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Reaction of Dimethyldichlorosilane, Phenylmethyldichlorosilane, or Diphenyldichlorosilane with Dimethyl Sulfoxide. Evidence for Silanone and Cyclodisiloxane Intermediates

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Summary: Dimethyldichlorosilane reacts with dimethyl sulfoxide (DMSO) in the presence of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane (I) to yield 2,2,4,4,7,7-hexamethyl-1,3-dioxa-2,4,7-trisilacycloheptane (Si-7), 2,2,4,4,6,6,9,9-octamethyl-1,3,5-trioxa-2,4,6,9-tetrasilacyclononane (Si-9), octamethylcyclotetrasiloxane (D$_4$), and decamethylcyclopentasiloxane (D$_5$). Similar reaction with phenylmethyldichlorosilane with DMSO and I yields 2,4,4,7,7-pentamethyl-2-phenyl-1,3-dioxa-2,4,7-trisilacycloheptane (^{Ph}Si-7), as well as an approximately 1:1 mixture of cis- and trans-2,4,6,6,9,9-hexamethyl-2,4-diphenyl-1,3,5-trioxa-2,4,6,9-tetrasilacyclononane (^{Ph}Si-9) and both 2,4,6-trimethyl-2,4,6-triphenylcyclotrisiloxane (^{Ph}D$_3$) and 2,4,6,8-tetramethyl-2,4,6,8-tetraphenylcyclotetrasiloxane (^{Ph}D$_4$). Likewise reaction of diphenyldichlorosilane with DMSO and I yields 4,4,7,7-tetramethyl-1,3-dioxa-2,2-diphenyl-2,4,7-trisilacycloheptane (^{PhPh}Si-7), 6,6,9,9-tetramethyl-1,3,5-trioxa-2,2,4,4-tetraphenyl-2,4,6,9-tetrasilacyclononane (^{PhPh}Si-9), and hexaphenylcyclotrisiloxane (^{PhPh}D$_3$).

Introduction

Over the last 30 years, there has been considerable interest in reactive π-multiple-bonded silicon intermediates.[1,2] Silanones, species which contain a silicon−oxygen double bond, have been generated by a variety of methods which involve high-energy processes such as pyrolysis or photolysis. Dimethylsilanone has been generated by pyrolysis of both D$_4$[3,4] and 3,3-dimethyl-6-oxa-3-silabicyclo[3,1,0]hexane.[5,6] Silanones have often been generated by methods which involve conversion of an initial reactive silicon-containing intermediate into a silanone. For example, dimethylsilene, produced by pyrolysis of 1,1-dimethylsilacyclobutane at ~500 °C, reacts with non-enolizable ketones such as benzophenone to yield dimethylsilanone.[7−9] Photochemically generated dimethylsilylene deoxygenates epoxides,[10,11] nitrous oxide,[12] or DMSO[13,14] to yield dimethylsilanone and alkenes, nitrogen, or dimethyl sulfide, respectively. Reactive dimethylsilanone is also formed in the low-temperature reactions of DMSO with either 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silirene or hexamethylsilirane.[15] The reactions described herein appear to generate silanone intermediates at low temperature.

Cyclodisiloxanes have been proposed as reactive intermediates in many reactions which involve silanone intermediates. Usually, cyclodisiloxanes are suggested to dimerize to yield stable cyclotetrasiloxane or to undergo insertion of a silanone intermediate to yield cyclotrisiloxane products.[16,17] Recently, stable cyclodisiloxanes, in which both of the silicon atoms are substituted by very large groups, have been prepared by the oxidation of stable disilenes.[18−20] Such cyclodisiloxanes are extremely unusually compounds which press the limits of current bonding theory.[21] We will present evidence that strongly suggests that both cyclodisiloxanes as well as silanones are involved as reactive intermediates in the reactions discussed in this paper.

We were attracted to a 30-year-old French patent by Goossens which reports that reaction of diphenyldichlorosilane with DMSO in heptane leads to ^{PhPh}D$_3$ (91%), and ^{PhPh}D$_4$ (9%).[22] While several other examples of this reaction are described in the patent, no products containing sulfur or chlorine were identified. Recently, this reaction has been rediscovered by Basenko and Voronkov.[23,24] They suggest, on the basis of trapping experi-

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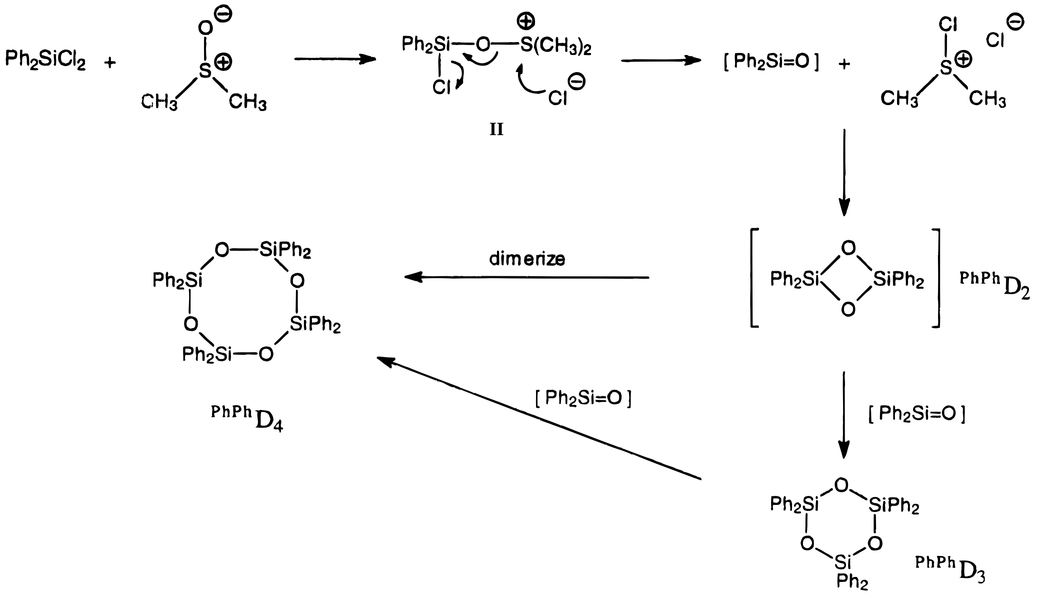
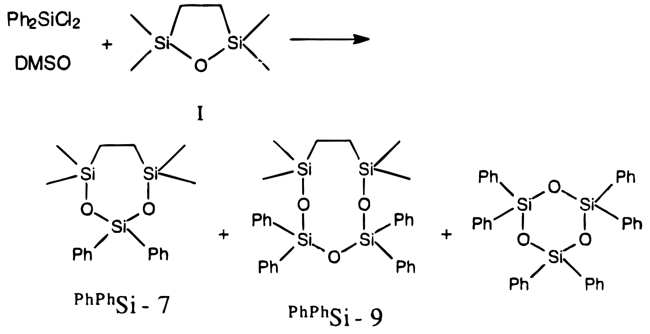
Scheme 1



ments with hexamethyldisiloxane (MM), that silanones are involved as intermediates in this reaction.

Consideration of possible mechanisms for the reaction of diphenyldichlorosilane with DMSO also lead us to speculate that diphenylsilanone might be involved as a reactive intermediate. Thus nucleophilic attack by the sulfoxide oxygen on the silyl center of diphenyldichlorosilane with loss of chloride would lead to a (diphenylchlorosiloxy)dimethylsulfonium/chloride ion pair (II). Collapse of this ion pair by attack of the chloride anion on the sulfonium ion center would lead to diphenylsilanone and a dimethylchlorosulfonium/chloride ion pair. Head to tail dimerization of diphenylsilanone would lead to $^{PhPh}D_2$. Subsequent insertion of diphenylsilanone into the reactive ring-strained Si−O single bonds of $^{PhPh}D_2$ would lead to $^{PhPh}D_3$, while dimerization of $^{PhPh}D_2$ or insertion of diphenylsilanone into one of the Si−O single bonds of $^{PhPh}D_3$ might yield $^{PhPh}D_4$. Dimethylchlorosulfonium/chloride ion pairs have been prepared by Corey and Kim by reaction of dimethyl sulfide and chlorine at low temperature.[25]

To test this hypothesis, we have carried out the reaction of diphenyldichlorosilane and DMSO in the presence of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane (I). Silanone intermediates have often been trapped in-situ by insertion of their Si−O double bond into the ring strained Si−O single bonds of I.[5] In fact, from this reaction we have isolated 4,4,7,7-tetramethyl-1,3-dioxa-2,2-diphenyl-2,4,7-trisilacycloheptane (^{PhPh}Si-7) and 6,6,9,9-tetramethyl-1,3,5-trioxa-2,2,4,4-tetraphenyl-2,4,6,9-tetrasilacyclononane (^{PhPh}Si-9), $^{PhPh}D_3$, and poly(2,2,5,5-tetramethyl-1-oxa-2,5-disilapentane) (polymer).[26,27] Dimethyl sulfide and HCl are given off in the reaction.



The formation of ^{PhPh}Si-7 may result from insertion of diphenylsilanone into a Si−O single bond of I. The formation of ^{PhPh}Si-9 may be a consequence of insertion of a second 1 equiv of diphenylsilanone into a Si−O single bond of ^{PhPh}Si-7. Alternatively, ^{PhPh}Si-9 may result from reaction of $^{PhPh}D_2$ with I. In a control experiment, we have attempted to react ^{PhPh}Si-7 with diphenylsilanone generated by reaction with diphenyldichlorosilane and DMSO. ^{PhPh}Si-7 is stable under the reaction conditions; no ^{PhPh}Si-9 is formed. Recovered ^{PhPh}Si-7 and $^{PhPh}D_3$ are the only silicon-containing reaction products. On this basis, we suggest that ^{PhPh}Si-9 is formed by reaction of the angle-strained Si−O bond of I with an extremely reactive Si−O bond of $^{PhPh}D_2$. Apparently, the Si−O single bonds of ^{PhPh}Si-7 are not sufficiently reactive to react with diphenylsilanone. The observation that no 8,8,11,11-tetramethyl-1,3,5,7-tetraoxa-2,2,4,4,6,6-hexaphenyl-2,4,6,8,11-pentasilacycloundecane is found suggests that ^{PhPh}Si-7 also does not react with $^{PhPh}D_2$. The dimethylchlorosulfonium/chloride ion pair will react with any adventious water to yield hydrochloric acid.[25] The polymer apparently results from acid-catalyzed ring-opening polymerization of I.

Similar reaction of dimethyldichlorosilane, DMSO, and I gave poly(2,2,5,5-tetramethyl-1-oxa-2,5-disilapentane), 2,2,4,4,7,7-hexamethyl-1,3-dioxa-2,4,7-trisilacycloheptane (Si-7), 2,2,4,4,6,6,9,9-octamethyl-1,3,5-trioxa-2,4,6,9-tetrasilacyclononane (Si-9), D_4, D_5, and polymer. We suggest that Si-7 is formed by the insertion of dimethylsilanone into one of the Si−O single bonds of I. In a control experiment between Si-7, dimethyldichlorosilane, and DMSO, no Si-9 was formed.

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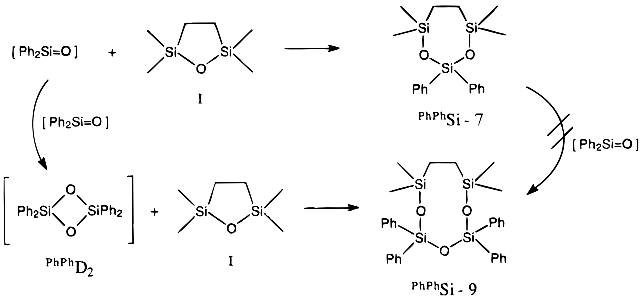

On the basis of a similar line of reasoning, we conclude that Si-9 is probably formed by reaction of D_2 with I.

Finally, reaction of phenylmethyldichlorosilane with DMSO and I gave 2,4,4,7,7-pentamethyl-2-phenyl-1,3-dioxa-2,4,7-trisilacycloheptane (^{Ph}Si-7), a 1:1 mixture of *cis*- and *trans*-2,4,6,6,9,9-hexamethyl-2,4-diphenyl-1,3,5-trioxa-2,4,6,9-tetrasilanonane (^{Ph}Si-9), 2,4,6-trimethyl-2,4,6-triphenylcyclotrisiloxane ($^{Ph}D_3$), 2,4,6,8-tetramethyl-2,4,6,8-tetraphenylcyclotetrasiloxane ($^{Ph}D_4$), and polymer.

Experiments which provide evidence for the formation of the dimethylchlorosulfonium/chloride ion pair in this reaction have been carried out. Thus reaction of DMSO and trimethylchlorosilane has been shown to yield a dimethylchlorosulfonium/trimethylsiloxyl ion pair which decomposes to yield methanesulfenyl chloride which undergoes electrophilic addition to alkenes.[28,29] Similarly, we have found that reaction of DMSO and diphenyldichlorosilane in the presence of cyclohexene yields *trans*-1-chloro-2-methylthiocyclohexane in addition to $^{PhPh}D_3$. We have also isolated dimethyl sulfide in these reactions.[30] It is possible that the dimethylchlorosulfonium/chloride ion pair breaks down to yield dimethyl sulfide and chlorine under our experimental conditions.[25]

We have also reexamined the system reported by Voronkov. We find, indeed, that the reaction of phenylmethyldichlorosilane and DMSO with $(Me_3Si)_2O$ (MM) yields 1,1,1,3,5,5,5-heptamethyl-3-phenyltrisiloxane, the expected product of insertion of phenylmethylsilanone into the Si–O single bond of MM, as well as 1,1,1,3,5,7,7,7-octamethyl-3,5-diphenyltetrasiloxane. The fact that octamethyltrisiloxane (MDM) does not react with DMSO and phenylmethyldichlorosilane under these conditions to yield 1,1,1,3,5,5,7,7,7-heptamethyl-3-phenyltetrasiloxane suggests that 1,1,1,3,5,7,7,7-octamethyl-3,5-diphenyltetrasiloxane probably is formed by reaction of MM with $^{Ph}D_2$. Apparently, there is a significant difference in reactivity between the Si–O bonds MM and MDM toward phenylmethylsilanone.

In conclusion, the reaction of I with dichlorosilanes and DMSO yields products which can economically be explained by reactions which involve silanone and cyclodisiloxane intermediates.

Experimental Section

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC-250 spectrometer operating in the FT mode. ^{29}Si NMR spectra were recorded on an IBM Bruker WP-270-SY spectrometer. Five percent weight/volume solutions in chloroform-*d* were used to obtain NMR spectra. ^{13}C NMR spectra were run with broad band proton decoupling. A heteronuclear gated decoupling pulse sequence (NONOE) with a 20 s delay was used to acquire ^{29}Si NMR spectra.[31] These were externally referenced to TMS. Chloroform ($CHCl_3$) was used as an internal standard for ^{1}H and ^{13}C NMR spectra. IR spectra of chloroform solutions were recorded on an IBM FT-IR spectrometer. UV spectra of cyclohexane solutions were acquired on a Shimadzu UV-260 ultraviolet visible spectrometer. GC/MS was performed on a Hewlett Packard 5890 GC equipped with a 30 m DB-5 capillary column and a MS detector. Elemental analysis was performed by Oneida Research Services Inc., Whitesboro, NY.

2,2,5,5-Tetramethyl-1-oxa-2,5-disilacyclopentane (I), dimethyldichlorosilane, phenylmethyldichlorosilane, and diphenyldichlorosilane were purchased from Gelest. DMSO was distilled from calcium hydride prior to use. During the course of our experiments, the commercial availability of I ceased. For this reason, a number of experiments were conducted with I prepared in our laboratories. I from either source gave identical results. $CHCl_3$ was dried over 4 Å molecular sieves. All reactions were conducted under a purified nitrogen atmosphere.

2,2,5,5-Tetramethyl-1-oxa-2,5-disilacyclopentane (I) was prepared by following literature procedures by hydrolysis of 1,2-bis(dimethylchlorosilyl)ethane which was prepared by platinum-catalyzed hydrosilation of dimethylvinylchlorosilane with dimethylchlorosilane.[32]

Reaction of Diphenyldichlorosilane, DMSO, and I. The reaction of diphenyldichlorosilane and DMSO was run in flame-dried glassware under a nitrogen atmosphere. Diphenyldichlorosilane (2.53 g, 10 mmol), I (1.60 g, 10 mmol), and $CHCl_3$ (10 mL) were placed in a 50 mL three neck flask, equipped with a reflux condenser, a Teflon-covered magnetic stirring bar, and a pressure-equalizing addition funnel. DMSO (0.78 g, 10 mmol) and chloroform (5 mL) were placed in the addition funnel and were added dropwise over the course of 0.5 h to the well-stirred solution of diphenyldichlorosilane and I. An exothermic reaction with gas evolution occurs. Acid was detected in these gases by use of litmus paper. The reaction mixture was stirred at room temperature for 12 h. Chloroform (20 mL) was added and the organic solution extracted three times with water. The $CHCl_3$ solution was dried over anhydrous magnesium sulfate and filtered, and the volatile solvents were removed by evaporation under reduced pressure. Absolute ethanol (10 mL) was added to the viscous residue. This caused the precipitation of a white solid which was separated by filtration. Evaporation of the ethanol solution gave an oily residue which was bulb to bulb distilled under high vacuum to give a 1.61 g, 45% yield of Ph_2Si-7. The white solid filtrate was partially soluble in hot hexane (10 mL). Evaporation of the hexane gave a white crystalline solid which was recrystallized from hexane. In this way, a 0.28 g, 10% yield of Ph_2Si-9 was isolated. The white material which was insoluble in hexane was recrystallized from a mixture of benzene and ethanol. In this way, a 0.56 g, 28% yield of $^{PhPh}D_3$, mp 185–186 °C (lit. mp 190 °C),[33] and polymer, 0.44 g, 28% yield, was obtained.[27]

4,4,7,7-Tetramethyl-1,3-dioxa-2,2-diphenyl-2,4,7-trisilacycloheptane (^{PhPh}Si-7) is a white crystalline solid, mp 54–55 °C (lit. mp 57–58 °C).[34] ^{1}H NMR: δ 0.13 (s, 12H), 0.81 (s, 4H), 7.36 (m, 6H), 7.59 (m, 4H). ^{13}C NMR: δ −0.17, 10.75, 127.60, 129.73, 134.07, 136.35. ^{29}Si NMR: δ −41.91, 13.75. IR: ν 3072, 3054, 3028, 3005, 2959, 2897, 1592, 1430, 1254,

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1126, 1118, 1060, 1027, 998, 909, 832, 789, 737, 701 cm^{-1}. UV (λ, nm (ϵ)): 271 (348), 265 (502), 260 (453), 255 (299). GC/MS (*m*/*e* (relative intensity, %)): 358 (22.7) M$^{\bullet+}$, 343 (39.4) M − 15$^+$, 329 (72.7), 315 (63.6), 313 (31.8), 299 (9.1), 280 (24.2), 265 (100.0), 251 (37.9), 237 (50.0), 193 (51.5).

6,6,9,9-Tetramethyl-1,3,5-trioxa-2,2,4,4-tetraphenyl-2,4,6,9-tetrasilacyclononane (^{PhPh}Si-9) is a white crystalline solid, mp 124−125 °C. ^{1}H NMR: δ −0.08 (s, 12H), 0.51 (s, 4H), 7.17 (p, 12H, J = 6 Hz), 7.45 (d, 8H, J = 6 Hz). ^{13}C NMR: δ −0.15, 8.79, 127.61, 129.77, 134.19, 135.97. ^{29}Si NMR: δ −34.01, 23.93. IR: ν 2952, 2876, 1695, 1592, 1482, 1454, 1417, 1351, 1333, 1310, 1249, 1169, 1133, 1084, 1054, 993, 911, 832, 779, 735 cm^{-1}. UV (λ, nm (ϵ)): 271 (736), 265 (1014), 260 (944), 255 (694). GC/MS (*m*/*e* (relative intensity, %)): 541 (19.7) M − 15$^+$, 527 (13.6), 479 (15.2), 449 (6.1), 337 (10.6), 315 (45.5), 259 (28.8), 253 (36.4), 197 (100.0). Anal. Calcd for $C_{30}H_{36}Si_4O_3$: C, 64.70; H, 6.52. Found: C, 64.77; H, 6.62.

Reaction of Phenylmethyldichlorosilane with DMSO and I. I (5 g, 31 mmol), phenylmethyldichlorosilane (11.9 g, 62 mmol), and DMSO (4.87 g, 62 mmol) were reacted as above. ^{Ph}Si-7 (3.7 g, 40% yield) and ^{Ph}Si-9 (1.6 g, 12% yield) were separated by column chromatography on a silica gel column with hexane as the eluent.

2,4,4,7,7-Pentamethyl-2-phenyl-1,3-dioxa-2,4,7-trisilacycloheptane (^{Ph}Si-7) had properties and ^{1}H, IR, and mass spectra in complete agreement with literature values.[35]

***cis*- and *trans*-2,4,6,6,9,9-Hexamethyl-2,4-diphenyl-1,3,5-trioxa-2,4,6,9-tetrasilacyclononane (^{Ph}Si-9).** The mixture of *cis*- and *trans*-^{Ph}Si-9 was not separated. IR, UV, and ^{29}Si NMR spectra of the mixture are reported. The isomers are separable by GC/MS on a capillary column. The lower intensity isomer, which we have assigned as *cis*, elutes first. The mass spectra of the *cis* and *trans* isomers are identical. It is possible to assign ^{1}H and ^{13}C resonances to individual stereoisomers due to consistent differences in peak intensities. The ratio of *cis* to *trans* stereoisomer is ∼44 to 55. IR: ν 3072, 2958, 2901, 1429, 1257, 1126, 1077, 1029, 998, 791, 758, and 728 cm^{-1}. UV (λ, nm (ϵ)): 270 (650), 264 (861), 259 (837), 253 (620). ^{29}Si NMR: δ 10.51 and −33.01. Mass spectra (*m*/*e* (rel intensity)): 423 (3) M$^{\bullet+}$, 417 (79) M − 15$^+$, 403 (36), 354 (15), 269 (18), 253 (53), 197 (53), 135 (100). Data for *cis*-^{Ph}Si-9: ^{1}H NMR δ 0.64 (s, 6H), 0.14 (s, 6H), 0.17 (s, 6H), 0.76 (s, 4H), 7.31−7.45 (m, 6H), 7.67−7.71 (m, 4H); ^{13}C NMR δ −0.26, 0.17, 9.73, 127.66, 129.48, 133.25, 137.97. Data for *trans*-^{Ph}Si-9: ^{1}H NMR δ 0.22 (s, 6H), 0.31 (s, 6H), 0.43 (s, 6H), 0.75 (s, 4H), 7.31−7.45 (m, 6H), 7.58−7.62 (m, 4H); ^{13}C NMR δ −0.16, 0.07, 9.28, 127.57, 129.57, 133.34, 137.64.

Reaction of Dimethyldichlorosilane with DMSO and I. I (8.0 g, 50 mmol), dimethyldichlorosilane (9.7 g, 75 mmol), and DMSO were added sequentially at −60 °C to 50 mL of $CHCl_3$. The reaction mixture was vigorously stirred and allowed to warm slowly to room temperature over 2 h. The reaction mixture was washed twice with aqueous sodium bicarbonate and once with distilled water. The organic layer was dried over anhydrous magnesium sulfate and filtered, and half of the chloroform was removed by evaporation under reduced pressure. Poly(2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane) (3.5 g, M_w/M_n = 16 500/14 300) was precipitated by addition of methanol. The rest of the chloroform was removed by evaporation under reduced pressure. Analysis of the crude reaction mixture by GC/MS showed 3% D_4, 74% Si-7, 1.1% decamethylcyclopentasiloxane, 7% Si-9, and 11% dodecamethylcyclohexasiloxane. The solution was fractionally distilled through a micro Teflon spinning band column which had 30 theoretical plates. In this way, 4.3 g, 42% Si-7 and 0.7 g, 4% Si-9 yields were obtained.

2,2,4,4,7,7-Hexamethyl-1,3-dioxa-2,4,7-trisilacycloheptane (Si-7) had ^{1}H NMR, IR, and GC/MS in agreement with literature values.[5] Neither ^{13}C nor ^{29}Si NMR data have been previously reported. ^{13}C NMR: δ −0.23, 0.74, 10.89. ^{29}Si NMR: δ 11.24, −14.50.

2,2,4,4,6,6,9,9-Octamethyl-1,3,5-trioxa-2,4,6,9-tetrasilanonane (Si-9) has the following properties. IR: ν 2963, 2902, 1261, 1079, 803, 700, 668 cm^{-1}. ^{1}H NMR: δ 0.03 (s, 12H), 0.06 (s, 12H), 0.61 (s, 4H). ^{29}Si NMR: δ 8.73, −20.57. GC/MS (*m*/*e* (rel intensity)): 293 (100), M − 15$^+$, 279 (17), 265 (33), 207 (38), 191 (18), 73 (32).

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