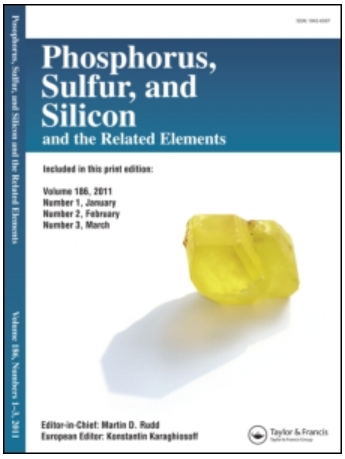

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Synthesis by FVT and Characterization of Unhindered Silanethiones

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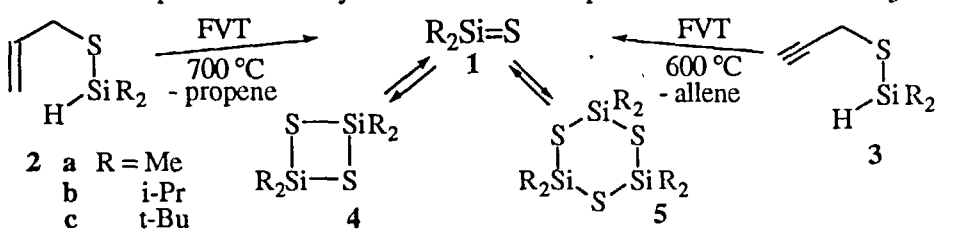
The retro-ene reaction of allylthio- and propargylthiosilanes led, under flash vacuum thermolysis (FVT) conditions, to unhindered silanethiones, characterized by their derivatives, and also directly by coupling of the FVT with gas-phase spectrometries. Monomeric silicon oxysulfide has been generated similarly. The unsubstituted silanethione was not obtained, but dehydrogenated into silicon monosulfide during FVT.

KEY WORDS: flash vacuum thermolysis, retro-ene, silanethione, silicon oxysulfide

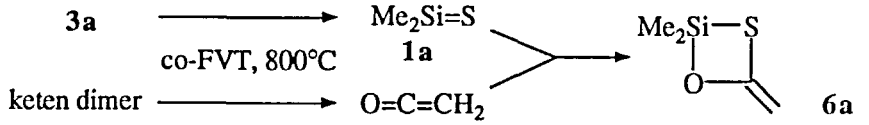
The direct observation of silanethiones ($R_2Si=S$), when compared to other compounds possessing a double bond on silicon, remains particularly scarce, owing to their extreme thermodynamic and kinetic unstability.[1] Two silanethiones, stabilized either by intramolecular coordination[2] or by bulky substituents,[3,4] have been however described. The unstabilized dimethylsilanethione has been generated by monomerization of its cyclotrimer under FVT conditions and characterized in the gas-phase by photoelectron spectrometry (PES).[5]

FVT is an excellent method of access to reactive, unhindered species having a silicon-heteroatom double bond[6] and we report here our recent results concerning the obtention of simple silanethiones (**1**) by retro-ene reaction. The investigated precursors are allylthio- (**2**) and propargylthiodialkylsilanes (**3**), the latter being preferred for their lower temperatures of decomposition. Compounds **2** and **3** have been prepared by reaction of mercaptans with dialkylchlorosilanes in the presence of n-BuLi or NEt_3.

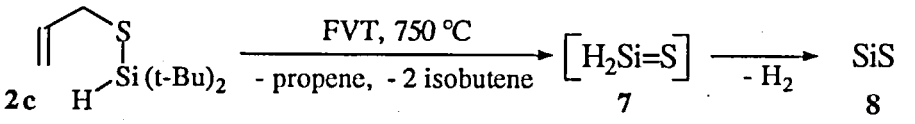


Dimethylsilanethione (**1a**) has been directly characterized by coupling of FVT with PES, showing the ionization potentials in agreement with those previously calculated and observed.[5] The FVT-PES investigation of silanethiones **1b** and **1c** is presently in progress.[7] **1b** and **1c** have been also identified by FVT-HRMS coupling. The generation

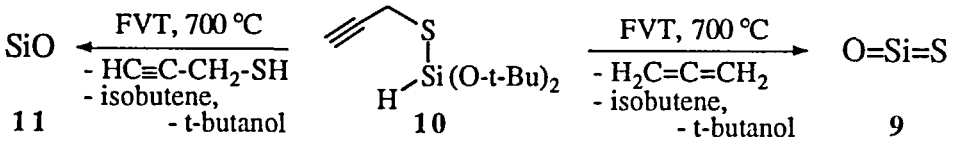
of silanethiones **1** has been confirmed by the obtention of cyclodimers **4a,b**, cyclotrimer **5a**, and of the cycloadduct **6a** obtained in the cothermolysis of **3a** with keten dimer [**6a**, δ^1H ($CDCl_3$): 0.43 (s, 6H), 4.40 and 4.57 (2d, J 1.7 Hz, 2H); δ^{13}C: -0.8, 94.7, 147.8].



Isobutene is easily eliminated from the t-butyl groups during the FVT of **2c** (precluding in that case the obtention of **1c** and **4c**) and the formation of silanethione (**7**), a postulated interstellar molecule, was thus expected. An investigation in coupling with millimeter wave spectrometry (MWS) showed however the dehydrogenation of **7** at the FVT temperature and only silicon monosulfide (**8**) was obtained.[8]



The synthesis of silicon oxysulfide (**9**), another compound of cosmochemical importance, has been undertaken from precursor **10**. The FVT of **10** showed the β-elimination of the t-butoxy groups and the competition of the retro-ene reaction giving **9** (characterized by its infrared spectrum at -196°C, in agreement with that reported in matrix[9]) with an α-elimination yielding silicon monoxide **11**.[8] Experiments aimed at the characterization of **9** by MWS are now in progress.[10]



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