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The generation of 1,1-dimethylsilanimine by flash vacuum thermolysis

Marguerite Letulle [a], Anne Systermans [a], Jean-Louis Ripoll [a,*], Pierre Guenot [b]

[a] *Laboratoire de Chimie des Composés Thio-organiques (Unité de Recherche Associée au CNRS no. 480), ISMRA, Université de Caen, 6 Boulevard Maréchal Juin, F-14050 Caen, France*

[b] *Centre Régional de Mesures Physiques de l'Ouest, Université de Rennes I, Avenue du Général Leclerc, F-35042 Rennes, France*

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Abstract

1,1-dimethylsilanimine ($Me_2Si{=}NH$) was generated from two different precursors, under flash vacuum thermolysis (FVT) conditions, either by retro-[2 + 2] or by retro-ene cleavage. This very reactive silanimine was characterized by formation of its cyclo-dimer, analyzed by FVT/HRMS, as well as by the production of its adduct with *t*-butanol. The generation in these thermolyses of *N*-*t*-butyl-1,1-dimethylsilanimine and *N*-dimethylsilyl-1,1-dimethylsilanimine was also demonstrated.

Keywords: Silanimines; Flash vacuum thermolysis; Synthesis; HRMS

1. Introduction

We published recently [1] the first experimental evidence for *N*-phenyl-1,1-dimethylsilanimine and *N*-isopropyl-1,1-dimethylsilanimine. These reactive unhindered silanimines were generated by retro-ene reaction of an *N*-allylsilanamine under flash vacuum thermolysis (FVT) conditions and by vacuum gas-solid reaction of a 1-chlorosilanamine, respectively. The silanimines obtained were identified by mass spectrometry, as well as by chemical trapping and from the dimerization products.

The present paper reports the generation of 1,1-dimethylsilanimine (**1**), unambiguously characterized by its cyclo-dimer **2** and its adduct **3** with *t*-butanol. To our knowledge, there is as yet no experimental evidence concerning this *N*-unsubstituted silanamine (see Ref. [2] for reviews on silicon double-bonded species).

2. Results and discussion

A preliminary investigation of several possible precursors of silanymine (**1**) by FVT led us to choose as the best candidates azasilacyclobutane (**4**) and the propargylic disilazane **5**. Compound **4** was prepared by intramolecular hydrosilylation of the allylic silanymine **6** in the presence of a platinum(0)-tetramethyldivinyldisiloxane complex [3]. The starting materials **5** and **6** were obtained by classical methods (see Experimental section).

Compound **4** was expected to undergo a retro-[2 + 2] cleavage [4] to give propene and silanimine **7** upon FVT. Silanimine **1** can also be formed in this thermolysis by β-elimination of isobutene from the *N*-*t*-butyl group.

No starting material was recovered when compound **4** was thermolyzed at 700°C. NMR analysis of products showed the presence of propene and of the dimer of silanimine **7**, cyclodisilazane (**8**) [5] in $\approx 5\%$ yield. At 800°C, isobutene was also eliminated. The thermolysis of **4** in the presence of *t*-butanol injected at the oven exit resulted in the formation of propene, isobutene, and of compound **3**, the addition product of silanimine **1** (yield 28% at 800°C). For the purpose of comparison, an authentic sample of **3** was prepared by reaction of dichlorodimethylsilane with *t*-butanol and then ammonia, according to a general procedure [6].

The monomeric silanimines **1** and **7** were not observed due to their high reactivity, but the formation of their cyclo-dimers **2** and **8** in the thermolysis of **4** was definitely confirmed by FVT/HRMS, showing that when the oven temperature is increased from 700 to

* Corresponding author.

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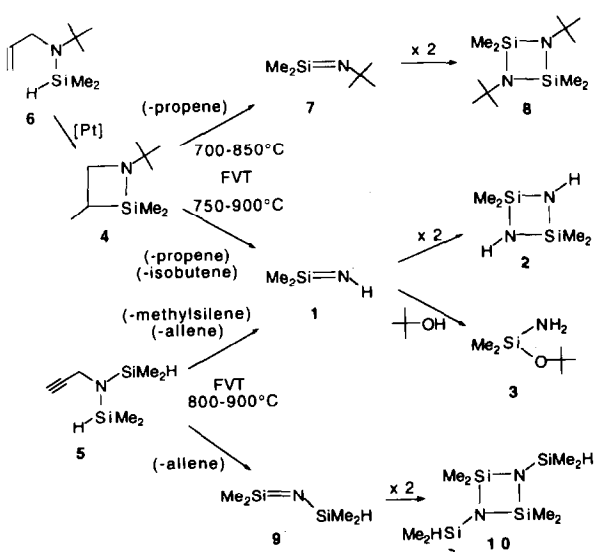
900°C, the peak at m/z 243.1727 (**8**, $M^+ - 15$, $C_{11}H_{27}N_2Si_2$, calcd. 243.1712) decreases and that at m/z 131.0457 (**2**, $M^+ - 15$, $C_3H_{11}N_2Si_2$, calcd. 131.0460) increases.

Upon FVT, the propargylic disilazane **5** was expected to give silanimine **9** by retro-ene cleavage [7]. Furthermore, the β-elimination of methylsilene from the other dimethylsilyl group present in the molecule can lead, as in the case of **4**, to silanimine **1**.

Compound **5**, totally thermolyzed above 800°C, also led to the silanimine **1**, although somewhat less specifically than **4**. The NMR analysis of the products of thermolysis between 800 and 900°C showed allene (yield ≈ 30%), azasilacyclopentenes resulting from a partial intramolecular thermal hydrosilylation of **5** and cyclodisilazane **10** [5] (≈ 5%), the dimer of silanimine **9**. Compound **3** was also obtained (≈ 20%) when this thermolysis was performed in the presence of *t*-butanol. The formation of silanimines **9** and **1** in the FVT of **5** has been confirmed by FVT (800°C)/HRMS, which showed particularly the presence of monomeric **9** at m/z 130.0504 ($M^+ - 1$, $C_4H_{12}NSi_2$, calcd. 130.0508), as well as that of cyclodisilazane **2**, the dimer of silanimine **1**, at m/z 131.0417 ($M^+ - 15$, $C_3H_{11}N_2Si_2$, calcd. 131.0460). The less-hindered cyclodisilazane **2** was expected to polymerize rapidly [8], and, unlike compounds **8** and **10**, it has been identified by FVT/MS only in the gas-phase.

3. Experimental section

Owing to the reactivity of the silanamines used and related compounds, all glassware was washed with a 5% solution of bis(trimethylsilyl)acetamide in pentane before drying. Reactions, transfers, and storing, were done under ultra-pure dinitrogen. FVT and GC apparatus were preconditioned by injection of hexamethyldisilazane. Spectrometers used were Varian-Mat 311 (MS), Perkin-Elmer 1420 (IR), and Bruker AM250 or WP80SY (NMR, δ referred to internal TMS).



3.1. *N-Allyl-N-t-butyl-1,1-dimethylsilanamine (6)*

Compound **6** was synthesized, according to the literature procedure [1], from allyl-*t*-butylamine [9] (2.26 g, 20 mmol), triethylamine (2.23 g, 22 mmol) and chlorodimethylsilane (1.89 g, 20 mmol): b.p. 52°C/15 hPa, yield 2.23 g (65%). HRMS: $C_9H_{21}NSi$, calcd. 171.1443, found 171.1444. MS (70 eV), m/z (%): 171 (7) [M^+], 156 (64), 114 (26), 100 (15), 98 (100), 69 (26), 59 (22), 58 (17), 57 (21), 56 (19), 42 (14), 41 (71), 39 (14). IR (film): $\nu = 2130$ cm^{-1} (Si–H), 1240 (Si–C), 900 (Si–N). ^{1}H NMR ($CDCl_3$): $\delta = 0.16$ [d, $J = 3.3$ Hz, 6H, $Si(CH_3)_2$], 1.17 [s, 9H, $C(CH_3)_3$], 3.41 [dm, $J = 4.8$ Hz, 2H, $N-CH_2-CH=CH_2$], 4.57 [sept, $J = 3.3$ Hz, 1H, Si–H], 4.96 [dm, $J = 10.2$ Hz, 1H] and 5.11 [dm, $J = 17.0$ Hz, 1H] [$N-CH_2-CH=CH_2$], 5.82 [m, 1H, $N-CH_2-CH=CH_2$]. ^{13}C NMR ($CDCl_3$): $\delta = 1.09$ [$Si(CH_3)_2$], 30.64 [$C(CH_3)_3$], 47.39 [$N-CH_2-CH=CH_2$], 53.75 [$C(CH_3)_3$], 113.02 [$N-CH_2-CH=CH_2$], 142.39 [$N-CH_2-CH=CH_2$]. ^{29}Si NMR ($CDCl_3$): $\delta = -12.47$.

3.2. *1-t-Butyl-2,2,3-trimethyl-1-aza-2-silacyclobutane (4)*

A 0.25 M solution of the complex of platinum(0) in 1,1,3,3-tetramethyl-1,3-divinyldisiloxane was prepared [10] by reaction of this disiloxane with hexachloroplatinic acid. This solution (40 μl, 0.01 mmol) was added at room temperature to silanamine **6** (1.71 g, 10 mmol). The reaction was complete after 4 h and compound **4** was obtained practically pure in nearly quantitative yield: $C_9H_{21}NSi$, calcd. C 63.08, H 12.35, N 8.18, found C 63.03, H 12.40, N 8.18%. HRMS: calcd. 171.1443, found 171.1434. MS (70 eV), m/z (%): 171 (2) [M^+], 157 (4), 156 (26), 116 (4), 115 (6), 114 (100), 100 (3), 86 (4), 84 (6), 72 (6), 59 (19), 58 (12), 57 (8), 56 (7). IR (film): $\nu = 1245$ cm^{-1} (Si–C), 840 (Si–N). ^{1}H NMR ($CDCl_3$): $\delta = 0.20$ and 0.23 [2s, 6H, $Si(CH_3)_2$], 1.00 [s, 9H, $C(CH_3)_3$], 1.09 [d, $J = 7.3$ Hz, 3H, $CH-CH_3$], 1.45 [ddq, $J = 8.4$, 4.3 and 7.3 Hz, 1H, $CH-CH_3$], 2.81 [dd, $J = 8.4$ and 5.9 Hz] and 3.55 [dd, $J = 5.9$ and 4.3 Hz], [2H, $N-CH_2$]. ^{13}C NMR ($CDCl_3$): $\delta = 0.33$ [$SiCH_3$], 3.57 [$SiCH_3$], 15.21 [$CH-CH_3$], 16.61 [$CH-CH_3$], 29.12 [$C(CH_3)_3$], 49.38 [$C(CH_3)_3$], 51.97 [$N-CH_2$]. ^{29}Si NMR ($CDCl_3$): $\delta = 8.64$.

3.3. *N-Propargyl-1,1,3,3-tetramethyldisilazane (5)*

Using the general procedure [11], propargylamine (0.55 g, 10 mmol), 1,1,3,3-tetramethyldisilazane (1.33 g, 10 mmol), and a 1% solution of chlorodimethylsilane in

pentane (10 μl, 10^{-3} mmol) were placed in a thoroughly dried, dinitrogen-flushed two-necked flask. The mixture was heated under reflux with magnetic stirring until ammonia no longer evolved (ca. 4 h) and the product was distilled bulb-to-bulb under vacuum. Compound **5**, obtained almost quantitatively in *ca.* 90% purity (NMR), was finally purified by preparative GC at 130°C, using a 5% SE30 column (3 m): $C_7H_{17}NSi_2$, calcd. C 49.05, H 10.00, N 8.17, found C 48.30, H 10.02, N 7.72%. HRMS: calcd. 171.0900, found 171.0911. MS (70 eV), *m/z* (%): 171 (12) [M^+], 170 (11), 157 (12), 156 (100), 148 (11), 147 (61), 130 (14), 118 (13), 116 (15), 100 (17), 98 (26), 96 (11), 86 (33), 83 (25), 72 (21), 69 (13), 66 (11), 59 (97), 54 (20), 45 (25), 43 (24). IR (film): $\nu = 3320$ cm^{-1} (≡C–H), 2130 (C≡C and Si–H), 1250 (Si–C), 880 (Si–N). ^1H NMR ($CDCl_3$): $\delta = 0.22$ [d, $J = 3.2$ Hz, 12H, $Si(CH_3)_2$], 2.17 [t, $J = 2.3$ Hz, 1H, $C{\equiv}CH$], 3.56 [d, $J = 2.3$ Hz, 2H, CH_2], 4.47 [sept, $J = 3.2$ Hz, 2H, Si–*H*]. ^{13}C NMR ($CDCl_3$): $\delta = -0.97$ [$Si(CH_3)_2$], 34.21 [CH_2], 70.15 [$C{\equiv}CH$], 84.93 [$C{\equiv}CH$]. ^{29}Si NMR ($CDCl_3$): $\delta = -9.09$.

3.4. 1-t-Butoxy-1,1-dimethylsilanamine (3)

Compound **3** was obtained by the general procedure [6], by reaction in hexane of dichlorodimethylsilane (1.29 g, 10 mmol), first with *t*-butanol (0.74 g, 10 mmol) in the presence of triethylamine (1.01 g, 10 mmol), and then with an excess of gaseous ammonia bubbled through the solution during 5 h. The crude product obtained was purified by bulb-to-bulb vacuum distillation, followed by GC at 130°C with a SE30 column: $C_6H_{17}NOSi$, calcd. C 48.92, H 11.63, found C 48.63, H 11.39%. IR (film): $\nu = 3480$ and 3400 cm^{-1} (NH_2), 1245 (Si–C), 1035 (Si–O), 855 (Si–N). ^1H NMR ($CDCl_3$): $\delta = 0.10$ [s, 6H, $Si(CH_3)_2$], 1.30 [s, 9H, $C(CH_3)_3$]. ^{13}C NMR ($CDCl_3$): $\delta = 1.62$ [$Si(CH_3)_2$], 32.08 [$C(CH_3)_3$], 72.05 [$C(CH_3)_3$]. ^{29}Si NMR ($CDCl_3$): $\delta = -8.88$.

3.5. Flash vacuum thermolysis of compounds 4 and 5

The FVT were performed at 700–900°C/10^{-4} hPa (oven dimensions: $l = 15$ cm, i.d. = 14 mm). For NMR analysis, $CDCl_3$ was first condensed on a cold finger at −196°C, ca. 50 mg of precursor were then thermolyzed, the products transferred upon melting in the NMR tube fitted below the trap, and the spectra immediately recorded. Trapping experiments were performed by gas-phase injection of *t*-butanol (1.5 equiv) into the oven exit during the whole-time of thermolysis. For purpose of comparison, cyclodisilazanes **8** and **10** were prepared according to Ref. [5]. A polymeric material, obtained in the FVT of **4** and **5** in addition to the reported products and arising possibly from **1** and **2** was not investigated further. For MS analysis, the oven was directly coupled to the mass spectrometer and the products analyzed in real time.

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