

# *N,N'*-Bis(trimethylsilylmethyl)thiocarbamide and *N,N'*-Bis(trimethylsilylmethyl)-λ<sup>6</sup>-thiocarbamide *S,S*-Dioxide

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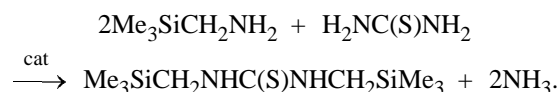
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**Abstract**—*N,N'*-Bis(trimethylsilylmethyl)-λ<sup>6</sup>-thiocarbamide *S,S*-dioxide was synthesized by oxidation of *N,N'*-bis(trimethylsilylmethyl)thiocarbamide with hydrogen peroxide. The synthesized dioxide is a less active reducing agent than previously studied *S,S*-dioxides of organosilicon thiocarbamides in which the silicon atom is separated from the thiocarbamide fragment by a –CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>– bridge.

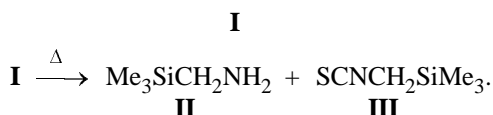
We previously reported the first synthesis of organosilicon derivatives of thiocarbamide dioxide [X<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH]<sub>2</sub>CSO<sub>2</sub>, X<sub>3</sub>Si = (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Si, N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>Si, and O<sub>1,5</sub>Si] [1–3]. With the purpose of preparing analogs of the general formula [X<sub>3</sub>Si·CH<sub>2</sub>NH]CSO<sub>2</sub>, we have synthesized formerly unknown *N,N'*-bis(trimethylsilylmethyl)thiocarbamide (**I**) and studied its oxidation to *N,N'*-Bis(trimethylsilylmethyl)-λ<sup>6</sup>-thiocarbamide *S,S*-dioxide.

Organosilicon thiocarbamide **I** was prepared analogously to *N,N'*-bis(triorganysilylpropyl)thiocarbamides [4] by condensation of (aminomethyl)trimethylsilane (**II**) with thiourea in the presence of a catalytic amount of ammonium sulfate at 150–160°C.



The starting (aminomethyl)trimethylsilane (**II**) was prepared by the procedure described in [5].

*N,N'*-Bis(trimethylsilylmethyl)thiocarbamide (**I**) is thermally labile. It easily decomposes when heated above 160°C to form compound **II** and (isothiocyanatomethyl)trimethylsilane (**III**).



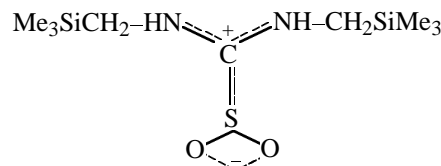
The composition and structure of compound **I** were confirmed by elemental analysis and IR and <sup>1</sup>H NMR spectroscopy. The IR spectrum contains absorption bands at 3196 [ν(NH)], 1420 [δ(NH)], 1260 [δ(Me<sub>3</sub>Si)], 1000 [ν(C=S)], and 850 cm<sup>-1</sup> [ν(Me<sub>3</sub>Si)] and lacks the ν(N=C=S) band at 2100–2000 cm<sup>-1</sup>.

Thiocarbamide **I**, like its analog *N,N'*-bis-[3-(triethylsilyl)propyl]thiocarbamide [1], is easily oxidized with 50% hydrogen peroxide in dioxane at (-5)- 0°C to give *N,N'*-bis(trimethylsilylmethyl)-λ<sup>6</sup>-thiocarbamide *S,S*-dioxide (**IV**) as a white solid (mp 197–199°C) almost insoluble in organic solvents and readily soluble in water.



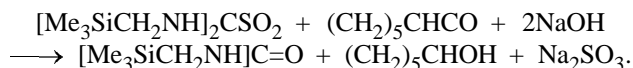
The IR spectrum of compound **IV** has no absorption band in the range 1695–1660 cm<sup>-1</sup>, characteristic of ν(C=N), which distinguishes it from the spectra of previously prepared organosilicon thiocarbamide *S,S*-dioxides [1, 3]. In this connection compound **IV** can not be regarded as an organosilicon derivative of formamidinesulfinic acid Me<sub>3</sub>SiCH<sub>2</sub>NHC(SOOH)=NCH<sub>2</sub>SiMe<sub>3</sub>.

At the same time, like thiocarbamide *S,S*-dioxide [6], dioxide **IV** evidently has a zwitterionic structure.

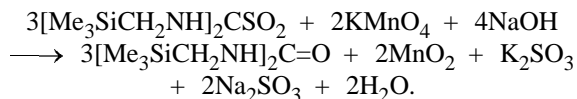


Evidence for this proposal is provided by the absence of the [ν(C=S)] band at 1000 cm<sup>-1</sup> [7], that is present in the IR spectrum of starting thiocarbamide **I**. At the same time, the IR spectrum of compound **IV** displays absorption bands at 3060 [ν(NH)], 1430 [δ(NH)], 1260 [ν (Me<sub>3</sub>Si)], 1080 [ν<sub>as</sub>(SO)], 1040 [ν<sub>s</sub>(SO)] and 850 cm<sup>-1</sup> [δ(Me<sub>3</sub>Si)], confirmatory of its structure.

*S,S*-dioxide (**IV**), like previously studied organosilicon thiocarbamide *S,S*-dioxides [1–3], is a reducing agent. It reacts with cyclohexanone to give cyclohexanol.



The reactions of compound **IV** with potassium permanganate in alkaline, neutral, or acidic media involve reduction of  $\text{Mn}^{+7}$  to  $\text{Mn}^{+4}$ .



The fastest reduction of  $\text{Mn}^{+7}$  with dioxide **IV** takes place in alkaline medium (1–2 h). At the same time, the same reaction in neutral and acidic media completes in 24 and 36 h, respectively. These data are nicely consistent the reductive ability of thiocarbamide *S,S*-dioxide [8].

Hence, *N,N'*-bis(trimethylsilylmethyl)thiocarbamide (**I**), like its analogs containing an  $[\text{X}_3\text{SiCH}_2 \cdot \text{CH}_2\text{CH}_2\text{NH}]_2$  fragment [1–3], is fairly easy oxidized without side processes. However, dioxide **IV** is a less active reducing agent than its silicon-containing  $\gamma$ -analog [1]. The latter reduces  $\text{Mn}^{+7}$  within 10–30 min at any pH of the medium. This fact suggests that compounds with the silicon atom and the dioxothiocarbamide group intervened with a methylene bridge are more difficultly reduced than compounds with a  $-\text{CH}_2\text{CH}_2\text{CH}_2-$  bridge. This effect evidently arises from the difference in the electronic and steric effects of the  $\text{R}_3\text{SiCH}_2$  and  $\text{R}_3\text{SiCH}_2\text{CH}_2\text{CH}_2$  groups.

## EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer in thin layer. The  $^1\text{H}$  NMR spectra were obtained on a Bruker DPX-400 spectrometer (400 MHz) in  $\text{D}_2\text{O}$  against internal HMDS. Gas chromatography was performed on an LKhM-8MDP chromatograph equipped with a thermal conductivity detector, carrier gas helium, column 1000x4 mm, packing 5% SE-30 on Chromaton N-AW-HMDS (0.2–0.25 mm).

***N,N'*-Bis(trimethylsilylmethyl)thiocarbamide (I).** A mixture of 3.3 g of trimethylsilylamine, 1.2 g of thiocarbamide, and 0.01 g of ammonium sulfate was heated in a sealed ampule for 5–6 h at 150–160°C. Compound **I**, 2.5 g (63%), was frozen out from the reaction mixture at –5 to 0°C, mp 24–25°C.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.1 s (18H,  $\text{CH}_2\text{Si}$ ), 2.6 s (4H,  $\text{CH}_2\text{Si}$ ), 7.15 s (2H, NH). Found, %: H 9.70; N 12.18; S 13.95.  $\text{C}_9\text{H}_{24}\text{N}_2\text{SSi}_2$ . Calculated, %: H 9.67; N 11.29; S 12.90.

***N,N'*-Bis(trimethylsilylmethyl)- $\lambda^6$ -thiocarbamide *S,S*-dioxide (IV).** To a solution of 2.0 g of thiocarbamide **I** in 15 ml of dioxane, 0.2 ml of 50% hydrogen peroxide was added at –5 to 0°C over the course of 30 min. A precipitate formed and was crystallized from acetone and washed with ether to obtain 1.1 g (49%) of compound **IV** as colorless needle-like crystals, mp 197–199°C.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.19 s (18H,  $\text{CH}_3$ ), 2.33 s (4H,  $\text{CH}_2\text{Si}$ ), 4.8 s (2H, NH). Found, %: H 9.14; N 10.78; S 13.02.  $\text{C}_9\text{H}_{24} \cdot \text{N}_2\text{O}_2\text{SSi}_2$ . Calculated, %: H 8.57; N 10.00; S 11.42.

**Reduction of cyclohexanone.** To a mixture of solutions of 0.21 g of cyclohexanone in 16 ml of ethanol and 0.05 g of sodium hydroxide in 6 ml of water, 0.6 g of dioxide **IV** was added. The reaction mixture was heated at 80°C for 6 h after that the ethanol was removed by distillation, and the residual aqueous solution was extracted with ether. After that the ether was distilled off, and the residue was analyzed by GLC to identify cyclohexanol.

**Reduction of Mn(VII).** To a solution of 0.1 g of compound **IV** in 100 ml of distilled water, 0.1 N  $\text{KMnO}_4$  was added dropwise from a burette until a stable pink color appeared. The same operation was carried out with a solution of compound **IV** with 10 ml of 0.1 N  $\text{H}_2\text{SO}_4$  or 0.2 g of NaOH added.

## ACKNOWLEDGMENTS

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