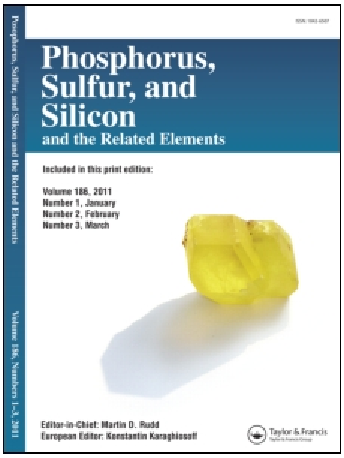

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GENERATION OF SILICON MONOXIDE, SILICON MONOSULFIDE AND HYDROGEN SILAISOCYANIDE BY FLASH VACUUM THERMOLYSIS

Agnes Chive[a]; Valerie Lefevre[a]; Anne Systermans[a]; Jean-Louis Ripoll[a]; Marcel Bogey[b]; Adam Walters[b]
[a] Laboratoire de Chimie des Composés Thio-organiques (Unité de Recherche Associée au CNRS n° 480), ISMRA, Université de Caen, Caen, France [b] Laboratoire de Spectroscopie Hertzienne (Unité de Recherche Associée au CNRS n° 249), Université des Sciences et Technologies de Lille, Villeneuve d'Ascq, France

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Communication

GENERATION OF SILICON MONOXIDE, SILICON MONOSULFIDE AND HYDROGEN SILAISOCYANIDE BY FLASH VACUUM THERMOLYSIS

AGNES CHIVE, VALERIE LEFEVRE, ANNE SYSTERMANS and JEAN-LOUIS RIPOLL*
Laboratoire de Chimie des Composés Thio-organiques (Unité de Recherche Associée au CNRS n° 480), ISMRA, Université de Caen,
6 Boulevard Maréchal Juin, F-14050 Caen, France

and

MARCEL BOGEY and ADAM WALTERS
Laboratoire de Spectroscopie Hertzienne (Unité de Recherche Associée au CNRS n° 249), Université des Sciences et Technologies de Lille,
F-59655 Villeneuve d'Ascq, France

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The flash vacuum thermolysis (650–1000°C) of unsaturated di-*t*-butylsilyl ether, sulfide, and amine **7–9** gave, upon retro-ene reaction, β-elimination of isobutene and dehydrogenation, silicon monoxide (**4**), silicon monosulfide (**5**), and hydrogen silaisocyanide (**6**), characterized in the gas-phase by millimeter wave spectrometry.

Key words: Flash vacuum thermolysis, retro-ene reaction, silicon-heteroatom double bond, millimeter wave spectrometry, interstellar molecules.

INTRODUCTION

The gas-phase generation of unsubstituted low-coordinated silicon species such as silanone (**1**), silanethione (**2**), and silanimine (**3**), remains presently challenging with only one experimental report concerning compound **1**.[1] Also, their dehydrogenated counterparts silicon monoxide (**4**), silicon monosulfide (**5**), and hydrogen silaisocyanide (**6**), are reactive molecules and only two gas-phase syntheses of **6** have been reported, using the flash vacuum thermolysis (FVT) of trimethylsilyl azide,[2] and the reaction of nitrogen with silane in a radio frequency discharge.[3] Compounds **4** and **5** have been more extensively investigated. All these silicon derivatives **1–6** are of cosmochemical importance as known (**4**, **5**) or postulated interstellar species.[4]

We have recently generated 1,1-dimethylsilanimine ($Me_2Si{=}NH$) by FVT of 1-

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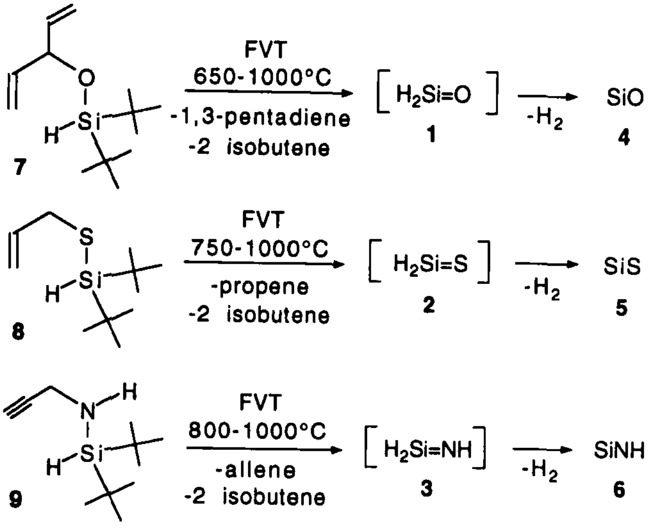
*To whom correspondence should be addressed.

t-butyl-2,2,3-trimethyl-1-aza-2-silacyclobutane, and of N-propargyl-1,1,3,3-tetramethyldisilazane.[5] These thermolyses included retro-ene reaction and β-elimination of isobutene from an N-*t*-butyl group. We report herein the FVT of compounds **7–9**, possible precursors of **1–3** by retro-ene reaction and β-elimination of isobutene from a Si-*t*-butyl group, as well as of **4–6** by the preceding reactions and dehydrogenation of the H_2Si group, theoretically investigated for **2** → **5**.[6] The obtained reactive species have been characterized in real time by coupling the FVT oven with a millimeter wave spectrometer.[7]

RESULTS AND DISCUSSION

The silyl ether **7**, the two double bonds of which conjugate by retro-ene reaction, as well as compounds **8** and **9**, for which this reaction is facilitated by the presence of the allylthio[8] and propargylic[9] groups, respectively, were expected to be cleaved at moderate FVT temperatures. The reaction of di-*t*-butylchlorosilane with 1,4-pentadien-3-ol in the presence of pyridine gave cleanly the silyl ether **7**. The allylthiosilane **8** and propargylic silanamine **9** have been prepared by reaction, in the presence of triethylamine, of allyl mercaptan and propargylamine, respectively, on di-*t*-butylchlorosilane.

Compound **7** was totally decomposed at 700°C, and 1,3-pentadiene (*E* + *Z* 80:20) and isobutene were identified by NMR. The FVT of **7** in coupling with millimeter wave spectrometry (MWS) also showed the presence of silicon monoxide (**4**), characterized particularly by its strong rotational transition *J*: 4 → 5 at 217104.610 MHz, in agreement with Reference 10. This line was detectable from 650°C, with an intensity increasing with the temperature up to 1000°C, the upper limit of the oven. The search for the lines of silanone (**1**), very recently observed by MWS in a plasma of $SiH_4/O_2/Ar$,[11] remained unsuccessful. It appears thus that **1**, if formed, should be dehydrogenated at the required FVT temperatures.



SCHEME

The thermolysis of allylthiosilane **8** was already practically complete at 600°C and the analysis of products by NMR showed the presence of propene and isobutene, the cyclo-dimer of 1,1-di-*t*-butylsilanethione[12] was not observed. The FVT/MWS experiments revealed for **8** the formation of silicon monosulfide (**5**), characterized by its *J*: 15 → 16 rotational transition at 290330.770 MHz.[13] This line was increasingly present from 750°C up to the maximum oven temperature of 1000°C.

The propargylic silanamine **9** was decomposed at 800°C and its FVT/MWS led to the observation of the *J*: 6 → 7 rotational transition of hydrogen silaisocyanide (**6**) at 266234.888 MHz.[14] Owing to the high reactivity of **6**, its concentration in the cell and the corresponding signal were however weaker than in the case of **4** and **5**.

In conclusion, the above mentioned decomposition reactions by FVT do not seem appropriate to the generation of molecules **1–3**, due to the thermal lability of the H_2Si group. On the other hand, the easily prepared compounds **7–9** can serve, upon FVT, as new sources for the reactive species **4–6**.

EXPERIMENTAL

General experimental conditions and details concerning FVT/NMR analysis were the same as already reported.[5,15] The millimeter wave spectrometer, as well as the technique of FVT/MWS coupling used in this work, have also been described previously.[7] Analytical samples of compounds **7–9** have been obtained, in view of the determination of their spectra and FVT/NMR experiments, by preparative GC at 170°C on a 3 m 5% SE30 column. Compounds **8** and **9** should be used immediately due to their high reactivity and, therefore, their complete microanalyses have not been obtained with sufficient reliability.

(1,4-pentadienyl-3-oxy)di-t-butylsilane (**7**): A mixture of 1,4-pentadien-3-ol (Aldrich, 0.84 g, 10 mmol), pyridine (0.79 g, 10 mmol) and di-*t*-butylchlorosilane (1.79 g, 10 mmol) in dry toluene (10 ml) was stirred at 100°C during 20 h. After elimination of the oily pyridinium chloride layer, the solution was diluted with ether (20 ml) and washed with icy water. After drying over magnesium sulfate and evaporation of solvents, the residue was bulb-to-bulb distilled under vacuum to give compound **7**, yield 1.72 g (76%): $C_{13}H_{26}OSi$, calcd. C 68.95, H 11.58, found C 68.79, H 11.91. - IR (film): ν = 2080 cm^{-1} (Si—H), 1110, 1050, 1020 and 915 (Si—C and Si—O). - ^1H NMR ($CDCl_3$): δ = 1.00 [s, 18 H, $(C(C\underline{H}_3)_3)_2$], 4.04 [s, 1 H, $Si-\underline{H}$], 4.63 [tm, *J* = 6.1 Hz, 1 H, $O-C\underline{H}-(CH=CH_2)_2$], 5.09 [dm, *J* = 10.2 Hz, 2 H] and 5.22 [dm, *J* = 17.1 Hz, 2 H] [$O-CH-(CH=C\underline{H}_2)_2$], 5.81 [m, 2 H, $O-CH-(C\underline{H}=CH_2)_2$]. - ^{13}C NMR ($CDCl_3$): δ = 20.01 [$(\underline{C}(CH_3)_3)_2$], 27.33 [$(C(\underline{C}H_3)_3)_2$], 78.41 [$O-\underline{C}H-(CH=CH_2)_2$], 114.43 [$O-CH-(CH=\underline{C}H_2)_2$], 139.79 [$O-CH-(\underline{C}H=CH_2)_2$]. - ^{29}Si NMR ($CDCl_3$): δ = 14.50.

Allylthiodi-t-butylsilane (**8**): Commercial 70% allyl mercaptan (Aldrich, 1.21 ml, 10 mmol) was added dropwise to a solution of chlorodi-*t*-butylsilane (1.79 g, 10 mmol) and triethylamine (1.01 g, 10 mmol) in anhydrous ether (10 ml). After stirring under reflux for 5 d and filtration of salts under inert atmosphere, the solvent was evaporated and the residue bulb-to-bulb distilled under vacuum to give practically pure **8**, yield 1.68 g (78%): $C_{11}H_{24}SSi$, calcd. S 14.81, found S 15.01. - IR (film): ν = 2100 cm^{-1} (Si—H), 1630 (C=C), 1220 (Si—C). - ^1H NMR ($CDCl_3$): δ = 1.09 [s, 18 H, $(C(C\underline{H}_3)_3)_2$], 3.25 [dm, *J* = 7.0 Hz, 2 H, $S-C\underline{H}_2-CH=CH_2$], 4.07 [s, 1 H, $Si-\underline{H}$], 5.02 [dm, *J* = 9.9 Hz, 1 H] and 5.14 [dm, *J* = 16.8 Hz, 1 H] [$S-CH_2-CH=C\underline{H}_2$], 5.89 [m, 1 H, $S-CH_2-C\underline{H}=CH_2$]. - ^{13}C NMR ($CDCl_3$): δ = 21.18 [$(\underline{C}(CH_3)_3)_2$], 28.25 [$(C(\underline{C}H_3)_3)_2$], 32.90 [$S-\underline{C}H_2-CH=CH_2$], 115.77 [$S-CH_2-CH=\underline{C}H_2$], 136.55 [$S-CH_2-\underline{C}H=CH_2$]. - ^{29}Si NMR ($CDCl_3$): δ = 27.23.

N-propargyl-1,1-di-t-butylsilanamine (**9**): Prepared according to the general procedure[15] from 10 mmol each of propargylamine, triethylamine and di-*t*-butylchlorosilane (reaction time: 20 h at room temp.) to give 1.62 g (82%) of **9** after bulb-to-bulb vacuum distillation. HRMS: $C_{11}H_{23}NSi$ [M^+], calcd. 197.1600, found 197.1614; $C_7H_{14}NSi$ [M^+ - C_4H_9], calcd. 140.0896, found 140.0905. - IR (film): ν = 3420 cm^{-1} (N—H), 3310 ($\equiv C-H$), 2090 (Si—H and $C\equiv C$), 1010 (Si—C), 820 (Si—N). - ^1H NMR ($CDCl_3$): δ = 1.00 [s, 18 H, $(C(C\underline{H}_3)_3)_2$], 2.20 (t, *J* = 2.4 Hz, 1 H, $C\equiv C\underline{H}$], 3.63 [dd, *J* = 7.7 and

2.4 Hz, 2 H, $C\underline{H}_2$], 3.79 [d, J = 4.6 Hz, 1 H, Si—$\underline{H}$]. - ^{13}C NMR ($CDCl_3$): δ = 22.42 [$(\underline{C}(CH_3)_3)_2$], 27.96 [$(C(\underline{C}H_3)_3)_2$], 34.57 [$\underline{C}H_2$], 69.59 [$C{\equiv}\underline{C}H$], 85.42 [$\underline{C}{\equiv}CH$]. - ^{29}Si NMR ($CDCl_3$): δ = 11.65.

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