



Dimethylsilanethione — Generation by Retro-ene Reaction and Cycloaddition with Ketene

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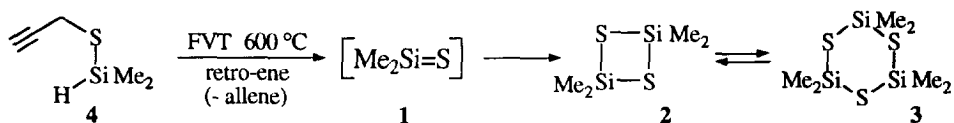
Abstract: Dimethylsilanethione was cleanly generated, under flash vacuum thermolysis conditions, by retro-ene cleavage of propargylthiodimethylsilane. The cothermolysis of this latter and ketene dimer led in 60 % yield to an only [2+2] cycloadduct, 2,2-dimethyl-4-methylene-2-sila-3-thiaoxetane, which in turn can be cleaved at higher temperature to give hexamethylcyclotrisiloxane.

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Amongst the species possessing a double bond on silicon,¹ silanethiones (R₂Si=S) have been scarcely investigated, due to their extreme thermodynamic and kinetic unstability. Two silanethiones, stabilized either by intramolecular coordination or by bulky substituents, have been described.^{2,3} The unhindered dimethylsilanethione (**1**) has been until now, when generated in the gas-phase, most often characterized by the cyclo-oligomers **2** and **3** resulting firstly from its cyclodimerization, the easiness of which usually overwhelms any other reaction of **1**. In these investigations, **1** was commonly generated by thermolysis of dimethylsilathietanes or cyclosilthianes **2** and **3**,^{4,5} and of allylthiodimethylsilane.⁶ Silanethione **1**, generated by flash vacuum thermolysis (FVT) of **3**, has been also directly characterized in the gas-phase by photoelectron spectrometry.⁷

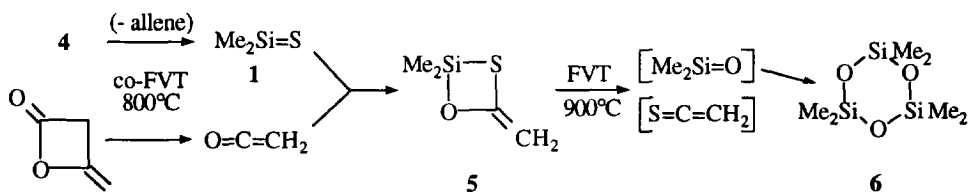
We report hereafter the generation of dimethylsilanethione (**1**) by FVT of propargylthiodimethylsilane (**4**), and its cycloaddition with ketene, resulting from the cothermolysis of **4** and ketene dimer. To our knowledge, this is the first example of cycloaddition between a double-bonded silicon and a ketene. The starting material **4** was prepared in 66 % yield by adding, to prop-2-ynethiol in ether, equimolar quantities of n-butyllithium, and then chlorodimethylsilane.⁸

The FVT of precursor **4** (FVT oven: 20 cm length x 1.6 cm i. d., pressure: 10⁻⁵ hPa) was complete at 600°C. Allene, cyclodisilthiane **2**, and cyclotrisilthiane **3** were obtained in 30, 65, and 3 % yield, respectively, as only thermolysis products, confirming the retro-ene reaction of **4** and the formation of silanethione **1** to be the exclusive thermal pathway occurring in that case.⁹



The co-FVT of **4** and ketene dimer was performed by simultaneous vaporization of these compounds, from two separate flasks, through the same oven heated at 800°C.¹⁰ A ten-fold excess of ketene was necessary to

avoid the formation of cyclodisilthiane **2**. The excess ketene, not trapped at -196°C , was pumped off and did not impede the isolation of the FVT products. Under these conditions, the main product, obtained in 60% yield, was silathioxetane **5**, a poorly stable compound (life time: *ca.* 24 h at room temperature in CDCl_3 solution), characterized by its NMR and HRMS spectra.¹¹ A small amount (< 5%) of hexamethylcyclotrisiloxane (**6**) was also characterized beside **5**. Compound **6**, formed as the main product by FVT of **5** at 900°C , resulted likely from the thermal fragmentation of this latter into dimethylsilanone and thioketene (similar thermal cleavages of silaoxetanes to give silanones have been often encountered in the literature¹).



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References and notes.

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8. *Propargylthiodimethylsilane* (**4**); b.p.: $75^{\circ}\text{C}/107$ hPa; ^1H NMR (CDCl_3): 0.38 (6 H, d, 3.4 Hz), 2.18 (1 H, t, 2.7 Hz), 3.18 (2 H, d, 2.7 Hz), 4.64 ppm (1 H, hept, 3.4 Hz); ^{13}C NMR: -1.6, 14.7, 71.1, 81.8 ppm; HRMS: M^+ 130.0285 (calcd. $\text{C}_5\text{H}_{10}\text{SSi}$ 130.02715), M^+ - CH_3 115.0002 (calcd. $\text{C}_4\text{H}_7\text{SSi}$ 115.00369); S%: calcd. $\text{C}_5\text{H}_{10}\text{SSi}$ 24.61, found 24.40.
9. The FVT products were characterized by NMR, IR, and HRMS, in agreement with the previously reported results⁴⁻⁶ [spectrometers: Bruker AC250 (NMR), Perkin-Elmer 1420 (IR), Jeol JMS D300 (HRMS)]. Yields were determined by NMR, using a quantitative standard of benzene; allene, being too volatile, was uncompletely trapped.
10. This temperature was necessary to allow the complete monomerization of ketene dimer.
11. *2,2-Dimethyl-4-methylene-2-sila-3-thioaxetane* (**5**): ^1H NMR (CDCl_3): 0.43 (6 H, s), 4.40 (1 H, d, 1.7 Hz), 4.57 ppm (1 H, d, 1.7 Hz); ^{13}C NMR: -0.8, 94.7, 147.8 ppm; HRMS: M^+ 132.0060 (calcd. $\text{C}_4\text{H}_8\text{OSSi}$ 132.00642), M^+ - CH_3 116.9802 (calcd. $\text{C}_3\text{H}_5\text{OSSi}$ 116.98692).

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