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FLASH VACUUM PYROLYSIS OF DIMETHOXYMETHYLSILYL-BIS(TRIMETHYLSILYL)AMINE: 1,3-SIGMATROPIC REARRANGEMENTS OF SILAIMINE INTERMEDIATES

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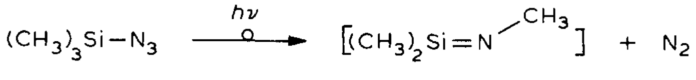
Summary

Pyrolysis of dimethoxymethylsilyl-bis(trimethylsilyl)amine has been carried out at low pressure. 1,2-Elimination of trimethylmethoxysilane gives *N*-trimethylsilylmethoxymethylsilaimine (II). 1,3-Sigmatropic rearrangements of II gives *N*-methoxydimethylsilyldimethylsilaimine (VII). Addition of trimethylmethoxysilane to VII gives trimethylsilyl-bis(methoxydimethylsilyl)amine (VIII) which may lose dimethyldimethoxysilane to give *N*-trimethylsilyl dimethylsilaimine (IX). Head-to-tail dimerization as well as [2 + 2]-cross cycloaddition reactions of these silaimines intermediates II, VII and IX lead to formation of substituted cyclodisilazanes as the major products.

There has been significant current interest in elucidating the chemical pathways followed by reactive doubly-bonded intermediates in organosilicon chemistry [1,2]. Rearrangement reactions provide not only methods to generate certain of these species but also channels to interconvert them.

Several types of rearrangement reactions have proved useful for the generation of reactive silicon doubly-bonded species. Both silenes [3,4] and silaimines have been produced by 1,2-rearrangement reactions. Thus photolysis or pyrolysis of silyl azides results in loss of nitrogen and rearrangement of a group from silicon to nitrogen to yield a silaimine [5–8].



$$(CH_3)_3Si{-}N_3 \xrightarrow[\Delta]{h\nu} [(CH_3)_2Si{=}N{-}CH_3] + N_2$$

1,3-Sigmatropic rearrangements of aryl [9–15], ethynyl [16,17] and vinyl [18,19] substituted disilanes under the influence of thermal or photochemical energy input result in the formation of silenes.

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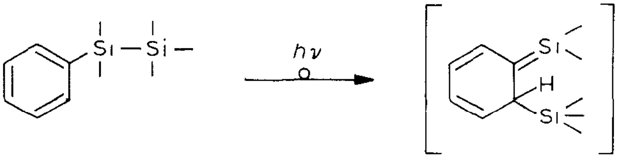
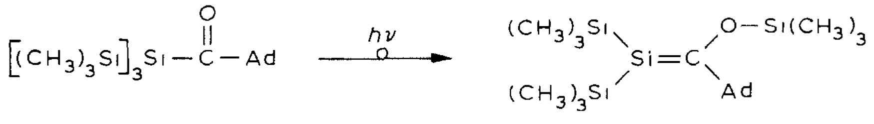
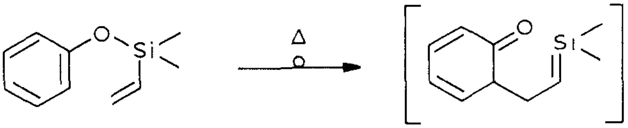


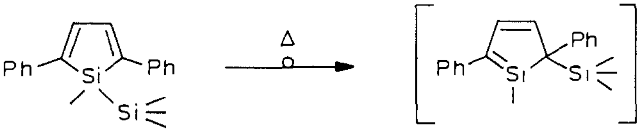
A sterically stabilized silicon–carbon doubly-bonded species has been prepared by photolysis of adamantoyl tris(trimethylsilyl)silane. This rearrangement involves a 1,3-sigmatropic migration of a trimethylsilyl group from silicon to oxygen [20].



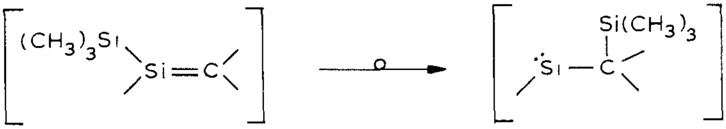
Reactive silenes result from Claisen rearrangement of dimethylphenoxyvinylsilanes [21].



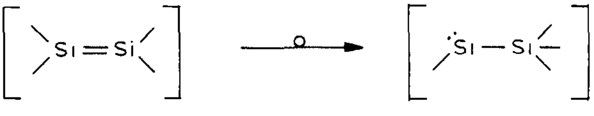
Silenes have also been generated by 1,5-sigmatropic rearrangements of dienyl substituted disilanes [22–24].



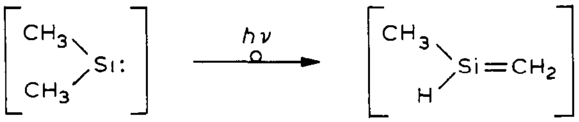
Most of the examples of interconversion of unsaturated silicon intermediates one into another involve the transformation of silenes or disilenes to silylenes by 1,2-rearrangements. For example, silyl silenes rearrange to silylenes [25,26].



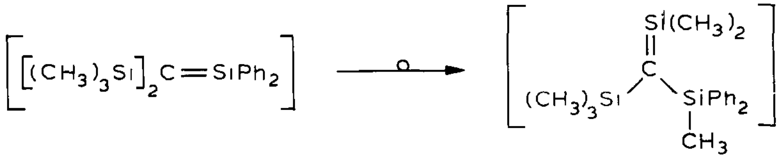
The interconversion of disilenes into silyl substituted silylenes has likewise been observed [27–30].



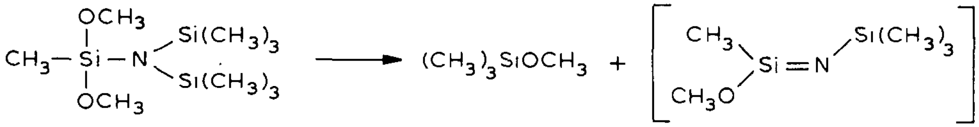
The reverse reaction, namely the transformation of dimethylsilylene into methylsilene on ultraviolet irradiation in an argon matrix, as well as, in the gas phase at high temperature has been reported [31–34].



The transformation of one silicon–nitrogen doubly-bonded species into another by 1,3-sigmatropic rearrangement has not been previously observed. The pyrolysis of dimethoxymethylsilyl-bis(trimethylsilyl)amine (I) which we would like to report provides several examples of this type of rearrangement. In fact, only one example of the interconversion of one silene into another by a 1,3-sigmatropic rearrangement has been observed [35].

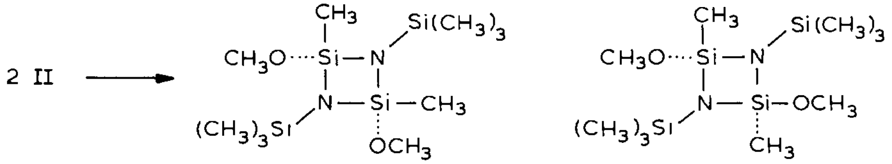


We undertook a study of the pyrolysis of dimethoxymethylsilyl-bis(trimethylsilyl)amine(I) with the expectation that it would undergo 1,2-elimination of trimethylmethoxysilane to yield *N*-trimethylsilylmethoxymethylsilaimine (II).



(I) (II)

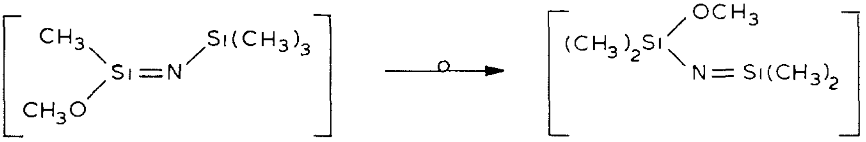
A number of silenes have been generated by such 1,2-elimination reactions of trimethylmethoxysilane [36–38]. As expected, pyrolysis of I results in loss of trimethylmethoxysilane (64%) and formation of *cis*- and *trans*-1,3-bis(trimethylsilyl)-2,4-dimethoxy-2,4-dimethylcyclodisilazane (III and IV) in 1.9 and 2.8% yields, respectively.



(III) (IV)

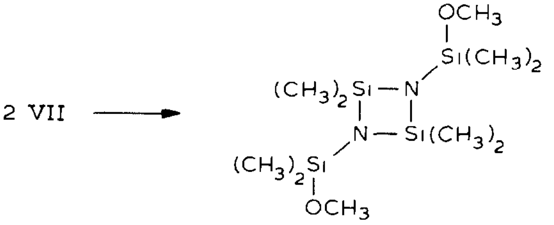
These cyclodisilazanes are expected products for the dimerization of the reactive intermediate *N*-trimethylsilylmethoxymethylsilaimine (II).

In addition to these anticipated products a number of unexpected products were isolated. Among these were 1,3-bis(methoxydimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (V) and 1-methoxydimethylsilyl-3-trimethylsilyl-2-methoxy-2,4,4-trimethylcyclodisilazane (VI) found in 14 and 24% yield, respectively. The former probably results from the head-to-tail dimerization of *N*-methoxydimethylsilyldimethylsilaimine (VII). This reactive species may be formed from II by a 1,3-rearrangement of a methyl group from one silyl center to the other.

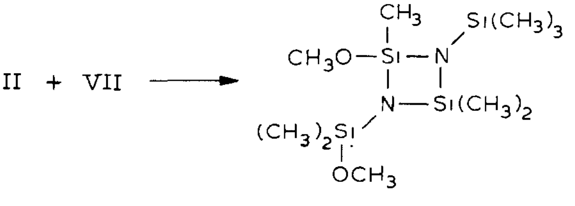


(II) (VII)

The latter disilazane results from head-to-tail reaction of reactive silaimines II and VII.

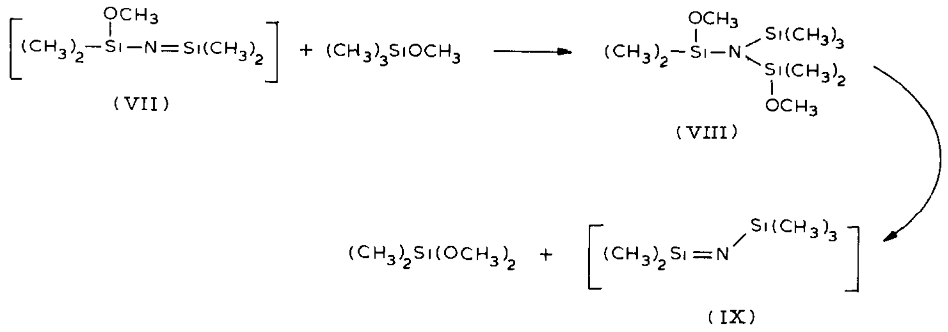


(V) 13.8%

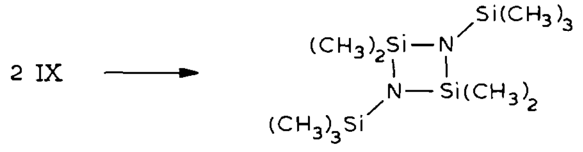


(VI) 24%

A second group of unexpected products results from the reactions of the silaimine found by loss of dimethyldimethoxysilane (32%) from I. The loss of dimethyldimethoxysilane may result from the following sequence of reactions. Reaction of the rearranged silaimine (VII) with trimethylmethoxysilane would be expected to yield trimethylsilyl-bis(methoxydimethylsilyl)amine (VIII) which undergoes 1,2-elimination of a methoxydimethylsilyl group and a methoxy group from an adjacent silyl center as dimethyldimethoxysilane with concurrent formation of *N*-trimethylsilyldimethylsilaimine (IX) [36–38]. In fact VIII is found in addition to recovered I in about 1% yield. The alternative possibility, the direct loss of a dimethoxymethylsilyl group and a methyl group from an adjacent silyl center is without precedent.

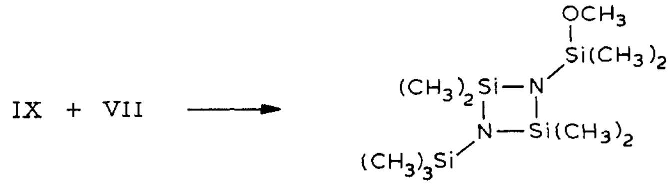


1,3-Bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (X), the expected dimer of the reactive silaimine intermediate IX, was found in 16.5% yield.

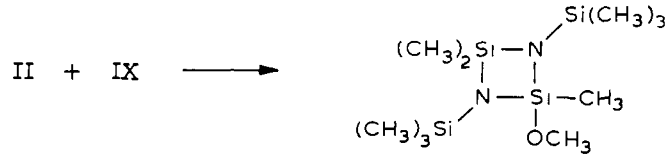


(X)

1-Methoxydimethylsilyl-3-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane (XI) and 1,3-bis(trimethylsilyl)-2-methoxy-2,4,4-trimethylcyclodisilazane (XII), products of cross reaction of silaimine IX with silaimines VII and II, are found in 11.1 and 16.7% yields, respectively.

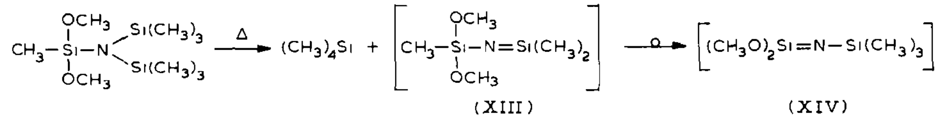


(XI)

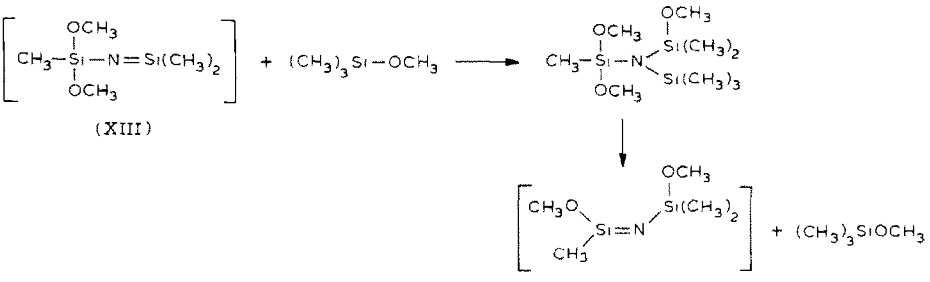


(XII)

A third group of products results from the reaction of the silaimine formed by loss of tetramethylsilane (4%) from I. This minor pathway is without precedent. Apparently it results in concurrent formation of *N*-dimethoxymethylsilyldimethylsilaimine (XIII). 1,3-Sigmatropic rearrangement of a methyl group from one silyl center of XIII to the other leads to *N*-trimethylsilyldimethoxysilaimine (XIV).

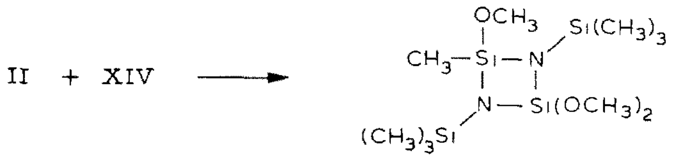


Reaction of trimethylmethoxysilane with XIII would lead to dimethoxymethylsilylmethoxydimethylsilyltrimethylsilylamine which could undergo loss of trimethylmethoxysilane in the opposite direction to yield *N*-methoxydimethylsilylmethoxymethylsilaimine (XV). These last three silaimines are formed in low yield, but nevertheless contribute to the formation of a variety of minor cyclodisilazanes which have been isolated and whose structures have been determined.

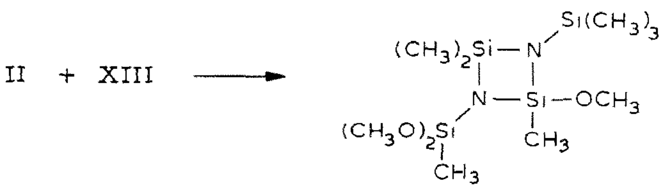

(XIII)

(XV)

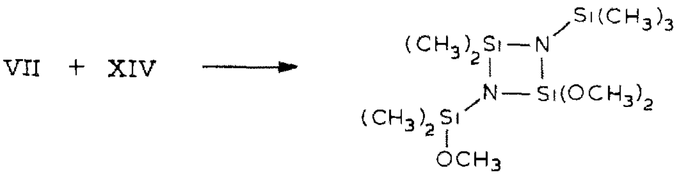
1,3-Bis(trimethylsilyl)-2,2,4-trimethoxy-4-methylcyclodisilazane (XVI) found in 1.5% yield probably results from the reaction of silaimines II and XIV.


(XVI)

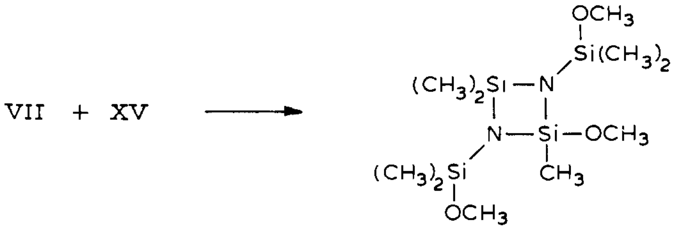
While 1-dimethoxymethylsilyl-3-trimethylsilyl-2-methoxy-2,4,4-trimethylcyclodisilazane (XVII) found in 2.4% results from reaction of II and XIII.


(XVII)

No product of reaction of II and XV was isolated. 1-Methoxydimethylsilyl-3-trimethylsilyl-2,2-dimethoxy-4,4-dimethylcyclodisilazane (XVIII, 1.4%) may result from reaction of VII and XIV.

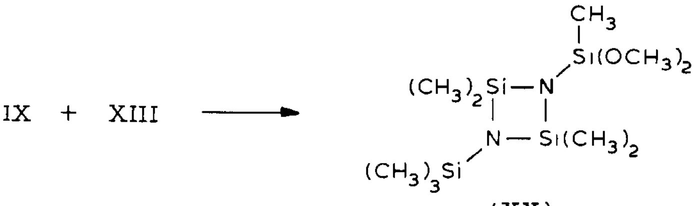

(XVIII)

1,3-Bis(methoxydimethylsilyl)-2-methoxy-2,4,4-trimethylcyclodisilazane (XIX, 0.3%) may arise from reaction of VII and XV.



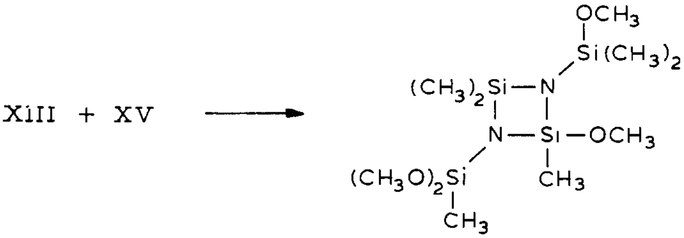
(XIX)

1-Dimethoxymethylsilyl-3-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane (XX) found in 1.5% yield may occur by reaction of IX and XIII.



(XX)

Finally, 1-dimethoxymethylsilyl-3-methoxydimethylsilyl-2-methoxy-2,4,4-trimethylcyclodisilazane (XXI, 1.2%) was found. It probably is formed by the reaction of XIII and XV.



(XXI)

A number of predicted products of self reaction and cross reaction of the silaimine intermediates XIII, XIV, and XV which are formed in very low yield were not detected.

Nevertheless, we have accounted for 96% of the material pyrolyzed. This is a remarkable analytical achievement. Further it should be noted that in control experiments we have shown that the products discussed are stable to the pyrolysis conditions. Once two silaimines react to form a cyclodisilazane they do not come apart again and equilibrate under the reaction conditions.

Finally, the pyrolysis of I provides products which can best be accounted for in terms of two 1,3-sigmatropic rearrangements interconverting one silaimine into another a previously unknown type of reaction.

Experimental

^1H NMR spectra were obtained on a Varian XL-100, IBM-Bruker WP-270-SY, or Bruker WM-500 spectrometer operating in the FT mode using a 5% solution in 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 [32,33]. ^{13}C NMR spectra were obtained on an IBM-Bruker WP-270-SY spectrometer 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 spectrometer 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. × 1/8 in. 2% OV-10 on 100/120 mesh Chromosorb W column was used in the gas chromatography inlet of the mass spectrometer. High resolution mass spectra were obtained on an A.E.I. MS-902 mass spectrometer at 70 eV. Exact masses were determined by peak matching against peaks of known mass of perfluoro kerosene. GLPC analysis were performed on a Hewlett-Packard F&M 700 using either a 4 ft. × 1/4 in 20% SE-30 on 60–80 mesh Chromosorb W column (A), a 15 ft. × 1/4 in 20% Carbowax on 60–80 mesh Chromosorb W column (B), or a 15 ft. × 1/4 in 20% β,β-ODPN on 60–80 mesh Chromosorb W column (C). 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 Systems Inc. Diethyl ether was distilled from sodium/benzophenone ketyl immediately prior to use.

Preparation of dimethoxymethylsilyl-bis(trimethylsilyl)amine (I) [39]

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 °C by liquid nitrogen and (10 g, 0.071 mol) of methyldimethoxychlorosilane in 30 ml of ether was added to the frozen solution. The reaction mixture was gradually warmed and then refluxed for 3 h. Lithium chloride was removed by filtration. The solvents were removed by evaporation under reduced pressure. Dimethoxymethylsilyl-bis(trimethylsilyl)amine was distilled from the residue bp. 44 °C/1 mmHg in 68% yield. It has the following spectral properties. ^1H NMR: δ 0.112 (s, 3H); 0.157 (s, 18H); 3.424 (s, 6H). ^{13}C NMR : δ 2.002 (1C), 4.012 (6C); 48.801 (2C). ^{29}Si NMR: δ −27.80 (1Si); 2.366 (2Si). MS; *m/e* (% rel. int.) 234 (100) $M^+ - 31$; 204 (5.7); 188 (6.8); 130 (27.3), 116 (7.1); 100 (7.8); 73 (8.1).

Flash vacuum pyrolysis of I

A 5 ml round bottom flask which contained (0.5 g, 1.88 mmol) compound I, was connected to a spiral pyrex tube (100 cm × 0.7 cm) which was placed inside an oven (450–475 °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 ($\sim 10^{-4}$ mmHg). The round bottom flask was heated to 60 °C to distill the sample of I through the pyrolysis tube.

Tetramethylsilane was formed in 4% yield.

Trimethylmethoxysilane was formed in 64% yield.

Dimethyldimethoxysilane was formed in 32% yield. Positive identification of each of the above was obtained by spectral comparison with authentic samples.

cis-1,3-Bis(trimethylsilyl)-2,4-dimethoxy-2,4-dimethylcyclodisilazane (III) was found in 1.88% yield. It was purified by preparative GLPC column C. It has the following spectral properties: ^{1}H NMR: δ 0.056 (s, 18H); 0.211 (s, 6H); 3.654 (s, 6H). IR: ν 1030 and 890 cm^{-1} [35]. MS: m/e (% rel. int.) 322 (3.9) $M^{+\cdot}$; 307 (100) $M^+ - 15$; 277 (47.4); 247 (11.2); 207 (13.8); 146 (13.8); 131 (19.7); 116 (19.1); 100 (4.6); 73 (12.5). Exact mass for $Si_4C_9H_{27}N_2O_2$ ($M^+ - 15$) 307.1152, calcd. 307. 1150.

trans-1,3-Bis(trimethylsilyl)-2,4-dimethoxy-2,4-dimethylcyclodisilazane (IV) was found in 2.82% yield. It was purified by preparative column C. It has the following spectral properties; ^{1}H NMR: δ 0.045 (s, 18H); 0.289 (s, 6H); 3.445 (s, 6H). IR: $\bar{\nu}$ 1025 and 880 cm^{-1}. MS: m/e (% rel. int.) 322 (2.0) $M^{+\cdot}$; 307 (100) $M^+ - 15$; 277 (47.9); 247 (12.9); 231 (4.2); 146 (11.6); 131 (20.4); 116 (19.1); 100 (5.0); 73 (2.6). Exact mass for $Si_4C_9H_{27}N_2O_2$ ($M^+ - 15$) 307.1152, calcd. 307.1150.

1,3-Bis(methoxydimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (V) was found in 13.8% yield. It was purified by preparative GLPC column B. It has the following spectral properties. ^{1}H NMR: δ 0.0372 (s, 12H); 0.3057 (s, 12H), 3.398 (s, 6H). ^{13}C NMR: δ −0.567 (4C); 4.858 (4C); 49.490 (2C). ^{29}Si NMR: δ −6.248 (2Si); 4.488 (2Si). IR: $\bar{\nu}$ 1090, 1020, 890 and 840 cm^{-1}. MS: m/e (% rel. int.) 322 (2.2) $M^{+\cdot}$; 307 (100) $M^+ - 15$; 277 (54.5); 247 (15.2); 131 (25.8); 116 (28.8); 100 (9.1); 73 (16.7). Exact mass for $Si_4C_9H_{27}N_2O_2$ ($M^+ - 15$) 307.1152, calcd. 307.1150.

1-Methoxydimethylsilyl-3-trimethylsilyl-2-methoxy-2,4,4-trimethylcyclodisilazane (VI) was found in 24% yield. It was purified by preparative GLPC column B. It has the following spectral properties: ^{1}H NMR: δ 0.034 (s, 9H); 0.067 (s, 6H); 0.253 (s, 3H); 0.279 (s, 3H); 0.301 (s, 3H); 3.393 (s, 3H); 3.473 (s, 3H). ^{13}C NMR: δ −0.830 (1C); −0.753 (1C); −0.251 (1C); 1.930 (3C); 3.824 (1C); 4.247 (1C); 49.208 (1C); 49.537 (1C). ^{29}Si: δ −27.045 (1Si); −6.434 (1Si); −3.238 (1Si); +1.651 (1Si). IR: $\bar{\nu}$ 1090, 1030, and 890 and 840 cm^{-1}. MS: m/e (% rel. int.) 322 (2.1) M^+; 307 (100) $M^+ - 15$; 277 (47.9); 247 (14.2); 231 (4.6); 146 (11.7); 131 (16.2); 116 (16.7); 100 (5.5); 73 (2.8). Exact mass for $Si_4C_9H_{27}N_2O_2$ ($M^+ - 15$) 307.1152, calcd. 307.1150.

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

1,3-Bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (X) [40] was found in 16.5% yield. It was purified by preparative GLPC on column A. It has the following spectral properties: ^{1}H NMR: δ 0.030 (s, 18H); 0.220 (s, 12H). ^{13}C NMR: δ 2.183 (4C); 5.145 (6C). ^{29}Si NMR: -4.125 (2Si); 3.7 (2Si). IR: $\bar{\nu}$ 1030 and 890 cm^{1} MS: *m/e* (% rel. int.) 290 (1.4) M^+ ; 275 (100) $M^+ - 15$; 187 (5.2); 130 (29); 100 (5.1); 73 (4.3).

1-Methoxydimethylsilyl-3-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane (XI) was found in 11.1% yield. It was purified by preparative GLPC column B. It has the following spectral properties. ^{1}H NMR: δ -0.009 (s, 9H); 0.022 (s, 6H); 0.252 (s, 12H); 3.385 (s, 3H). ^{13}C NMR: δ -0.595 (2C); 2.156 (3C); 5.012 (4C); 49.457 (1C). IR: $\bar{\nu}$ 1030 and 880 cm^{-1}, MS: *m/e* (% rel. int.) 306 (2.1) M^+ ; 291 (100) $M^+ - 15$; 275 (5.8) $M^+ - 31$; 261 (60.0); 245 (6.0); 138 (9.3); 123 (21.9); 100 (4.0); 73 (2.4). Exact mass for $Si_4C_9H_{27}N_2O$ ($M^+ - 15$) 291.1192, calcd. 291.1201.

1,3-Bis(trimethylsilyl)-2-methoxy-2,4,4-trimethylcyclodisilazane (XII) was found in 16.7% yield. It was purified by preparative GLPC column B. It has the following spectral properties: ^{1}H NMR: δ 0.023 (s, 18H); 0.206 (s, 3H); 0.238 (s, 3H); 0.260 (s, 3H); 3.462 (s, 3H). ^{13}C NMR: δ 0.008 (1C); 2.050 (6C); 3.948 (1C); 4.398 (1C); 48.222 (1C); IR: $\bar{\nu}$ 1080, 1030 and 890 cm^{-1}. MS: *m/e* (% rel. int.) 306 (2.1) M^+ ; 291 (100) $M^+ - 15$; 275 (5.7) $M^+ - 31$; 261 (64.0); 245 (6.4); 138 (11.0); 123 (25.8); 100 (6.4); 73 (4.4). Exact mass for $Si_4C_9H_{27}N_2O$ ($M^+ - 15$) 291.1192, calcd. 291.1201.

1,3-Bis(trimethylsilyl)-2,2,4-trimethoxy-4-methylcyclodisilazane (XVI) was formed in 1.5% yield. It was purified by preparative GLPC column B. It has the following spectral properties. ^{1}H NMR: δ 0.071 (s, 18H); 0.292 (s, 3H) 3.470 (s, 3H); 3.508 (s, 3H); 3.601 (s, 3H). MS: *m/e* (% rel. int.) 338 (2.0) M^+ ; 323 (100) $M^+ - 15$; 307 (3.3) $M^+ - 31$; 293 (46.3); 263 (14.5); 247 (8.0); 233 (10.3); 154 (10.5); 139 (20.3); 124 (17.7); 116 (15.2); 73 (3.8). Exact mass for $Si_4C_9H_{27}N_2O_3$ ($M^+ - 15$) 323.1090, calcd. 323.1099.

1-Dimethoxymethylsilyl-3-trimethylsilyl-2-methoxy-2,4,4-trimethylcyclodisilazane (XVII) was formed in 2.4% yield. It was purified by preparative GLPC column B. It has the following spectral properties: ^{1}H NMR: δ 0.029 (s, 9H); 0.055 (s, 3H); 0.260 (s, 3H); 0.294 (s, 3H); 0.305 (s, 3H); 3.455 (s, 3H); 3.457 (s, 3H), 3.495 (s, 3H). MS: *m/e* (% rel. int.) 338 (2.0) M^+ ; 323 (100) $M^+ - 15$; 307 (3.3) $M^+ - 31$; 293 (46.3); 263 (14.5); 247 (8.0); 233 (10.3); 154 (10.5); 139 (20.3); 124 (17.7); 116 (15.2); 73 (3.8). Exact mass for $Si_4C_9H_{27}N_2O_3$ ($M^+ - 15$) 323.1090, calcd. 323.1099.

1-Methoxydimethylsilyl-3-trimethylsilyl-2,2-dimethoxy-4,4-dimethylcyclodisilazane (XVIII) was formed in 1.4% yield. It was purified by preparative GLPC column B. It has the following spectral properties: ^{1}H NMR: δ 0.059 (s, 9H); 0.087 (s, 6H); 0.325 (s, 6H); 3.434 (s, 3H); 3.465 (s, 6H). MS: *m/e* (% rel. int.) 338 (2.0) M^+ ; 323 (100) $M^+ - 15$; 307 (3.3) $M^+ - 31$; 293 (46.3); 263 (14.5); 247 (8.0); 233 (10.3); 154 (10.5); 139 (20.3); 124 (17.7); 116 (15.2); 73 (3.8). Exact mass for $Si_4C_9H_{27}N_2O_3$ ($M^+ - 15$) 323.1090, calcd. 323.1099.

1,3-Bis(methoxydimethylsiyl)-2-methoxy-2,4,4-trimethylcyclosilazane (XIX) was formed in 0.3% yield. It has the following spectral properties: ^{1}H NMR: δ 0.075 (s, 12H); 0.292 (s, 3H); 0.326 (s, 3H); 0.332 (s, 3H); 3.414 (s, 6H); 3.508 (s, 3H). MS: *m/e* (% rel. int.) 338 (2.0) M^+ ; 323 (100) $M^+ - 15$; 307 (3.3) $M^+ - 31$; 293 (46.3); 263 (14.5); 247 (8.0); 233 (10.3); 154 (10.5); 139 (20.3); 124 (17.7); 116 (15.2); 73 (3.8). Exact mass for $Si_4C_9H_{27}N_2O_3$ ($M^+ - 15$) 323.1090, calcd. 323.1099.

1-Dimethoxymethylsilyl-3-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane (XX) was formed in 1.5% yield. It was purified by preparative GLPC column B. It has the following spectral properties: ^{1}H NMR: δ −0.016 (s, 9H); −0.012 (s, 3H); 0.257 (s, 12H); 3.426 (s, 6H). IR: $\bar{\nu}$ 1030 and 890 cm^{-1}. MS: *m/e* (% rel. int.) 322 (3.2) $M^{+\cdot}$; 307 (100) $M^+ - 15$; 291 (2.3) $M^+ - 31$; 277 (46.8); 247 (15.8); 146 (15.6); 131 (21.7); 116 (25.2); 100 (7.9); 73 (5.9). Exact mass for $Si_4C_9H_{27}N_2O_2$ ($M^+ - 15$) 307.1152, calcd. 307.1150.

1-Dimethoxymethylsilyl-3-methoxydimethylsilyl-2-methoxy-2,4,4-trimethylcyclodisilazane (XXI) was formed in 1.2% yield. It was purified by preparative GLPC column B. It has the following spectral properties: ^{1}H NMR: δ 0.068 (s, 3H); 0.075 (s, 6H); 0.304 (s, 3H); 0.334 (s, 3H); 0.343 (s, 3H); 3.414 (s, 3H); 3.462 (s, 3H); 3.465 (s, 3H); 3.519 (s, 3H). MS: *m/e* (% rel. int.) 354 (3.0) M^+; 339 (100) $M^+ - 15$; 325 (13.3); 309 (47.8); 293 (10.0); 279 (16.9); 233 (8.5); 219 (10.0); 162 (14.2); 147 (23.4); 132 (25.8); 116 (11.8); 102 (7.1); 73 (4.7). Exact mass for $Si_4C_9H_{27}N_2O_4$ ($M^+ - 15$) 339.1026, calcd. 339.1048.

Control experiments

Co-pyrolysis of 1,3-bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (X) and hexamethylcyclotrisiloxane

1,3-Bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (X) (0.2 g, 0.68 mmol) and hexamethylcyclotrisiloxane (1.5 g, 6.8 mmol) were placed in a 5 ml round bottom flask. The flask was connected to a quartz pyrolysis tube as above which was placed inside a tube oven (450–475 °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^{-4} mmHg). The round bottom flask was heated to 60°C to distill the mixture through the pyrolysis tube. GLPC analysis of the product mixture indicated only recovered 1,3-bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane in greater than 95% yield. Hexamethylcyclotrisiloxane has previously been shown to be an efficient trapping reagent for silaimine intermediates [41,42].

Co-pyrolysis of a mixture of substituted cyclodisilazanes from the pyrolysis of I and hexamethylcyclotrisiloxane

A mixture of 0.4 g of 1,3-bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (X, 19.8%), 1,3-bis(trimethylsilyl)-2-methoxy-2,4,4-trimethylcyclodisilazane (XII, 20%), 1,3-bis(methoxydimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (V, 16.5%), 1-methoxydimethylsilyl-3-trimethylsilyl-2-methoxy-2,4,4-trimethylcyclodisilazane (VI, 28.9%), and 1-methoxydimethylsilyl-3-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane (XI, 13.0%) was combined with 2.8 g of hexamethylcyclotrisiloxane in a 5 ml round bottom flask. The flask was connected to a quartz pyrolysis tube as above. The mixture was distilled through the pyrolysis tube in a manner previous described. The ratio of the isomer present before and after the pyrolysis were the same.

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