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Oligocyclic Ladder Polysiloxanes: Alternative Synthesis by Oxidation

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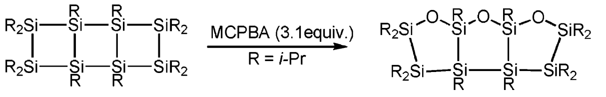
Summary: A series of ladder polysiloxanes was prepared by oxidation of the corresponding ladder polysilanes with mCPBA (m-chloroperbenzoic acid), and their structures were determined. Complete oxidation of all Si−Si bonds was accomplished with a large excess of mCPBA using long reaction times.

Introduction

Highly regular silsesquioxanes, especially those with ladder structures, have received considerable attention.[1] Evidence from IR and ^{29}Si NMR spectra as well as X-ray powder diffraction[2] has suggested the formation of ladder-type polysilsesquioxanes under certain conditions. However, such evidence is not universally accepted.[3] Thus, it is worthwhile to prepare ladder polysiloxanes with defined structures, since they can serve as models for ladder polysilsesquioxanes. Recently, we reported the synthesis of a pentacyclic ladder polysiloxane by a sequential route.[4] Alternatively, herein we report the one-step synthesis of a series of ladder polysiloxanes by oxidation of ladder polysilanes. The X-ray crystal structures, NMR, and IR of these ladder polysiloxanes are reported.

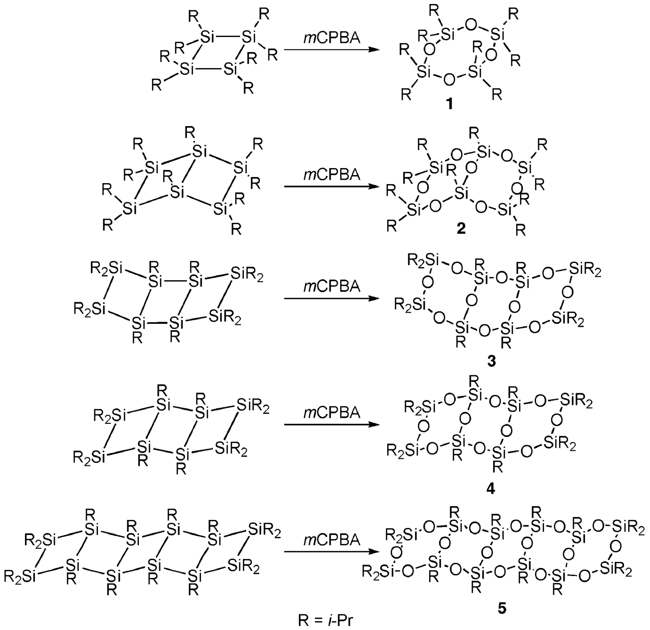
Results and Discussion

Synthesis of Ladder Polysiloxanes. The starting ladder polysilanes[5] are known compounds.[6−10] Oxidation of these with various reagents was examined. With *m*CPBA (*m*-chloroperbenzoic acid), the oxidation occurred only on one side of the molecules ("domino oxidation"; see eq 1).[11] Interestingly, the oxidation of octasilacubane, (*t*-BuMe$_2$SiSi)$_8$, with *m*CPBA affords (*t*-BuMe$_2$SiSi)$_8$O$_{12}$ (T$_8$).[12] On the basis of these results, we searched for an effective oxidant for complete oxidation of all Si−Si bonds. Although trimethylamine oxide seemed promising, no significant oxidation was observed with ladder polysilanes. While photoreaction of octasilacubane in DMSO gave oxygen insertion products in good yields,[13] the fact that ladder polysilanes give cyclotetrasilene by photoreaction[9] made this approach inapplicable. The reaction of bicyclic polysilanes with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) gave only mono-oxidized products. Confronted with these results, we decided to study the oxidation with *m*CPBA under more forcing conditions. This was successful (Scheme 1).



(1)

Scheme 1. Synthesis of Ladder Polysiloxanes



*m*CPBA oxidation of monocyclic polysilanes is well-known. West reported the oxidation of (*t*-BuSi)$_4$ with *m*CPBA to give (*t*-BuSi)$_4$O and (*t*-BuSi)$_4$O$_2$.[14] Similarly,

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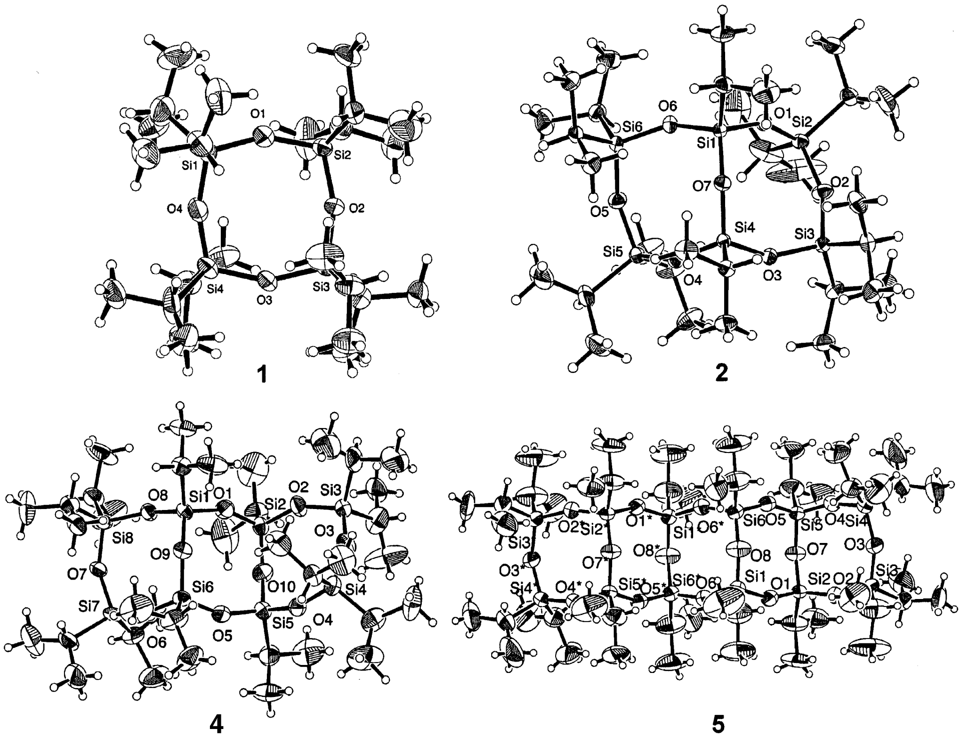

Figure 1. Crystal structures of ladder polysiloxanes. Thermal ellipsoids are drawn at the 30% probability level.

Kumada and Ishikawa reported the generation of $(MeSi)_4O$ from $(MeSi)_4$,[15] while Weber isolated $(MeSi)_6O_n$ ($n = 1-6$) from the reaction of $(MeSi)_6$ with *m*CPBA.[16] We have found that when octaisopropylcyclotetrasilane[17] was treated with a large excess (20 equiv) of *m*CPBA for 1 day, cyclotetrasiloxane **1** was obtained in 46% yield after purification. The structure of **1** was established by X-ray crystal analysis as well as by spectroscopic methods. In a similar manner, oxidation of ladder polysilanes was performed, and bicyclic (**2**), syn-tricyclic (**3**), anti-tricyclic (**4**), and anti-pentacyclic (**5**) ladder polysiloxanes were obtained. Compound **5** is the first example of an all-anti pentacyclic ladder polysiloxane, and **2**−**5** are the only known ladder polysiloxanes with single substituents. With these, more drastic reaction conditions were required; the pentacyclic ladder polysiloxane was obtained using 50 equiv of *m*CPBA in benzene after 113 h. Interestingly, temperature did not affect the reaction time or yields; the reaction with *m*CPBA in benzene or CH_2Cl_2 proceeded similarly at 50 °C and at room temperature. The structures of bicyclic,[18] syn-tricyclic,[19] anti-tricyclic,[20] and our pentacyclic[4] ladder polysiloxanes were determined previously.

Table 1. Crystallographic Data for 1, 2, 4, and 5

	1	**2**	**4**	**5**
formula	$C_{24}H_{56}Si_4O_4$	$C_{30}H_{70}Si_6O_7$	$C_{36}H_{84}Si_8O_{10}$	$C_{48}H_{112}Si_{12}O_{16}$
mol wt	521.05	711.39	901.74	1282.43
temp, °C	−100.0	−100.0	15.0	13.0
cryst size, mm	0.09 × 0.12 × 0.13	0.10 × 0.20 × 0.20	0.10 × 0.10 × 0.10	0.10 × 0.10 × 0.20
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$C2/c$	$P\bar{1}$
a, Å	10.445(1)	11.0665(4)	33.670(3)	11.552(2)
b, Å	15.746(1)	18.2356(7)	16.227(2)	18.738(3)
c, Å	19.817(2)	21.3040(7)	26.185(2)	9.449(1)
α, deg				98.28(1)
β, deg	98.645(1)	91.736(2)	131.220(4)	104.711(8)
γ, deg				100.054(6)
V, Å^3	3225.0(6)	4297.3(3)	10761(1)	1909.4(5)
Z	4	4	8	1
D_{calcd}, g cm^{-3}	1.073	1.099	1.110	1.115
μ_{calcd}, cm^{-1}	2.08	2.30	2.43	2.54
$2\theta_{max}$, deg	45.2	55.2	54.8	55.1
no. of rflns measd	3703	8273	7847	6212
no. of obsd rflns ($I > 2.00\sigma(I)$)	3484	7657	6515	5412
no. of params	290	389	506	380
R1 ($I > 2.00\sigma(I)$)	0.084	0.063	0.098	0.092
wR2 (all rflns)	0.241	0.164	0.279	0.316
S	1.11	1.127	1.11	1.39
$(\Delta/\sigma)_{max}$	0.015	0.002	0.001	0.095
$(\Delta\rho)_{max}$, e Å^{-3}	0.69	0.78	0.53	0.56
$(\Delta\rho)_{min}$, e Å^{-3}	−0.47	−0.61	−0.56	−0.41

Structures of Ladder Polysiloxanes. The structure determination was based on X-ray crystallographic analysis, except for syn-tricyclic **3**, whose structure was already reported.[19b] The ORTEP drawings are depicted in Figure 1; crystallographic data are summarized in Table 1, and selected bond lengths and angles are shown in Tables 2−5. Because of the small energy differences between the conformers, disorders of isopropyl groups were observed for **4** and **5**. In **4**, isopropyl groups on Si(6) and Si(7) atoms were disordered. In pentacyclic **5**,

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for (i-Pr$_2$SiO)$_4$ (1)

Si(1)–O(1)	1.602(5)	Si(3)–O(2)	1.622(4)
Si(2)–O(2)	1.617(4)	Si(4)–O(4)	1.592(5)
Si(4)–O(3)	1.627(5)	Si(2)–O(1)	1.615(4)
Si(1)–O(4)	1.607(5)	Si(3)–O(3)	1.623(5)
O(1)–Si(1)–O(4)	110.0(2)	Si(1)–O(1)–Si(2)	153.5(3)
O(3)–Si(4)–O(4)	110.9(2)	Si(1)–O(4)–Si(4)	159.4(4)
Si(3)–O(3)–Si(4)	154.7(3)	O(2)–Si(3)–O(3)	110.4(2)
O(1)–Si(2)–O(2)	111.0(2)	Si(2)–O(2)–Si(3)	160.7(3)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Bicyclic Ladder Polysiloxane 2

Si(1)–O(1)	1.609(2)	Si(4)–O(3)	1.617(2)
Si(2)–O(1)	1.626(2)	Si(5)–O(4)	1.617(2)
Si(3)–O(3)	1.632(2)	Si(6)–O(6)	1.632(2)
Si(4)–O(7)	1.612(2)	Si(1)–O(7)	1.612(2)
Si(6)–O(5)	1.617(2)	Si(3)–O(2)	1.622(2)
Si(1)–O(6)	1.615(2)	Si(4)–O(4)	1.621(2)
Si(2)–O(2)	1.609(2)	Si(5)–O(5)	1.614(2)
O(1)–Si(1)–O(6)	108.8(1)	O(5)–Si(6)–O(6)	110.4(1)
O(6)–Si(1)–C(1)	110.1(1)	Si(3)–O(3)–Si(4)	150.3(1)
O(3)–Si(4)–O(4)	108.8(1)	Si(1)–O(6)–Si(6)	150.4(1)
O(4)–Si(5)–O(5)	109.4(1)	O(6)–Si(1)–O(7)	109.3(1)
Si(2)–O(2)–Si(3)	155.8(2)	O(2)–Si(3)–O(3)	110.3(1)
Si(5)–O(5)–Si(6)	156.4(1)	O(4)–Si(4)–O(7)	110.4(1)
O(1)–Si(1)–O(7)	110.2(1)	Si(1)–O(1)–Si(2)	151.6(2)
O(1)–Si(2)–O(2)	109.0(1)	Si(4)–O(4)–Si(5)	148.9(1)
O(3)–Si(4)–O(7)	109.6(1)	Si(1)–O(7)–Si(4)	150.8(1)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for the Anti Tricyclic Ladder Polysiloxane 4

Si(1)–O(1)	1.598(7)	Si(5)–O(4)	1.601(5)
Si(2)–O(1)	1.591(8)	Si(6)–O(5)	1.601(9)
Si(3)–O(2)	1.613(7)	Si(7)–O(6)	1.624(5)
Si(4)–O(4)	1.643(4)	Si(8)–O(8)	1.634(6)
Si(5)–O(10)	1.600(6)	Si(1)–O(9)	1.622(5)
Si(6)–O(9)	1.638(5)	Si(2)–O(10)	1.598(6)
Si(8)–O(7)	1.634(4)	Si(4)–O(3)	1.638(5)
Si(1)–O(8)	1.613(5)	Si(5)–O(5)	1.624(8)
Si(2)–O(2)	1.614(5)	Si(6)–O(6)	1.611(5)
Si(3)–O(3)	1.630(6)	Si(7)–O(7)	1.635(6)
O(1)–Si(1)–O(8)	108.2(3)	O(6)–Si(6)–O(9)	110.2(3)
O(1)–Si(2)–O(2)	105.3(3)	Si(1)–O(1)–Si(2)	156.2(3)
O(2)–Si(3)–O(3)	109.2(3)	Si(4)–O(4)–Si(5)	158.5(4)
O(4)–Si(5)–O(10)	109.8(3)	Si(7)–O(7)–Si(8)	149.1(3)
O(5)–Si(6)–O(9)	110.1(3)	Si(2)–O(10)–Si(5)	145.7(4)
O(7)–Si(8)–O(8)	109.4(3)	O(8)–Si(1)–O(9)	109.2(2)
Si(3)–O(3)–Si(4)	155.0(3)	O(2)–Si(2)–O(10)	110.8(4)
Si(6)–O(6)–Si(7)	162.9(3)	O(4)–Si(5)–O(5)	108.9(3)
Si(1)–O(9)–Si(6)	142.5(3)	O(5)–Si(6)–O(6)	107.9(3)
O(1)–Si(1)–O(9)	110.6(4)	O(6)–Si(7)–O(7)	110.1(2)
O(1)–Si(2)–O(10)	111.9(3)	Si(2)–O(2)–Si(3)	151.8(5)
O(3)–Si(4)–O(4)	110.4(3)	Si(5)–O(5)–Si(6)	154.6(4)
O(5)–Si(5)–O(10)	111.3(4)	Si(1)–O(8)–Si(8)	151.5(3)

disorder was observed for four isopropyl groups on Si(1), Si(2), Si(3), and Si(6). Average Si–O bond lengths were 1.613 Å for **1**, 1.618 Å for **2**, 1.621 Å for **3**, 1.618 Å for **4**, and 1.599 Å for **5**. These values are similar within error.

Cyclotetrasilanes are known to show various dihedral angles of their frameworks due to different substituents or differences in stereostructure.[21] On the other hand, the frameworks of cyclotetrasiloxanes are less affected by substituents due to their longer Si–O–Si distances. Monocyclic **1** shows a slightly folded structure, with a dihedral angle of the cyclotetrasiloxane ring of 24.1°. The torsion angle between Si(1)···Si(2) and Si(3)···Si(4) lines was 16.9°. Similarly, torsion angles for **2** were 15.8 and 16.0°, for a total of 31.8° (this value indicates the torsion angle for both terminal rungs). For syn-tricyclic **3**, torsion angles were 10.9, 2.3, and 12.8°, for a total of 26.0°. The anti-tricyclic ladder polysiloxane **4** showed a more helical structure, and torsion angles were 14.4, 5.7, and 16.0°, for a total of 36.1°. These four compounds possess no symmetry elements. However, there exists a symmetry center in the pentacyclic ladder polysiloxane **5**. Therefore, torsion angles for **5** were 5.5, 0.3, 0, −0.3, and −5.4°. The terminal rungs are parallel. In all cases, the middle rings show smaller torsion angles. In the case of ladder polysilanes, skewed structures were observed, and torsion angles of the terminal rungs increase as the number of rings increases. Thus, the torsion angle for the anti-tricyclic compound was 44.0°, reflecting the larger steric repulsion of the substituents. Ladder polysilsesquioxanes are expected to be less skewed.

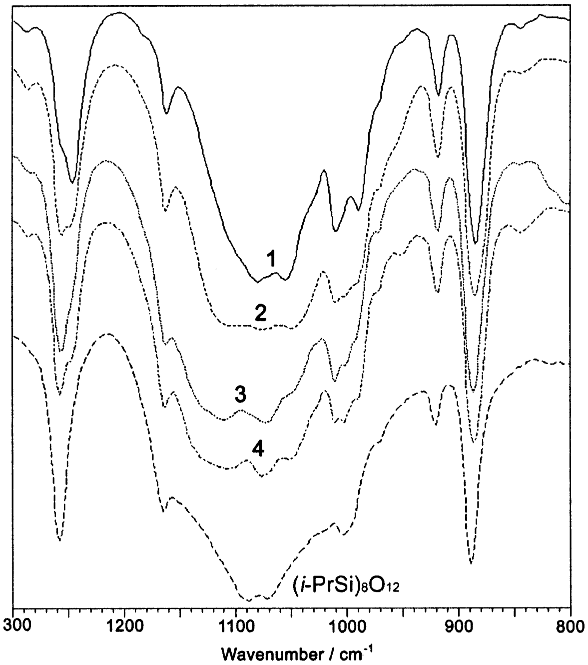

Figure 2. IR spectra of ladder polysiloxanes.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for the Pentacyclic Ladder Polysiloxane 5

Si(1)–O(1)	1.577(4)	Si(3)–O(3)	1.621(3)
Si(2)–O(1)	1.593(4)	Si(5)–O(4)	1.578(4)
Si(3)–O(2)	1.603(3)	Si(6)–O(5)	1.582(4)
Si(4)–O(4)	1.621(4)	Si(1)–O(8)	1.587(4)
Si(5)–O(7)	1.620(3)	Si(2)–O(7)	1.619(4)
Si(6)–O(8)	1.587(4)	Si(4)–O(3)	1.629(4)
Si(1)–O(6)	1.591(3)	Si(5)–O(5)	1.606(4)
Si(2)–O(2)	1.587(3)	Si(6)–O(6*)	1.589(4)
O(1)–Si(1)–O(6)	108.5(2)	O(5)–Si(5)–O(7)	109.3(2)
O(1)–Si(2)–O(2)	108.5(2)	O(6*)–Si(6)–O(8)	112.1(2)
O(2)–Si(3)–O(3)	110.7(2)	Si(3)–O(3)–Si(4)	154.1(2)
O(4)–Si(5)–O(7)	110.2(2)	Si(1)–O(6)–Si(6*)	159.4(3)
O(5)–Si(6)–O(8)	109.7(2)	O(6)–Si(1)–O(8)	111.3(2)
Si(2)–O(2)–Si(3)	162.2(3)	O(2)–Si(2)–O(7)	109.5(2)
Si(5)–O(5)–Si(6)	154.9(3)	O(4)–Si(5)–O(5)	107.9(2)
Si(1)–O(8)–Si(6)	145.3(3)	O(5)–Si(6)–O(6*)	108.1(2)
O(1)–Si(1)–O(8)	109.6(2)	Si(1)–O(1)–Si(2)	155.3(3)
O(1)–Si(2)–O(7)	109.5(2)	Si(4)–O(4)–Si(5)	160.2(3)
O(3)–Si(4)–O(4)	110.0(2)	Si(2)–O(7)–Si(5)	146.1(2)

Spectral Features of Ladder Polysiloxanes. Because of the difficulty in obtaining structural information, ladder-type polysilsesquioxanes have been identified previously, mostly by IR and NMR spectroscopy. Thus, it is worthwhile to summarize the spectral data of various ladder polysiloxanes of well-defined structures. In Figure 2, IR spectra of **1**–**4** and the cage silsesquioxane (i-PrSi)$_8$O$_{12}$ [22] are shown.

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Table 6. ^{29}Si NMR Chemical Shifts of Ladder Polysiloxanes (ppm)

1 (monocyclic)	−29.24		
2 (bicyclic)	−28.42	−71.97	
3 (anti tricyclic)	−23.40	−66.77	
4 (syn tricyclic)	−23.72	−67.16	
5 (pentacyclic)	−22.46	−65.21	−65.80

^{29}Si NMR spectra of ladder polysiloxanes were less characteristic. As summarized in Table 6, the chemical shift of inner-rung Si atoms (T unit) moves from −71.97 (for bicyclic) to −65.21 and −65.80 ppm (pentacyclic). As the chemical shift of (i-PrSi)$_8$O$_{12}$ is observed at −66.26 ppm,[22] distinguishing cage and ladder structures is difficult from ^{29}Si NMR spectra. For polyphenylsilsesquioxanes (PPSQ), ^{29}Si NMR peaks in the −75 to −85 ppm region have been assigned to ladder polysilsesquioxanes.[2] However, it is difficult to distinguish structures of ladder, cage, or mixed structures. In addition, ^{29}Si NMR spectra of silsesquioxanes are affected by the ring sizes but not by the stereostructures. The chemical shifts are similar in anti- and syn-tricyclic ladder polysiloxanes. We conclude that ladder polysilsesquioxanes will show the peaks in regions similar to those of octasilsesquioxanes (T$_8$).

In summary, we have prepared monocyclic to pentacyclic ladder polysiloxanes and determined their structures.

Experimental Section

Solvents were purified and dried according to literature procedures. All NMR spectra were recorded on a JEOL α-500 (^{1}H, 500.00 MHz, ^{13}C, 125.65 MHz, ^{29}Si, 99.25 MHz) spectrometer. EI mass spectra were performed with a JEOL JMS-DX302 instrument. IR spectra were recorded on a Shimadzu FTIR-8700 spectrometer. Analytical HPLC was performed on a Jasco UV-970/880-PU instrument with a Chemcosorb 4.6 mm × 250 mm 5-ODS-H column.

General Procedure of Oxidation: Preparation of Octaisopropylcyclotetrasiloxane (1). A solution of octaisopropylcyclotetrasilane[17] (23 mg, 0.05 mmol) and mCPBA (173 mg, 1.0 mmol) in benzene (5 mL) was stirred at 20 °C for 24 h. Then the solvent was removed, and the residue was purified by column chromatography (silica gel, hexane) to afford cyclotetrasiloxane **1** (12 mg, 46%). Single crystals suitable for X-ray crystallography were obtained by slow evaporation of a MeOH solution. Octaisopropylcyclotetrasiloxane (**1**): mp 130−135 °C; ^{1}H NMR (CDCl$_3$) δ 0.90 (sept, 8H, J = 7.3 Hz), 1.03 (d, 48H, J = 7.3 Hz); ^{13}C NMR (CDCl$_3$) δ 14.45, 17.50; ^{29}Si NMR (CDCl$_3$) δ −29.24; MS (30 eV) m/z (%) 477 ([M − i-Pr]$^+$, 100), 435 (16); IR (KBr, cm^{-1}) 2943, 2866, 1464, 1384, 1364, 1246, 1085, 1055, 1009, 989, 885. Anal. Calcd for C$_{24}$H$_{56}$Si$_4$O$_4$: C, 55.23; H, 10.85. Found: C, 55.32; H, 10.83.

Preparation of the Bicyclic Ladder Polysiloxane 2. The reaction of decaisopropylbicyclo[2.2.0]hexasilane[6] (102 mg, 0.18 mmol) with mCPBA (733 mg, 4.2 mmol) in benzene (15 mL) was effected in a similar manner (20 °C, 24 h) to produce the bicyclic ladder polysiloxane **2** (59 mg, 48%). Single crystals suitable for X-ray crystallography were obtained by slow evaporation of an EtOH solution. Decaisopropylbicyclo[5.5.1]-hexasiloxane (**2**): mp 166−168 °C; ^{1}H NMR (CDCl$_3$) δ 0.83−0.95 (m, 10H), 1.01 (d, 12H, J = 6.8 Hz), 1.02 (d, 24H, J = 6.8 Hz), 1.03 (d, 24H, J = 6.8 Hz); ^{13}C NMR (CDCl$_3$) δ 12.78, 14.05, 14.44, 17.14, 17.27, 17.38 (overlapped), 17.45; ^{29}Si NMR (CDCl$_3$) δ −71.97, −28.42; MS (30 eV) m/z (%) 667 ([M − i-Pr]$^+$, 70); IR (KBr, cm^{-1}) 2945, 2868, 1464, 1385, 1364, 1256, 1076, 1049, 1010, 885. Anal. Calcd for C$_{30}$H$_{70}$O$_7$Si$_6$: C, 51.16; H, 10.02. Found: C, 50.65; H, 9.92.

Preparation of the Syn Tricyclic Ladder Polysiloxane 3. The reaction of syn-dodecaisopropyltricyclo[4.2.0.0^{2,5}]octasilane[8] (96 mg, 0.13 mmol) with mCPBA (673 mg, 3.9 mmol) in benzene (15 mL) was effected in a similar manner (20 °C, 71 h) to give the bicyclic ladder polysiloxane **3** (86 mg, 73%). All spectral data were identical with those of the previously reported **3**. syn-Dodecaisopropyltricyclo[9.5.1.1^{3,9}]octasiloxane (**3**): mp 156−158 °C; ^{1}H NMR (CDCl$_3$) δ 0.84−0.94 (m, 12H), 1.02 (d, 24H, J = 6.8 Hz), 1.03 (d, 24H, J = 6.8 Hz), 1.04 (d, 24H, J = 6.8 Hz); ^{13}C NMR (CDCl$_3$) δ 12.76, 14.08, 14.72, 16.99, 17.15, 17.26, 17.41 (overlapped), 17.45; ^{29}Si NMR (CDCl$_3$) δ −67.16, −23.72; MS (30 eV) m/z (%) 857 ([M − i-Pr]$^+$, 40); IR (KBr, cm^{-1}) 2945, 2868, 1466, 1387, 1366, 1258, 1115, 1072, 1010, 887.

Preparation of the Anti Tricyclic Ladder Polysiloxane 4. The reaction of $anti$-dodecaisopropyltricyclo[4.2.0.0^{2,5}]octasilane[23] (30 mg, 0.04 mmol) with mCPBA (344 mg, 2.0 mmol) in benzene (5 mL) was effected in a similar manner (20 °C, 221 h) to afford the bicyclic ladder polysiloxane **4** (9.2 mg, 25%). Single crystals suitable for X-ray crystallography were obtained by slow evaporation of a THF−EtOH solution. $anti$-Dodecaisopropyltricyclo[9.5.1.1^{3,9}]octasiloxane (**4**): mp 88−89 °C; ^{1}H NMR (CDCl$_3$) δ 0.82−0.94 (m, 12H), 1.00 (d, 48H, J = 7.2 Hz), 1.03 (d, 48H, J = 7.2 Hz); ^{13}C NMR (CDCl$_3$) δ 12.54, 13.89, 13.97, 16.96, 16.99, 17.25 (overlapped), 17.20 (overlapped); ^{29}Si NMR (CDCl$_3$) δ −66.77, −23.40; MS (30 eV) m/z (%) 857 ([M − i-Pr]$^+$, 44); IR (KBr, cm^{-1}) 2945, 2866, 1466, 1385, 1366, 1258, 1107, 1073, 1003, 887. Anal. Calcd for C$_{24}$H$_{56}$O$_{12}$Si$_8$: C, 48.58; H, 9.51. Found: C, 47.95; H, 9.39.

Preparation of the Anti,anti,anti Pentacyclic Ladder Polysiloxane 5. The reaction of $anti,anti,anti$-hexadecaisopropylpentacyclo[4.4.0.0.^{2,5}0^{7,10}]dodecasilane[10] (18 mg, 0.02 mmol) with mCPBA (178 mg, 1.0 mmol) in benzene (5 mL) was effected in a similar manner (20 °C, 113 h) to afford the bicyclic ladder polysiloxane **5** (6.4 mg, 31%). Single crystals suitable for X-ray work were obtained by slow evaporation of a THF−EtOH solution. $anti,anti,anti$-Hexadecaisopropyltetracyclo-[17.5.1.1^{3,17}.1^{5,15}.1^{7,13}]dodecasiloxane (**5**): mp 199−202 °C; ^{1}H NMR (CDCl$_3$) δ 0.94−1.30 (m, 112H); ^{13}C NMR (CDCl$_3$) δ 17.59, 17.52, 17.51, 17.49, 17.33, 17.28, 17.21, 17.17, 14.31, 14.18, 12.99, 12.82; ^{29}Si NMR (CDCl$_3$) δ −65.80, −65.21, −22.46; MS (30 eV) m/z (%) 1239 ([M − i-Pr]$^+$, 5), 169 (100); IR (KBr, cm^{-1}) 2945, 2868, 1466, 1387, 1259, 1121, 1090, 1001, 887.

X-ray Crystallography (General Procedure). Intensity data were collected on a Rigaku RAXIS-IV diffractometer with Mo Kα radiation (λ = 0.710 70 Å). An empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects. All calculations were performed using the teXsan software of Molecular Structure Corp.

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Supporting Information Available: Crystallographic information files (CIF) for **1**, **2**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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