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Pentacyclic Laddersiloxane

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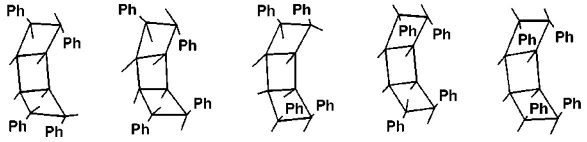
Much effort has been directed toward the syntheses of ladder-type polysilsesquioxanes[1] since 1960, when Brown and co-workers proposed a ladder structure for phenylsilsesquioxanes (PhSiO$_{1.5}$)$_n$ obtained by treatment of the hydrolysate of trichlorophenysilane with 0.1% KOH in toluene.[2] Some evidence, such as IR spectra, ^{29}Si NMR spectra, and X-ray powder diffraction,[1] has suggested that ladder structures resulted under certain conditions. Such evidence, however, is not universally accepted by organosilicon chemists.[3] Thus, the construction of polysilsesquioxanes having true ladder structures represents an important synthetic goal in this field.

During the course of our investigation on the construction of oligosilsesquioxanes with well-defined structures,[4] we have found that the all-*cis*-1,3,5,7-cyclotetrasiloxanetetraol, (*i*-PrSi(OH)O)$_4$ (**1**)[5] is a versatile precursor of the tricyclic laddersiloxane,[6] hexasilsesquioxane,[7] octasilsesquioxane,[5] and hydrogen-bonded supermolecule.[8] These previous results have prompted us to construct a true ladder oligosilsequioxane from **1**. The primary goal of our research is to assess the physical properties including spectral features arising from the true laddersiloxane framework. To our knowledge, it has thus far been impossible to construct laddersiloxane consisting of more than three Si$_4$O$_4$ rings.[9] Herein, we report a novel method for the construction of laddersiloxanes and the first synthesis of pentacyclic laddersiloxane **6**.

The synthesis of **6** began with the dehydrochlorinative condensation of **1** and (*i*-PrPhSiCl)$_2$O (**2**), leading to the tricyclooligosiloxane **3**. To date, prior work showed several procedures including treatments of silanols and chlorosilanes in the presence of triethylamine in ether,[10] in benzene,[11] in THF/hexane,[12] or with pyridine in ether.[13] Nevertheless, these procedures did not produce satisfactory results in our case. We found, however, that condensation of **1** and **2** could be effected by using pyridine as a solvent. Thus, mixing **1** and **2** in pyridine resulted in the formation of **3** in 85% yield, as a mixture of five stereoisomers (Scheme 1).

We separated these isomers by recycle-type reverse-phase HPLC and determined their structures by X-ray crystallography. Reflecting the all-*cis* configuration of **1**, all the isomers have a *syn* structure. Under this condition, stereoselectivity in the terminal phenyl group orientation is unobserved (Figure 1). The crystallographic results also revealed that all the bond lengths and angles of **3a**−**e** are within normal ranges.



3a (14%) **3b** (17%) **3c** (15%) **3d** (26%) **3e** (13%)

Figure 1. All isopropyl groups are omitted for clarity. Cyclotetrasiloxane rings are represented as rectangles.

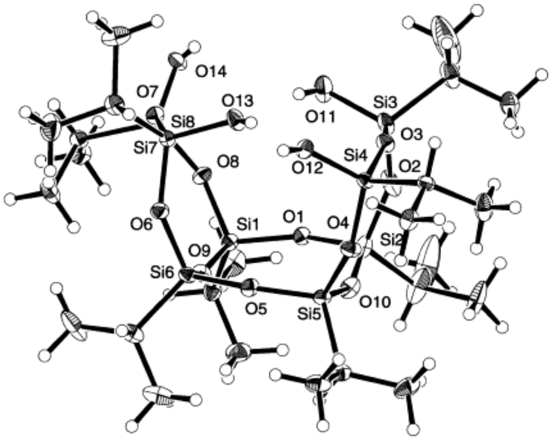
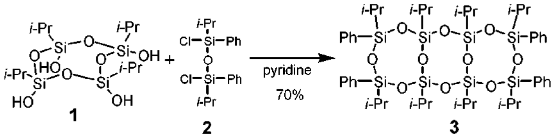
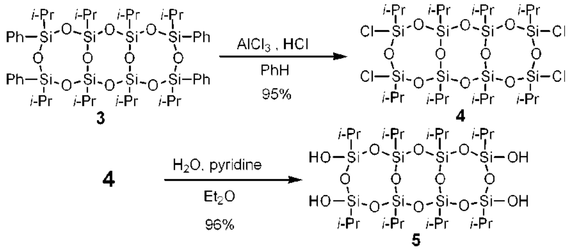


Figure 2. ORTEP drawing of **5a**. Thermal ellipsoids are drawn at the 50% probability level.

Scheme 1



Scheme 2



The key step of the entire procedure is the chlorodephenylation of **3**. Previous studies show that aluminum trichloride cleaves Si−O bonds and induces a disproportionation in the case of cyclic methylsiloxane.[14] In our laboratory, however, the dephenylchlorination of (*i*-PrPh$_2$Si)$_2$O with AlCl$_3$/HCl was found to be effected by passing dry HCl gas through its solution in benzene containing 2 equiv. of AlCl$_3$, giving (*i*-PrCl$_2$Si)$_2$ in quantitative yield.[15] Similarly, when a stereoisomeric mixture of **3** was subjected to chlorodephenylation under the same condition, tetrachloride **4** was produced in a 95% yield. Subsequent hydrolysis of **4** in water/pyridine/ether led to the formation of **5** in a yield of 96% (Scheme 2). Tetraol **5** was also found to be a mixture of stereoisomers, and we successfully determined the structure of one of the isomers, **5a** (Figure 2).[16] An interesting aspect of the structural result is the observation of the *cis*-fused ring and hydrogen bonding between diagonal hydroxyl groups (O(11) and O(13)). In the lattice, one water molecule is

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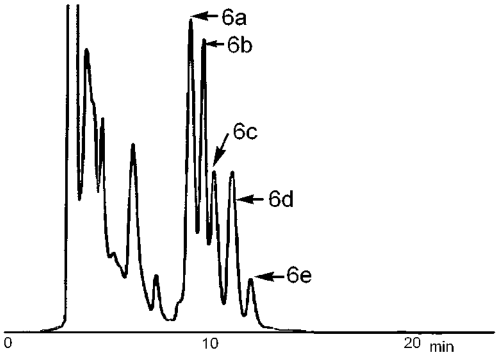


Figure 3. HPL chromatogram (ODS, MeOH/THF = 7/3).

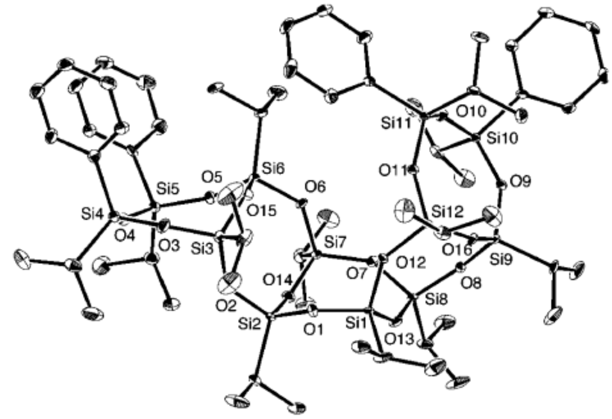
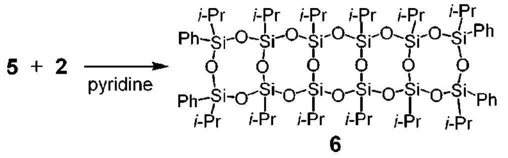


Figure 4. ORTEP drawing of **6b**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Scheme 3



included, and two molecules of **5a** are connected via water with hydrogen bonding. It is noted that tetraol **5** and tetrachloride **4** are the first examples of the sila-functional tricyclic laddersiloxanes.

The dehydrochlorinative condensation of **5** (a mixture of stereoisomers) with **2** was achieved as in the case of **3**, resulting in the isolation of five isomers **6a**−**e** (Scheme 3). The HPLC chart at the end of the reaction is shown in Figure 3. Separation by recycle-type HPLC (ODS, MeOH/THF = 7/3) gave **6a** (12%), **6b** (9%), **6c** (8%), **6d** (7%), and **6e** (3%).

Among the five isomers, we obtained single crystals of **6b**, and as a result, we present the first structure of pentacyclic laddersiloxane.[17] In addition, the spectroscopic data[18] supported the structure of **6b**. As shown in Figure 4, the pentacyclic rings assume a *anti,syn,syn*-conformation, and each eight-membered ring is significantly twisted, resulting in the double-helix structure.[19] Thus, the dihedral angles were 38.6° for Si1−Si2−Si7−Si8, 9.2° for Si2−Si3−Si6−Si7, 37.3° for Si3−Si4−Si5−Si6, and 28.9° for Si1−Si8−Si9−Si12 rings. Our laboratory has previously reported the double-helix structure of the ladder polysilane.[20] In this study, **6b** showed a similar structure (see Figure 4).

Important to note are the results of the thermal analysis of **6b** in a N_2 atmosphere; TG-DTA analysis showed that **6b** sublimed at 422.6 °C, without loss of any substituents below that temperature. Clearly, this result indicates the high thermal stability of the pentacyclic laddersiloxane.

In summary, we have explored a novel method to extend ladder silsesquioxanes, and synthesized the pentacyclic laddersiloxane for the first time. The crystallographic analysis unequivocally showed its unique structure, and the thermal analysis showed its high stability.

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Supporting Information Available: Details of experimental procedure, spectra of all compounds (PDF), and data for crystallographic analysis for **5a** and **6b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Crystallographic data of **5a**: colorless plate, $C_{24}H_{56}O_{14}Si_8 \cdot 0.5H_2O$, T = 209 K, M_r = 806.42, monoclinic, $C2/c$, a = 33.670(4) Å, b = 14.448(1) Å, c = 18.511(1) Å, β = 109.013(1)°, V = 8414(1) Å^3, Z = 8, R = 0.0655, R_w = 0.0617 for 6117 data with 441 parameters.

(17) Crystallographic data of **6b**: colorless plate, $C_{60}H_{104}O_{16}Si_{12}$, T = 195 K, M_r = 1418.50, triclinic, P-1, a = 14.6572(5) Å, b = 21.730(1) Å, c = 12.7694(5) Å, α = 90.326(1)°, β = 102.540(3)°, γ = 97.132(1)°, V = 3937.1(2) Å^3, Z = 2, R1 = 0.0569, wR2 = 0.1793 for all 10970 data with 794 parameters.

(18) Spectral data of **6b**: ^{1}H NMR ($CDCl_3$) δ 0.54−1.15 (m, 84H), 7.18−7.70 (m, 20H). ^{13}C NMR ($CDCl_3$) δ 11.24, 11.46, 11.59, 11.89, 12.03, 12.13, 12.24, 12.33, 12.40, 12.56, 12.68, 12.86, 12.92, 13.03, 13.13, 14.08, 14.25, 14.43, 14.48, 14.59, 14.68, 14.84, 14.96, 15.14, 16.29, 16.40, 16.49, 16.57, 16.61, 16.74, 16.77, 16.81, 16.85, 16.90, 16.95, 17.04, 127.25, 127.37, 127.41, 127.47, 129.62, 134.04, 134.07, 134.14, 134.21, 134.49, 134.53, 134.67, 134.73, 134.89, 135.02, 135.13. ^{29}Si NMR ($CDCl_3$) δ −65.99, −65.69, −65.30, −64.92, −64.08, −63.68, −63.37, −33.54, −32.78, −32.70, −31.97, −31.86. MS (35 eV) m/z (%) 1374 (M^+ − *i*-Pr, 100). IR (NaCl) ν 3071, 2949, 2868, 1954, 1884, 1819, 1466, 1429, 1385, 1366, 1258, 1107, 1063, 1038, 995, 920, 889, 785, 764, 700, 646, 573. Anal. Calcd for $C_{60}H_{104}O_{16}Si_{12}$: C, 50.80; H, 7.39. Found: C, 50.82; H, 7.28.

(19) The torsion angles of Si-(O)-Si-(O)-Si-(O)-Si in the rings were 26.8°, 6.8°, −27.5°, −20.0°, and 11.1° from Si4−Si5 to Si10−Si11.

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