

## CO-PYROLYSIS OF DIMETHOXYMETHYLSILYL-BIS(TRIMETHYLSILYL)AMINE AND HEXAMETHYLCYCLOTRISILOXANE. 1,3-SIGMATROPIC REARRANGEMENTS OF SILAIMINE INTERMEDIATES \*

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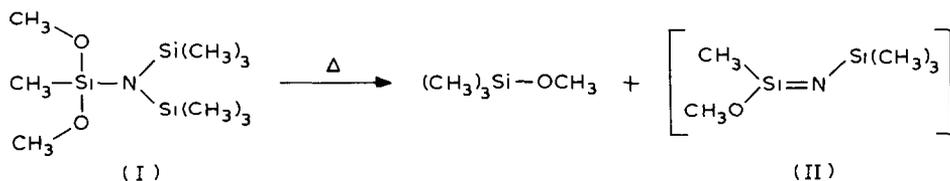
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### Summary

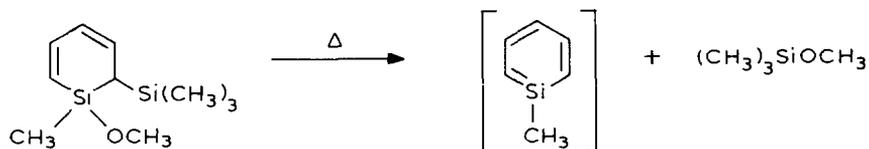
Co-pyrolysis of dimethoxymethylsilylbis(trimethylsilyl)amine (I) with hexamethylcyclotrisiloxane ( $D_3$ ) at low pressure has been carried out. 1,2-Elimination of trimethylmethoxysilane from I gives *N*-trimethylsilylmethylmethoxysilamine (II), which reacts with  $D_3$  to give 6-methoxy-2,2,4,4,6,8,8-heptamethyl-7-trimethylsilyl-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacyclooctane (40.5%) (III). 1,3-Sigmatropic rearrangement of a methyl group from one silyl center to the other converts II into *N*-methoxydimethylsilyldimethylsilamine, which reacts with  $D_3$  to yield 2,2,4,4,6,6,8,8-octamethyl-7-methoxydimethylsilyl-1,3,5-trioxa-4-7-aza-2,4,6,8-tetrasilacyclooctane (19.5%) (IV). Co-pyrolysis of III and  $D_3$  gives 1-aza-2,2,4,4,6,6,8,10,10,12,12,14,14-tridecamethyl-3,5,7,9,11,13-hexaoxa-2,4,6,8,10,12,14-heptasilabicyclo[6.6.0]tetradecane (65%) (VII). These results are discussed.

There has been considerable interest in the generation and chemical reactivity of silicon doubly bonded intermediates [1,2]. We undertook a study of the flash vacuum pyrolysis of dimethoxymethylsilylbis(trimethylsilyl)amine (I) in the hope that it would undergo 1,2-elimination of a molecule of trimethylmethoxysilane to yield *N*-trimethylsilylmethylmethoxysilamine (II).

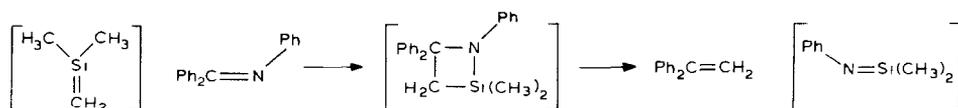


\* This paper is dedicated to Professor M. Kumada, whose excellent work and high standards of achievement in silicon chemistry have contributed much to our understanding in this area.

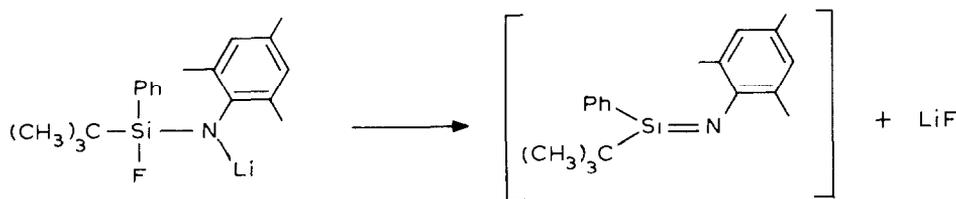
This approach has been successfully used to generate a number of silicon-carbon doubly bonded intermediates [3-5].



Silaimines have previously been generated by photolysis or pyrolysis of silyl azides. This involves loss of nitrogen and rearrangement of a group from silicon to nitrogen to yield a reactive silaimine [6-9]. Silicon-nitrogen doubly bonded intermediates have also been suggested to result from [2 + 2] cycloaddition reactions of silenes with imines to yield unstable *N*-silazetidines, which decompose to yield an alkene and a silaimine [10].

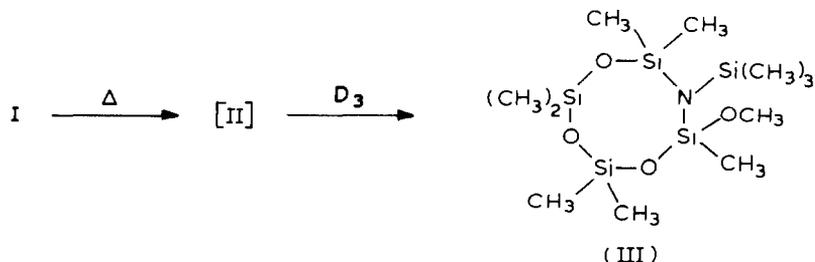


Silaimine intermediates are formed by loss of lithium fluoride from *N*-lithioamino-fluorosilane [11-13].



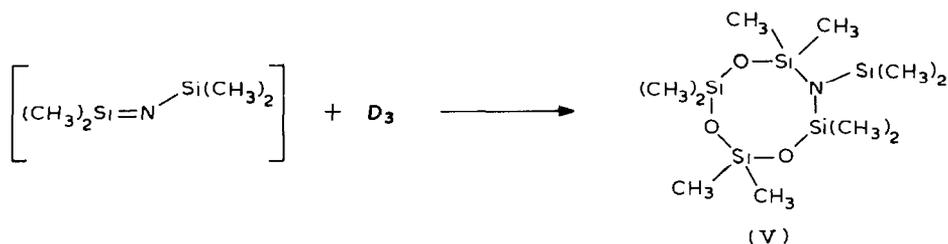
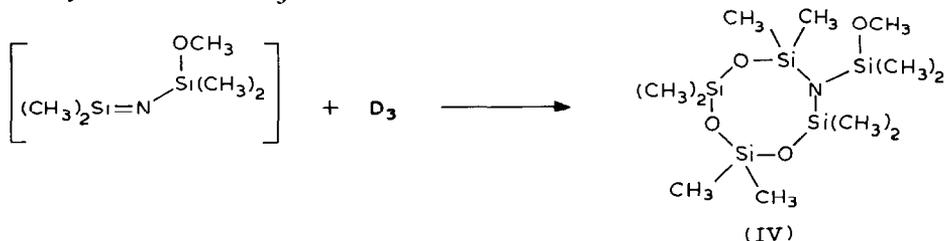
Finally, thermal decomposition of 3,5,5-tris(trimethylsilyl)-4,4-dimethyl-4-sila-1,2,3-triazoline yields a reactive silaimine [14].

In fact, flash vacuum pyrolysis of I in the presence of hexamethylcyclotrisiloxane ( $D_3$ ) led to 6-methoxy-2,2,4,4,6,8,8-heptamethyl-7-trimethylsilyl-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacyclooctane (III), the expected product of reaction of  $D_3$  with II (40.5% yield) and trimethylmethoxysilane. Hexamethylcyclotrisiloxane has previously been shown to trap efficiently silicon-carbon [15,16], silicon-oxygen [16,17], silicon-sulfur [18,19], and even silicon-nitrogen [20] doubly bonded intermediates.



Perhaps of greater significance, in addition to the expected product III, 2,2,4,4,6,6,8,8-octamethyl-7-methoxydimethylsilyl-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacyclooctane (IV) (19% yield), 2,2,4,4,6,6,8,8-octamethyl-7-trimethylsilyl-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacyclooctane (V) (3.3% yield) and dimethyldimethoxysilane were

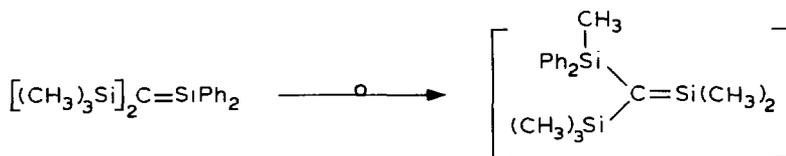
also isolated. Product IV may result from the reaction of *N*-methoxydimethylsilyldimethylsilaimine with  $D_3$ , while V may arise by reaction of *N*-trimethylsilyldimethylsilaimine with  $D_3$ .



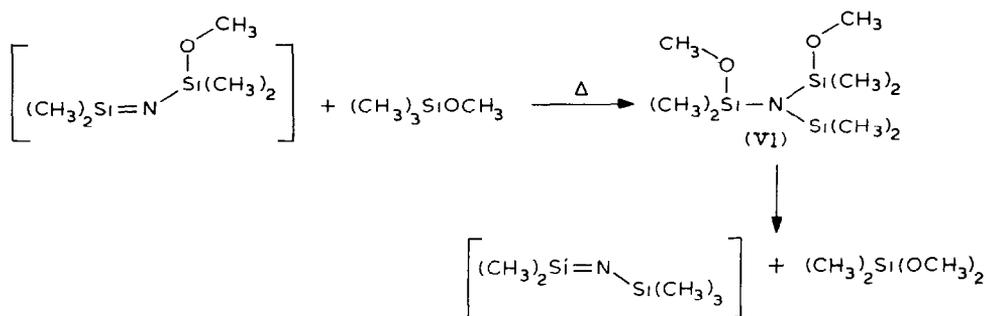
*N*-Methoxydimethylsilyldimethylsilaimine may result from a 1,3-sigmatropic rearrangement of a methyl group from one silicon to another of the initially formed *N*-trimethylsilylmethylmethoxysilaimine intermediate (II).



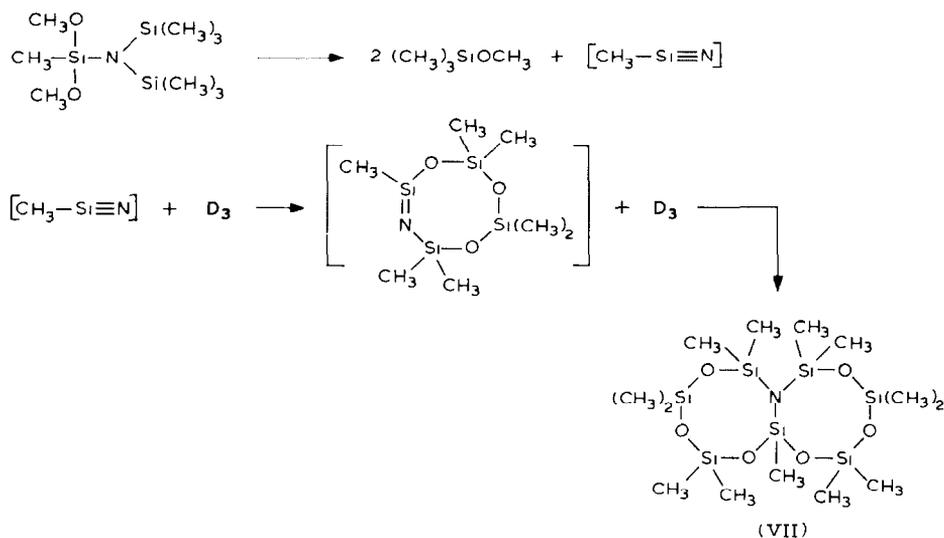
No previous example of isomerizations of one silicon–nitrogen doubly bonded intermediate into another has been reported, but interconversions of silicon–carbon doubly bonded intermediates via 1,3-sigmatropic rearrangements have been observed [21]:



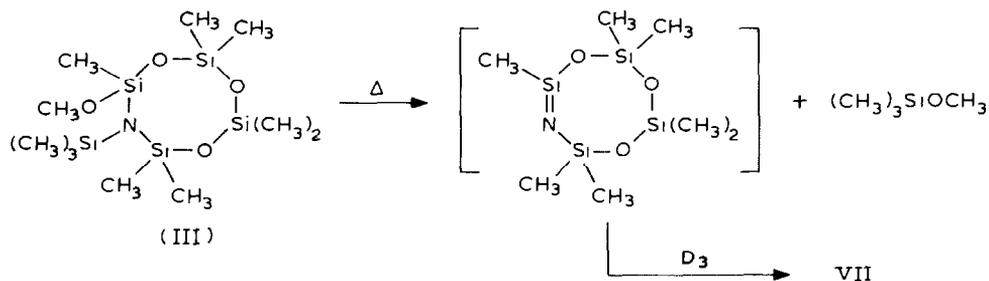
*N*-Trimethylsilyldimethylsilaimine may arise by the following reaction sequence. Reaction of trimethylmethoxysilane with the rearranged silaimine intermediate, *N*-methoxydimethylsilyldimethylsilaimine yields trimethylsilylbis(dimethylmethoxysilyl)amine (VI). 1,2-Elimination of a dimethylmethoxysilyl group and a methoxy group as dimethyldimethoxysilane from VI would result in generation of *N*-trimethylsilyldimethylsilaimine as a reactive intermediate [3–5]. In support of this proposal small amounts (1%) of VI have in fact been isolated in addition to unreacted starting material I.



In addition small amounts of 1-aza-2,2,4,4,6,6,8,10,10,12,12,14,14-tridecamethyl-3,5,7,9,11,13-hexaoxa-2,4,6,8,10,12,14-heptasilabicyclo[6.6.0]tetradecane (VII) were found (6%). This product might result from loss of two molecules of trimethylmethoxysilane from I to form silacetonitrile an intermediate which possesses a reactive silicon–nitrogen triply bond. Sequential reaction of this species with two molecules of  $\text{D}_3$  may yield VII.



However, an alternative mechanism for the formation of VII exists, specifically, initial 1,2-elimination of trimethylmethoxysilane from III to form 1-aza-



2,4,4,6,6,8,8-heptamethyl-3,5,7-trioxa-2,4,6,8-tetrasilacycloocta-1-ene, a reactive silaimine, which then reacts with a silicon-oxygen single bond of  $D_3$  to yield VII. Consistent with this latter possibility we have found that co-pyrolysis of III and  $D_3$  at higher temperature results in formation of VII (65%) and trimethylmethoxysilane. On the other hand, co-pyrolysis of either IV or V and  $D_3$  results only in recovered starting materials IV or V. This result is expected since neither IV nor V can lose trimethylmethoxysilane in a 1,2-sense.

## Experimental

$^1H$  NMR spectra were obtained on a Varian XL-100, IBM-Bruker WP-270-SY, or Bruker WM-500 spectrometer operating in a FT mode using 5% solution at deuteriochloroform. Chloroform was utilized as the internal standard. The integration of the NMR spectra sometimes gave too small intensities for the Si- $CH_3$  signals because of saturation problems. However, in all cases the integration was within 10% of the calculated value.  $^{13}C$  NMR spectra were obtained on an IBM-Bruker WP-270-SY using 10–15% solution in deuteriochloroform. Chloroform was utilized as an internal standard.  $^{13}C$  spectra were run with broad band proton decoupling.  $^{29}Si$  spectra were run on a Bruker WM-500 using 10–15% solution in deuteriochloroform. Tetramethylsilane was utilized as an internal standard.  $^{29}Si$  spectra were run with gated decoupling.

IR spectra were obtained on a Perkin-Elmer 281 or Nicolet MX-1 Fourier Transform spectrometers. Low resolution mass spectra were obtained on a Hewlett-Packard 5985 GC-MS at an ionizing voltage of 70 eV. A 20 in  $\times$  1/8 in 2% OV-10 on 100/120 mesh Chromosorb W column was used in the gas chromatograph inlet of the mass spectrometer. High resolution mass spectra were obtained on an A.E.I. MS-902 at 70 eV. Exact mass were determined by peak matching against peaks of known mass of perfluoro kerosene. GLPC analysis was performed on a Hewlett-Packard F&M 700 using either a 4 ft  $\times$  1/4 in 20% SE-30 on 60–80 mesh Chromosorb W column (A), a 15 ft  $\times$  1/4 in 20% Carbowax on 60–80 mesh Chromosorb W column (B), a 15 ft  $\times$  1/4 in 20%  $\beta,\beta$ -ODPN on 60–80 mesh Chromosorb W column (C), a 6 ft  $\times$  1/8 in 5% OV-101 on 80–100 mesh Chromosorb W column (D), or an 16 ft  $\times$  1/8 in 5% OV-202 on Chromosorb W 80/100 mesh column (E). Product yields were calculated using mesitylene as an internal standard.

Hexamethyldisilazane and n-butyllithium were purchased from Aldrich. Dimethylmethoxychlorosilane and hexamethylcyclotrisiloxane were obtained from Petrarch System Inc. Diethyl ether was distilled from sodium/benzophenone ketyl immediately prior to use.

*Preparation of dimethoxymethylsilylbis(trimethylsilyl)amine (I) [22].* In a 250 ml three-necked round bottom flask equipped with a pressure equalizing addition funnel, condenser and a rubber septum were placed (18.8 g, 0.071 mol) of hexamethyldisilazane and a Teflon covered magnetic stirring bar. The flask was flushed with purified nitrogen. n-Butyllithium (1.5 M in hexane) (57 ml, 0.071 mol) was added to the flask over a period of 1 h. During addition, the reaction mixture was cooled in an ice-water bath. The solution was refluxed for 3 h and then was stirred at 20°C overnight. The solution was then cooled to  $-196^\circ C$  by liquid nitrogen and (10 g, 0.071 mol) of methyl dimethoxychlorosilane in 30 ml of ether was

added to the frozen solution. The reaction mixture was gradually warmed and then refluxed for 3 h. LiCl was removed by filtration. The solvents were removed by evaporation under reduced pressure. Dimethoxymethylsilylbis(trimethylsilyl)amine was distilled from the residue b.p. 44 °C/1 mmHg in 68% yield. It has the following spectral properties: <sup>1</sup>H: δ 0.112 (s, 3H); 0.157 (s, 18H); 3.424 (s, 6H). <sup>13</sup>C NMR: δ 2.002 (1C), 4.012 (6C); 48.801 (3C) <sup>29</sup>Si NMR: δ -27.80 (1Si); 2.366 (2Si). MS: *m/e* (% rel. int.) 250 (21) *M*<sup>+</sup> - 15; 234 (100) *M*<sup>+</sup> - 31; 204 (5.7); 188 (6.8); 130 (27.3), 116 (7.1); 100 (7.8); 73 (8.1).

*6-Methoxy-2,2,4,4,6,8,8-heptamethyl-7-(trimethylsilyl)-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacyclooctane (III)*. III was formed in 40.3% yield. It was purified by preparative GLPC column B. It has the following spectral properties: <sup>1</sup>H NMR: δ 0.078 (s, 6H); 0.095 (s, 3H); 0.133 (s, 3H); 0.152 (s, 9H); 0.165 (s, 3H); 0.177 (s, 3H); 0.219 (s, 3H); 3.424 (s, 3H). MS: *m/e* (% rel. int.) 368 (100) *M*<sup>+</sup> - 15; 352 (2.3) *M*<sup>+</sup> - 31; 280 (7.4); 264 (20.3); 250 (12.0); 190 (8.3); 130 (5.5); 100 (5.5); 89 (19.6); 73 (42.5). Exact mass for Si<sub>5</sub>C<sub>10</sub>H<sub>30</sub>NO<sub>4</sub> (*M*<sup>+</sup> - 15) 368.1047, calcd. 368.1021.

*2,2,4,4,6,6,8,8-Octamethyl-7-(methoxydimethylsilyl)-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacyclooctane (IV)*. IV was formed in 19% yield. It was purified by preparative GLPC column B. It has the following spectral properties: <sup>1</sup>H NMR: δ 0.077 (s, 12H); 0.171 (s, 6H); 0.205 (s, 12H); 3.378 (s, 3H). MS: *m/e* (% rel. int.) 368 (100) *M*<sup>+</sup> - 15; 352 (2.3) *M*<sup>+</sup> - 31; 280 (7.4); 264 (20.3); 250 (12.0); 190 (8.3); 130 (5.5); 100 (5.5); 89 (19.6); 73 (42.5). Exact mass for Si<sub>5</sub>C<sub>10</sub>H<sub>30</sub>NO<sub>4</sub> (*M*<sup>+</sup> - 15) 368.1047, calcd. 368.1021.

*2,2,4,4,6,6,8,8-Octamethyl-7-(trimethylsilyl)-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacyclooctane (V) [22]*. V was formed in 3.3% yield. It was purified by preparative GLPC column B. It has the following spectral properties: <sup>1</sup>H NMR: δ 0.077 (s, 12H); 0.156 (s, 9H); 0.202 (s, 12H). MS: *m/e* (% rel. int.) 352 (86.0) *M*<sup>+</sup> - 15; 264 (26.6); 248 (12); 190 (7.3); 73 (100).

*Trimethylsilylbis(dimethylmethoxysilyl)amine (VI)*. VI was isolated in about 1% yield. It was purified by preparative GLPC column D. It has the following spectral properties: <sup>1</sup>H NMR: δ 0.175 (s, 9H); 0.187 (s, 12H); 3.384 (s, 6H). MS: *m/e* (% rel. int.) 250 (100.0), *M*<sup>+</sup> - 15; 234 (21.3) *M*<sup>+</sup> - 31; 220 (12.8); 174 (10.6); 130 (63.8).

#### *Flash vacuum pyrolysis of I*

A 5 ml round bottom flask which contained (0.5 g, 1.88 mmol) of compound I and hexamethylcyclotrisiloxane (**D**<sub>3</sub>) (1.26 g, 5.66 mmol) was connected to a spiral pyrex tube (200 cm × 0.7 cm) which was placed inside an oven (450–470 °C). The other end of the pyrolysis tube was connected to a liquid nitrogen cooled trap which in turn was attached to a mercury diffusion pump (10<sup>-4</sup> mmHg). The round bottom flask was heated to 60 °C to distill the sample of I through the pyrolysis tube. This procedure took between 30–45 min.

*1-Aza-2,2,4,4,6,6,8,10,10,12,12,14,14-tridecamethyl-3,5,7,9,11,13-hexaoxa-2,4,6,8,10,12,14-heptasilabicyclo[6.6.0]tetradecane (VII)*. A mixture of III (100 mg, 0.26 mmol) and **D**<sub>3</sub> (440 mg, 2 mmol) was placed in a 5 ml round bottom flask which was connected to a spiral quartz pyrolysis tube as above. The mixture was distilled through the pyrolysis tube under high vacuum at a temperature of 510 °C over 0.5 h. VII was found in 65% yield based on recovered starting materials. It was purified by preparative GLPC on column E. It has the following spectral properties: <sup>1</sup>H NMR: δ 0.065 (s, 6H); 0.08 (s, 6H); 0.092 (s, 6H); 0.114 (s, 6H); 0.171 (s, 6H); 0.190 (s, 6H);

0.204 (s, 3H). IR: 1104, 1070, 1023  $\text{cm}^{-1}$  Si-O. MS:  $m/e$  (% rel. int.) 486 (89.2)  $M^+ - 15$ ; 398 (14.4); 147 (3.0); 73 (100). Exact mass for  $\text{Si}_7\text{C}_{12}\text{H}_{36}\text{NO}_6$  ( $M^+ - 15$ ) 486.0932, calcd. 486.0926.

Co-pyrolysis of either IV and  $\text{D}_3$  or V and  $\text{D}_3$  as above resulted in only recovered starting materials IV or V respectively.

### Acknowledgements

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