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

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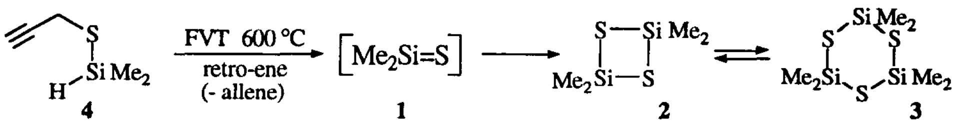
***Abstract:*** Dimethylsilanethione was cleanly generated, under flash vacuum thermolysis conditions, by retro-ene cleavage of propargylthiodimethylsilane. The cothermolysis of this latter and ketene dimer led in 60 % yield to an only [2+2] cycloadduct, 2,2-dimethyl-4-methylene-2-sila-3-thiaoxetane,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

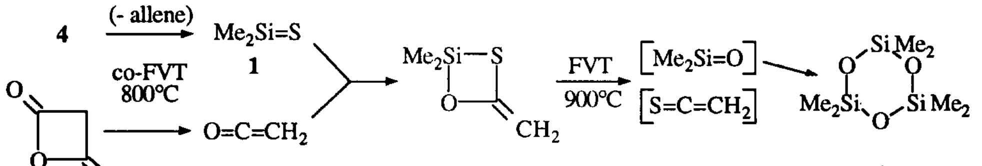
Amongst the species possessing a double bond on silicon,[1] silanethiones ($R_2Si=S$) have been scarcely investigated, due to their extreme thermodynamic and kinetic unstability. Two silanethiones, stabilized either by intramolecular coordination or by bulky substituents, have been described.[2,3] The 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 occuring 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 silathiaoxetane **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 literature[1]).



**5** **6**

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8. *Propargylthiodimethylsilane* (**4**); b.p.: 75°C/107 hPa; $^1$H 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: $M^{+\cdot}$ 130.0285 (calcd. $C_5H_{10}SSi$ 130.02715), $M^{+\cdot}$ - $CH_3$ 115.0002 (calcd. $C_4H_7SSi$ 115.00369); S%: calcd. $C_5H_{10}SSi$ 24.61, found 24.40.
9. The FVT products were characterized by NMR, IR, and HRMS, in agreement with the previously reported results[4-6] [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-thiaoxetane* (**5**): $^1$H 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: $M^{+\cdot}$ 132.0060 (calcd. $C_4H_8OSSi$ 132.00642), $M^{+\cdot}$ - $CH_3$ 116.9802 (calcd. $C_3H_5OSSi$ 116.98692).

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