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FINAL REPORT

from

UNIVERSITY OF SOUTHERN CALIFORNIA

UNIVERSITY PARK

LOS ANGELES, CALIFORNIA 90089-1062

Project Coordinator: William P. Weber

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August 1, 1984

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Instrumentation Purchased

→ The instrument purchased was a routine Fourier transform nuclear magnetic resonance spectrometer for use by graduate students, research associates and faculty at the University of Southern California. The instrument is a JEOL (USA) Inc. Model JNM/FX-90Q equipped with a dual $^1\text{H}/^{13}\text{C}$ omni probe and includes a micro insert. In September 1983, the instrument was received and was fully installed and meeting specifications by October 1983. Since installation the equipment has operated continuously and has had virtually no downtime.

Mr. Allan Kershaw has been the instrument technician who has been in charge of the oversight of the operation of this instrument. He has aided in the training of the more than 40 graduate students, research associates and faculty who are qualified as operators of this equipment. Usage of the instrument has developed to more than 100 hours per week and is now on a scheduled usage basis.

Research Progress: Current DOD Support

Two research groups were listed as currently receiving DOD support when the proposal was submitted. Both of these continue to receive DOD support. Progress on these research projects is described in the reports from the individual investigators. In addition recent manuscripts arising from this research is appended.

William P. Weber
Air Force Office of Scientific Research
Grant No. AFOSR 82-0333
Support for 9/30/83 to 9/30/84
\$106,356
Title: Chemistry of New Silicon Contain Polymers and
Triple Bonded Silicone Intermediates
Contract Monitor: Dr. Anthony Matuszko

George A. Olah
U.S. Army Research Office
Grant No. DAAG29-82-K-0009
Support for 11/15/83 thru 11/14/84
\$71,350.00
Title: Nitration and Preparation of Nitrocompounds
Contract: Monitor: Dr. G. Ronald Husk

Research Progress: Non DOD Contractors

The instrumentation has aided the research programs of the following non DOD contractors.

Robert Bau
"Preparation and Structure Determination of Metal-Hydride,
Metal-Phenyl and Metal-Nucleotide Complexes"

Colin G. Francis
"The Application of Metal Vapor Synthesis to the Preparation
of Electroconducting Polymers"

Christopher A. Reed
"Synthetic Coordination Chemistry"

Lawrence A. Singer
"Photochemical and Photophysical Studies"

Geoffrey B. Wong
"Applications of NMR Spectroscopy to Coordination Complexes"

Recent manuscripts arising from these research programs is included in the Appendix.

APPENDIX A

Preprints of manuscripts resulting from research supported by the grant:

Appendix I - "Flash Vacuum Pyrolysis of Dimethoxymethylsilyl-bis-trimethylsilylamine 1,3-Sigmatropic Rearrangements of Silamine Intermediates"

by Samih Amine Kazoura and William P. Weber

Appendix II - "Co-Pyrolysis of Dimethoxymethylsilyl-Bis(Trimethylsilyl)-amine and Hexamethylcyclotrisiloxane-1,3-Sigmatropic Rearrangements of Silamine Intermediates" by Samih Amine Kazoura and William P. Weber

Appendix III - Preparation of 1-Silyl and 1,3-Bis(Silyl)Adamantanes"

by Yi-Ming Pai, Erich Wanek and William P. Weber

Appendix IV - "Thermolysis of 6-Oxa-3-Sila Bicyclo [3,1,0] Hexanes: A New Convenient Route to Silicon-Oxygen π -Bonded Species" by Georges Manuel and Guy Bertrand

Appendix V - "Photolysis of Dodecamethylcyclohexasilane - Formation of Both Methylsilene and Dimethylsilylene" by I.S. Alnaimi and W.P. Weber

Appendix VI - "Dimethylsilylene: Its Optical Absorption Spectrum and Reaction Kinetics" by I.S. Alnaimi, W.P. Weber, A.S. Nazran, J.A. Kawari and D. Griller

Appendix VII - "Adamantyldimethylsilyl Ethers. Preparation and Properties" by Erich Wanek, Yi-Ming Pai and William P. Weber

Appendix VIII - "Silicon-29 NMR Studies of Polymethylhydrosiloxanes" by Yi-Ming Pai, William P. Weber and Kenneth L. Servis

APPENDIX I

FLASH VACUUM PYROLYSIS OF DIMETHOXYMETHYLSILYL-BIS-TRIMETHYLSILYLAMINE
1,3-SIGMATROPIC REARRANGEMENTS OF SILAIMINE INTERMEDIATES

by

Samih Amine Kazoura and William P. Weber*

Department of Chemistry

University of Southern California

Los Angeles, California 90089-1062

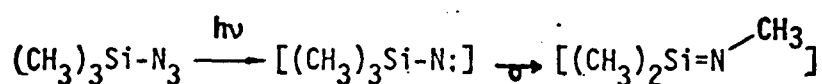
ABSTRACT

Pyrolysis of dimethoxymethylsilyl-bis-trimethylsilylamine has been carried out at low pressure. 1,2-Elimination of trimethylmethoxysilane gives N-trimethylsilyl methoxymethylsilamine (II). 1,3-Sigmatropic rearrangements of II gives N-methoxydimethylsilyl dimethylsilamine (III). Addition of trimethylmethoxysilane to III may give trimethylsilyl-bis-(methoxydimethylsilyl) amine which loses dimethyldimethoxysilane to give trimethylsilyl dimethylsilamine (IV). Head-to-tail dimerization as well as [2+2] cross cycloaddition reactions of these silamine intermediates II, III and IV lead to formation of substituted cyclodisilazanes as the major product.

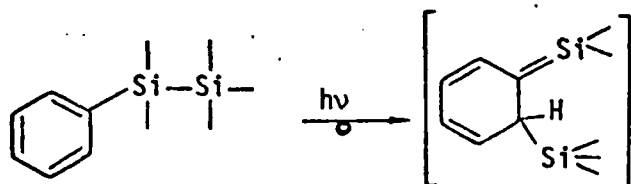
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There has been significant current interest in elucidating the chemical pathways followed by reactive doubly bonded intermediates in organosilicon chemistry.^{1,2} Rearrangement reactions provide not only methods to generate certain of these species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

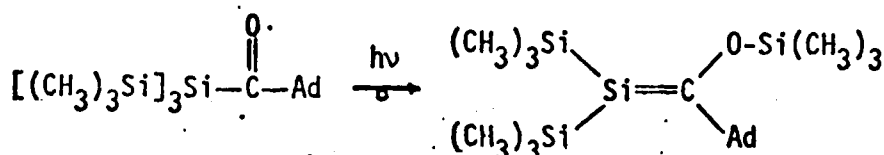
Several types of rearrangement reactions have proved useful for the generation of reactive silicon doubly bonded species. Both silenes^{3,4} and silanimines have been produced by 1,2-rearrangement reactions. Thus photolysis or pyrolysis of silyl azides initially results in loss of nitrogen to form a silyl nitrene which rearranges by a 1,2-migration of a group from silicon to nitrogen to yield a silimine.⁵⁻⁸



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.



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



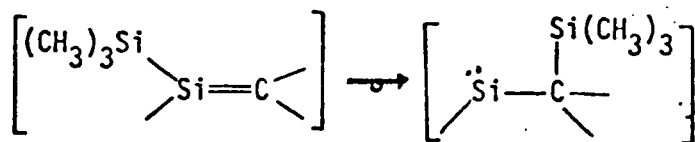
Reactive silenes result from Claisen rearrangement of dimethylphenoxyvinylsilanes.²¹



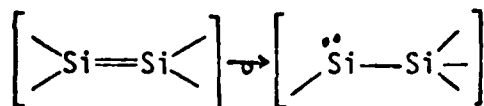
Silenes have also been generated by 1,5-sigmatropic rearrangements of dieny substituted disilanes.²²⁻²⁴



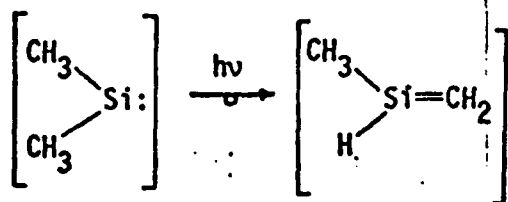
Most of the examples of interconversion of unsaturated silicon intermediates one into another by rearrangement reactions involve the transformation of silenes or disilenes to silylenes by 1,2-rearrangements. For example, 1,2-rearrangements convert silyl substituted silenes into silylenes.^{25,26}



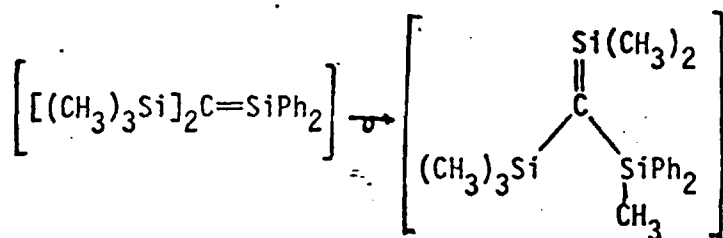
The interconversion of disilenes into silyl substituted silylenes has likewise been observed.²⁷⁻³⁰



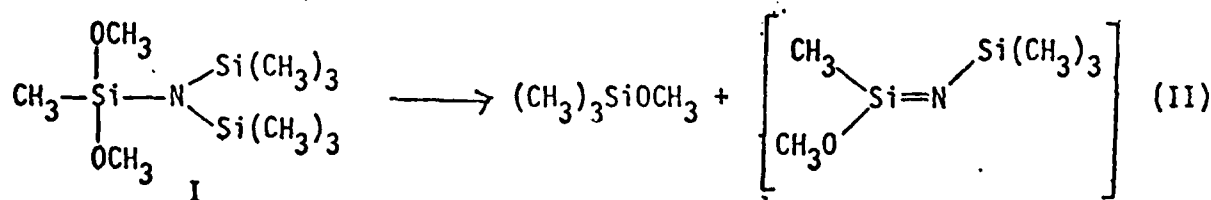
The reverse reaction, namely the transformation of dimethylsilylene into methylsilene on ultraviolet irradiation in an argon matrix, as well as, in the gas phase at high temperature has been reported.³¹⁻³⁴



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



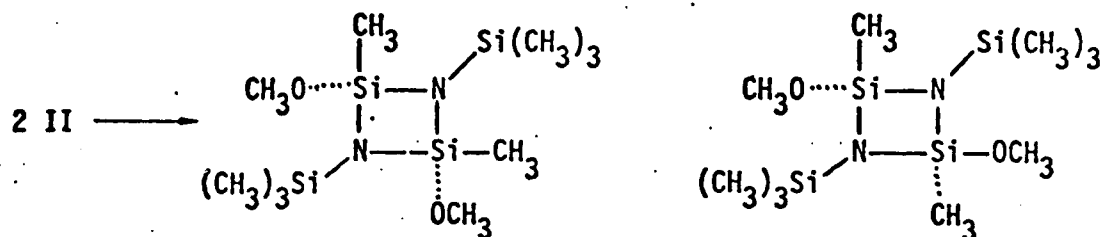
We undertook a study of the pyrolysis of dimethoxymethylsilyl-bis-(trimethylsilyl)amine (I) with the expectation that it would undergo 1,2-elimination of trimethylmethoxysilane to yield N-trimethylsilyl methylmethoxysilamine (II).



A number of silenes have been generated by such 1,2-elimination reactions of trimethylmethoxysilane.³⁶⁻³⁸

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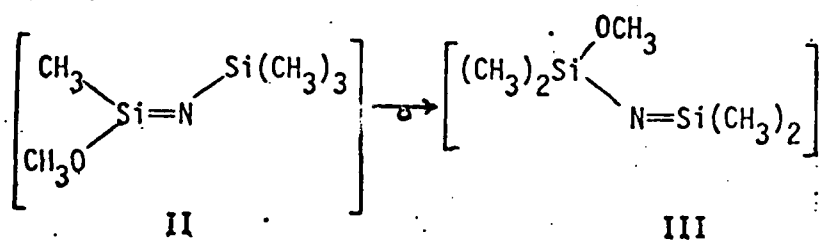
As expected, pyrolysis of I results in loss of trimethylmethoxysilane (64%) and formation of cis and trans-1,3-bis-(trimethylsilyl)-2,4-dimethoxy-2,4-dimethylcyclodisilazane in 1.9% and 2.8% yields respectively.



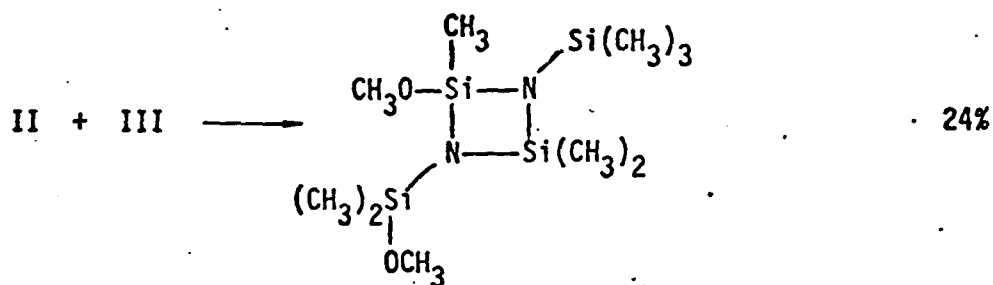
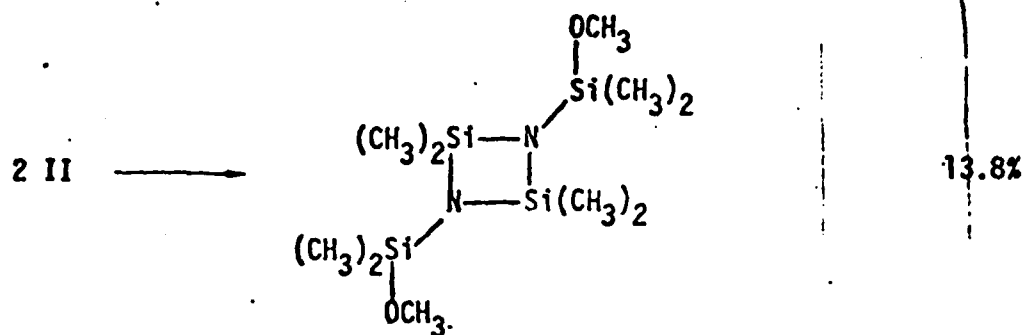
These cyclodisilazanes are expected products for the dimerization of the reactive intermediate N-trimethylsilyl methylmethoxysilamine (II).

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 and 1-methoxydimethylsilyl-3-trimethylsilyl-2-methoxy-2,4,4-trimethylcyclodisilazane found in 14% and 24% yield respectively.

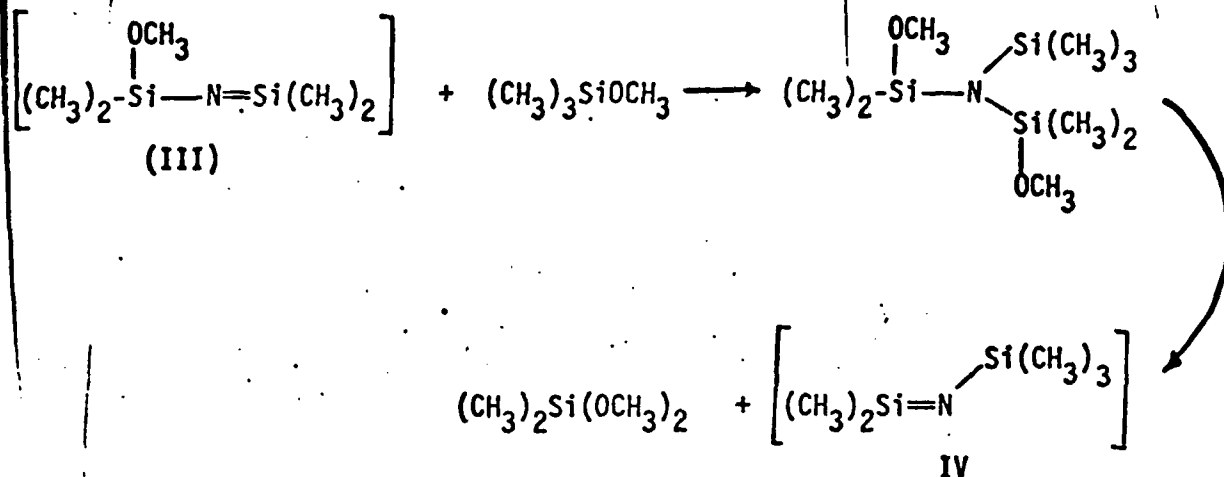
The former probably results from the head-to-tail dimerization of N-methoxydimethylsilyl dimethylsilamine (III). This reactive species may be formed from II by a 1,3-rearrangement of a methyl group from one silyl center to the other.



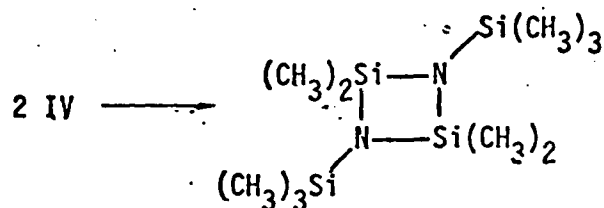
The latter disilazane results from head-to-tail reaction of reactive silamines II and III.



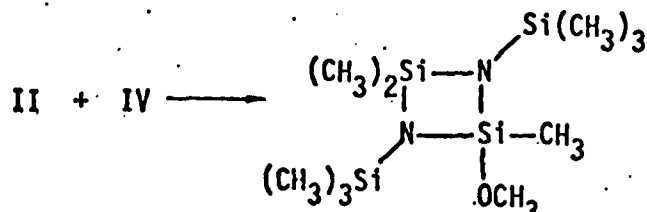
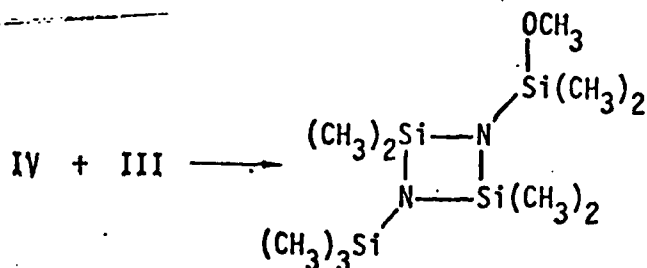
A second group of unexpected products results from the reactions of the silaimine found by loss of dimethyldimethoxysilane (32%) from I. The loss of dimethyldimethoxysilane may result from the following sequence of reactions. Reaction of the rearranged silaimine (III) with trimethylmethoxysilane would be expected to yield trimethylsilyl-bis(methoxydimethylsilyl)-amine 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-trimethylsilyl dimethylsilaimine (IV).³⁶⁻³⁸ The alternative possibility, the direct loss of a dimethoxymethylsilyl group and a methyl group from an adjacent silyl center is without precedent.



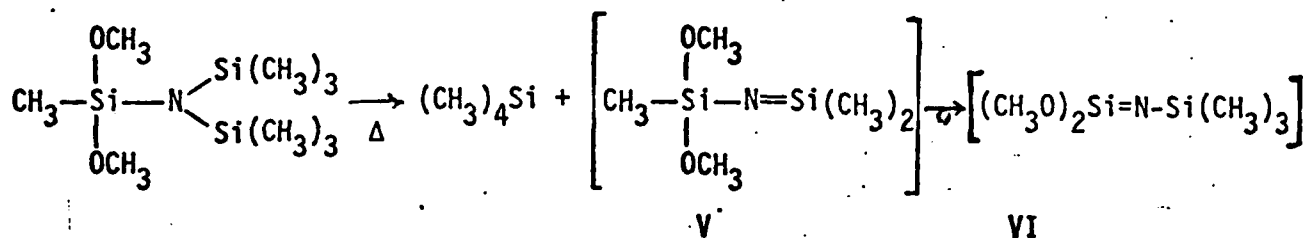
1,3-bis(Trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane the expected dimer of the reactive silaimine intermediate IV was found in 16.5% yield.



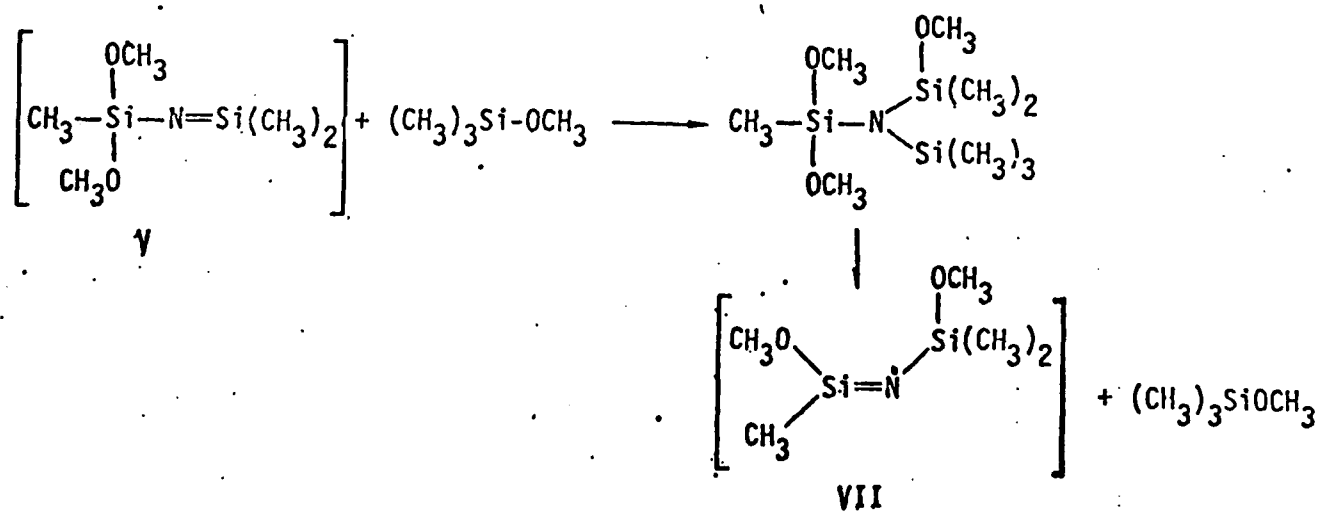
1-Methoxydimethylsilyl-3-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane and 1,3-bis(trimethylsilyl)-2-methoxy-2,4,4-trimethylcyclodisilazane, products of cross reaction of silaimine IV with silaimines III and II are found in 11.1% and 16.7% yields respectively.



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-dimethoxymethylsilyl dimethylsilaimine (V). 1,3-Sigmatropic rearrangement of a methyl group from one silyl center of V to the other leads to N-trimethylsilyl dimethoxysilaimine (VI).

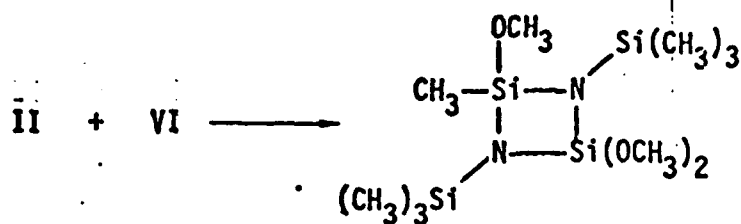


Reaction of trimethylmethoxysilane with V would lead to dimethoxymethylsilyl-methoxydimethylsilyl-trimethylsilylamine which could undergo loss of trimethylmethoxysilane in the opposite direction to yield N-methoxydimethylsilyl methoxymethylsilaimine (VII). These last three silaimines are formed in low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

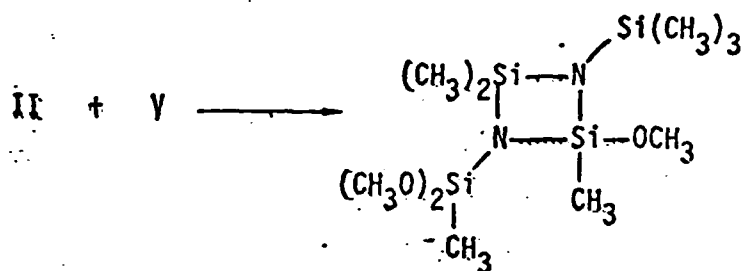


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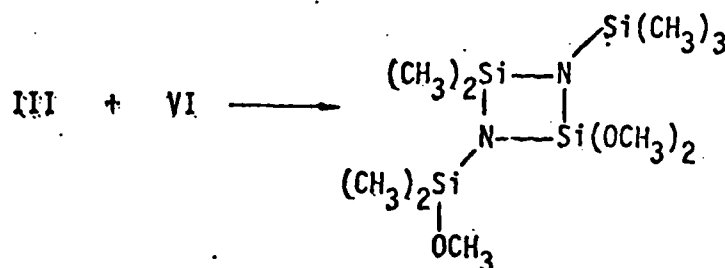
1,3-bis(trimethylsilyl)-2,4,4-trimethoxy-2-methylcyclodisilazane found in 1.5% yield probably results from the reaction of silaimines II and IV.



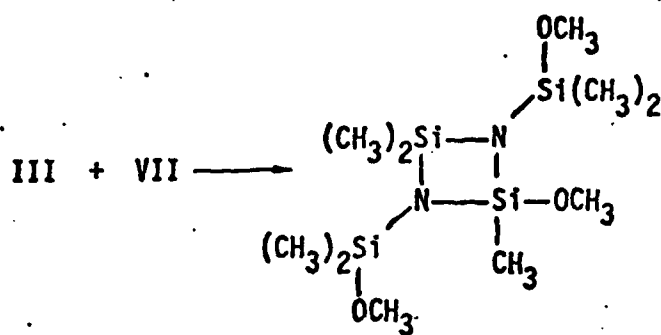
While 1-dimethoxymethylsilyl-3-trimethylsilyl-2-methoxy-2,4,4-trimethylcyclodisilazane found in 2.4% results from reaction of II and V.



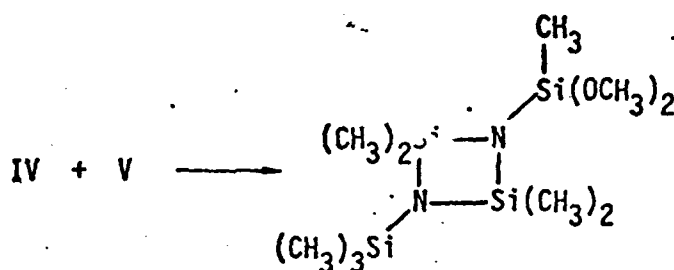
No product of reaction of II and VII was isolated. 1-Methoxydimethylsilyl-3-trimethylsilyl-2,2-dimethoxy-4,4-dimethylcyclodisilazane 1.4% may result from reaction of III and VI.



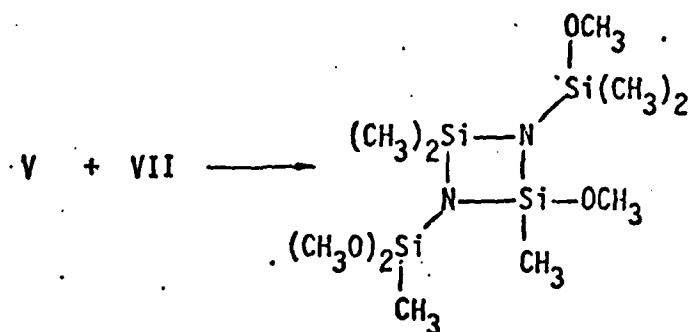
1,3-bis(Methoxydimethylsilyl)-2-methoxy-2,4,4-trimethylcyclodisilazane 0.3% may arise from reaction of III and VII.



1-Dimethoxymethylsilyl-3-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane found in 1.5% yield may occur by reaction of IV and V.



Finally, 1-dimethoxymethylsilyl-3-methoxydimethylsilyl-2-methoxy-2,4,4-trimethylcyclodisilazane 1.2% yield was found. It probably is formed by the reaction of V and VII.



(XX)

A number of predicted products of self reaction and cross reaction of the silaimine intermediates V, VI, VII which are found in very low yield were not detected.

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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 silamine 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 silamine into another a previously unknown type of reaction.

Experimental

^1H NMR spectra were obtained on a Varian XL-100, IBM-Brucker WP-270-XY, or Brucker WM-500 spectrometer operating in the 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.^{32,33} ^{13}C NMR spectra were obtained on an IBM-Brucker 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 Brucker 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 x 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

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on an A.E.I. MS-902 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 x 1/4 in 20% SE-30 on 60-80 mesh Chromosorb W column (A), a 15 ft x 1/4 in 20% Carbowax on 60-80 mesh Chromosorb W column (B), or a 15 ft x 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 System Inc. Diethylether 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, .071 mol) of hexamethyldisilazane and a Teflon covered magnetic stirring bar. The flask was flushed with purified nitrogen. n-Butyl lithium (1.5 M in hexane) (57 mL, .071 mol) was added to the flask over a period of 1 hr. During addition, the reaction mixture was cooled in an ice-water bath. The solution was refluxed for 3 hr and then was stirred at 20°C overnight. The solution was then cooled to -196°C by liquid nitrogen and (10 g, .071 mol) of methyl dimethoxychlorosilane in 30 mls of ether was added to the frozen solution. The reaction mixture was gradually warmed and then refluxed for 3 hr. LiCl 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 mm 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 (3C). ^{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 x 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 ($\sim 10^{-4}$ mm Hg). 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

was found in 1.88% yield. It was purified by preparative GLPC column C. It has the following spectral properties: ^1H NMR: δ = 0.056 (s, 18H); 0.211 (s, 6H); 3.654 (s, 6H). IR: $\bar{\nu}$ = 1030 and 890 cm^{-1} . ^{35}S MS: m/e (% rel. int.) 322 (3.9) M^+ ; 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 $\text{Si}_4\text{C}_9\text{H}_{27}\text{N}_2\text{O}_2$ (M^+ -15) 307.1152, Calcd. 307.1150.

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trans-1,3-bis(Trimethylsilyl)-2,4-dimethoxy-2,4-dimethylcyclodisilazane

was found in 2.82% yield. It was purified by preparative column C. It has the following spectral properties; ^1H 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^+ ; 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 $\text{Si}_4\text{C}_9\text{H}_{27}\text{N}_2\text{O}_2$ (M^+-15) 307.1152, calcd. 307.1150.

1,3-bis(Trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane⁴⁰ was found

in 16.5% yield. It was purified by preparative GLPC on column A. It has the following spectral properties: ^1H 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).

1,3-bis(Trimethylsilyl)-2-methoxy-2,4,4-trimethylcyclodisilazane was

found in 16.7% yield. It was purified by preparative GLPC column B. It has the following spectral properties: ^1H 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); 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 $\text{Si}_4\text{C}_9\text{H}_{27}\text{N}_2\text{O}$ (M^+-15) 291.1192, calcd. 291.1201.

1,3-bis(Trimethylsilyl)-2,2,4-trimethoxy-4-methylcyclodisilazane was

formed in 1.5% yield. It was purified by preparative GLPC column B. It has the following spectral properties. ^1H 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.

1,3-bis(Methoxydimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane was

found in 13.8% yield. It was purified by preparative GLPC column B. It has the following spectral properties. 1H 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^+ ; 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, 307.1150.

1-Methoxydimethylsilyl-3-trimethylsilyl-2-methoxy-2,4,4-trimethylcyclo-

disilazane was found in 24% yield. It was purified by preparative GLPC column B. It has the following spectral properties: 1H 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.

1-Methoxydimethylsilyl-3-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane

was found in 11.1% yield. It was purified by preparative GLPC column B.

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It has the following spectral properties. ^1H 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 $\text{Si}_4\text{C}_9\text{H}_{27}\text{N}_2\text{O}$ (M^+-15) 291.1192, calcd. 291.1201.

1-Dimethoxymethylsilyl-3-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane

was formed in 1.5% yield. It was purified by preparative GLPC column B.

It has the following spectral properties: ^1H 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^+ ; 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 $\text{Si}_4\text{C}_9\text{H}_{27}\text{N}_2\text{O}_2$ (M^+-15) 307.1152, calcd. 307.1150.

1-Dimethoxymethylsilyl-3-trimethylsilyl-2-methoxy-2,4,4-trimethylcyclo-

disilazane was formed in 2.4% yield. It was purified by preparative GLPC column B. It has the following spectral properties: ^1H 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 $\text{Si}_4\text{C}_9\text{H}_{27}\text{N}_2\text{O}_3$ (M^+-15) 323.1090, calcd. 323.1099.

1-Methoxydimethylsilyl-3-trimethylsilyl-2,2-dimethoxy-4,4-dimethylcyclo-

disilazane was formed in 1.4% yield. It was purified by preparative

GLPC column B. It has the following spectral properties: ^1H 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 $\text{Si}_4\text{C}_9\text{H}_{27}\text{N}_2\text{O}_3$ (M^+-15) 323.1090, calcd. 323.1099.

1,3-bis-(Methoxydimethylsilyl)-2-methoxy-2,4,4-trimethylcyclasilazane

was formed in 0.3% yield. It has the following spectral properties: ^1H 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 $\text{Si}_4\text{C}_9\text{H}_{27}\text{N}_2\text{O}_3$ (M^+-15) 323.1090, calcd. 323.1099.

1-Dimethoxymethylsilyl-3-methoxydimethylsilyl-2-methoxy-2,4,4-trimethyl-cyclodisilazane was formed in 1.2% yield. It was purified by preparative

GLPC column B. It has the following spectral properties: ^1H 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 $\text{Si}_4\text{C}_9\text{H}_{27}\text{N}_2\text{O}_4$ (M^+-15) 339.1026, calcd. 339.1048.

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Control Experiments:Co-pyrolysis of 1,3-bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane and hexamethylcyclotrisiloxane.

1,3-bis(Trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (0.2g, 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} mm Hg). 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 grams of 1,3-bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (19.8%), 1,3-bis(trimethylsilyl)-2-methoxy-2,4,4-trimethylcyclodisilazane (20%), 1,3-bis(methoxydimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (16.5%), 1-methoxydimethylsilyl-3-trimethylsilyl-2-methoxy-2,4,4-trimethylcyclodisilazane (28.9%), and 1-methoxydimethylsilyl-3-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane (13.0%) was combined with 2.8 grams 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 isomers present before and after the pyrolysis were the same.

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APPENDIX II

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

by

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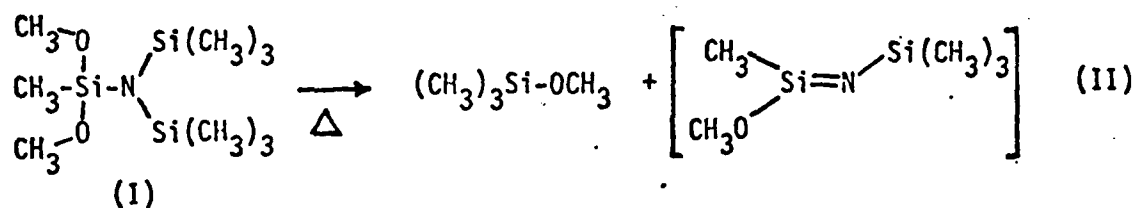
Los Angeles, California 90089-1062

ABSTRACT

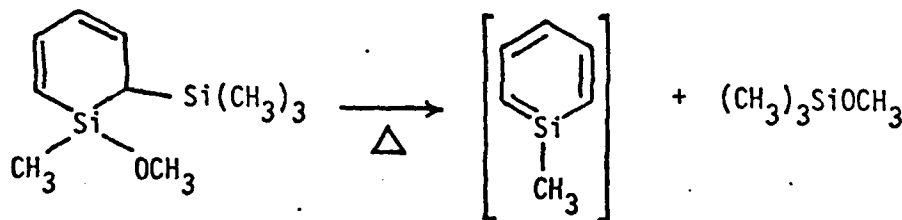
Co-pyrolysis of dimethoxymethylsilyl-bis(trimethylsilyl)amine (I) with hexamethylcyclotrisiloxane (D_3) at low pressure has been carried out. 1,2-Elimination of trimethylmethoxysilane from I gives N-trimethylsilyl-methoxymethylsilamine (II) which reacts with D_3 to give 8-methoxy-2,2,4,4,6,6,8-heptamethyl-7-trimethylsilyl-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacyclooctane (40.5%) (III). 1,3-Sigmatropic rearrangements 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-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.

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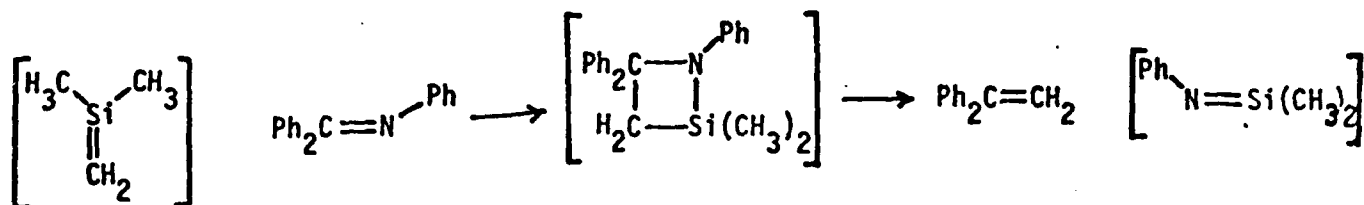
There has been considerable interest in the generation and chemical reactivity of silicon doubly bonded intermediates.^{1,2} We undertook a study of the flash vacuum pyrolysis of dimethoxymethylsilyl-bis(trimethylsilyl)amine (I) in the hope that it would undergo 1,2-elimination of a molecule of trimethylmethoxysilane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



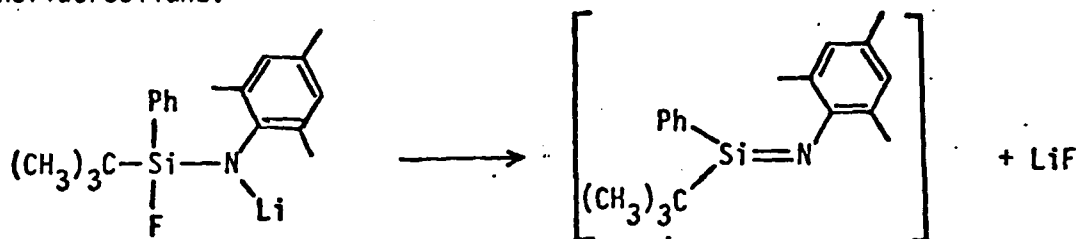
This approach has been successfully used to generate a number of silicon-carbon doubly bonded intermediates.³⁻⁵



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 proposed to result from [2+2] cycloaddition reactions of silenes with imines to yield unstable N-sila-azetidines which decompose to yield an alkene and a silaimine.¹⁰

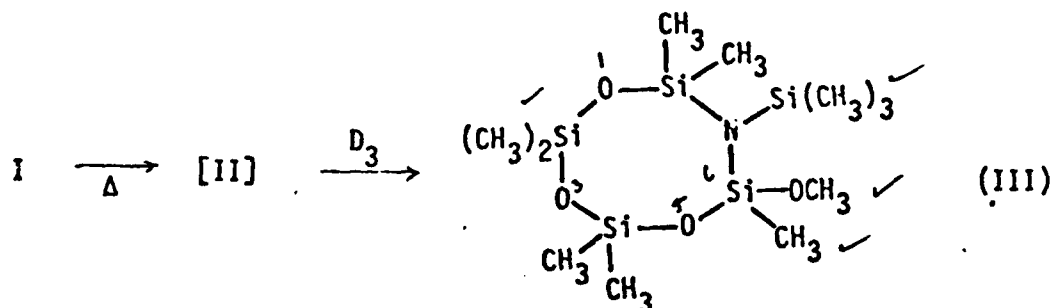


Silaimine intermediates are formed by loss of lithium fluoride from N-lithio aminofluorosilane.¹¹⁻¹³



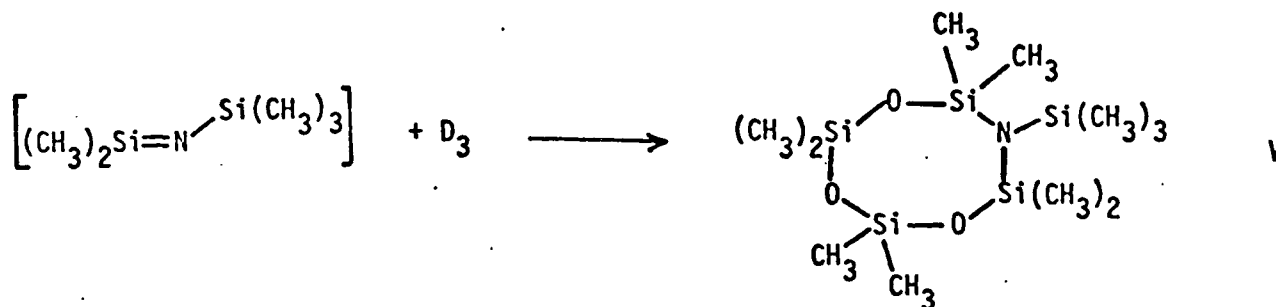
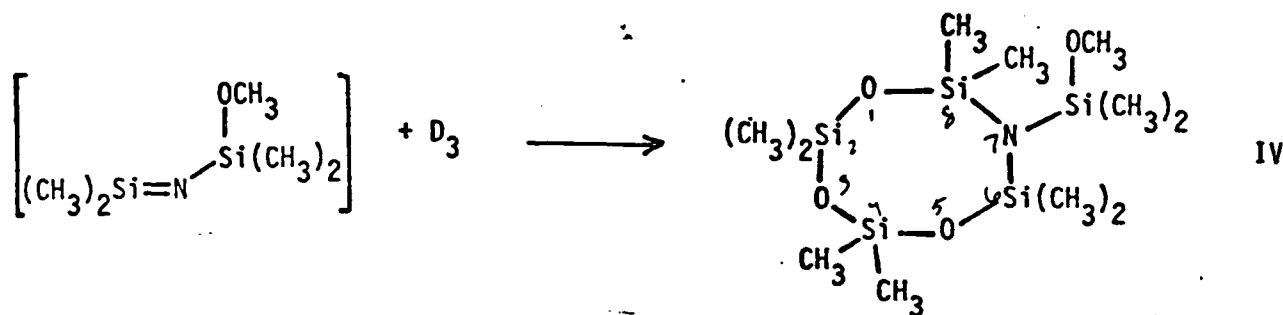
Finally, thermal decomposition of 3,5,5-tris-trimethylsilyl-4,4,-dimethyl-4-sila-1,2,3-triazoline yields a reactive silaimine.¹⁴

In fact, flash vacuum pyrolysis of I in the presence of hexamethylcyclotrisiloxane (D_3) led to 8-methoxy-2,2,4,4,6,6,8-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 efficiently trap silicon-carbon,^{15,16} silicon-oxygen,^{16,17} silicon-sulfur,^{18,19} and even silicon-nitrogen²⁰ doubly bonded intermediates.

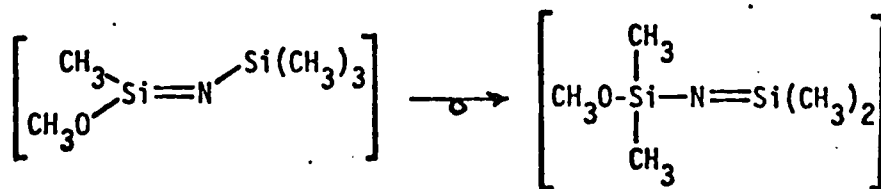


Perhaps of greater significance, in addition to the expected product (III),

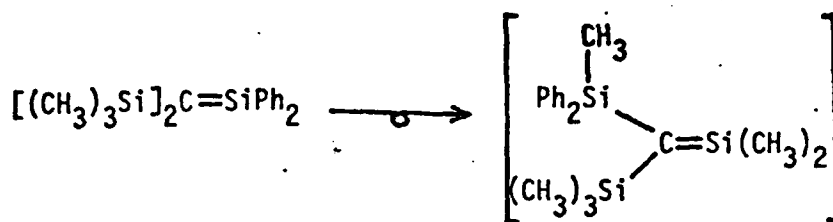
2,2,4,4,6,6,8,8-octamethyl-7-methoxydimethylsilyl-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacyclooctane (IV) (19% yield), 2,2,4,4,6,6,8,8-octamethyl-7-trimethylsilyl-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacyclooctane (V) (3.3% yield) and dimethyldimethoxysilane were also isolated. Product IV may result from the reaction of N-methoxydimethylsilyldimethylsilamine with D_3 , while V may arise by reaction of N-trimethylsilyldimethylsilamine with D_3 .



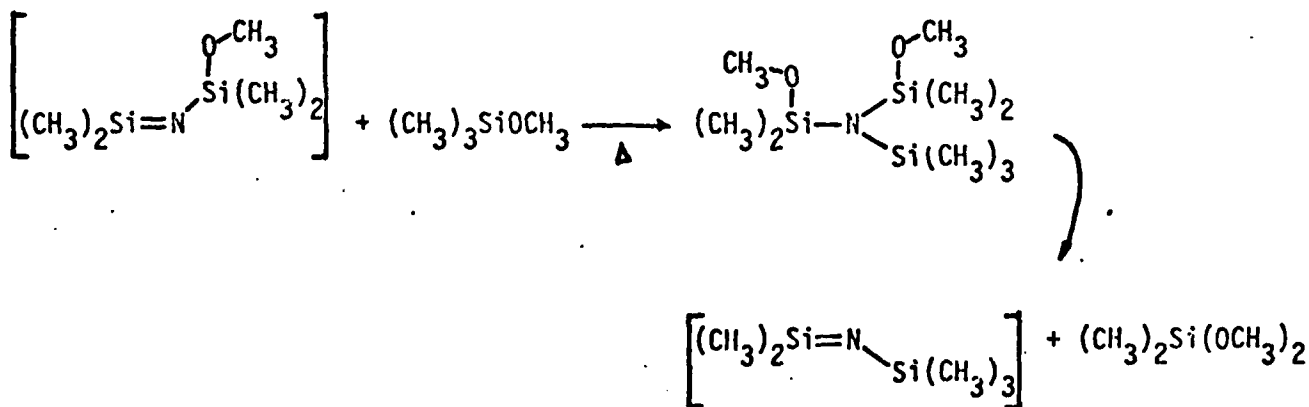
N-Methoxydimethylsilyldimethylsilamine may result from a 1,3-sigmatropic rearrangement of a methyl group from one silicon to another of the initially formed N-trimethylsilylmethylmethoxysilamine intermediate (II).



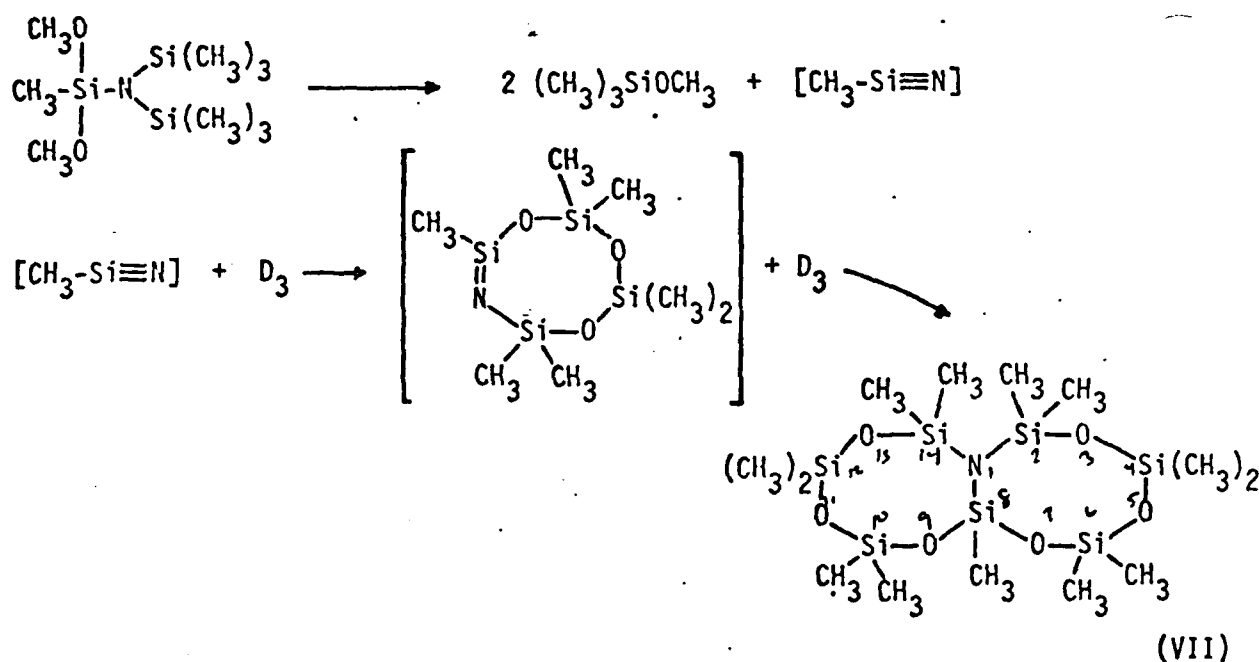
While interconversion of silicon-carbon doubly bonded intermediates via 1,3-sigmatropic rearrangements have been observed,²¹ no previous example of isomerizations of one silicon-nitrogen doubly bonded intermediate into another has been reported.



N-Trimethylsilyldimethylsilamine may arise by the following reaction sequence. Reaction of trimethylmethoxysilane with the rearranged silamine intermediate, N-methoxydimethylsilyldimethylsilamine yields trimethylsilyl-bis(dimethylmethoxysilyl)amine (VI). 1,2-Elimination of a dimethylmethoxysilyl group and a methoxy group as dimethyldimethoxysilane from VI would result in generation of N-trimethylsilyldimethylsilamine 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).

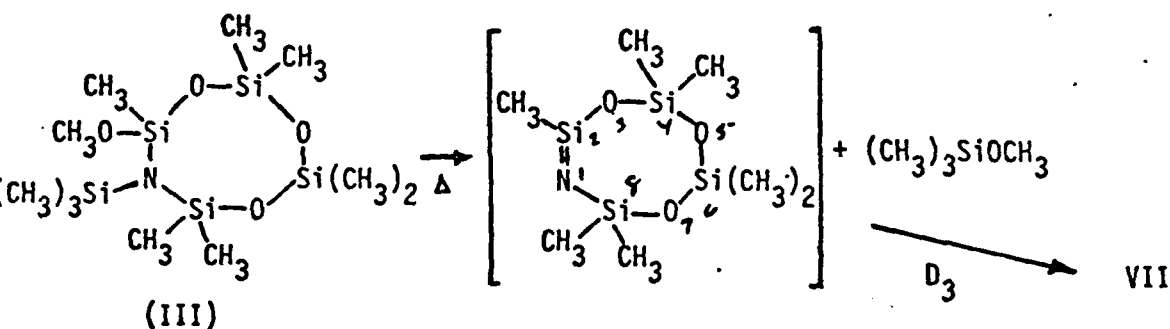


In addition small amounts of 1-aza-2,2,4,4,6,6,8,10,10,12,12,14,14-tridecamethyl-3,5,7,9,11,13-hexaoxa-2,4,6,8,10,12,14-heptasilabicyclo[6,6,0]-tetradecane (VII) were found (6%). This product might result from loss of two molecules of trimethylethoxysilane from I to form silaacetonitrile an intermediate which possesses a reactive silicon-nitrogen triply bond. Sequential reaction of this species with two molecules of 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-2,4,7,8-tetrasilacycloocta-1-ene, a reactive silamine, 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-Brucker WP-270-XY, or Brucker 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-CH₃ 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-Brucker 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 Brucker 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 x 1/8 in 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 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 x 1/4 in 20% SE-30 on 60-80 mesh Chromosorb W column (A), a 15 ft x 1/4 in 20% Carbowax on 60-80 mesh Chromosorb W column (B); a 15 ft x 1/4 in 20% β,β -ODPN on 60-80 mesh Chromosorb W column (C), a 6 ft x 1/8 in 5% OV-101 on 80-100 mesh Chromosorb W column (D), or a 16 ft x 1/8 in 5% OV-202 on Chromsorb 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. Diethylether was distilled from sodium/benzophenone ketyl immediately prior to use.

Preparation of dimethoxymethylsilyl-bis(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, .071 mol) of hexamethyldisilazane and a Teflon covered magnetic stirring bar. The flask was flushed with purified nitrogen. *n*-Butyl lithium (1.5 M in hexane) (57 mL, .071 mol) was added to the flask over a period of 1 hr. During addition, the reaction mixture was cooled in an ice-water bath. The solution was refluxed for 3 hr and then was stirred at 20°C overnight. The

solution was then cooled to -196°C by liquid nitrogen and (10 g, .071 mol) of methyldimethoxychlorosilane in 30 mls of ether was added to the frozen solution. The reaction mixture was gradually warmed and then refluxed for 3 hr. LiCl was removed by filtration. The solvents were removed by evaporation under reduced pressure. Dimethoxymethylsilyl-bis(trimethylsilyl)amine was distilled from the residue bp $44^{\circ}\text{C}/1\text{ mm}$ in 68% yield. It has the following spectral properties: ^1H : 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 (3C) ^{29}Si NMR: δ -27.80 (1Si); 2.366 (2Si). MS; m/e (% rel. int.) 250 (21) M^+-15 ; 234 (100) M^+-31 ; 204 (5.7); 188 (6.8); 130 (27.3), 116 (7.1); 100 (7.8); 73 (8.1).

8-Methoxy-2,2,4,4,6,6,8-heptamethyl-7-(trimethylsilyl)-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacyclooctane (III) was formed in 40.3% yield. It was purified by preparative GLPC column B. It has the following spectral properties: ^1H 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^+-15 ; 352 (2.3) M^+-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 $\text{Si}_5\text{C}_{10}\text{H}_{30}\text{NO}_4$ (M^+-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) was formed in 19% yield. It was purified by preparative GLPC column B. It has the following spectral properties: ^1H 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^+-15 ; 352 (2,3) M^+-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 $\text{Si}_5\text{C}_{10}\text{H}_{30}\text{NO}_4$ (M^+-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-tetrasilacyclooctane²² (V) was formed in 3.3% yield. It was purified by preparative GLPC column B. It has the following spectral properties: ^1H NMR: δ 0.077 (s, 12H); 0.156 (s, 9H); 0.202 (s, 12H). MS: m/e (% rel. int.) 352 (86.0) M^+-15 ; 264 (26.6); 248 (12); 190 (7.3); 73 (100).

Trimethylsilyl-bis-(dimethylmethoxysilyl)amine (VI) was isolated in about 1% yield. It was purified by preparative GLPC column D. It has the following spectral properties: ^1H 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).

Flash vacuum pyrolysis of I

A 5 ml round bottom flask which contained (0.5 g, 1.88 mol) of compound I and hexamethylcyclotrisiloxane (D_3) (1.26 g, 5.66 mmol) was connected to a spiral pyrex tube (200 cm x 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^{-4} mm Hg). 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, .26 mmol) and D_3 (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 .5 hr. VII was found in 65% yield based on recovered starting materials. It was purified by preparative GLPC on column E. It had the following spectral properties: ^1H NMR: δ 0.065 (s, 6H); 0.08 (s, 6H); 0.092 (s, 6H); 114 (s, 6H); 0.171 (s, 6H); 0.190 (s, 6H); 0.204 (s, 1H). IR: 1104, 1070, 1023 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 D_3 or V and D_3 as above resulted in only recovered starting materials IV or V respectively.

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APPENDIX III

PREPARATION OF 1-SILYL AND 1,3-BIS(SILYL)ADAMANTANES

by

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ABSTRACT: 1-Dimethylsilyl- and 1,3-bis(dimethylsilyl)adamantane have been prepared in low yield by Wurtz reaction of dimethylchlorosilane with 1-chloroadamantane or 1,3-dichloroadamantane respectively. On the other hand, reaction of phenyldimethylsilyl lithium with 1-bromoadamantane or 1,3-dibromoadamantane gives essentially quantitative yields of 1-phenyldimethylsilyladamantane or 1,3-bis(phenyldimethylsilyl)adamantane, respectively.

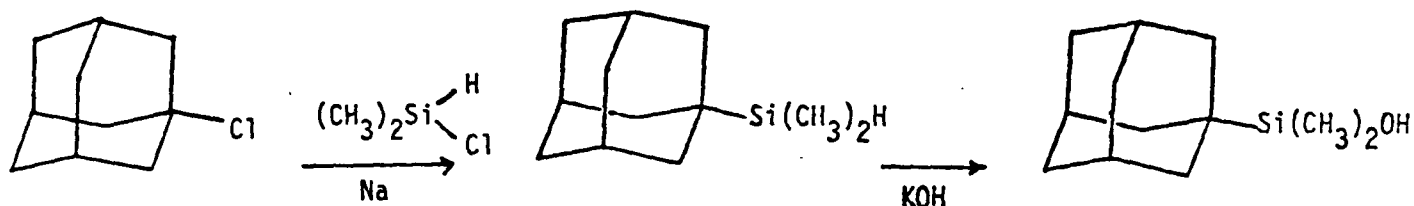
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The high symmetry and thermodynamic stability of the adamantane polyhedron have stimulated considerable interest in the chemistry of its many derivatives.¹ Surprisingly only a few silyl derivatives of adamantane have been reported.² We should like to report two methods which permit the preparation of 1-silyl and 1;3-disilyladamantane derivatives.

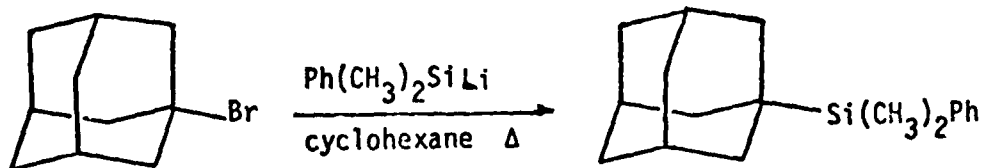
Organosilicon compounds are often prepared by the reaction of organometallic reagents with chlorosilanes.³ The difficulty in preparing silyl adamantane derivatives by this approach results from the fact that organometallic derivatives of adamantane are extremely hard to prepare.³⁻¹² Similarly, Wurtz type reactions of 1-chloroadamantane (I) are unsuccessful with most chlorosilanes.^{2,13} Hydrosilation reactions are frequently used to prepare organosilicon compounds. In this regard, the chloroplatinic acid catalyzed addition of the Si-H bond of trichlorosilane across the strained C-C single bond of 1,3-dehydroadamantane yields 1-trichlorosilyladamantane.¹⁴ Many adamantane derivatives have been prepared by Lewis acid catalyzed rearrangements.¹⁵ While 1-trimethylsilyladamantane (II) has been reported to result from the aluminum bromide catalyzed Wagner-Meerwein rearrangement of 3-trimethylsilyl tricyclo [5,2,1,0^{2,6}] decane,¹⁶ we have been unable to repeat this work. Finally the insertion of dichlorosilylene into tertiary C-H bond of adamantane or into a tertiary C-Cl bond of I is reported to yield 1-dichlorosilyladamantane or 1-trichlorosilyladamantane, respectively.¹⁷

Against this background, we find that the success of the Wurtz reaction of I and 1,3-dichloroadamantane (III) with chlorosilanes and sodium is highly dependent on solvent. The reaction fails in ether solvents, resulting in formation of adamantane and 1,1'-biadamantane.⁷ On the other hand, in aromatic hydrocarbon solvents low yields of II, 1-dimethylsilyladamantane (IV) and 1,3-bis(dimethylsilyl)adamantane (V) can be obtained. The high stability

of the adamantyl free radicals⁸⁻¹¹ is the problem. Thus reaction of III, dimethylchlorosilane (VI), and sodium yields IV as the major product, with only minor amounts of V. Similarly, reaction of 1,3,5-trichloroadamantane (VII) with VI and sodium gives IV and V. None of the expected 1,3,5-tris-(dimethylsilyl)adamantane (VIII) was found. The reactive Si-H bond of IV permits the preparation of other 1-adamantyl dimethylsilane derivatives. For example, 1-adamantyl dimethylsilanol (IX) was prepared by reaction of IV with potassium hydroxide.¹⁸



An alternative route to 1-silyl and 1,3-disilyladamantane derivatives involves the reaction of phenyldimethylsilyl lithium (X)¹⁹ with 1-bromo (XI) or 1,3-dibromoadamantane (XII), respectively. Choice of solvent in this case is also critical. In ether or THF only adamantane and 1,1'-biadamantane are found. On the other hand, in hydrocarbon solvent the reaction proceeds in close to quantitative yield. This is a most unusual example of coupling between a silyl lithium reagent and a tertiary alkyl halide.



Experimental

¹H NMR spectra were obtained on a IBM-Brucker WP-270-SY spectrometer

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operating in the FT mode using 5% solution in deuteriochloroform. Chloroform was utilized as the internal standard. ^{13}C NMR spectra were obtained on an IBM-Brucker WP-270-SY spectrometer using 10-15% solutions in deuteriochloroform or on a JEOL-90 FXQ spectrometer using 20% solution in deuteriobenzene. Chloroform and benzene were utilized as an internal standards, respectively. ^{13}C spectra were run with broad band proton decoupling. IR spectra were obtained on a Perkin-Elmer 281 spectrometer. Low resolution mass spectra were obtained on a Hewlett-Packard 5985 GC-MS at an ionizing voltage of 70 eV. High resolution mass spectra were obtained on an A.E.I. MS-902 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 1/4" x 18" 20% polyphenylether on 60-80 mesh Chromosorb W column (A) or a 1/4" x 10' 20% carbowax on 60-80 mesh Chromosorb P column (B). Product yields were calculated using octadecane as an internal standard. Elemental analysis were performed by Galbraith Laboratories Knoxville, Tennessee.

Dimethylchlorosilane (VI), trimethylchlorosilane (XIII) and phenyl-dimethylchlorosilane (XIV) were obtained from Petrarch System Inc. and were redistilled immediately prior to use. Tetrahydrofuran was distilled from sodium/benzophenone ketyl immediately prior to utilization.

1,2 Diphenyltetramethyldisilane was prepared by reaction of XIV with lithium metal in THF.¹⁹

1-Chloroadamantane (I), 1,3-dichloroadamantane (III), and 1,3,5-trichloro-adamantane (VII) were prepared by electrophilic chlorination of adamantane by aluminum chloride and carbon tetrachloride.²⁰ 1-Bromoadamantane (XI) and

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1,3-dibromoadamantane (XII) were prepared by bromination of adamantane with bromine and boron tribromide.²¹

Wurtz reaction of 1,3-dichloroadamantane (III) and dimethylchlorosilane (VI).
Preparation of 1-dimethylsilyladamantane (IV) and 1,3-bis(dimethylsilyl)-
adamantane (V). In a dry 200 ml pressure bottle equipped with a Teflon covered magnetic stirring bar which has been flushed with purified nitrogen were placed III (1.4 g, 6.8 mmol), dry xylene (2 ml), sodium (1.4 g, 61 mmol) and VI (3 ml, 27 mmol). The bottle was sealed with a silicone rubber gasket and the contents stirred at 120-130°C over a period of 5 hrs. Sodium chloride was removed by filtration and was thoroughly washed with hexane. Solvents were removed from the combined organic phase by evaporation under reduced pressure. Adamantane (0.67 g, 72%) was isolated by crystallization and was identified by comparison of its spectral properties with an authentic sample. Mp 268-270°C (lit. mp 269.6-270.8).²²

1-Dimethylsilyladamantane (IV) was formed in 22% yield. It was purified by preparative GLPC column B. It has the following spectral properties: ¹H NMR: δ -0.045 (d, J=3.6 Hz, 6H), 1.64 (d, J=2.7 Hz, 6H), 1.75 (d, J=2.7 Hz, 6H), 1.84 (br m, 3H), 3.43 (septet, J=3.6 Hz, 1H). ¹³C NMR: δ -8.25 (2C), 20.81 (1C), 28.02 (3C), 37.81 (3C), 38.19 (3C); IR: $\bar{\nu}$ = 2900, 2090 (Si-H) and 1250 cm⁻¹. MS: m/e (% rel. int.) 194 (56), 149 (37), 135 (100), 107 (13), 93 (26), 91 (32), 79 (78). Exact mass for SiC₁₂H₂₂ (M⁺) 194.1495, calcd. 194.1491.

1,3-bis(Dimethylsilyl)adamantane (V) was formed in 2% yield. It was purified by preparative GLPC column A. It has the following spectral properties: ¹H NMR: δ -0.043 (d, J=3.7 Hz, 12 H), 1.54, 1.64, 1.75 and 1.81 (14 H), 3.42

(septet, $J=3.7$ Hz, 2H). ^{13}C NMR: δ -8.13 (4C), 19.84 (2C), 27.29 (2C), 37.67 (1C), 37.99 (4C), 38.56 (1C). IR: $\bar{\nu}$ = 2900, 2090 (Si-H) and 1250 cm^{-1} . MS: m/e (% rel. int.) 252 (52), 193 (100), 149 (81), 138 (21), 133 (14), 113 (12), 73 (20). Exact mass for $\text{Si}_2\text{C}_{14}\text{H}_{28}$ (M^+) 252.1726, calcd. 252.1729.

Wurtz reaction of 1,3,5-trichloroadamantane (VII) and dimethylchlorosilane (VI). Reaction of VII (0.3 g, 1.25 mmol), dry xylene (1 ml), sodium (0.4 g, 17 mmol) and VI (0.83 ml, 7.5 ml) as above gave adamantane 24%, IV 59%, and V 9% yield. No 1,3,5-tris(dimethylsilyl)adamantane (VIII) was found.

Trimethylsilyladamantane (II) was prepared in an analogous reaction of XIII and I in 12% yield. It was purified by preparative GLPC column B. Mp = 36.5°C (lit. mp . 35°C).² It has the following spectral properties: ^1H NMR: δ -0.14 (s, 9H), 1.61 (d, $J=2.3$ Hz, 6H), 1.73 (d, $J=2.3$ Hz, 6H), 1.82 (br, 3H). ^{13}C NMR: δ -5.48 (3C), 21.33 (1C), 28.10 (3C), 37.37 (3C), 37.97 (3C). IR: $\bar{\nu}$ = 2900 and 1250 cm^{-1} . MS: m/e (% rel. int.) 208 (28), 193 (14), 165 (13), 135 (197), 73 (100). Exact mass for $\text{SiC}_{13}\text{H}_{24}$ (M^+) 208.1650, calcd. 208.1647.

Preparation of 1-Adamantyltrimethylsilanol (IX). 1-Dimethylsilyladamantane (IV) (0.085 g, 0.44 mmole) and powdered KOH ($\sim 10\%$ H_2O) (0.3 g, 5.3 mmole) were stirred in xylene (1 ml) at 120°C for 5 hours.¹⁸ The reaction mixture was cooled, poured into 2 N HCl (10 ml) and extracted with hexane. The organic solvents were dried, filtered and removed by evaporation under reduced pressure to yield IX as white needles in 87%. An analytic sample was purified by preparative GLPC column A. mp $91-2^\circ\text{C}$. It has the following spectral properties: ^1H NMR: δ 0.024 (s, 6H), 1.45 (br, 1H), 1.68 (d, $J=2.8$ Hz, 6H), 1.75 (d, $J=2.6$ Hz, 6H), 1.86 (br, 3H). ^{13}C NMR: δ -4.46 (2C), 22.86 (1C),

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27.58 (3C), 36.59 (3C), 37.66 (3C). IR: $\bar{\nu}$ = 3640 cm^{-1} (s) (Si-O-H), 23 2880 cm^{-1} , and 1250 cm^{-1} . MS: m/e (% rel. int.) 210 (49), 195 (15), 167 (14), 149 (19), 135 (27), 79 (16), 46 (100). Exact mass for $\text{SiC}_{12}\text{H}_{22}\text{O}(\text{M}^+)$ 210.1446, calcd. 210.1440.

Preparation of 1-dimethylphenylsilyladamantane (XV). A 10 ml aliquot of a THF solution of dimethylphenylsilyl lithium (X) (prepared by reaction of 5.0 g of 1,2-diphenyltetramethyldisilane and 0.7 g of lithium in 75 ml of THF over 10 hrs)¹⁹ was placed in a pressure bottle. The THF was removed by evaporation under high vacuum. The dark-brown residue was dissolved in 3 ml of cyclohexane. To the above solution was added a solution of 178 mg of XI in 2 ml of cyclohexane. The reaction mixture was heated in a sealed pressure bottle at 100°C for 3 hrs, cooled to room temperature. The reaction was quenched with H_2O . XV was obtained in 93% yield. It has the following spectral properties: ^1H NMR: δ 0.205 (s, 6H); 1.49-1.80 (m, 15H); 7.31-7.47 (m, 10H). ^{13}C NMR: δ -7.28 (2C); 21.67 (1C); 27.78 (3C); 37.30 (3C); 37.59 (3C); 127.36 (2C); 128.65 (1C); 134.63 (2C); 137.29 (1C). IR (CDCl_3): $\bar{\nu}$ = 3140 (w), 2970 (s), 1470 (m), 1490 (m), 1280 (s), 1140 (s) cm^{-1} . MS: m/e (rel. int.) 270 (3.4) M^+ ; 255 (0.5) $\text{M}^+ - 15$; 135 (100) $\text{M}^+ - 135$. Anal. Calcd. for $\text{C}_{18}\text{H}_{26}\text{Si}$: C, 79.92; H, 9.68. Found: C, 79.72; H, 9.82.

Preparation of 1,3-bis(dimethylphenylsilyl)adamantane (XVI). A 15 ml aliquot of a THF solution of X (as above) was placed in a pressure bottle. The THF was removed and the residue was dissolved in 5 ml cyclohexane. To the above solution was added a solution of 250 mg of XII in 3 ml of cyclohexane. The reaction mixture was heated in a sealed pressure bottle to 100°C for 6 hrs. The reaction was cooled to room temperature and quenched with H_2O . XVI was

obtained in 95% yield. It has the following spectral properties: ^1H NMR: δ 0.40 (s, 12H); 1.78-1.95 (m, 14H); 7.51-7.65 (m, 10H). ^{13}C NMR: δ -7.27 (4C); 20.60 (2C); 27.13 (2C); 37.03 (1C); 37.23 (4C); 37.48 (1C); 127.38 (4C); 128.67 (2C); 134.58 (4C); 137.215 (2C). IR (CDCl_3): $\bar{\nu}$ = 3050 (w), 2980 (s), 1430 (w), 1260 (s), 1150 (s), cm^{-1} . MS: m/e (rel. int.) 404 (5.8) M^+ ; 389 (1.0) M^+ -15; 269 (7.8) M^+ -135; 135 (100) M^+ -269. Anal. calcd. for $\text{C}_{26}\text{H}_{36}\text{Si}_2$: C, 77.15; H, 8.97. Found: C, 76.80; H, 9.08.

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APPENDIX IV

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Thermolysis of 6-Oxa-3-silabicyclo[3.1.0]hexanes: A New Convenient Route to Silicon-Oxygen π -Bonded Species

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The direct generation of silanones and germanones from easily prepared 6-oxa-3-metallabicyclo[3.1.0]hexanes is reported. Application of this method to the transient formation of an $[O=Si=O]$ species is given. This silicon analogue of carbon dioxide was trapped by hexamethylcyclotrisiloxane to yield 2,2,4,4,6,6,10,10,12,12,14,14-dodecamethyl-2,4,6,8,10,12,14-heptasila-1,3,5,7,9,11,13,15-octaoxaspiro[7.7]-pentadecane, the expected spiro adduct, in 60% yield.

Silanones, compounds containing a silicon-oxygen double bond, have been postulated as transient intermediates in a variety of reactions.¹ Most of these reactions involve the conversion of other unsaturated silicon intermediates into silanones. For example, reaction of non-enolizable aldehydes or ketones with silenes,²⁻⁶ silamines,^{7,8}

or disilenes⁹⁻¹¹ yield silanones. Likewise, reaction of silylenes with sulfoxides give silanones.¹²⁻¹⁷ On the other

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Scheme I

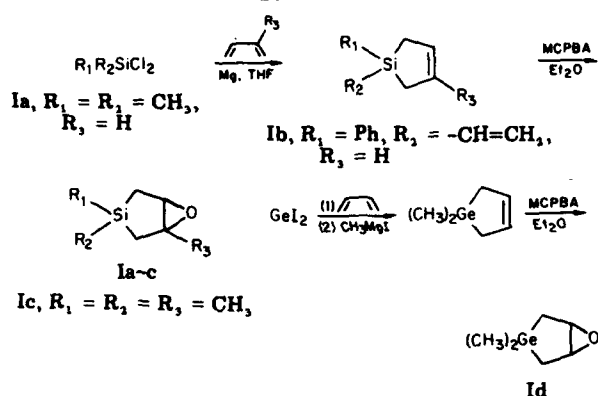


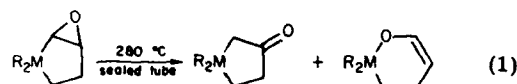
Table I. Absolute Yields of Derivatives II and III and Percentage Decomposition Observed in the Pyrolysis of I

I	M	R ₁	R ₂	% butadiene	% II	% III	% decompn
a	Si	Me	Me	85	61	7	95
b	Si	Ph	Vi	75	61	12	90
d	Ge	Me	Me	88	70	0	90

hand, silapyran-Diels Alder adducts extrude silanones directly.^{18,19}

We wish to report a simple general route to generate a variety of silicon²⁰ (or germanium) analogues of carbonyl derivatives including the carbon dioxide isologue.

In previous papers,^{21,22} it has been shown that thermolysis of 6-oxa-2-sila(or germa)bicyclo[3.1.0]hexanes leads to 3-sila (or germa) cyclopentan-1-ones and 1-oxa-2-sila(or germa)cyclohex-5-enes (eq 1).



Formation of 1-oxa-2-sila(or germa)cyclohex-5-enes is of particular interest since it demonstrates the existence of intramolecular interactions between the oxygen and the metal atom. For this reason, we investigated the thermal behavior of 6-oxa-3-sila(or germa)bicyclo[3.1.0]hexanes (I) in the hope that a transannular reaction would lead to silanones or germanones.²³⁻²⁵

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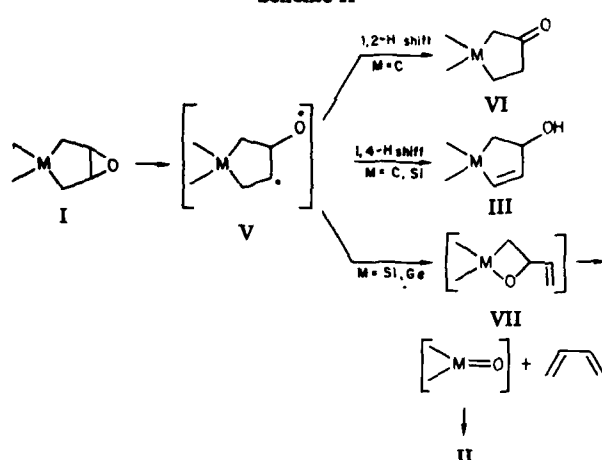
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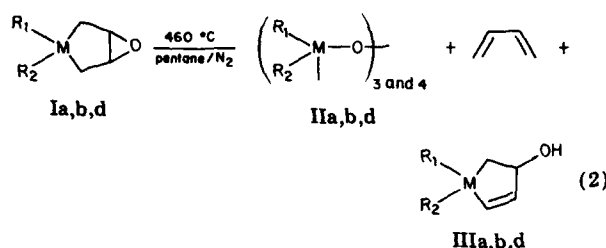
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Scheme II

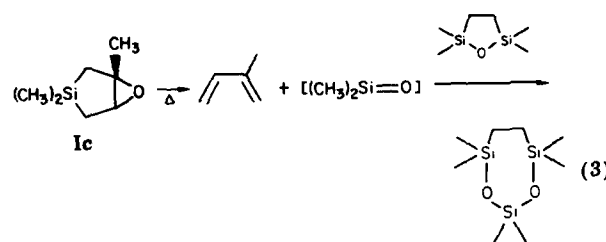


The starting epoxides I were synthesized in two steps²⁶⁻³⁰ in up to 90% yield (Scheme I).

Thermolysis of derivatives Ia,b,d in a flow system, at 460 °C, gave rise to cyclosiloxanes (or germoxanes) (II) and 1,3-butadiene. Depending on the nature of the metal atom and substituents, a small quantity of 3-metallacyclopent-4-en-1-ols (III)^{31,32} was also detected (Table I).



Copyrolysis of Ic and an excess of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane (IV) leads to isoprene and 2,2,4,4,7,7-hexamethyl-1,3-dioxo-2,4,7-trisilacycloheptane, the expected product of trapping dimethylsilanone by IV.^{33,34}



The formation of cyclosiloxanes and germoxanes (II) has often been interpreted as evidence for the intermediacy

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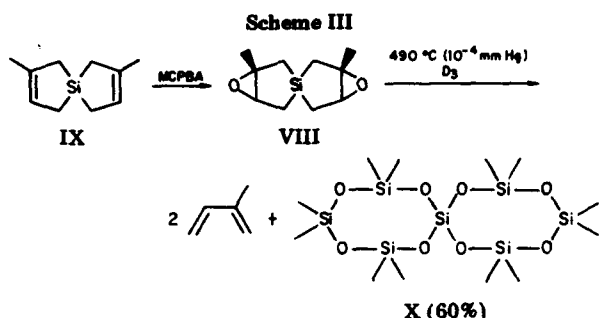
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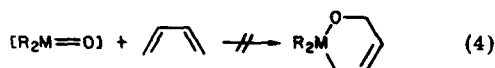
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of silanones and germanones. This result along with the trapping experiment and the observation of 1,3-butadiene or isoprene is consistent with extrusion of metallanones from I. No [2 + 4] cycloaddition reaction of metallanones was observed with 1,3-butadiene or isoprene even when the thermolysis reactions were carried out in the presence of an excess of diene (eq 4). 1-Oxa-2-silacyclohex-4-enes have been shown to be stable under the pyrolysis conditions.¹³



It is interesting to compare our findings with those reported in the case of the carbon isologue. Flowers and Penny³⁶ studied the gas-phase thermolysis of 6-oxabicyclo[3.1.0]hexane (I) between 400 and 470 °C and observed formation of cyclopentanone (VI) (66%) and cyclopent-2-en-1-ol (III) (34%). A mechanism involving homolytic cleavage of a carbon-oxygen bond that leads to diradical (V), followed by 1,2- and 1,4-hydrogen shift has been postulated (Scheme II).

In the silicon and germanium series, initial formation of diradical (V) also seems reasonable. However, a 1,2 hydrogen shift that would lead to 3-metallacyclopentan-1-one (VI) was not observed under our experimental conditions, where this derivative is stable. The 1,4-hydrogen shift that gives rise to 3-metallacyclopent-4-en-1-ols (III) is a minor process. For this reason, a third route, specific to metal 4B epoxides, must be considered. We propose attack on the metal atom by the oxygen radical, with transient formation of unstable metallaoxetanes (VII)³⁶ that decomposes to silanones or germanones and 1,3-butadiene or isoprene (Scheme II).

To illustrate the wide applicability of this reaction, the possibility of generating the silicon isologue of carbon dioxide was investigated. Several diagonal silicon intermediates such as 2-silaallene³⁷⁻⁴⁰ [$\text{CH}_2=\text{Si}=\text{CH}_2$], silaketene³⁷ [$\text{CH}_2=\text{Si}=\text{O}$], and silacarbidimides⁴¹ [$\text{RN}=\text{Si}=\text{NR}$] have been the subject of experimental as well as theoretical studies. Note that an $[\text{O}=\text{Si}=\text{O}]$ species has already been postulated.^{37,42}

With this goal in mind, 2,7-dimethyl-2,3,7,8-diepoxy-5-silaspiro[4.4]nonane (VIII) was synthesized by treatment of 2,7-dimethyl-5-silaspiro[4.4]nona-2,7-diene (IX) with *m*-chloroperbenzoic acid.⁴³ It was copolymerized with a fivefold excess of hexamethylcyclotrisiloxane (D_3). Isoprene was found in essentially quantitative yield. In addition 2,2,4,4,6,6,10,10,12,12,14,14-dodecamethyl-2,4,6,8,10,12,14-heptasila-1,3,5,7,9,11,13,15-octaoxaspiro[7.7]pentadecane (X)^{44,45} was isolated in 60% yield (Scheme III).

These results may be interpreted in terms of insertion of a reactive intermediate $[\text{O}=\text{Si}=\text{O}]$ into the silicon-oxygen single bond of two molecules of hexamethylcyclotrisiloxane. Obviously, an alternative possibility is that the reactive silicon-oxygen double bonds are generated stepwise.

Conclusion

These results emphasize the role of the metallic Si or Ge heteroatoms on the thermal behavior of 6-oxa-3-metallabicyclo[3.1.0]hexanes. In contrast with the carbon series, a transannular reaction takes place leading to transient metallaoxetanes. Since the starting materials are easily available, this method allows the facile generation of various metal 4B-oxygen π -bonded species.

Experimental Section

¹H NMR spectra were obtained on JEOLCO-90FX-Q or IBM-Brucker WP-270-SY spectrometer operating in the FT mode using 5% solution of deuteriochloroform. Chloroform was utilized as the internal standard. The integration of the NMR spectra sometimes gave too small intensities for the SiCH_3 signals because of saturation problems. However, in all cases the integration was within 10% of the calculated value. ¹³C NMR spectra were obtained on an IBM-Brucker WP-270-SY using 10–15% solution in deuteriochloroform. Chloroform was utilized as an internal standard. ¹³C spectra were run with broad-band proton decoupling.

IR spectra were obtained on a Perkin-Elmer 281 or Nicolet MX-1 Fourier Transform spectrometer. 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. 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 at 70 eV. Exact mass were determined by peak matching against peaks of known mass of perfluoro kerosene. GLPC analysis as performed on a Hewlett-Packard F&M 700.

1,1-Dimethyl-1-silacyclopent-3-ene,^{36,46} 1,1,3-trimethyl-1-silacyclopent-3-ene,^{36,46} 1,1-dimethyl-1-germacyclopent-3-ene,^{36,46} and the corresponding epoxides 3,3-dimethyl-6-oxa-3-silabicyclo[3.1.0]hexane,³⁷ 1,3,3-trimethyl-6-oxa-3-silabicyclo[3.1.0]hexane,³⁷ 3,3-dimethyl-6-oxa-3-germabicyclo[3.1.0]hexane,³⁸ and 3,3-dimethyl-3-silacyclopent-4-en-1-ol^{31,47} were prepared by previously reported methods and had spectral and physical properties in complete agreement with literature values.

Synthesis of 3-Phenyl-3-vinyl-6-oxa-3-silabicyclo[3.1.0]hexane (Ib). A solution of 1-phenyl-1-vinyl-1-silacyclopent-3-ene³⁶ (9.45 g, 0.05 mol) in ether (50 mL) was added dropwise to a stirred solution of *p*-nitroperbenzoic acid (10.2 g, 0.05 mol) in ether (50 mL), at 0 °C. After filtration, the solution was washed with a 10% NaOH solution and then with water. After drying

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over Na_2SO_4 , ether was removed at reduced pressure (15 mmHg). Distillation led to 8.1 g of Ib (79% yield): bp 170 °C (30 mmHg); n_D^{20} 1.5578; IR (neat) ν 1590 cm^{-1} ($\text{CH}=\text{CH}_2$); ^1H NMR (CCl_4) δ 0.8–1.7 (m, 4 H, SiCH_2), 3.3 (m, 2 H, CH), 5.4–6.7 (m, 3 H, $\text{CH}=\text{CH}_2$), 7.1–7.7 (m, 5 H). Anal. Calcd: C, 71.23, H, 6.97. Found: C, 71.26; H, 6.87.

Synthesis of 3-Phenyl-3-vinyl-3-silacyclopent-4-en-ol (IIIb). A pure sample of IIIb was prepared by photooxygenation of 1-phenyl-1-vinyl-1-silacyclopent-3-ene followed by reduction of the resulting hydroperoxide according to the procedure previously described by Laporterie et al.³²

The photooxygenation of 1-phenyl-1-vinyl-1-silacyclopent-3-ene (3.7 g, 0.02 mol) was followed by reduction of the crude hydroperoxide in methanol by NaBH_4 (5 g, excess). After removal of the solvent, the residue was extracted with ether (200 mL) and the etheral solution washed with water (2 $\times$ 50 mL). After the solution was dried over Na_2SO_4 , the ether was removed. Fractional distillation led to 2.7 g of IIIb (66% yield): bp 120 °C (0.2 mmHg); IR (neat) 3310 (OH), 1590 ($\text{HC}=\text{CH}_2$), 1560 cm^{-1} ($\text{CH}=\text{CH}_2$); ^1H NMR (CCl_4) SiCH_2 (two AB parts of two ABX systems corresponding to the two diastereoisomers 50/50, δ_A 1.56, δ_B 0.99, $J_{AB} = 15$ Hz, $J_{AX} = 2$ Hz, $J_{BX} = 1.4$ Hz and δ_A 1.69, δ_B 0.88, $J_{AB} = 15.2$ Hz, $J_{AX} = 2$ Hz, $J_{BX} = 1.4$ Hz), OH (4.3 ppm), CHOH (4.9 ppm, m), $\text{CH}=\text{CH}_2$ and $\text{SiCH}=\text{CH}$ (5.6–6.8 ppm, m), $\text{SiCH}=\text{CH}$ (rest A of an ABX system centered at 7.05 ppm, $J_{AB} = 10$ Hz, $J_{AX} = 2$ Hz), (7.2–7.8 ppm, 5 H). Anal. Calcd: C, 71.26; H, 7.07. Found: C, 71.35; H, 7.11.

Synthesis of 2,7-Dimethyl-5-silaspiro[4.4]nona-2,7-diene (IX).⁴³ Crude diethoxydichlorosilane, obtained by heating SiCl_4 (34 g, 0.2 mol) and $\text{Si}(\text{OEt})_4$ (41.6 g, 0.2 mol), in a sealed tube, at 160 °C, for 3 days, is added to a THF solution (500 mL) containing Mg (24.3 g, 1 mol) and isoprene (68 g, 1 mol). The mixture was stirred under reflux for 24 h under a nitrogen atmosphere. Water (200 mL) was added dropwise to the reactive mixture, and the organic layer was separated and evaporated. The pentane extracts of the residue were dried over CaCl_2 . Evaporation and distillation gave 55.1 g of IX (84% yield from SiCl_4 (lit.⁴³ 52%)): bp 104–106 °C (30 mmHg) (lit.⁴³ 140 °C (105 mmHg)); ^1H NMR (CCl_4) δ 1.3–1.6 (m, 8 H, SiCH_2), 1.7–1.9 (m, 6 H, CH_3), 4.5–5.70 (m, 2 H, CH).

Synthesis of 2,7-Dimethyl-2,3,7,8-diepoxy-5-silaspiro[4.4]nonane (VIII). To a stirred solution of *m*-chloroperbenzoic acid (8.7 g, 0.05 mol) in ether (100 mL), at –10 °C, was added a solution of IX (4.1 g, 0.025 mol) in ether (30 mL) dropwise. The resulting mixture was stirred at room temperature for 10 h, then washed with a 10% NaOH solution (3 $\times$ 40 mL) and with water (2 $\times$ 50 mL), and dried on CaCl_2 . Evaporation and distillation gave 3.8 g of VIII (77% yield (lit.⁴³ 65.3%)): bp 81 °C (0.4 mmHg) (lit.¹⁹ 80 °C (0.45 mmHg)); ^1H NMR (CCl_4) δ 0.7–1.3 (m, 8 H, SiCH_2), 1.35 (s, 6 H, CH_3), 3.05 (br s, 2 H, CHO).

Pyrolysis of 6-Oxa-3-metallabicyclo[3.1.0]hexanes (Ia,b,d). The pyrolysis were conducted in a 30-cm vertical Pyrex tube packed with Pyrex chips and enclosed in a tube furnace heated to 460 °C. A 20% solution of I in pentane was mechanically added at a rate of 2 mL/h concomitant with a nitrogen flow of 20 mL/min. The pyrolysate was collected in a liquid-nitrogen-cooled

trap, and the major products were identified. One of these was identified as 1,3-butadiene by comparison of its GC retention time and its GC-MS with those of an authentic sample. Cyclosiloxanes and cyclogermoxanes as well as 3-silacyclopent-4-en-1-ols were purified by preparative GC on a 20 ft $\times$ 0.25 in. 15% SE-30 column and their IR and ^1H NMR spectra compared with those of authentic samples. Yields were determined by gas chromatography using authentic samples of the products as internal standards. Percentage of decomposition and yield of 1,3-butadiene were estimated by ^1NMR of the crude pyrolysate.

Pyrolysis of 2,7-Dimethyl-2,3,7,8-diepoxy-5-silaspiro[4.4]nonane (VIII). Compound VIII was copolyolyzed with a fivefold excess of hexamethylcyclotrisiloxane through a 30-cm quartz tube that was heated to 490 °C with a pressure of 10^{-4} torr. The pyrolysate was collected in a liquid-nitrogen-cooled trap. Isoprene was found in essentially quantitative yield. In addition, 2,2,4,4,6,6,10,10,12,12,14,14-dodecamethyl-2,4,6,8,10,12,14-heptasil-1,3,5,7,9,11,13,15-octaoxaspiro[7.7]pentadecane was isolated, in 60% yield, by preparative GLPC on a 4 ft $\times$ 0.25 in. 20% SE-30 column: ^1H NMR (CDCl_3) δ 0.103 (s, 24 H), 0.075 (s, 12 H); ^{13}C NMR (CDCl_3) δ 0.761 (8 C), 0.599 (16 C); IR 1100, 1060 cm^{-1} ($\nu_{\text{Si-O}}$); mass spectrum, *m/e* (relative intensities) 489 (30%, $M - 15^+$), 401 (69%), 385 (15), 227 (12.6), 147 (11.3), 73 (100); high-resolution mass spectrum ($M - 15$)⁺ calcd for $\text{Si}_7\text{C}_{11}\text{H}_{33}\text{O}_8^+$ 489.0560, found 489.0577.

Copolyrolysis of 1,3,3-Trimethyl-6-oxa-3-silabicyclo[3.1.0]hexane (Ic) and 2,2,5,5-Tetramethyl-1-oxa-2,5-disilacyclopentane (V). 1,3,3-Trimethyl-6-oxa-3-silabicyclo[3.1.0]hexane (Ic) (1 g, 7 mmol) was copolyolyzed with 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane (3.5 g, 21.86 mmol) through a 30-cm quartz tube that was heated to 490 °C with a pressure of 10^{-3} torr. The pyrolysate was collected in a liquid-nitrogen-cooled trap. Isoprene was found in quantitative yield. In addition, D_3 (40%), D_4 (18%), and 2,2,4,4,7,7-hexamethyl-1,3-dioxo-2,4,7-trisilacycloheptane (41%) were isolated. 2,2,4,4,7,7-Hexamethyl-1,3-dioxo-2,4,7-trisilacycloheptane has the following spectral properties:^{33,34} ^1H NMR (CDCl_3) δ 0.714 (s, 4 H), 0.071 (s, 12 H), 0.040 (s, 6 H); mass spectrum, *m/e* (relative intensities) 219 (100, $M^+ - 15$), 191 (87), 141 (61), 133 (14), 117 (71), 88 (28), 74 (90), 73 (63).

Acknowledgment. W.P.W. and S.A.K. thank the U.S. Air Force Office of Scientific Research (Grant No. 82-0333) for financial assistance; G.M. and G.B. thank Drs. J. Dubac and A. Laporterie for the use of photochemical equipment. W.P.W. and G.M. acknowledge a NATO research Grant No. 845/83.

Registry No. Ia, 75-78-5; Ib, 50694-32-1; Ic, 33460-17-2; Id, 51343-29-4; IIIb, 90991-61-0; *cis*-IIIb, 90991-59-6; *trans*-IIIb, 90991-60-9; VIII, 63683-92-1; XI, 54767-28-1; X, 34060-11-2; SiCl_4 , 10026-04-7; $\text{Si}(\text{OEt})_4$, 78-10-4; diethoxydichlorosilane, 4667-38-3; isoprene, 78-79-5; hexamethylcyclotrisiloxane, 541-05-9; 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane, 7418-20-4; 2,2,4,4,7,7-hexamethyl-1,3-dioxo-2,4,7-trisilacycloheptane, 71245-77-7.

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APPENDIX V

PHOTOLYSIS OF DODECAMETHYLCYCLOHEXASILANE -
FORMATION OF BOTH METHYLSILENE AND DIMETHYLSILYLENE

by

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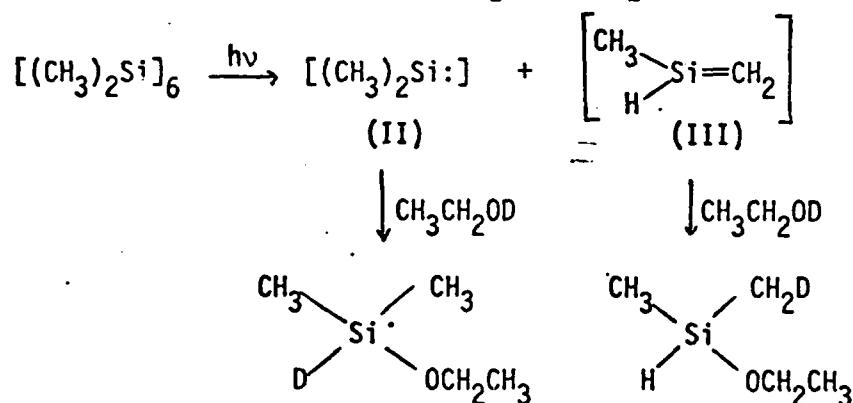
Division of Chemistry

National Research Council of Canada

Ottawa, Ontario, Canada K1A 0R6

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Photolysis of dodecamethylcyclohexasilane (I) with light of 254 nm has been reported to yield decamethylcyclopentasilane and dimethylsilylene (II).¹⁻³ This procedure is in fact the standard method to generate II in solution. We would like to report experimental and spectroscopic observations which demonstrate that this system is more complicated. Specifically that photolysis of I in the presence of ethanol-0-d₁ leads to both II and methylsilene (III). Dimethylsilylene (II) reacts with ethanol-0-d₁ to yield dimethylethoxysilane-d₁-Si (IV-d₁-Si)^{4,5} while III reacts with ethanol-0-d₁ to yield dimethylethoxysilane-d₁-C (IV-d₁-C).⁶⁻⁹

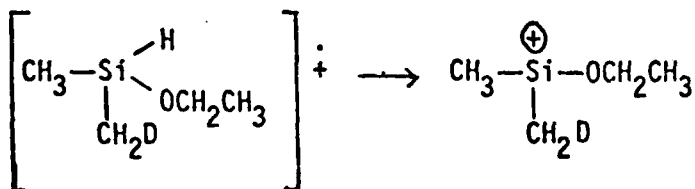
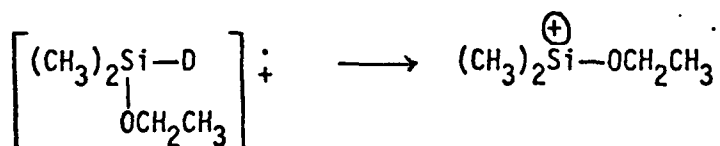


There has been considerable recent experimental¹⁰⁻¹² and theoretical¹³⁻¹⁶ interest in the interconversion of II and III under pyrolysis conditions.

Photolysis of a deoxygenated THF (1.5 ml) solution of I (23 mmol) and ethanol-0-d₁ (44 mmol)¹⁷ with a 450 W medium pressure Hanovia Hg lamp at 0°C gave IV-d₁ as expected. It was isolated by preparative GLPC¹⁸ and had the following spectral properties: ¹H NMR δ 4.59 (sept. small J=2.8 Hz),¹⁹ 3.68 (q, 2H, J=7 Hz), 1.19 (t, 3H, J=7 Hz) and 0.19 (s, 6H). IR-FT (gas phase) Si-H 2120 cm⁻¹ (w) with a shoulder at 2128 cm⁻¹ and Si-D 1542 cm⁻¹ (s). The most critical data is the deuterium NMR (²H NMR) which was run on an

IBM-Brucker WP-270-SY spectrometer operating at 41.467 megahertz in the FT mode. Deuterium chemical shifts are reported relative to chloroform- d_1 . With proton decoupling two singlets were observed: Si-D at 4.57 δ and C-D at 0.118 δ . In the decoupled spectrum the Si-D was still a singlet but the C-D signal was now a triplet $J=1.9$ Hz. Under conditions where toluene- d_8 gave a correct 5:3 ratio integration, the ratio of the Si-D to C-D was 93:7. Analysis of the mass spectrum of this sample on the assumption that each molecule of IV- d_1 contains one deuterium and the known fragmentation patterns of dimethylsilyl ethers, which lose methyl groups or hydrogen from the silyl center to form siliconium ions,^{20,21} yields a ratio of Si-D to C-D 93.7 in remarkable agreement with that obtained by 2H NMR. MS parent 105 (4.8%), P-1 (11.6%), P-2 (71%), P-15 (100%) and P-16 (14.1%).²²

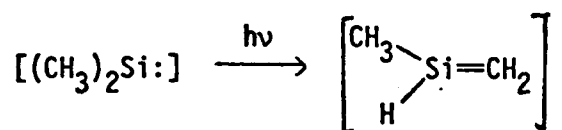
Similar results have been obtained from the photolysis of a diethyl ether solution of I and D_2O .



Additional evidence in support of the generation of III on photolysis of I is the observation of a transient absorption at 275 nm on laser flash

photolysis of a 3-methylpentane solution of I.²³ The uv absorption maximum of III in a matrix at low temperature has been reported at 260 nm.²⁴

A more mundane interpretation of our data is that II undergoes photoisomerization to III by absorption of a second photon of light prior to reaction with ethanol-0-d₁.



This process has in fact been observed in matrices at low temperature.^{25,26} The fact that III is quenched by methanol in THF with a rate constant of greater than $10^6 \text{ M}^{-1} \text{ sec}^{-1}$,²⁷ strongly argues against this interpretation. At the very least, the possibility of simultaneous production of III or its secondary formation faster than reaction of II with various substrates must be considered in evaluation of all experiments in which II is generated by the photolysis of I.

Further experiments to clarify this situation are in progress.

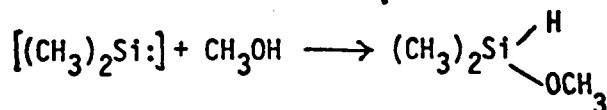
Acknowledgement: I.S. Alnaimi and W.P. Weber thanks the Air Force Office of Scientific Research under grant number 80-0006 for its generous support.

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APPENDIX VI

Dimethylsilylene: Its Optical Absorption Spectrum and Reaction Kinetics¹

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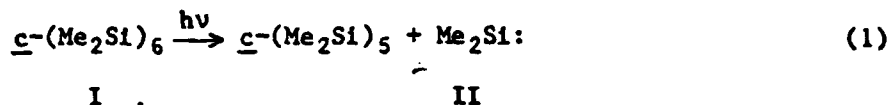
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Abstract

The photochemistry of dodecamethylcyclohexasilane, I, was investigated using laser flash photolysis. The photodecomposition of, I, at 308 nm, gives a transient which has an absorption spectrum at 350 nm. Evidence from quenching and product studies suggests that this is due to dimethylsilylene.

The rate constant for reaction of dimethylsilylene with triethylsilane at 298K in cyclopentane as solvent was found to be $2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$; that for the reaction with methanol in tetrahydrofuran solvent was $3.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

Photolysis of dodecamethylcyclohexasilane, I, has been used as a convenient source of dimethylsilylene, II, in solution³⁻⁹ and in the gas phase¹⁰, eq. 1.



The reaction has also been used to generate the silylene in hydrocarbon and argon matrices so that its infrared,¹¹ ^($\lambda_{\text{max}} = 450 \text{ nm}$) uv-visible,¹² and fluorescence spectra¹² ^($\lambda_{\text{max}} = 650 \text{ nm}$) could be recorded. In fact, irradiation in the uv-visible band at 450 nm has been used to induce rearrangements of II which have been monitored by infrared spectroscopy.¹¹ We report results which show that this system is more complicated than the current literature suggests and which demonstrate that the uv-visible spectrum of II has been incorrectly assigned.

Laser flash photolysis¹³ ($\lambda = 308 \text{ nm}$, pulse width 8 ns, power 10 mJ per pulse) of I (10^{-4} M) in 3-methylpentane or cyclopentane solvent at 293K gave an absorption band at 350 nm. This transient grew with a lifetime of 74 ns and decayed in 8 μs . No band was detected at 450 nm.

Quenching experiments suggest that the transient absorption at 350 nm was due to dimethylsilylene, II. Addition of triethylsilane, an effective silylene scavenger,^{4,9} quenched the transient absorption, eq. 2. The rate constant for this reaction, k_2 ,



III

was measured by monitoring the pseudo-first order rate constant, k_{obs} , for the disappearance of the transient as a function of substrate concentration, eq. 3,

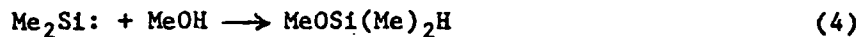
where k_0 describes the decay of the transient in the absence of the quencher.

✓ It was found that $k_2 = 2.0 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ in cyclopentane as solvent.

$$k_{\text{obs}} = k_0 + k_2[\text{Et}_3\text{SiH}] \quad (3)$$

Product studies were carried out by photolyzing I (0.05 M) and triethylsilane (2.5 M) in cyclopentane in a photochemical reactor (250 nm). Analysis by g.c./mass spec. showed that III had been formed in 85% yield at 64% conversion of I.

In similar vein, methanol quenched the absorption spectrum at 350 nm, eq. 4, although the reaction



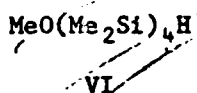
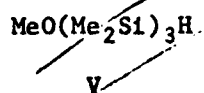
IV

kinetics were a little unusual. At methanol concentrations below 0.05 M the rate constant for quenching, k_q , was found to be $4.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ while above this concentration it was $4.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$. Similar effects have been observed in competition studies of the insertion reactions of dimethylsilylene into Si-H and O-H bonds. They are presumably related to the distribution of methanol monomers and oligomers which occur when the alcohol concentration is varied. However, we were unable to account for the sharp change in reaction kinetics by quantitative analysis of the data in these terms although such an effect was successful for arylchlorocarbenes.¹⁴

The methanol quenching experiment was repeated in tetrahydrofuran as solvent which was chosen for its ability to prevent oligomerization of the methanol.¹⁵ The absorption spectrum was "blue shifted" by the solvent such

that $\lambda_{\text{max.}} = 300 \text{ nm}$. In the absence of methanol the absorption grew with a lifetime of 30 ns and decayed with one of 8 μs . The rate constant for reaction with methanol was found to be $3.1 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$. As expected, tetrahydrofuran eliminated the unusual kinetic behaviour and the rate constant measured in this solvent was quite similar to that observed at low methanol concentrations in cyclopentane.

Product studies were carried out in cyclopentane solution as described above using methanol (0.38 M) as substrate. ~~While the simple insertion product, IV was formed in >95% yield V and VI were~~



~~detected in yields of 1 and 2% respectively at 43% conversion of I. Similar results were obtained when decamethylcyclopentasilane, VII, was used as the dimethylsilylene source. These products did not arise by repeated insertion of dimethylsilylene into IV since photolysis of 1,4,5,6-tetraphenyl-2,3-benzo-7,7-dimethyl-7-silanorbornadiene, VIII, a clean source of dimethylsilylene, under the same conditions gave only the mono-insertion product, eq. 4. We therefore conclude that photolysis of the cyclic polysilanes leads to the elimination of 3 and 4 dimethylsilylene units which can be scavenged by methanol.~~

To confirm that the absorption spectrum at 350 nm was indeed due to dimethylsilylene we carried out a competition under the conditions of the preparative experiments by photolyzing I (0.04 M) methanol (0.27 M) and triethylsilane (0.22 M) in 3-methylpentane to 80% conversion of I. Product analysis indicated that the ratio k_4/k_2 was 2.5 whereas the laser flash photolysis results (vide supra) give 2.1.

While we were unable to detect the ~~450~~^{470 nm} nm absorption previously assigned to dimethylsilylene by photolysis at 308 nm, we were able to detect an absorption at ~~that wavelength~~^{470 nm} by photolysis with much higher energy radiation (249 nm, pulse width 8 ns, power up to 250 mJ per pulse. The 470 nm band was detected along with the 350 nm band. The former was present immediately after the laser flash and decayed in 192 ns and could not be trapped by silylene ~~scavenger~~^{triethylsilane a scavenger}.

Product studies carried out on the methanol system with photolysis at 250 nm of the cyclic polysilanes I and VII, revealed no new products which was consistent with this observation and implied that the 470 nm ~~was a highly~~ coloured species which gave insignificant yields of chemical products or that it decomposed to give dimethylsilylene.

The present results imply that the photolysis of I gives dimethylsilylene which has an absorption spectrum at 350 nm and that I or its photolysis products can extrude, in very low yields, fragments containing 3 or 4 dimethylsilylene units. The absorption spectrum at ~~470~~⁵ nm previously reported to be due to dimethylsilylene has ~~been~~^{e apparently been} incorrectly assigned. ~~or else~~^{a mistake}.
Acknowledgement

We thank Dr. J.C. Scaiano for the use of the laser flash photolysis equipment and for helpful discussions. Two of us, I.S.A. and W.P.W. thank the Air Force Office of Scientific Research (Grant number 80-0006) for its generous support.

Tetra ethyldisilene the expected dimerization of dimethylsilylene is apparent it presents present under an condition since

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APPENDIX VII

Adamantyldimethylsilyl Ethers. Preparation and Properties.

by

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Abstract:

Adamantyldimethylsilyl ethers have been prepared by reaction of the corresponding chloride with alcohols in DMF/imidazole. Alternatively these ethers are available by tris(triphenylphosphine) rhodium chloride catalyzed reaction of adamantyldimethylsilane with alcohols. Adamantyldimethylsilyl ethers are comparable to t-butyldimethylsilyl ethers in their hydrolytic stability. Methods to convert the hydrolysis product adamantyldimethylsilanol back to the corresponding chloride or silanes are given.

Silyl ether derivatives of alcohols have a number of useful properties. The volatility of trimethylsilyl¹⁻⁷ and dimethylsilyl^{8,9} ether derivatives make them an attractive choice for separation and structure elucidation by a combination of gas chromatography and mass spectrometry. On the other hand, the ease of hydrolysis of these derivatives limits their utility as protecting groups.¹⁰ The fact that the hydrolysis of silyl ether derivatives proceeds by nucleophilic attack at silicon, under either acid or base catalysis, makes this reaction sensitive to steric hinderance at the silyl center.^{11,12} Based on this concept, t-butyldimethylsilyl,^{13,14} di-t-butylmethylsilyl,¹⁵ tri-isopropylsilyl,¹⁶ and t-butyldiphenylsilyl,^{17,18} ether derivatives have been developed and have proved highly useful protecting groups for hydroxyl groups under a wide range of reaction conditions. In particular, they are comparatively stable to hydrolysis under basic conditions.

A common property of most silyl ethers is that they are liquids or oils. We have recently prepared adamantyldimethylsilane⁹¹ in the hope that the diamond like structure of the adamantane nucleus²⁰ would confer crystallinity on these derivatives. At the same time it was anticipated that from a steric point of view the adamantyl group would be similar to the t-butyl group. In fact, adamantyldimethylsilyl ether derivatives have hydrolytic stability under either acid or base catalysis almost identical to that of t-butyldimethylsilyl ether derivatives (see Table 1). On the other hand, while some adamantyldimethylsilyl ether derivatives are crystalline solids, others are not and so this desired property has only been partially achieved. For example, the adamantyldimethylsilyl ether derivatives of n-butanol melts at 72°C while that of cyclohexanol is an oil.

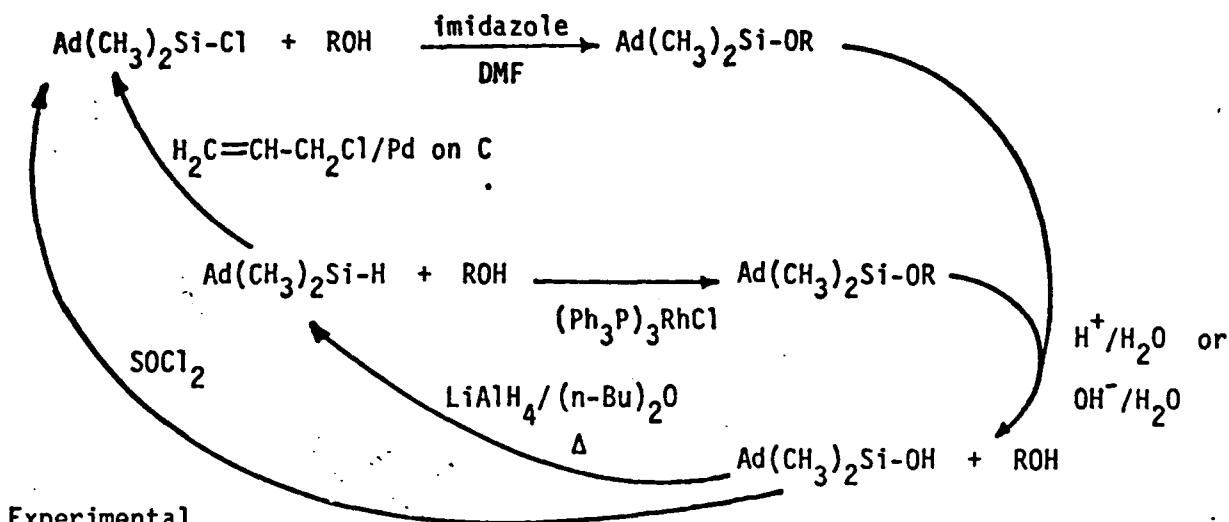
Adamantyldimethylsilyl ethers were prepared by reaction of

adamantyl dimethylchlorosilane with the desired alcohol in DMF solvent in the presence of imidazole, conditions identical to these used by Corey to prepare t-butyl dimethylsilyl ether derivatives.¹³ The necessary adamantyl dimethylchlorosilane was prepared from adamantyl dimethylsilane by catalytic chlorination with allyl chloride over a palladium on carbon catalyst.^{21,22} As can be seen from the table I, neither adamantyl dimethylsilyl nor t-butyl dimethylsilyl ethers of primary alcohols are very stable to acid hydrolysis conditions. This makes the removal of imidazole by an aqueous acidic extraction a problem.

A seldom utilized alternate procedure to prepare silyl ethers is the reaction of silanes with alcohols catalyzed by tris(triphenylphosphine)-rhodium chloride.^{23,24} We have utilized this procedure to prepare adamantyl dimethylsilyl ethers in essential quantitative yield in benzene. Less than 10^{-3} molar equivalents of rhodium catalyst were necessary. This procedure has the advantage that no aqueous work-up is required. Further, silanes are less subject to hydrolysis than the corresponding chlorides. Thus adamantyl dimethylsilane requires less care in handling and storage than the corresponding chloride, although it should be stored under nitrogen.

Finally, an often expressed concern is the high cost of t-butyl dimethylchlorosilane. This comment will certainly apply to adamantyl dimethylchlorosilane or the corresponding silane. Nevertheless, after hydrolysis of adamantyl dimethylsilyl ethers the corresponding silanol can be isolated. This silanol¹⁹ can be converted back to the chloride quantitatively by reaction with thionyl chloride.²⁵⁻²⁷ Alternatively, the silanol may be reduced to the silane by treatment with LiAlH_4 .²⁸⁻³⁰ These transformations which proceed in very high yield should further stimulate the use of such

silyl ethers by minimizing their costs, are outlined below.



Experimental

^1H NMR spectra were obtained on an IBM WP-270-SY spectrometer operating in the FT mode using 5% solution in deuteriochloroform. Chloroform was utilized as the internal standard. ^{13}C NMR spectra were obtained on an IBM WP-270-SY spectrometer using 10-15% solutions in deuteriochloroform or on a JEOL-90 FXQ spectrometer using 20% solution in deuteriobenzene. Chloroform and benzene were utilized as an internal standards, respectively. ^{13}C spectra were run with broad band proton decoupling. IR spectra were obtained on a Perking-Elmer 281 spectrometer. Low resolution mass spectra were obtained on a Hewlett-Packard 5985 GC-MS at an ionizing voltage of 70 eV. High resolution mass spectra were obtained on a an A.E.I. MS-902 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. Product yield were calculated using internal standards. Elemental analysis were performed by Galbraith Laboratories, Knoxville, Tennessee.

Preparation of Adamantyldimethylsilyl Ethers by the tris-Triphenylphosphine

Rhodium Chloride Catalyzed Reaction of Adamantyldimethylsilane with Alcohols.

Adamantyldimethylsilane 2.5 mmole (0.49 g) was added to a solution containing 5 mg tris(triphenylphosphine) rhodium (I) chloride and 2.5 mmol of the dry alcohol in 3 ml dry benzene. The mixture was refluxed until complete conversion was observed by GLPC (10-18 hrs). The solvent was removed in vacuo. The silyl ether was distilled into a cold trap in greater than 90% yield. Analytical samples were purified by preparative GLPC on a 1/4" x 3-1/2' 20% PPE on 60/80 mesh Chromosorb W column.

Adamantyl-n-butoxydimethylsilane was obtained in 94% yield. It had the following properties: mp 72-74°C. ^1H NMR: δ -0.03 (d, $J=1.5$ Hz, 6H), 0.89 (d of t, $J_1 = 7$ Hz, $J_2 = 1.2$ Hz, 3H), 1.21-1.37 (m, 2H), 1.43-1.52 (m, 2H), 1.68 (s, 6H), 1.74 (s, 6H), 1.83 (s, 3H), 3.56 (d of t, $J_1 = 6$ Hz, $J_2 = 1.4$ Hz, 2H). ^{13}C -NMR: δ -6.10 (2C), 13.94 (1C), 19.03 (1C), 23.26 (1C), 27.59 (3C), 35.12 (1C), 36.75 (3C), 37.73 (3C), 63.08 (1C). IR (CDCl_3): 1090 (s) cm^{-1} Si-O. MS: m/e (% rel. int.) 266 (16), 251 (12), 135 (5), 131 (100), 75 (38). Exact mass for $\text{SiC}_{16}\text{H}_{30}\text{O}$ (M^+) 266.2071, calcd. 266.2065.

Adamantylcyclohexoxydimethylsilane was obtained in 92% yield. It had the following properties: ^1H NMR: δ -0.03 (s, 6H), 1.1-1.6 (m, 10H), 1.67 (d, $J=2.5$ Hz, 6H), 1.74 (s, 6H), 1.82 (s, 3H), 3.6 (br m, 1H). ^{13}C -NMR: δ -5.56 (2C), 23.10 (1C), 24.13 (2C), 25.64 (1C), 27.59 (3C), 35.94 (3C), 36.64 (3C), 37.73 (2C), 70.72 (1C). IR: (CDCl_3): 1090 (s) cm^{-1} Si-O. MS: m/e (% rel. int.) 292 (3), 277 (2), 195 (2), 157 (33), 135 (5), 75 (100), 59 (10). Exact Mass for $\text{SiC}_{18}\text{H}_{32}\text{O}$ (M^+) 292.2220, calcd. 292.2222.

Reaction of Adamantyldimethylchlorosilane with Alcohols, Preparation of Adamantylbenzyloxydimethylsilane

Sublimed adamantyldimethylchlorosilane (100 mg, 0.44 mmol) was dissolved in dry DMF (~ 1 ml). To this solution was added imidazole (75 mg, 1.1 mmol) and benzyl alcohol (45 μ l, 47 mg, 0.44 mmol). The mixture was stirred at room temperature overnight. GLPC showed a 98% conversion. The mixture was quickly separated between cold aqueous 0.1 N HCl and hexane. The organic phase was dried over anhydrous MgSO_4 . After filtration and evaporation of the solvent, adamantylbenzyloxydimethylsilane (120 mg) was obtained in 91% yield. It had the following properties: ^1H NMR: δ 0.035 (s, 6H), 1.64-1.85 (m, 15H), 4.72 (s, 2H), 7.24-7.32 (m, 5H). ^{13}C -NMR: δ -6.14 (2C), 23.58 (1C), 27.80 (3C), 36.97 (3C), 37.83 (3C), 65.16 (1C), 126.18 (2C), 126.85 (1C), 128.17 (2C), 141.68 (1C). IR (CDCl_3): 1100 (s) and 1090 (s) cm^{-1} Si-O. MS: m/e (% rel. int.) 300 (4), 285 (1), 165 (45), 149 (7), 135 (32), 91 (100) 79 (14), 65 (11). Exact mass for $\text{SiC}_{19}\text{H}_{28}\text{O}$: 300.1903, calc. 300.1909.

Preparation of Adamantyldimethylchlorosilane³² from Adamantyldimethylsilane.

Allyl chloride (1.5 ml) and 10% palladium on charcoal (53 mg, 0.05 mmol), were heated at reflux for 10 min, at which time adamantyldimethylsilane (0.56 g, 2.9 mmol), was added. The mixture was refluxed for 1 hr. The catalyst was filtered off and excess allyl chloride was removed in vacuo. The residue was purified by sublimation under reduced pressure (1 mm) to give adamantyldimethylchlorosilane (0.6 g) 91% yield. It has the following properties: Mp: 52°C ^1H -NMR: δ 0.30 (s, 6H), 1.71 (d, $J=2.6$ Hz, 6H), 1.74 (d, 3.1 Hz, 6H), 1.89 (br, m, 3H). ^{13}C -NMR: δ -2.58 (2C), 23.48 (1C), 27.32 (3C), 35.94 (3C), 37.29 (3C). IR: (CDCl_3): 2920 (m), 2900 (s), 2850 (m),

1450 (w), 1255 (m) cm^{-1} . MS: m/e (% rel. int.) 230 (4.4), 228 (11.8), 187 (1.3), 185 (4.4), 149 (18.6), 135 (100), 95 (9.1), 93 (35.7), 79 (22.2). The parent to parent +2 ratio is consistent with the presence of one chlorine.

Preparation of Adamantyldimethylchlorosilane from Adamantyldimethylsilanol.

Adamantyldimethylsilanol¹⁹ 140 mg (0.67 mmol) was stirred with freshly distilled SOCl_2 (1-2 ml). After gas evolution has ceased, the mixture was stirred for two more hours. Excess SOCl_2 was distilled off, leaving a solid yellowish residue which was sublimed under reduced pressure (1 mm) to yield 150 mg, 92% yield of adamantyldimethylchlorosilane as white crystals, mp 52°C .

Preparation of Adamantyldimethylsilane from Adamantyldimethylsilanol

Adamantyldimethylsilanol¹⁹ 94.5 mg (0.45 mmol) was refluxed with LiAlH_4 (100 mg, 2.5 mmol) in di-n-butyl ether at $110-115^\circ\text{C}$ for 1-1/2 hour. After an aqueous work up, the organic layer was dried over anhydrous MgSO_4 , filtered and the solvent removed by evaporation under reduced pressure. Adamantyldimethylsilane (75 mg) was obtained in 86% yield. It had properties in complete agreement with those previously reported.¹⁹

Preparation of t-Butyldimethylsilyl ethers

These silyl ethers were prepared according to the procedure Cunico and Bedell.⁶ The products showed IR and NMR data in complete agreement with literature values. In the case where ^{13}C NMR MS data have not been published we have included this data.

n-Butoxy-t-butyldimethylsilane had the following properties:

^{13}C -NMR: δ -5.29 (2C), 13.94 (1C), 18.44 (1C), 19.03 (1C), 26.02 (3C), 35.12 (1C), 63.02 (1C). MS: 188 (2), 173 (2), 131 (100), 115 (2), 89 (12), 75 (55).

Cyclohexoxy-*t*-butyldimethylsilane had the following properties:

^{13}C -NMR: δ -4.64 (2C), 18.28 (1C), 24.13 (2C), 25.70 (1C), 25.91 (3C), 35.94 (2C), 70.82 (1C).

Kinetic measurements to determine the half-life for hydrolysis of adamantyldimethylsilyl and *t*-butyldimethylsilyl ethers were carried out under conditions reported by Barton and Tully¹⁵ and by Cunico and Bedell¹⁶. All silyl ethers showed first order dependence of their base catalyzed hydrolysis rates over at least two half lives. The adamantyl silyl ethers hydrolyze somewhat faster than the corresponding *t*-butyl silyl ethers.

Table I
Half Life of Hydrolysis

	H^+	OH^-
<i>n</i> -butoxy- <i>t</i> -butyldimethylsilane	< 1 min	1 hr
adamantyl- <i>n</i> -butoxydimethylsilane	< 1 min	1 hr
cyclobutoxy- <i>t</i> -butyldimethylsilane	< 4 min	26 hr
adamantylcyclohexoxydimethylsilane	< 3 min	24 hr

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APPENDIX VIII

Silicon-29 NMR Studies of Polymethylhydrosiloxanes

by

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Abstract:

Si-29 NMR spectra of polymethylhydrosiloxanes $M-D_n^H-M$ from $n=3$ to 8 and 25 have been determined. Both chemical shifts and spin-lattice relaxation times have been measured. The stereochemistry at the adjacent chiral $-CH_3HSiO-$ unit influences the nearest neighbor Si-29 chemical shift. The T_1 values measured for $M-D_n^H-M$ systems are discussed.

Introduction

The high structural sensitivity of chemical shifts makes silicon-29 NMR a powerful tool for determination of the structure of oligomeric and polymeric siloxanes.¹ Detailed information can be obtained for the characterization of the different structural units,² for the determination of average chain lengths¹³ or for the degree of condensation of the siloxane framework.⁴

In the case of low molecular weight linear polydimethylsiloxane, both the Si-29 chemical shift and the spin-lattice relaxation time of each silicon atom have been determined.⁵ In the Si-29 NMR spectra, individual resonance lines can be found for each distinct silicon nucleus present in oligomers from $(\text{CH}_3)_3\text{Si-O}[(\text{CH}_3)_2\text{SiO}]_1\text{Si}(\text{CH}_3)_3$ to $(\text{CH}_3)_3\text{Si-O}[\text{Si}(\text{CH}_3)_2\text{O}]_8\text{Si}(\text{CH}_3)_3$. This degree of chemical shift resolution surpasses that observed in the ^{13}C or ^1H NMR of the same materials.⁶

Spin lattice relaxation times give information about the mobility at different points in polymer chains.⁷ The relatively high values of the Si-29 T_1 values found in polydimethylsiloxanes are consistent with high mobility of these polymer chains.⁸

In the case of polymethylhydrosiloxanes, some of the long range substituent chemical shifts are obscured.⁹ These spectral complications result from the asymmetry of the $-\text{CH}_3\text{HSiO}- (\text{D}^{\text{H}})$ unit. Silicon-29 chemical shifts for $(\text{CH}_3)_3\text{SiO}-[\text{CH}_3\text{H SiO}]_n\text{Si}(\text{CH}_3)_3$ ($n=1$ to 6 and ~ 50) have been reported.^{9,10} In the Si-29 NMR spectra the terminal trimethylsilyl (M) groups and the D^{H} moieties exhibit resonances in substantially different regions of the Si-29 NMR spectrum. Tacticity effects are essential in understanding the stereochemical features of substituted vinyl polymer chains. Harris and Kimber have reported two examples in which tacticity effects the Si-29 NMR

spectra of polymethylhydrosiloxanes.¹⁰ Tacticity and end group effects were used to interpret the observed fine structure in the proton decoupled spectrum of $(\text{CH}_3)_3\text{SiO}[\text{CH}_2\text{HSi-O}]_5\text{Si}(\text{CH}_3)_3$ ($\text{M-D}_5^{\text{H}}\text{-M}$): a triplet and a doublet. Analogous features in the Si-29 NMR of $\text{M-D}_n^{\text{H}}\text{-M}$ ($n=50$) to those observed with $\text{MD}_5^{\text{H}}\text{M}$ were explained as a result of either a completely atactic polymer or from the presence of equal amounts of the chains of the different tacticity. We have investigated in detail both the Si-29 chemical shifts and spin-lattice relaxation times¹¹ for $\text{MD}_n^{\text{H}}\text{M}$ ($n=3-8$ and 25). These results are presented here and interpreted in terms of tacticity and chain mobility.

Experimental Section

Materials

Polymethylhydrosiloxane, $\text{MD}_n^{\text{H}}\text{M}$ $n=25$, was obtained from Alfa Products and was used as received. $\text{MD}_n^{\text{H}}\text{M}$ oligomeric mixtures were prepared by cohydrolysis of trimethylchlorosilane and dichloromethylsilane.¹² Each of $\text{MD}_n^{\text{H}}\text{M}$ ($n=3-8$) oligomers was purified by glpc (5.5 ft column, 10% SE-30 on Chromosorb W). Their properties were in agreement with literature values.¹²

NMR Measurements

All Si-29 NMR spectra were recorded on an IBM WP-270SY NMR spectrometer (63.51 MHz for Si-29) equipped with an Aspect 2000 computer. All samples were run as 80% solution in acetone- d_6 in 10 mm OD NMR tubes. Nitrogen was bubbled through the solution for at least 30 minutes in order to remove dissolved oxygen. The ^2H signal of the solvent was used as an internal lock. Chemical shifts were calculated from the line positions in proton noise-decoupled spectra at ambient probe temperature (37°C). Hexamethyldisiloxane was used as

an external standard. For the ^1H decoupled Si-29 spectra, the experiments were performed by using the "gated decoupling without NOE effect" technique.¹³ In this technique, the decoupling rf power is switched on at the same time as the measuring rf pulse, and the decoupler is switched off when data acquisition stops. The following parameters were used: time pulse = 9 μs ($\alpha=45^\circ$), delay time=100 sec.

Spin Lattice Relaxation Measurements

The spin-lattice relaxation time (T_1) for all Si-29 nuclei were measured simultaneously by the inversion-recovery pulse method under conditions of proton noise decoupling.⁸ The pulse sequence utilized in these measurements was $(180^\circ-t-90^\circ-T)_n$ where the pulse interval time, t , is experimentally varied and T is set to at least five times the longest T_1 measured.¹⁴ In this sequence, a semilog plot of $(A_\infty - A_t)$ vs t results in a straight line with a slope equal to $-1/T_1$ where A_∞ and A_t were the transformed signals intensities from the 90° and 90°_t pulses. For each determination 8-12 sets of measurements were taken. The delay between pulse sequence was set at 300 sec.⁸

Results and Discussion

The Si-29 chemical shifts for the series $\text{MD}_n^{\text{H}}\text{M}$ ($n=3-8, 25$) reported in Table 1 were obtained by gated decoupling in order to eliminate the NOE effect.¹³ The values are reported relative to hexamethyldisiloxane, with positive values when the sample resonates at higher frequency than the reference. The group multiplicities which can be seen in each spectrum must be caused by asymmetry effects. The results are consistent with literature

values previously reported for $M-D_n^H-M$ oligomers ($n=3$ to 6). The value for $n=7,8$ are new. The number of peaks indicates that only the stereochemistry at the nearest-neighbor D^H influences the adjacent Si-29 resonance frequencies in the D^H region. The spectrum appears as a doublet and a triplet for either MD_3^H-M or MD_4^H-M . Since MD_3^H-M and MD_4^H-M are atactic the sequences $ddd=lll$, $ddl=ldd=lld=dll$, and $ldl=dld$ are equally probable. This gives a 1:2:1 triplet for D_b^H position in MD_3^H-M and MD_4^H-M . For the D_a^H position, the sequences $Mdd=Mll$ and $Mdl=Mld$ are equally probable. The results is a doublet for the D_a^H position in MD_3^H-M and MD_4^H-M .

The Si-29 spectrum of MD_n^H-M ($n=5-8, 25$) oligomers show four distinct areas of resonance, M at 8.13 to 8.50 ppm, D_a^H from -37.60 to -37.75 ppm, D_b^H from -36.69 to -37.25 ppm, and D_x^H ($x=3-n$) from -36.59 to -36.84. The predominant feature, a triplet at -36.6 to -36.8 ppm, can be assigned as that of the D^H groups which are three or more D^H groups away from the terminal M group of the oligomer. These coalesce to a triplet structure. Hence there is no detectable change in these chemical shifts and no new stereochemical effects for oligomers $M-D_n^H-M$ beyond $n=5$. (See Figure 1)

Once the spectra were fully assigned, it became feasible to investigate the Si-29 spin-lattice relaxation time of these polymethylhydrosiloxanes in order to provide useful information about their molecular motion. From the data in Table 1 the general trends in T_1 values can be rationalized. First, it seems to be reasonable that M had the longest T_1 because M units are able to spin freely at the ends of the chain while D^H units may only rotate through a restricted angle which obviously decreases their T_1 values. These values decrease gradually as the D^H units approach the middle of the chain. Second, all D^H units have comparable relaxation times within one molecule. This

implies that the motional process along the chains are quite similar. Third, since all the values of T_1 are relatively long it is clear that these systems are quite mobile. This is to be expected in the absence of crosslinking of linear MD_n^H chains. Fourth, the T_1 values of the different stereoisomers do not change significantly in oligomers and polymer systems. Tacticity has little effect on the motion occurring in these systems. The Si-29 T_1 measurements on the series of linear polymethylhydrosiloxanes demonstrate that localized motions along segments of the oligomer or polymer backbone result in Si-29 relaxation that rapidly becomes independent of chain length. Fifth, the T_1 values for the D^H groups in the polymethylhydrosiloxanes are consistently shorter than the T_1 values for the dimethylsiloxy group in polydimethylsiloxanes.³ Because of the Si-H bonds, the dipolar contribution is more effective and the relaxation times are shorter.

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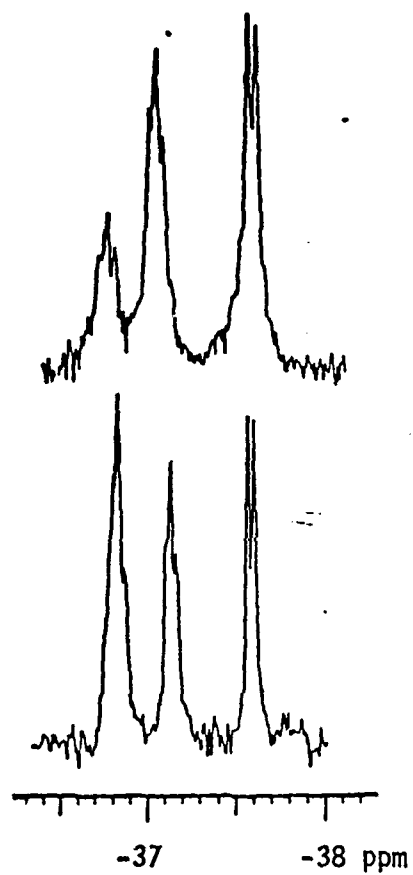


Figure 1. Si-29 {¹H} NMR of the D^H region of M-D₅^H-M (upper); and M-D₇^H-M (lower) oligomers.

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Table 1. Si-29 Chemical Shifts and T_1 Values for Polymethylhydrosiloxane

Compound ^c	M	$\delta^a (T_1)^b$			
		D_a^H	D_b^H	D_c^H	D_x^H
MD_3^H	7.97(50)	-37.87(42) -37.91(42)	-37.70 -37.73(30) -37.75		
MD_4^H	8.19(50)	-37.63(44) -37.68(38)	-37.14(32) -37.18(36) -37.22(41)		
MD_5^H	8.22(52)	-37.60(43) -37.64(44)	-37.04(44) -37.08(39) -37.12(38)	-36.75(42) -36.79(42) -36.84(41)	
MD_6^H	8.13(47)	-37.67(44) -37.72(46)	-37.11 -37.15(43) -37.19	-36.75 -36.79(43) -36.84	
MD_7^H	8.18(48)	-37.63(48) -37.67(43)	-37.05 -37.09(41) -37.13	-36.68(35) -36.69(35) -36.72(32)	
MD_8^H	8.24(49)	-37.61(46) -37.64(46)	-36.69 -37.02(42) -37.07	-36.59 -36.61(36) -36.63	
MD_{25}^H	8.13(59)	-37.67 -37.71	-37.11 -37.14 -37.19		-36.62(67) -36.66(37) -36.71(77)

^a Chemical shifts in ppm from hexamethyldisiloxane

^b In seconds; T_1 values where determined are in parenthesis

^c For the definition of the symbols, see the text. The D^H units are numbered from the end: $MD_{a b c}^H$.