with hydrogen sulfide in acetonitrile in the presence of triethylamine [1]. In this case analytically pure dithione **I** separates from the reaction mixture in 70–80% yield.

## EXPERIMENTAL

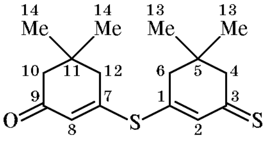
The $^{1}H$ and $^{13}C$ NMR spectra were recorded on Jeol FX-90Q and Bruker DPX-400 instruments using HMDS as external reference. The two-dimensional NMR spectra (HETCOR) were obtained on a Bruker DPX-400 spectrometer operating at 400.13 ($^{1}H$) and

100.6 MHz ($^{13}C$). The IR spectra were recorded on an IFS-25 spectrometer from samples pelleted with KBr. The progress of reactions was monitored, and the purity of products was checked, by TLC on Silufol UV-254 plates.

**3-(4-Oxa-1-azoniacyclohexylidene)-3′-thioxobis-(5,5-dimethyl-1-cyclohexenyl) sulfide perchlorate (III).** A cooled solution of 0.86 g (5 mmol) of 3-mercapto-5,5-dimethyl-2-cyclohexenethione (**V**) in a mixture of 10 ml of dry acetonitrile and 3 ml of dry chloroform was added dropwise to a solution of 1.64 g (5 mmol) of 1-(3-chloro-5,5-dimethyl-2-cyclohexenylidene)morpholinium perchlorate (**IV**) in 10 ml of dry acetonitrile, while stirring under argon at 10°C. The mixture was stirred for 2.5 h (until hydrogen chloride no longer evolved) and was poured into ice water. The product was extracted into chloroform, and the extract was washed with ice water and dried over $CaCl_2$ at 5°C. The solvent was removed, and the residue (a red–brown oily substance) was washed with cold methanol and dried in a vacuum at reduced temperature. Yield 0.9 g (39%); dark orange powder, decomposing at 117–121°C. The decomposition point and $^1H$ NMR and IR spectral parameters of the product were identical to those reported in [1]. Found, %: C 50.91; H 7.04; Cl 7.62; N 2.27; S 13.48. $C_{20}H_{30}ClNO_5S_2$. Calculated, %: C 51.78; H 6.47; Cl 7.66; N 3.02; S 13.81.

**Reaction of 3-(4-oxa-1-azoniacyclohexylidene)-3′-thioxobis(5,5-dimethyl-1-cyclohexenyl) sulfide perchlorate (III) with hydrogen sulfide.** Dry hydrogen sulfide was passed over a period of 10 min through a solution of 0.46 g (1 mmol) of perchlorate **III** in 15 ml of dry acetonitrile, cooled to –40°C. Triethylamine, 0.02 ml, was added, and hydrogen sulfide was passed through the mixture over a period of 4 h at –40°C. The mixture was allowed to gradually warm up to –15°C, and hydrogen sulfide was passed through the mixture for an additional 4 h at that temperature. The progress of the reaction was monitored by TLC using chloroform–ethyl acetate (3 : 1) as eluent. The mixture was purged with argon to remove hydrogen sulfide and was evaporated under reduced pressure. The dark red solid residue was dissolved in ethyl acetate, and the solution was passed through a column charged with silica gel (40/100 mesh). The column was eluted with ethyl acetate to isolate 0.09 g (40%) of 5,5-dimethyl-3-morpholino-2-cyclohexenethione (**VI**) as orange crystals with mp 160–162°C (published data [5]: mp 161–162°C). Found, %: C 64.67; H 8.59; N 6.19; S 13.83. $C_{12}H_{19}NOS$. Calculated, %: C 64.00; H 8.45; N 6.22; S 14.22.

**Reaction of bis(5,5-dimethyl-3-oxo-1-cyclohexenyl) sulfide (VII) with hydrogen sulfide.** A solution of 0.8 g (3 mmol) of dioxo sulfide **VII** in 40 ml of anhydrous methanol was saturated with gaseous HCl for 1 h at –40°C, and hydrogen sulfide was passed through the solution for 10 h at –40 to –30°C. The mixture was left to stand for 12 h at –70°C, purged with argon at –30°C to remove HCl and $H_2S$, filtered, poured onto ice, and extracted with ether. The extract was washed with ice water to pH 4–5, dried over $Na_2SO_4$ at 5°C, and evaporated under reduced pressure. The residue, 0.31 g, was a dark violet thick oil with an unpleasant odor. It contained 26 ± 1.7% of sulfide **VIII**. $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 2.22 (4H, 10-H), 2.35 (4H, 6-H), 2.36 (4H, 12-H), 2.74 (4H, 4-H), 6.08 t (1H, 8-H, $^4J$ = 1.3 Hz), 6.93 t (1H, 2-H, $^4J$ = 1.3 Hz). $^{13}C$ NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 27.19 ($C^{13}$), 27.55 ($C^{14}$), 33.99 ($C^{12}$), 34.32 ($C^5$), 42.22 ($C^{11}$), 42.37 ($C^6$), 50.27 ($C^{10}$), 59.36 ($C^4$), 123.12 ($C^8$), 134.14 ($C^2$), 157.78 ($C^1$), 158.15 ($C^7$), 195.21 ($C^9$), 230.67 ($C^3$).



**VIII**

**Reaction of 3-chloro-5,5-dimethyl-2-cyclohexenethione (IX) with $Na_2S_2O_3$.** Anhydrous sodium thiosulfate, 0.16 g (1 mmol), was added in portions over a period of 15 min to a solution of 0.37 g (2 mmol) of chlorothione **IX** in 10 ml of anhydrous methanol, stirred at –45°C. The mixture was allowed to slowly warm up to –20 to –30°C and was stirred for 7 h at that temperature. TLC analysis (eluent chloroform) revealed formation of dithioxo sulfide **I** in 40 min after the reaction started. The unreacted $Na_2S_2O_3$ was filtered off, and the filtrate was poured into 60 ml of ice water and extracted with benzene. The extract was washed with ice water and dried over $Na_2SO_4$. Removal of the solvent left 0.18 g of a residue which contained dithioxo sulfide **I**, initial chlorothione **IX**, and a number of unidentified products. IR spectrum, ν, $cm^{-1}$: 1110 (C=S), 1545 (C=C–S) (compound **I**); 1123 (C=S), 1579 (C=C) (compound **IX**).

**Condensation of 3-mercapto-5,5-dimethyl-2-cyclohexenethione (V).** *a.* Compound **V**, 0.1 g, was placed in a flask which was then purged with argon and left to stand for 20 days at –10°C. TLC analysis (eluent chloroform–ethyl acetate, 3 : 1) showed the presence of dithioxo sulfide **I**, and hydrogen sulfide was detected via reaction with $Pb(CH_3COO)_2$.

*b.* A solution of 0.1 g of compound **V** in 10 ml of anhydrous chloroform was stirred for 2 h at –10 to –15°C under argon. Evolution of hydrogen sulfide and formation of dithioxo sulfide **I** (TLC) were observed.

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