Acid-Catalyzed Condensation Reaction of Phenylsilanetriol: Unexpected Formation of *cis,trans*-1,3,5-Trihydroxy-1,3,5-triphenylcyclotrisiloxane as the Main Product and Its Isolation

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Ⓢ *Supporting Information*

ABSTRACT: *cis,trans*-1,3,5-Trihydroxy-1,3,5-triphenylcyclotrisiloxane was successfully isolated and fully characterized by spectroscopic methods and single-crystal X-ray diffraction. This compound was believed to be highly unstable and only exist as a transient species in low concentration during the condensation reaction of phenylsilanetriol or its precursors. The isolated pure cyclotrisiloxane is, however, surprisingly stable even in acidic solution and partially isomerizes to the *cis,cis* isomer.
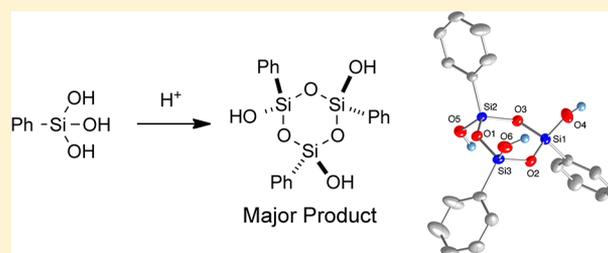
Silicone resins containing phenylsilsesquioxane units $((PhSiO_{1.5})_n)$ are widely used in industry, and their importance is increasing in a number of applications such as sealing materials for LED lights and organic electroluminescence diodes and as an antireflective layer for extreme lithography for semiconductor production.[1] The production of silicone resins is usually performed by polycondensation reaction of alkoxysilanes or chlorosilanes under hydrolytic conditions. For the development of silicone materials having improved properties, an understanding of the reaction details and control of the polysiloxane structure are indispensable. In spite of the long history of the research on phenylsilsesquioxane materials, the initial stages of the condensation reaction have not been very well understood.[2]

It has been established that cyclotetrasiloxanes as four isomeric forms are produced on hydrolytic condensation of trialkoxyphenylsilanes and trichlorophenylsilane.[3] On the other hand, the corresponding cyclotrisiloxanes have been believed to be highly unstable and could be stabilized only under special circumstances; Fujita and co-workers succeeded in stabilizing the *cis,cis*-cyclotrisiloxane by using a cage that could incorporate the cyclotrisiloxane in it.[4] Several cyclotrisiloxanetriols stabilized by bulky substituents such as (2,6-dimethylphenyl)- (trimethylsilyl)amino,[5a] bis(trimethylsilyl)methyl,[5b] and 2,4,6-triisopropylphenyl[5c] groups have been isolated. In 2004, Unno and Matsumoto revealed that a cyclotrisiloxanetriol having relatively small substituents, isopropyl groups, could be isolated.[6,7] During the course of our research to clarify the condensation process of phenylsilsesquioxane, we found that

the cyclotrisiloxanes are unexpectedly stable and can be isolated without any special stabilization agents such as cage compounds. Here we wish to report the isolation, structural characterization, and properties of cyclotrisiloxanes from phenylsilanetriol **1**.

We selected phenylsilanetriol **1**[8] as the starting material because its condensation reaction is simpler and easier to analyze than those of trialkoxyphenylsilanes and trichloro-(phenyl)silane, which have usually been used for such condensation reactions. By using **1**, it is possible (1) to avoid complexity arising from partially hydrolyzed intermediates such as alkoxyhydroxysilanes and chlorohydroxysilanes and (2) to control condensation reaction rates by avoiding the formation of hydrochloric acid resulting from the hydrolysis of trichloro-(phenyl)silane. In addition, **1** is easily available by a known method[8] and has sufficient stability. Acid-catalyzed condensation reactions of compound **1** under various conditions were studied. Scheme 1 shows the condensation pathways of compound **1**. We found that HPLC analysis is highly useful to follow the condensation reaction.

Chromatograms obtained from the reaction of **1** in the presence of 1000 ppm[9] of methanesulfonic acid (MSA) in tetrahydrofuran (THF) using a UV detector at 263 nm are shown in Figure 1. Peaks observed are labeled A−L.[10] Among these peaks, A−D and H were assigned to compound **1**, disiloxane **2**, linear trisiloxane **3**, and cyclotrisiloxanes *cis,trans*-**4**

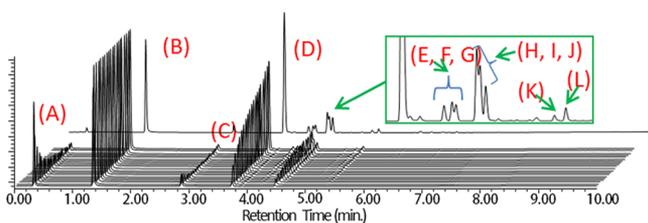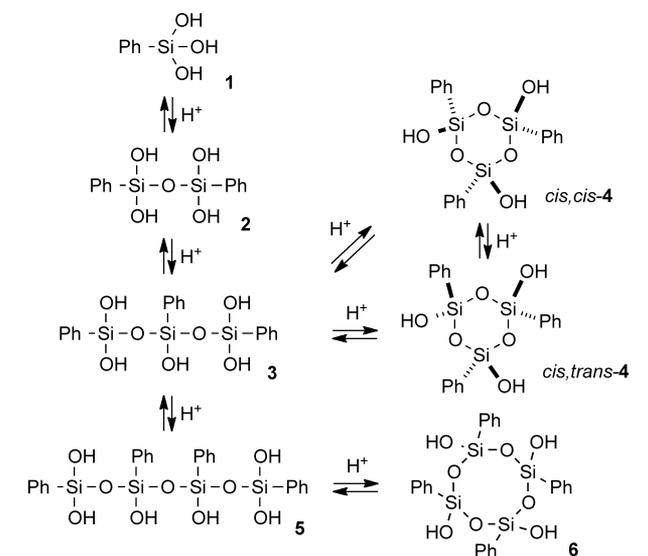**Scheme 1. Condensation Pathways of Phenylsilanetriol 1**

Figure 1. Chromatograms of the condensation reaction of **1** (initial concentration, 5.34×10^{-2} mol/L) with 1000 ppm of MSA in THF at 5 °C. Each chromatogram was obtained at a 30 min interval except the last one, which was obtained by injecting the sample after 42.5 h.
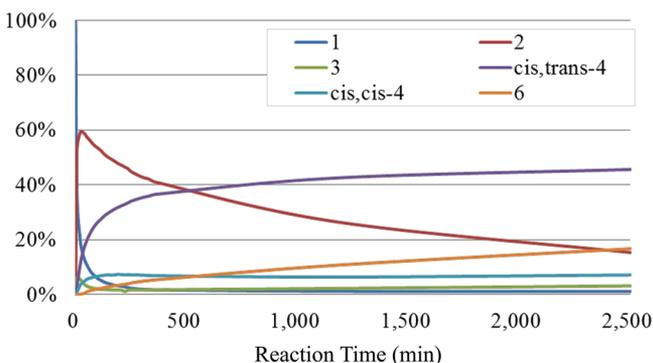

Figure 2. Time-dependent composition of **1** and condensation products **2**, **3**, *cis,trans*-**4**, *cis,cis*-**4**, and cyclotetrasiloxanes **6**.

and *cis,cis*-**4**, respectively. Details of their identification are shown below. Figure 2 gives a graphical presentation of the time-dependent composition of **1**–**3**, *cis,trans*-**4**, *cis,cis*-**4**, and cyclotetrasiloxanes **6** in the same reaction. Unexpectedly, considerable amounts of cyclotrisiloxanes **4**, especially the *cis,trans* isomer, were formed under these reaction conditions.

Figure 3 shows the chromatograms obtained by LC-ESI-TOF MS analysis of the condensation reaction of **1** with 1000 ppm of MSA in THF at 20 °C. The mass chromatogram for *m/z* 432, which corresponds to the ammonium cation adduct of dehydrated trisiloxane ($[C_{18}H_{18}O_6Si_3 \cdot NH_4]^+$), showed three peaks (C, D, and H). High-resolution mass analysis of these peaks by ESI techniques (Figure S2 in the Supporting
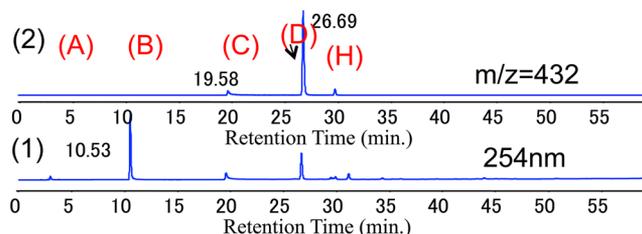

Figure 3. LC-ESI-TOF MS chromatograms of the condensation reaction of **1** with 1000 ppm of MSA in THF: (1) chromatogram by UV absorption at 254 nm by PDA detector; (2) mass chromatogram for *m/z* 432.

Information) clearly suggested that C is the linear trisiloxane **3** (calcd for $[C_{18}H_{20}O_7Si_3 \cdot NH_4]^+$ 450.0855; found 450.0874) and D and H are the cyclotrisiloxanes **4** (calcd for $[C_{18}H_{18}O_6Si_3 \cdot NH_4]^+$ 432.0749; found 432.0758 and 432.0752, respectively).

To our surprise, cyclotrisiloxane D could be isolated by silica gel column chromatography by careful tuning of the separation conditions.[11] Addition of a small amount of CF_3CO_2H is highly effective for the stabilization of the cyclotrisiloxane during the separation. So far, the isolation of *cis,trans*-**4** has been successful only for a sample at an early stage of reaction (∼3 h), and the isolated yield was 9.9%. As shown in Figure 1, *cis,trans*-**4** became the main product after a longer reaction time (45.7% by HPLC area ratio after 42.5 h). However, attempts to isolate *cis,trans*-**4** by using these samples resulted in the formation of an unidentified complex mixture of products, which have longer retention times by HPLC analysis. We also tried to isolate *cis,cis*-**4** but failed, because *cis,cis*-**4** was formed only in a low yield and its retention time under the separation conditions was probably similar to those of other products, as observed in the HPLC chromatograms in Figure 1.

We obtained single crystals of *cis,trans*-**4** from its ether solution and succeeded in an unambiguous determination of its structure. The crystal contained ether molecules, which are severely disordered. Figure 4(1) shows the molecular structure of *cis,trans*-**4**. In the crystal, this compound forms a cylindrical arrangement along the *a* axis through hydrogen bonds by the three hydroxy groups (Figure 4(2)). A similar arrangement through hydrogen bonds is also observed for isopropyl-substituted cyclotrisiloxanetriol.[6] One of the hydrogen atoms of the three OH groups seems to form another hydrogen bond between the oxygen atom of the disordered ether molecule. The average Si–O bond length of the six-membered ring is 1.633 Å, and the average O–Si–O and Si–O–Si angles are 108.4 and 131.8°, respectively. The cyclotrisiloxane six-membered ring has good planarity, and the highest deviation from the least-squares plane of the six atoms is 0.132(1) Å (O2). These bonding parameters and the planarity are similar to those of the other cyclotrisiloxanetriols.[4b,5b,c,6]

With this information in hand, we further analyzed the condensation mixture by ^{29}Si NMR spectroscopy. With a lower concentration of MSA, 10 ppm in THF-d_8, the condensation reaction was slow and signals of monomer **1** (−53.3 ppm),[8c] disiloxane **2** (−62.3 ppm),[12,13] and linear trisiloxane **3** (−61.8 and −71.4 ppm)[13] were clearly observed for the sample after 17.6 h at 25 °C (Figure S3 in the Supporting Information). The ^{29}Si NMR spectrum of the condensation solution with more concentrated MSA (1000 ppm) after 11.5 h is shown in Figure 5. New signals corresponding to cyclotrisiloxanes **4** were
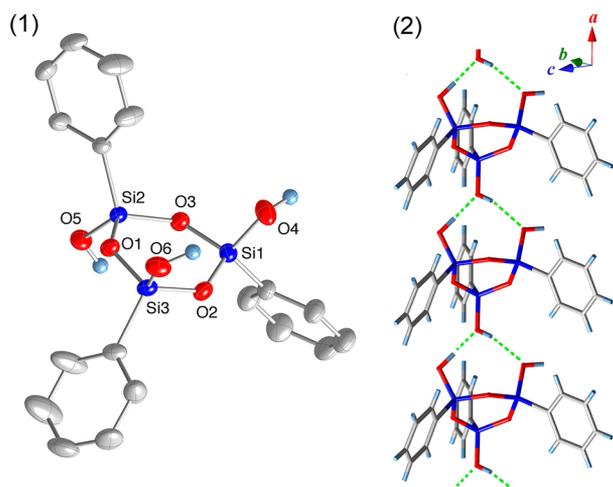
Figure 4. X-ray crystallographic analysis of *cis,trans*-4: (1) thermal ellipsoid plot (50% probability level) of *cis,trans*-4; (2) cylindrical arrangement of cyclotrisiloxane rings through hydrogen bonds. Selected bond lengths (Å) and angles (deg): Si1−O2 1.628(2), Si1−O3 1.633(2), Si1−O4 1.630(3), Si2−O1 1.631(2), Si2−O3 1.633(2), Si2−O5 1.625(3), Si3−O1 1.636(2), Si3−O2 1.639(2), Si3−O6 1.618(3); O2−Si1−O3 107.40(12), O2−Si1−O4 105.28(14), O3−Si1−O4 110.35(14), O1−Si2−O3 107.27(12), O1−Si2−O5 108.31(13), O3−Si2−O5 109.64(13), O1−Si3−O2 106.26(12), O1−Si3−O6 111.71(13), O2−Si3−O6 109.14(14), Si1−O3−Si2 131.37(14), Si1−O2−Si3 131.06(14), Si2−O1−Si3 133.07(15).
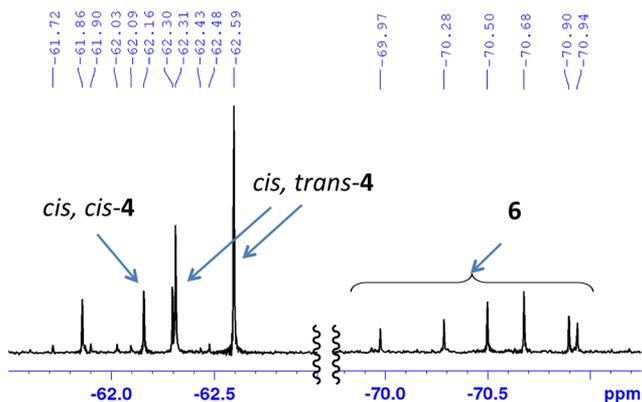

Figure 5. ^{29}Si inverse gated ^{1}H-decoupled NMR spectrum of the condensation reaction mixture of **1** (42.4 mg) with 1000 ppm of MSA in THF-d_8 (0.7 mL) after 11.5 h (measurement duration 37 min) at 25 °C (−61.5 to −63.0 ppm and −69.75 to −71.25 ppm regions).

observed at −62.16, −62.31, and −62.59 ppm in addition to six signals observed at −70 to −72 ppm assignable to six different silicon atoms belonging to four stereoisomers of cyclo-tetrasiloxanes **6**.[14]

It was generally observed that ^{29}Si NMR signals of the silicon atoms consisting of cyclotrisiloxane six-membered rings appear at about 10 ppm lower magnetic field positions in comparison to those of the similarly substituted silicon atoms of linear and cyclic tetrasiloxane or larger ring siloxanes.[15] In consideration of the ^{29}Si NMR chemical shifts of **2** and **3**, we now can confirm this general observation and unambiguously assign the larger signal at −62.59 ppm to two identical silicon atoms of *cis,trans*-**4** and the smaller signal at −62.31 ppm to the remaining silicon atom. In addition, we can conclude that the signal at −62.16 ppm belongs to the silicon atoms of *cis,cis*-**4**.
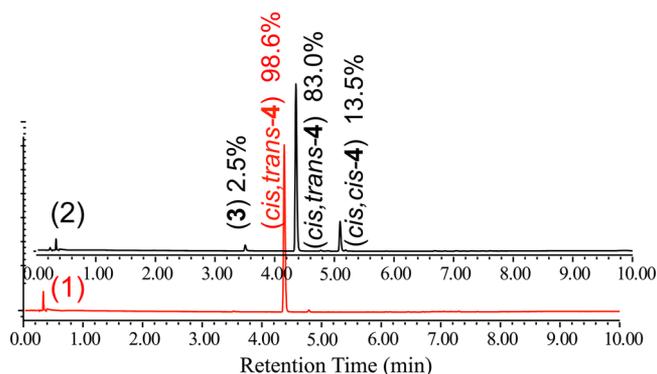

Figure 6. Chromatograms for 1.5 mg of *cis,trans*-4 (1) before the reaction and (2) after the reaction with 1000 ppm of MSA in THF at 5 °C for 21.7 h.

It became clear that, once *cis,trans*-**4** was isolated in a pure crystalline form, it is unexpectedly stable and does not change for months. Furthermore, it is also stable in THF or CH$_3$CN solution for more than 1 week. Even with 1000 ppm of MSA in THF solution, only a small amount of *cis,trans*-**4** was consumed by a ring-opening reaction to form the linear trisiloxane **3** and an isomerization reaction to form *cis,cis*-**4** without any other degradations or polymerizations. Under these conditions, an equilibration mixture was obtained at 5 °C after 21.7 h. Figure 6 shows the HPLC chromatograms before and after the equilibration of *cis,trans*-**4**. From the relative ratio of *cis,trans*-**4** and *cis,cis*-**4** (86.0/14.0),[16] the free energy difference between the two isomers was calculated to be 4.2 kJ/mol.

Cyclotrisiloxanes from phenylsilanetriol have long been considered as short-lived kinetic products and to be rapidly converted to thermodynamically favored tetrasiloxanes and further condensed products. However, this investigation clearly shows that the cyclotrisiloxanes **4** are unexpectedly stable not only in the solid state but also even in acidic solution. Therefore, the cyclotrisiloxanes would play an important role in the condensation process to form polyphenylsilsesquioxanes. We expect these findings will help to control silicone resin structures and will lead to the improvement of silicone materials properties such as shelf life and brittleness.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, and a CIF file giving experimental details and characterization and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(9) All ppm values in this paper are by weight.

(10) Other peaks were assigned as follows: E, **6**; F, unidentified; G, **6**; I, unidentified; J, **6**; K, **6**; L, unidentified. See the Supporting Information for details.

(11) Synthesis and isolation of *cis,trans*-**4**: to a stirred mixture of **1** (2.0 g, 12.8 mmol) and anhydrous $MgSO_4$ (20 g) in 40 mL of Et_2O was added 40 μL of MSA. The mixture was stirred at room temperature for 3 h. After the mixture was filtered through Celite, a small amount of CF_3CO_2H was immediately added to the filtrate to make about a 100 ppm solution. After evaporation of the solvent to 5 mL, the mixture was subjected to chromatography over silica gel. Elution was done using solvents (hexane/Et_2O) containing 100 ppm of CF_3CO_2H for the stabilization of products with gradient conditions 10% Et_2O for 2 min, then up to 100% Et_2O for 18 min, and further for 20 min with 100% Et_2O at a rate of 20 mL/min. *cis,trans*-**4** eluted as the first fraction, which was evaporated to just before dryness and kept at 5 °C to give 175 mg (1.27 mmol, 9.9% yield) of crystalline *cis,trans*-**4** with a purity of 98.6% as judged by HPLC. Anal. Calcd for $C_{18}H_{18}O_6Si_3$: C, 52.15; H, 4.38. Found: C, 52.14, H, 4.41. ^1H NMR (600 MHz, THF-d_8): δ 6.57 (1H, br s, O*H*), 6.62 (2H, br s, O*H*), 7.26 (4H, m, *m-Ph*), 7.33 (2H, m, *p-Ph*), 7.34 (2H, m, *m-Ph*), 7.39, 1H, m, *p-Ph*), 7.68 (4H, m, *o-Ph*), 7.83 (2H, m, *o-Ph*), ^{13}C NMR (151 MHz, THF-d_8): 128.17 (*m-Ph*), 128.20 (*m-Ph*), 130.63 (*p-Ph*), 130.66 (*p-Ph*), 134.58 (*ipso-Ph*), 134.80 (*ipso-Ph*), 135.13 (*o-Ph*), 135.24 (*o-Ph*). ^{29}Si NMR (119 MHz, THF-d_8): −62.59, −62.31.

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(16) The relative ratio of isomers was obtained from the peak intensities of the HPLC analysis. See the Supporting Information on the reliability of these values.