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SYNTHESIS OF SPIROCYCLOSILOXANES BY FLASH VACUUM PYROLYSIS OF 2,7-DIMETHYL-2,3 : 7,8-DIEPOXY-5-SILASPIRO[4.4]NONANE AND CYCLOSILOXANES

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Summary

Flash vacuum pyrolysis (FVP) of 2,7-dimethyl-2,3 : 7,8-diepoxy-5-silaspiro[4.4]-nonane with cyclotetra- or cyclopenta-siloxanes (D_4 or D_5) leads to products which apparently result from transannular insertion of [O=Si=O] or an equivalent synthon into Si–O single bonds of D_4 or D_5: 2,4,6,8,10-pentasila-1,3,5,7,9,11-hexaoxa-spiro[5.5]undecane (D_2QD_2) and 2,4,6,8,10,12-hexasila-1,3,5,7,9,11,13-heptaoxa-spiro[5.7]tridecane (D_3QD_2) respectively. The scope of this reaction has been explored with substituted cyclotetrasiloxanes such as heptamethylcyclotetrasiloxane, vinylheptamethylcyclotetrasiloxane, phenylheptamethylcyclotetrasiloxane, and chloromethylheptamethylcyclotetrasiloxane. In all cases, substituted spirocyclosiloxane products (D_2QDD^x) were obtained. ^{29}Si NMR has proved particularly useful for the assignment of structure of these spirocyclosiloxanes.

Silanones, reactive species which possess a Si–O double bond, have been generated as transient intermediates in a variety of reactions [1]. For example, silenes [2–6], silaimines [7,8], and disilenes [9–11] have been proposed to react with non-enolizable ketones and aldehydes via an initial [2 + 2] cycloaddition to yield silaoxetanes, 1-oxa-2-sila-3-azacyclobutanes or 1,2-disilaoxetanes, respectively. These unstable heterocyclic intermediates decompose by a retro [2 + 2] cycloaddition reaction to yield reactive silanones and alkenes, imines or silenes respectively. Silanones have also been proposed as intermediates in the pyrolysis of cyclotetrasiloxanes [13–16]. An unstable silaoxetane which decomposes by a retro [2 + 2] cycloaddition to yield dimethylsilanone and 2-methyl-2-butene has been generated by the platinum catalyzed intramolecular hydrosilation reaction of α,α-dimethylal-

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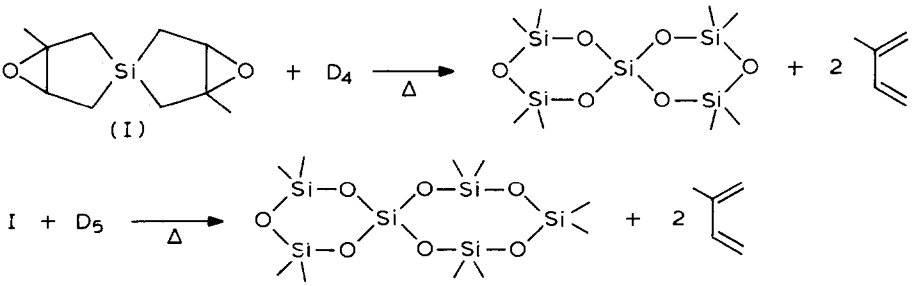
lyloxydimethylsilane [12]. Alternatively, silylenes can be oxidized to silanones by reaction with sulfoxides [17,18], N_2O [19] or epoxides [20]. Both silirenes and siliranes react with DMSO to yield silanones and respectively alkynes or alkenes [21]. Retro Diels–Alder reaction of unstable 7-oxa-8-silabicyclo[2.2.2]octadienes also yields silanones and benzene derivatives [22]. Reactive silanones, in general, undergo cyclooligomerization to yield cyclotri- and cyclotetra-siloxanes.

We have recently reported that flash vacuum pyrolysis (FVP) of 6-oxa-3-silabicyclo[3.1.0]hexanes provides a convenient route to silanones [23,28]. Likewise, FVP of 2,7-dimethyl-2,3 : 7,8-diepoxy-5-silaspiro[4.4]nonane (I) serves to generate a synthon for silicon dioxide [O=Si=O] which inserts into Si–O single bonds of trapping reagents. Thus, co-pyrolysis of I with hexamethylcyclotrisiloxane (D_3) gave isoprene and 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 (D_3QD_3). This 2/1 product may be formed by sequential insertion of the Si–O double bonds resulting from the stepwise decomposition of I into Si–O single bonds of two molecules of D_3 [23–25]. These experiments do not require the existence of free [O=Si=O].

Although [O=Si=O] is an unusual species, it has been previously produced by reaction of silicon monoxide with atomic oxygen in an argon matrix. The infrared spectrum of [O=Si=O] has been reported [26]. Silicon dioxide has also been detected by both negative and positive ion mass spectrometry in the upper atmosphere [27,28].

We should like to report that co-pyrolysis of I and octamethylcyclotetrasiloxane (D_4) or I and decamethylcyclopentasiloxane (D_5) on the other hand yield 1/1 adducts of [O=Si=O] and D_4 or D_5, respectively. These apparently result from initial insertion of a Si–O double bond of [O=Si=O] into one of the Si–O single bonds of D_4 or D_5 followed by an intramolecular trans-annular insertion of the other Si–O double bond into a Si–O single bond across the ring. In the case of D_4 this yields 2,2,4,4,8,8,10,10-octamethyl-2,4,6,8,10-pentasila-1,3,5,7,9,11-hexaoxaspiro[5.5]undecane (D_2QD_2) while with D_5 the product is 2,2,4,4,8,8,10,10,12,12-decamethyl-2,4,6,8,10,12-hexasila-1,3,5,7,9,11,13-heptaoxaspiro[5.7]tridecane (D_3QD_2). These spirosiloxanes (D_2QD_2) and (D_3QD_2) have previously been prepared in low yield (~ 1%) by the co-hydrolysis of dimethyldichlorosilane and silicon tetrachloride followed by thermal equilibration at 375–600°C [29,30]. As far as we are aware no other spiro-siloxanes are known.



^{29}Si NMR chemical shifts have been particularly useful in the assignment of structure to the spirosiloxane products. Thus a significant effect of ring size has been previously observed on the ^{29}Si NMR chemical shifts in cyclic siloxanes. Specifically, the ^{29}Si NMR chemical shift for D_3 comes at -9.2 ppm while that for

D_4 comes at −20.0 ppm. Silicate silicon atoms have been previously observed at −105 ppm.[31] The ^{29}Si NMR data for D_2QD_2 (−5.78 and −95.34 ppm) (4/1) is consistent with the symmetrical spirosiloxane structure. Likewise the ^{29}Si NMR of D_3QD_2 (−6.41, −17.14, −18.64, and −100.28 ppm) (2/2/1/1/) is in accord with the D_3QD_2 structure in which there are two equivalent silicon atoms in a six-membered siloxane ring, two non-equivalent types of silicon atoms in a ratio of 2/1 in an eight-membered siloxane ring, and one silicate silicon atom.

The versatility of this new approach to the synthesis of spirosiloxanes has been explored by conducting co-pyrolysis reactions of I with a number of substituted cyclotetrasiloxanes: heptamethylcyclotetrasiloxane (D_3D^H), phenylheptamethylcyclotetrasiloxane (D_3D^{Ph}), vinylheptamethylcyclotetrasiloxane (D_3D^{Vi}), and chloromethylheptamethylcyclotetrasiloxane ($D_3D^{CH_2Cl}$). D_3D^H, D_3D^{Ph}, and D_3D^{Vi} were prepared by co-hydrolysis of 1,5-dichlorohexamethyltrisiloxane and methyldichlorosilane, phenylmethyldichlorosilane or vinylmethyldichlorosilane, respectively. $D_3D^{CH_2Cl}$, on the other hand, was prepared by free radical chlorination of D_4. In all cases the ^{29}Si NMR spectra and other properties of the trapped products were consistent with the expected spirosiloxane product (D_2QDD^x). The fact that I is easily prepared in two steps starting from isoprene and diethoxydichlorosilane makes this new approach to the preparation of specific spirosiloxanes viable [23,32].

Experimental

All products were purified by preparative GLPC on a GOW-MAC 550 GC. A 1.5′(A), 6′(B), or 10′(C) × 1/4″ copper column which was packed with 20% SE-30 on Chromosorb W NAW 60/80 mesh was employed for the purification. These columns were deactivated immediately prior to use by silation with hexamethyldisilazane. ^{1}H and ^{29}Si NMR spectra were obtained on a Bruker WP-270-SY spectrometer operating in the Fourier Transform mode. Ten to fifteen percent solutions in chloroform-*d* were used to obtain ^{29}Si spectra while five percent solutions were used for ^{1}H and ^{13}C spectra. ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer operating in the Fourier Transform mode. ^{29}Si NMR spectra were run with gated broad band proton decoupling with a 100 sec pulse delay to minimize the NOE effect [39]. A DEPT pulse sequence was used to obtain ^{29}Si NMR spectra of compounds in which all silicon atoms have at least one methyl group bonded to them [40]. For ^{1}H, ^{13}C, and ^{29}Si NMR spectra chloroform was utilized as an internal standard. All chemical shifts reported are referenced to tetramethylsilane. IR spectra were recorded on a Perkin–Elmer 281 spectrometer. The IR spectra of oils were measured as neat samples on NaCl plates while those of solids were determined utilizing 5% chloroform solution in NaCl solution cells. Low resolution mass spectra were obtained on a Hewlett Packard 5985A GC-MS at an ionizing voltage of 70 eV. A 20″ × 1/8″ column packed with 2% OV-101 on 80/100 mesh Chromosorb W was used in the gas chromatographic inlet of the mass spectrometer. High resolution mass spectra were obtained with an A.E.I. MS-902 mass spectrometer at an ionizing voltage of 20 eV. Exact masses were determined by peak matching against known masses of perfluorokerosene.

2,7-Dimethyl-5-silaspiro[4.4]nona-2,7-diene and the corresponding diepoxide: 2,7-dimethyl-2,3 : 7,8-diepoxy-5-silaspiro[4.4]nonane (I) were prepared by literature methods. Their spectral and physical properties were in complete agreement with those previously reported [23,32].

Octamethylcyclotetrasiloxane (D_4), decamethylcyclopentasiloxane (D_5), 1,5-dichlorohexamethyltrisiloxane, methyldichlorosilane, phenylmethyldichlorosilane, and vinylmethyldichlorosilane were purchased from Petrarch Systems Inc. D_5 was purified by preparative GLPC on column C immediately prior to use. All other reagent were used as received.

Yields of spirosiloxane products obtained from the pyrolysis experiments are those actually obtained by preparative GLPC. These are based on the available "[O=Si=O]" produced after correction for reaction of this reactive species with the walls of the pyrolysis tube. This loss was based on the increased weight of the pyrolysis tube measured after the experiment. Before and after each pyrolysis reaction, the pyrolysis tube was baked at 560°C at atmospheric pressure for 18 h before weighing it. When 2 g of I was utilized, the theoretical amount of "[O=Si=O]" available is 0.6 g (10 mmol). The usual weight gain of the pyrolysis tube under these conditions was about 0.36 g. Thus yields of spirosiloxane products are thus calculated on the basis of 0.24 g (4 mmol) of "[O=Si=O]" available.

Heptamethylcyclotetrasiloxane (D_3D^H) [33]

A 2-l round-bottom three-necked flask was equipped with a pressure equalizing addition funnel, Tru-bore mechanical stirrer equipped with a Teflon propeller blade and a reflux condenser topped with a nitrogen gas inlet. The apparatus was flame dried under an atmosphere of nitrogen. 1,5-Dichlorohexamethyltrisiloxane (45 g), (0.16 mol) and methyldichlorosilane (18.4 g, 0.16 mol) were dissolved in 450 ml of dry THF and the solution was placed in the addition funnel. The flask was charged with 1200 ml of THF, water (5.8 ml, 0.32 mol) and triethylamine (90 ml, 0.64 mol). The flask was cooled in a dry-ice acetone bath while the THF solution of chlorosilanes was added dropwise over 5 h with vigorous stirring. After allowing the solution to warm to room temperature overnight, the precipitated triethylammonium chloride was removed by suction filtration through a Buchner funnel. The THF solution was then washed with 300 ml aliquots of 0.05 *N* aqueous H_2SO_4 until the aqueous layer tested acidic with pH paper. The THF solution was then washed with two 300 ml portions of saturated aqueous NaCl, dried over anhydrous $MgSO_4$, filtered and the THF removed by distillation at atmospheric pressure until about 400 ml of solution remained. The remaining solution was fractionally distilled through a 10 cm vacuum jacketed Vigreux column. A fraction (b.p. 40–50°C/0.5 mmHg) was further purified by preparative GLPC. D_3D^H, 2.1 g, 5% yield was obtained. ^1H NMR: δ 0.08 (s, 6H), 0.10 (s, 6H), 0.11 (s, 6H), 0.15 (d, 3H, J 1.46 Hz), 4.66 (q, 1H, J 1.46 Hz). These values were in agreement with those previously reported [34]. ^{13}C NMR: δ 0.37 (2C), 0.74 (4C), 0.91 (1C). ^{29}Si NMR: δ -17.67 (2Si), -18.82 (1Si), -34.81 (1Si). IR: ν 1076 cm^{-1} Si–O–Si, and 2155 cm^{-1} Si–H. MS m/e (rel. intensity): 281 (5.8%) $M-1^+$; 267 (100%) $M-15^+$; 207 (24.5%); 193 (15.7%).

Vinylheptamethylcyclotetrasiloxane (D_3D^{Vi}) [35]

1,5-Dichlorohexamethyltrisiloxane (55.4 g, 0.2 mol) and vinylmethyldichlorosilane (28.2 g, 0.2 mol) were co-hydrolyzed as above. D_3D^{Vi} distilled at 32–33°C/1 mmHg and 5% (3 g) yield was obtained. A small impurity of *sym*-trivinyltrimethylcyclotrisiloxane was detected by GLPC. ^{1}H NMR: δ 0.07 (s, 6H), 0.08 (s, 6H), 0.09 (s, 6H), 0.14 (s, 3H), 5.75–6.07 (m, 3H). ^{13}C NMR: δ -0.84 (1C), 0.69 (4C), 0.73 (2C), 132.90 (1C), 136.92 (1C). ^{29}Si NMR: δ -18.49 (2Si), -18.91 (1Si), -33.47 (1Si). IR: ν 1600 cm^{-1} C=C, 1068 cm^{-1} Si-O-Si. MS *m/e* (rel. intensity): 293 (100%) $M-15^+$, 281 (11.8%) $M-27^+$, 265 (26.7%).

Phenylheptamethylcyclotetrasiloxane (D_3D^{Ph}) [36]

1,5-Dichlorohexamethyltrisiloxane (45 g, 0.16 mol) and phenylmethyldichlorosilane (32.8 g, 0.16 mol) were co-hydrolyzed as above. The resulting oil was separated by fractional distillation. D_3D^{Ph} distilled at 55°C/10^{-4} mmHg. This material was shown to be 91% pure by GLPC. D_3D^{Ph} was purified on column A. In this way, 5.1 g, a 9% yield was obtained. ^{1}H NMR: δ 0.05 (s, 9H), 0.11 (s, 3H), 0.14 (s, 6H), 0.31 (s, 3H), 7.27–7.64 (m, 5H). ^{13}C NMR: δ -0.18 (1C), 0.65 (2C), 0.75 (4C), 127.71 (2C), 129.68 (1C), 133.31 (2C), 137.63 (1C). ^{29}Si NMR: δ -18.19 (2Si), -18.74 (1Si), -32.77 (1Si). IR: ν 1065 cm^{-1} Si–O–Si. MS *m/e* (rel. intensity): 343 (100%) $M-15^+$, 327 (29.4%), 253 (8.2%), 249 (8.2%), 207 (1.9%).

Chloromethylheptamethylcyclotetrasiloxane ($D_3D^{CH_2Cl}$) [37]

D_4 (62 ml, 0.2 mol), SO_2Cl_2 (8 ml, 0.1 mol) and 60 ml of freshly distilled CCl_4 were added to a 250 ml round-bottom flask equippped with a Teflon covered magnetic stirring bar, reflux condenser and a nitrogen gas inlet. Benzoyl peroxide (2.47 g, 0.01 mol) dissolved in 10 ml of CCl_4 was added through the reflux condenser. The mixture was heated to reflux for 6 h and then allowed to cool to room temperature. The solvent was evaporated under reduced pressure. The resulting oil was fractionally distilled. The fraction with b.p. 80°C/4 mmHg (11.2 g, 9% yield) was found to contain 98% $D_3D^{CH_2Cl}$. ^{1}H NMR: δ 0.08 (s, 6H), 0.10 (s, 6H), 0.11 (s, 6H), 0.21 (s, 3H), 2.66 (s, 2H). ^{13}C NMR: δ -2.68 (1C), 0.60 (2C), 0.63 (2C), 0.69 (2C), 29.06 (1C). ^{29}Si NMR: δ -17.87 (2Si), -18.72 (1Si), -30.29 (1Si). IR: ν 1072 cm^{-1} Si-O-Si. MS *m/e* (rel. intensity): 317 (29.4%), 315 (59.5%) $M-15^+$, 289 (26.4%), 287 (56.3%), 281 (100%) $M-CH_2Cl^+$, 265 (13.6%), 249 (15.5%), 193 (31.4%).

Flash vacuum pyrolysis of cyclosiloxanes with 2,7-dimethyl-2,3 : 7,8-diepoxy-5-silaspiro[4.4]nonane (I)

Flash vacuum pyrolysis experiments were carried out as follows. A Pyrex tube 35.5 cm long with an ID of 5 mm was wrapped in a helical spiral such that the tube fit into the heated zone of a tube furnace 13″ length by 1″ diameter. The temperature in the oven was determined by use of an iron-constantan thermocouple connected to an Omega 871 digital thermometer. Pyrolysis reactions were carried out at 520°C. A vessel containing the reactants was joined to one end of the pyrolysis tube. The other end of the pyrolysis tube was attached to a liquid nitrogen cooled cold finger, which in turn was connected to a mercury diffusion pump (10^{-4} mm). A typical pyrolysis involved simultaneous evaporation of 1 to 2 g of I and 1 to 3 equivalents of cyclosiloxane into the heated Pyrex pyrolysis tube. External heating above the boiling point of both reactants was used to minimize fractionation of reactants. After the pyrolysis was complete, the cold finger was warmed to room temperature, and the reaction mixture was recovered as a light yellow green oil. The products were purified by preparative GLPC.

2,2,4,4,8,8,10,10-Octamethyl-2,4,6,8,10-pentasila-1,3,5,7,9,11-hexaoxaspiro[5.5]undecane (D_2QD_2)

I (2 g, 10.2 mmol) and D_4 (4.55 g, 15 mmol) were mixed together in a 50 ml round-bottom flask which was attached to the pyrolysis tube. The flask was frozen in liquid nitrogen while the system was heated to temperature and evacuated to 10^{-4} mmHg. Once equilibrated, the round-bottom flask was brought to room temperature and heated to ca. 100°C. The distillation of the reactants into the pyrolysis tube required 2.5 h. The desired product was purified by preparative GLPC on column B to give 97.2 mg, 9% yield of D_2QD_2 as white crystalline needles, m.p. 120–121°C (lit. [29] m.p. 121°C). ^{1}H NMR: δ 0.18 (s, 24H). ^{13}C NMR: δ 0.62 (8C). ^{29}Si NMR: δ −5.78 (4Si), −95.34 (1Si). IR: ν 1030 cm^{-1} Si–O–Si. MS *m/e* (rel. intensities): 341 (100%) $M - 15^+$, 325 (23.4%), 73 (36.5%). High resolution MS *m/e* calcd. for $Si_5C_7H_{21}O_6$ $(M - 15^+)$ 341.0194; found 341.0189.

2,2,4,4,8,8,10,10,12,12-Decamethyl-2,4,6,8,10,12-hexasila-1,3,5,7,9,11,13-heptaoxaspiro[5.7]tridecane (D_3QD_2)

I (1 g, 5.1 mmol) was added to a 20 ml round-bottom flask. D_5 (5.3 g, 14.4 mmol) was placed in a separate 20 ml round-bottom flask. The two flasks were connected via a glass "Y" joint to the pyrolysis tube. The reaction was run as above except that the heating of the two round-bottom flasks was controlled in an attempt to provide a stoichiometric mixture of the two reactants in the pyrolysis tube. The reactants were distilled into the pyrolysis tube over a 3.25 h period. After the usual work-up, the reaction mixture was purified by preparative GLPC on column B. D_3QD_2, white needles m.p. 56–57°C, 90.5 mg, 9% yield was isolated (lit. [29] m.p. 57°C). ^{1}H NMR: δ 0.08 (s, 6H), 0.11 (s, 12H), 0.16 (s, 12H). ^{13}C NMR: δ 0.50 (4C), 0.60 (4C), 0.71 (2C). ^{29}Si NMR: δ −6.14 (2Si), −17.14 (2Si), −18.64 (1Si), −100.28 (1Si). IR: ν 1032 cm^{-1} Si–O–Si. MS *m/e* (rel. intensities): 415 (77.1%) $M - 15^+$, 400 (4.1%), 327 (100%) and 73 (77.1%). High resolution MS *m/e* calcd. for $Si_6C_9H_{27}O_6$ $(M - 15^+)$ 415.0372; found 415.0377.

2-Vinyl-2,4,4,8,8,10,10-heptamethyl-2,4,6,8,10-pentasila-1,3,5,7,9,11-hexaoxaspiro[5.5]undecane (D_2QD^{Vi})

I (1 g, 5.1 mmol) and D_3D^{Vi} (3.0 g, 10 mmol) were added to separate 25 ml round-bottom flasks. The reactants were heated separately as in the D_5 experiment. The reactants were added over a 3.75 h period. After work-up, the reaction mixture was purified by preparative GLPC on column C. D_2QDD^{Vi}, white crystalline needles m.p. 75°C, 60 mg, 12% yield was recovered. ^{1}H NMR: δ 0.18 (s, 12H), 0.19 (s, 6H), 0.25 (s, 3H), 5.84–6.05 (m, 3H). ^{13}C NMR: δ −1.21 (1C), 0.48 (6C), 134.37 (1C), 135.24 (1C). ^{29}Si NMR: δ −4.92 (1Si), −5.41 (1Si), −5.46 (1Si), −20.89 (1Si), −95.21 (1Si). IR: ν 1596 cm^{-1} $CH{=}CH_2$, 1035 cm^{-1} Si–O–Si. MS *m/e* (rel. intensities): 353 (100%) $M - 15^+$, 325 (20.6), 156 (39.4%), 155 (23.6%), and 73 (51%). High resolution MS *m/e* calcd. for $Si_5C_8H_{21}O_6$ $(M - 15^+)$ 353.0179; found 353.0182.

2-Chloromethyl-2,4,4,8,8,10,10-heptamethyl-2,4,6,8,10-pentasila-1,3,5,7,9,11-hexaoxaspiro[5.5]undecane ($D_2QDD^{CH_2Cl}$)

I (1 g, 5.1 mmol) is added to a 10 ml pressure equalizing addition funnel. $D_3D^{CH_2Cl}$ was added to a second pressure equalizing addition funnel. Both of these were connected via a jacketed steam heated glass "Y" to the inlet of the pyrolysis tube. This apparatus allows for careful measurement of reactant volumes under vacuum. Addition of the reactants required 4.5 h. After the usual work-up, the product was isolated by preparative GLPC on a 10′ × 1/4″ 20% DC-QF1 on 60/80 mesh Chromosorb W Column. $D_2QDD^{CH_2Cl}$, white crystalline needles m.p. 105–107°C, 104 mg, 22% yield was obtained. ^{1}H NMR: δ 0.18 (s, 6H), 0.19 (s, 6H), 0.21 (s, 3H), 0.22 (s, 3H), 0.31 (s, 3H), 2.74 (s, 2H). ^{13}C NMR: δ −2.92 (1C), 0.38 (1C), 0.46 (5C), 28.42 (1C). ^{29}Si NMR: δ −3.98 (1Si), −5.16 (1Si), −5.21 (1 Si), −17.31 (1 Si), −95.31 (1Si). IR: ν 1034 cm^{-1} Si–O–Si. MS *m/e* (rel. intensities): 377 (33.3%), 375 (55.7%) $M-15^+$, 341 (85.4%) $M-49^+$, $M-CH_2Cl^+$, 325 (23.6%), 281 (20.8%), 163 (50.%), and 73 (100%). High resolution MS *m/e* calcd. for $Si_5C_7H_{20}O_6Cl$ ($M-15^+$) 374.9795; found 374.9794.

2,4,4,8,8,10,10-Heptamethyl-2,4,6,8,10-pentasila-1,3,5,7,9,11-hexaoxaspiro[5.5]undecane (D_2QDD^H)

I (1.19 g, 5.8 mmol) and D_3D^H (1.64 g, 5.8 mmol) were combined in a pressure equalizing addition funnel. The reaction was run according to the procedure used for $D_3D^{CH_2Cl}$. The addition required 2.5 h. The reaction mixture was purified by preparative GLPC on column. B. D_2QDD^H, white needles m.p. 85°C, 125 mg, 20% yield was isolated. ^{1}H NMR: δ 0.19 (s, 12H), 0.20 (s, 3H), 0.21 (s, 3H), 0.26 (d, 3H, J 1.53 Hz), 4.81 (q, 1H, J 1.53 Hz). ^{13}C NMR: δ 0.34 (1C), 0.58 (4C), 0.68 (1C), 0.99 (1C). ^{29}Si NMR: δ −4.33 (1Si), −5.26 (1Si), −5.32 (1Si), −21.49 (1Si), −95.37 (1Si). IR: ν 2162 cm^{-1} Si–H, 1032 cm^{-1} Si–O–Si. MS *m/e* (rel. intensities): 341 (7.0%) $M-1^+$, 327 (100%) $M-15^+$, 311 (14.9%), 239 (2.1%), and 73 (14%). High resolution MS *m/e* calcd. for $Si_5C_7H_{21}O_6$ ($M-1^+$) 341.0185; found 341.0182. MS *m/e* calcd. for $Si_5C_6H_{19}O_6$ ($M-15^+$) 327.0028; found 327.0029.

2-Phenyl-2,4,4,8,8,10,10-heptamethyl-2,4,6,8,10-pentasila-1,3,5,7,9,11-hexaoxaspiro-[5.5]undecane (D_2QDD^{Ph})

I (1 g, 5.2 mmol) and D_3D^{Ph} (1.73 g, 4.8 mmol) were combined in a pressure equalizing addition funnel. The experiment was run according to the procedure above. The addition of reactants required 8 h. The reaction mixture was separated by preparative GLPC on column A. D_2QDD^{Ph}, a viscous yellow oil, 190 mg, 30% yield was recovered. ^{1}H NMR: δ 0.15 (s, 3H), 0.16 (s, 3H), 0.17 (s, 3H), 0.20 (s, 3H), 0.22 (s, 3H), 0.25 (s, 3H), 0.44 (s, 3H), 7.37–7.68 (m, 5H). ^{13}C NMR: δ −0.78 (1C), 0.61 (6C), 128.70 (2C), 131.15 (1C), 133.93 (2C), 136.61 (1C). ^{29}Si NMR: δ −4.82 (1Si), −5.50 (1Si), −5.58 (1Si), −20.16 (1Si), −94.97 (1Si). IR: ν 1026 cm^{-1} Si–O–Si. MS *m/e* (rel. intensities): 418 (3.6%) M^+, 403 (100%) $M-15^+$, 387 (16.7%), 135 (28.2%), and 73 (4.2%). High resolution MS *m/e* calcd. for $Si_5C_{13}H_{26}O_5$ ($M^{+\cdot}$) 418.0576; found 418.0572.

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