Article

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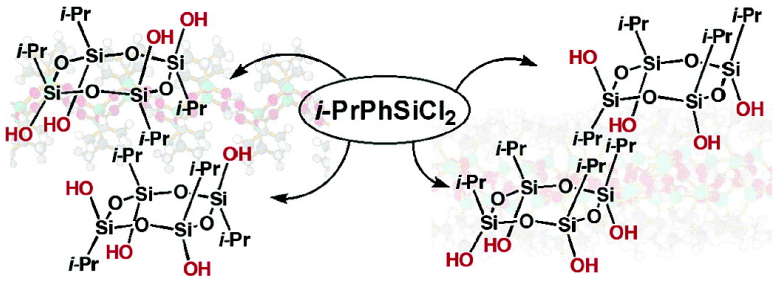

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Stereoisomers of 1,3,5,7-Tetrahydroxy-1,3,5,7-tetraisopropylcyclotetrasiloxane: Synthesis and Structures in the Crystal

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Abstract: The first synthesis of all four stereoisomers of 1,3,5,7-tetrahydroxy-1,3,5,7-tetraisopropylcyclotetrasiloxane, [*i*-PrSiO(OH)]$_4$ (all-*trans*-, *cis*-*cis*-*trans*-, *cis*-*trans*-*cis*-, and all-*cis*-**1**), is presented. The starting compounds, all-*trans*-, *cis*-*cis*-*trans*-, *cis*-*trans*-*cis*-, and all-*cis*-1,3,5,7-tetraaryl-1,3,5,7-tetraisopropylcyclotetrasiloxanes, were prepared by the hydrolysis of the corresponding arylisopropyldichlorosilanes, *i*-PrArSiCl$_2$ (Ar = Ph, *p*-tolyl), and subsequent separation of isomers. A combination of dephenylchlorination of tetraarylcyclotetrasiloxanes and the following hydrolysis proved to be an efficient method for the stereospecific transformation of aryl-substituted cyclotetrasiloxanes into (*i*-PrSiO(OH))$_4$. For example, treatment of *cis*-*trans*-*cis*-1,3,5,7-tetraphenyl-1,3,5,7-tetraisopropylcyclotetrasilane with HCl and AlCl$_3$, followed by hydrolysis in the presence of pyridine, resulted in the exclusive formation of *cis*-*trans*-*cis*-**1** in 92% yield. The structures of *cis*-*cis*-*trans*-**1**, *cis*-*trans*-*cis*-**1**, and all-*cis*-**1** were determined by X-ray crystallography. All isomers were found to construct unique packing structures by intermolecular hydrogen bonding; *cis*-*trans*-*cis*-**1** composed an infinite antiladder structure, and *cis*-*cis*-*trans*-**1** formed a sheetlike structure.

Introduction

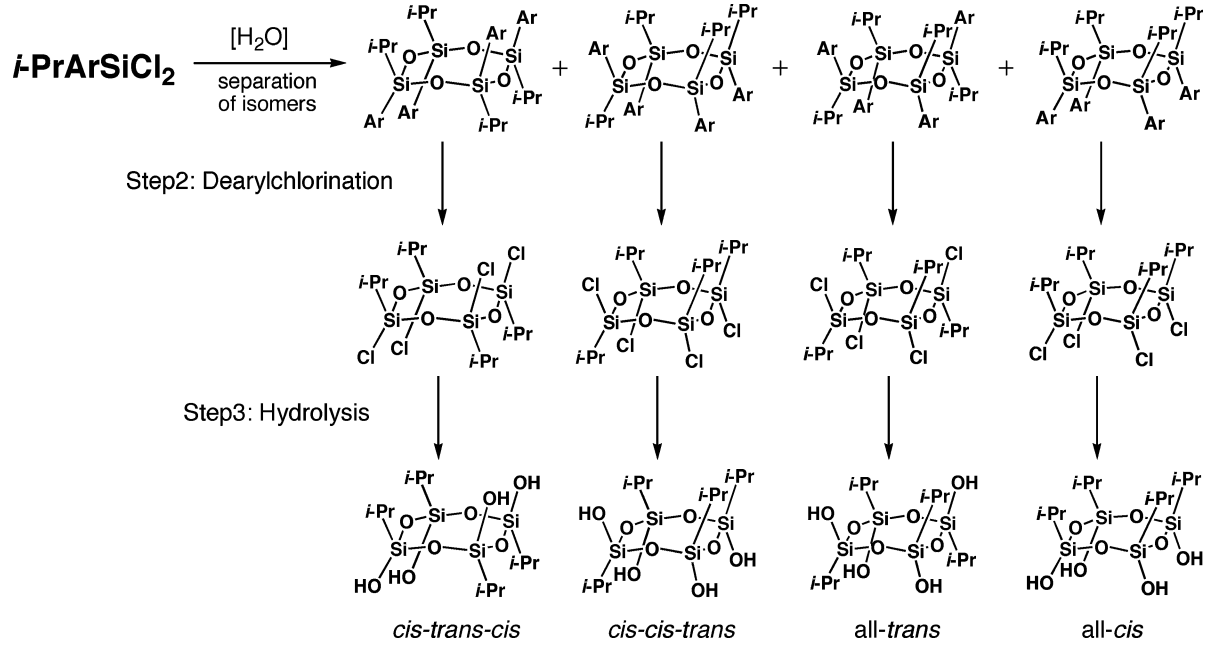
In the past decade, there was a great deal of investigation on the synthesis and applications of polysilanols.[1] Among such polysilanols, 1,3,5,7-tetrahydroxy-1,3,5,7-tetraorganocyclotetrasiloxanes have shown their utility as precursors of polysilsesquioxanes with cage and ladder structures.[2−5] The first synthesis of cyclotetrasiloxanetetraols was reported in 1965, when Brown and Vogt reported that 1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane and 1,3,5,7-tetrahydroxy-1,3,5,7-tetracyclohexylcyclotetrasiloxane were obtained by the hydrolytic condensation of trichlorophenylsilane and trichlorocyclohexylsilane, respectively.[6] They assigned the structure of both compounds to be all-*cis* isomer from the IR spectra of their derivatives, and later, the structure of (PhSiO(OH))$_4$ was confirmed by Feher in 1996 by X-ray crystallography.[7] These are the only examples of cyclotetrasiloxanetetraols, and no isomers other than the all-*cis* form have been reported to our best knowledge. This result is explained by the following two facts: (1) the absence of a synthetic pathway to other isomers; and (2) the possibility that condensation of the silanepolyols causes difficulties in the separation and purification step.

As a part of our work related to silsesquioxane chemistry,[8] we have prepared (*i*-PrSiO(OH))$_4$ with a stepwise transformation from *i*-PrPhSiCl$_2$.[3] Again, the obtained isomer was only all-*cis* form, and we attributed this rather unusual (sterically or statistically unfavorable) selectivity to the stabilization by hydrogen bonding at the final stage of the reaction. Incidentally, this tetraol is very versatile as the precursors of various siloxanes; we have reported the preparation of tricyclic laddersiloxanes,[3] pentacyclic laddersiloxanes,[4] hexasilsesquioxanes,[3] octasilsesquioxanes,[2] and supramolecular nanosize aggregates.[5] This remarkable diversity prompted us to prepare other isomers of cyclotetrasiloxanetetraols, which are also considered to be potential precursors of various siloxanes, for example, ladder silsesquioxanes. Regarding the other stereoisomers, a Russian group reported the isomerization of all-*cis*-(PhSiO(OH))$_4$ with Me$_3$SiCl to give an equilibrium mixture of all isomers.[9,10] Other than this report, there have been no examples thus far.

(1) (a) Lickiss, P. D. *Adv. Inorg. Chem.* **1995**, *42*, 147. (b) Lickiss, P. D. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Z., Eds.; Wiley: Chichester, U.K., 2001; Vol. 3, Chapter 12. (c) Feher, F. J.; Budzichowski, T. A. *Polyhedron* **1995**, *14*, 3239. (d) Duchateau, R. *Chem. Rev.* **2002**, *102*, 3525. (e) *The Chemistry of Organic Silicon Compounds*; Jutzi, P., Schubert, U., Eds.; Wiley-VCH: Weinheim, Germany, 2003; Chapter III.
(2) Unno, M.; Takada, K.; Matsumoto, H. *Chem. Lett.* **1998**, 489.
(3) Unno, M.; Suto, A.; Takada, K.; Matsumoto, H. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 215.
(4) Unno, M.; Suto, A.; Matsumoto, H. *J. Am. Chem. Soc.* **2002**, *124*, 1574.
(5) Unno, M.; Takada, K.; Matsumoto, H. *Chem. Lett.* **2000**, 242.
(6) (a) Brown, J. F., Jr.; Vogt, L. H., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 4313. (b) Brown, J. F., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 4317.
(7) Feher, F. J.; Schwab, J. J.; Soulivong, D.; Ziller, J. W. *Main Group Chem.* **1997**, *2*, 123.
(8) (a) Unno, M.; Shamsul, B. A.; Saito, H.; Matsumoto, H. *Organometallics* **1996**, *15*, 2413. (b) Unno, M.; Shamsul, B. A.; Arai, M.; Takada, K.; Tanaka, R.; Matsumoto, H. *Appl. Organomet. Chem.* **1999**, *13*, 1. (c) Unno, M.; Imai, Y.; Matsumoto, H. *Silicon Chem.* **2003**, *2*, 175. (d) Unno, M.; Tanaka, T.; Matsumoto, H. *J. Organomet. Chem.* **2003**, *686*, 175. (e) Unno, M.; Matsumoto, T.; Mochizuki, K.; Higuchi, K.; Goto, M.; Matsumoto, H. *J. Organomet. Chem.* **2003**, *685*, 156.
(9) Klement'ev, I. Yu.; Shklover, V. E.; Kulish, M. A.; Tikhonov, V. S.; Volkova, E. V. *Dokl. Akad. Nauk SSSR* **1981**, *259*, 1371.
(10) Unfortunately, our attempts to reproduce this result have not been successful; trials to separate the products met with the decomposition.

10.1021/ja043894m CCC: $30.25

Scheme 1. Strategy for the Synthesis of All Isomers of Cyclotetrasiloxanetetraols



Cyclotetrasiloxanetetraol, especially the phenyl-substituted one, lacks enough stability to be chromatographically separated or purified. Feher also mentioned its instability in his successful crystallographical identification of all-*cis*-$(PhSiO(OH))_4$ with careful handling.[7] In contrast, all-*cis*-$(i\text{-}PrSiO(OH))_4$ was stable in air or in basic or acidic media. Thus, we chose isopropyl groups as substituents in this project. One expected problem was the separation of isomers. We have shown that reverse-phase HPLC was very effective in separating stereoisomers.[4] However, this method could not be applied to alkyl-substituted silsesquioxanes because of the lack of an appropriate detector for these compounds.

Confronted with the fact that separating isomers of cyclotetrasiloxanetetraols is difficult, we devised a strategy as illustrated in Scheme 1. By overcoming the following two synthetic hurdles, we were able to accomplish this task. (1) The first hydrolytic condensation gives all four isomers of $(i\text{-}PrArSiO)_4$, and they are separated. (2) Two consecutive reactions (dearylchlorination and hydrolysis) proceed while maintaining the stereostructures.

The stereochemistry of organosilicon compounds has been intensively studied,[11] and several reports described the stereochemistry of dearylchlorination of silicon compounds. Kumada's group reported that dephenylchlorination of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane always gave a mixture of isomers regardless of whether pure *cis* or *trans* isomer was employed, indicating the reaction proceeded in a nonstereospecific manner.[12] They also observed that isomeric pure 1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane underwent epimerization slowly by the action of atmospheric moisture or rapidly with ethanol, and suggested that this epimerization was responsible for the nonstereospecific dearylhalogenation. The facile racemization of (+) or (−)-naphthylphenylchlorosilane resulting in a mixture of diastereomers in the mentholysis was also reported.[11d] Additionally, racemization of halosilanes was reported to be enhanced by the addition of nucleophiles (e.g., HMPA, DMF, or pyridine).[13] Although the hydrolysis of acyclic chlorosilanes is recognized to proceed invariably in inversion of configuration,[14] Corriu demonstrated that in the presence of nucleophiles, the hydrolysis of methyl(1-naphthyl)phenylchlorosilane took place with retention of configuration,[15] and this was rationalized by a recent theoretical study.[16] All of these previous results imply that the stereospecific preparation of cyclic silanols is a difficult task. Nonetheless, these reports deal with methyl-substituted silanes, and the bulkiness of the substituents has considerable effect on the stability against racemization. With these considerations in mind, we adopted isopropyl groups for substituents.

In our recent synthesis of pentacyclic laddersiloxane,[4] we succeeded in the transformation of phenyl groups to chlorine atoms with the siloxane rings remaining intact. Although the stereostructure of a ladder framework was maintained, stereochemistry at the silicon atoms was not elucidated. In the present paper, we employed phenyl and *p*-tolyl groups on the silicon atoms, and stereospecific transformation via chlorosiloxanes to silanols was demonstrated. As expected, the obtained cyclic silanols were shown to compose a variety of hydrogen-bonded aggregates.

Results and Discussion

Preparation of Aryl-Substituted Cyclotetrasiloxanes. Although preparations of cyclotetrasiloxanes bearing two different

(11) For reviews, see: (a) Bassindale, A. R.; Glynn, S. J.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Z., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Chapter 9. (b) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. V. *Chem. Rev.* **1993**, *93*, 1371−1448. (c) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17. (d) Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Chapter 4.

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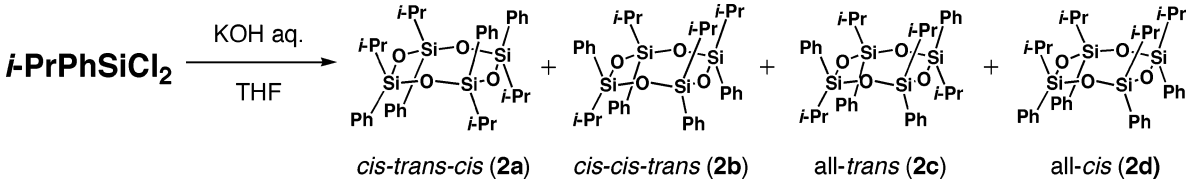
(13) Bassindale, A. R.; Lau, J. C.-Y.; Taylor, P. G. *J. Organomet. Chem.* **1995**, *490*, 75.

(14) See ref 11a, p 496.

(15) Corriu, R. J. P.; Dabosi, G.; Martineau, M. *J. Organomet. Chem.* **1978**, *154*, 33.

(16) Ignatyev, I.; Schaefer, H. F., III. *Organometallics* **2001**, *20*, 3113.

Scheme 2. Preparation and Separation of the Isomers of (*i*-PrPhSiO)$_4$ **2**



substituents have been known for years,[17] only stereoisomers of (MePhSiO)$_4$ have been separated to date. The first synthesis of this compound was reported in 1948 by Lewis,[18] followed by the report in which partial separation and IR measurement were performed.[19] Eighteen years later, isolation of a *cis*−*trans*-*cis* isomer was effected by distillation and fractional crystallization over a period of 2 months.[20] Since then, structure elucidation by ^{1}H NMR[21] and X-ray crystallographic analysis of a *cis*-*trans*-*cis* isomer have been accomplished.[22] However, the molecular structures of other isomers have not yet been determined, and only a few reactions starting from a single stereoisomer have emerged.[23] It is thus worthwhile to determine the structures of all isomers and to transfer them into the versatile compounds. In view of the fact that facile separation and further transformation may demand stability, isopropyl-substituted compounds are more favorable.

The reaction of *i*-PrPhSiCl$_4$ with aqueous KOH or NaOH proceeded smoothly to give cyclotetrasiloxane, (*i*-PrPhSiO)$_4$ (**2**), as a mixture of isomers (Scheme 2). The reverse-phase HPLC chromatogram at the end of the reaction is shown in Figure 1. This chart clearly indicates that all four isomers were generated in the reaction. For methyl-substituted cyclic siloxanes, KOH cleaves Si−O bonds and equilibrium was observed.[18] By repeating the reactions under conditions of various scales, concentrations, and reaction time, we observed no difference in the ratio of isomers. Thus, the reaction promptly came to the final mixture, and no further equilibrium occurred. This is another advantage for isopropyl-substituted siloxanes, showing the stability of their frameworks. The separation of four isomers was performed by recycle-type HPLC, and **2a** (18%), **2b** (46%), **2c** (9%), and **2d** (8%) were obtained. It is noteworthy that the total yield (81%) is quite high, compared to the result of (MePhSiO)$_4$. In the latter case, a trimer (D_3) and pentamer (D_5) were also obtained as well as polymeric compounds, and thus the yield was lower.[19] One of the isomers, the *cis*-*cis*-*trans* isomer, could be assigned to **2b** from the NMR spectra (three different silicon atoms and substituents). However, the structures of the remaining three isomers could not be determined by spectroscopic methods. Fortunately, two of the isomers (**2a** and **2d**) gave suitable single crystals, and the structure was assigned to *cis*-*trans*-*cis* and all-*cis* isomer, respectively. In consequence, all four isomers were unequivocally determined. Crystal structures are shown in Figure 2, and the result of crystallographic data is summarized in Table 1.

The ratio of four isomers (22:57:11:10) is similar to that of the statistical abundance (25:50:12.5:12.5), but all-*cis* and all-*trans* isomers were less formed than in the case of (MePhSiO)$_4$ (ratio was 20:50:13:17).[17c] In this reaction, *cis*-*cis*-*trans* isomer **2b** was generated predominantly (46%), whereas *cis*-*trans*-*cis* isomer **2a**, which is mostly desired for the construction of laddersiloxanes, was obtained in 18% yield. Since we could not observe any equilibrium between isomers for **2a**−**d**, we then tried *p*-tolyl as an aryl substituent, aiming for a better yield of the *cis*-*trans*-*cis* isomer. The reaction is depicted in Scheme 3; the HPLC chart is shown in Figure 3, and all four isomers were separated. Again, compound **3b** was assigned to be *cis*-*cis*-*trans* isomer from the NMR spectra, and the structures of the remaining three isomers were determined by X-ray crystallography. The result of analysis is shown in Figure 4 and Table 1. Although it was expected that the isomer ratio might not be affected (steric environment around the silicon atoms seems to be barely different), yields of isomers (22, 32, 11, and 8% for **3a**−**d**, respectively) were different; we obtained *cis*-*trans*-*cis* isomer with improved yield.

Structure of (*i*-PrArSiO)$_4$. The structural parameters for cyclotetrasiloxane rings for **2a**, **2d**, **3a**, **3c**, and **3d** are summarized in Table 2. Average Si−O bond lengths and O−Si−O bond angles are identical within errors, whereas the Si−O−Si angle varies from 147.6 to 159.6°, showing flexibility of the bonding. Additionally, dihedral angles of four Si atoms in the

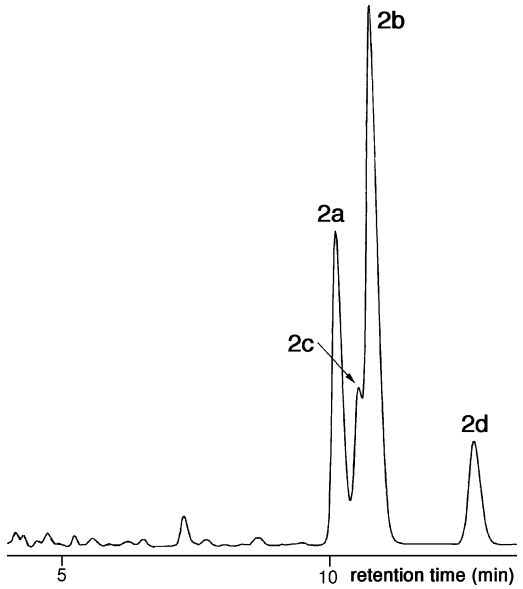


Figure 1. HPL chromatogram at the end of the reaction (ODS, MeOH).

(17) (a) Sakiyama, M.; Nishizawa, Y.; Okawara, R. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 2182. (b) Pelletier, E.; Harrod, J. F. *Can. J. Chem.* **1983**, *61*, 762. (c) Harrod, J. F.; Pelletier, E. *Organometallics* **1984**, *3*, 1064. (d) Park, M. J.; Yim, E. S.; Lee, S. J.; Park, M. K.; Han, B. H. *Main Group Met. Chem.* **1999**, *22*, 713.
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(19) Young, C. W.; Servais, P. C.; Currie, C. C.; Hunter, J. *J. Am. Chem. Soc.* **1948**, *70*, 3758.
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(23) (a) Sommer, L. H.; Frye, C. L. *J. Am. Chem. Soc.* **1960**, *82*, 3796. (b) ref 14.

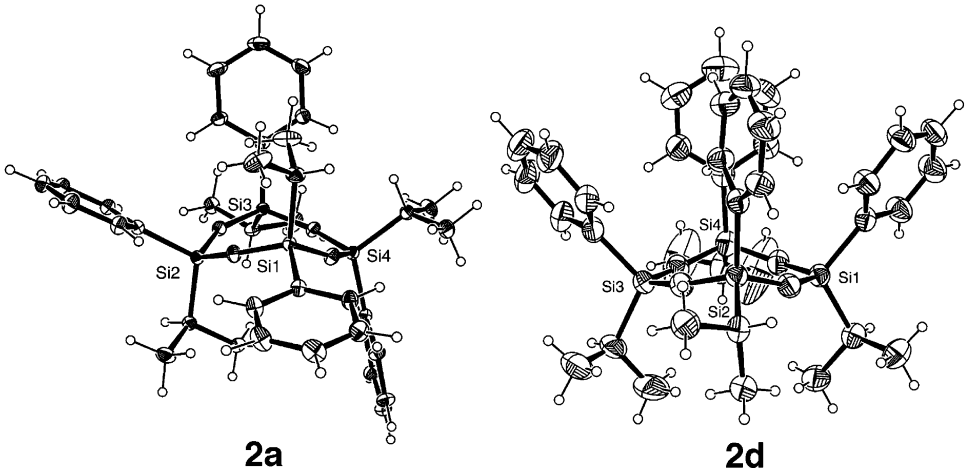
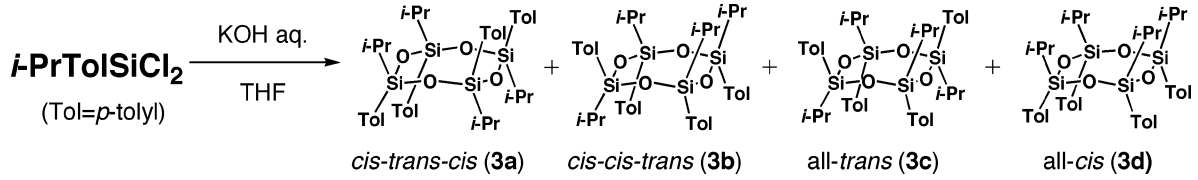


Figure 2. ORTEP drawings of compounds **2a** and **2d** derived from X-ray crystallographic analysis.

Table 1. Crystallographic Data for **2a**, **2d**, **3a**, **3c**, and **3d**

	2a	2d	3a	3c	3d
formula	$C_{36}H_{48}O_4Si_4$	$C_{36}H_{48}O_4Si_4$	$C_{40}H_{56}O_4Si_4$	$C_{40}H_{56}O_4Si_4$	$C_{40}H_{56}O_4Si_4$
formula weight	657.11	657.11	713.22	713.22	713.22
crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/a$	$P\bar{1}$	$P\bar{1}$	Cc
a, Å	13.393(1)	19.782(2)	10.0898(2)	10.8849(4)	10.785(1)
b, Å	18.750(2)	10.279(1)	10.8738(2)	12.3267(5)	18.662(2)
c, Å	14.822(1)	19.450(2)	11.1989(2)	15.1563(6)	21.071(3)
α, deg			75.44(1)	78.373(5)	
β, deg	94.359(3)	105.265(3)	67.62(1)	81.219(5)	97.383(4)
γ, deg			67.20(1)	77.132(5)	
V, Å^3	3711.4(6)	3815.5(7)	1039.5(1)	2056.7(2)	4205.7(9)
Z	4	4	1	2	4
μ, mm^{-1}	0.195	0.190	0.179	0.181	0.177
2θ max, deg	64.6	64.7	64.6	64.6	64.3
independent reflns	10774	11075	5379	10664	10145
observed reflns	8821	9751	4410	9550	6957
solution	SIR97	SIR97	SIR92	SIR97	SIR92
$R1$	0.047	0.094	0.065	0.041	0.051
$wR2$	0.145	0.275	0.181	0.112	0.159
S	1.12	0.98	1.31	1.08	1.52
$(\Delta/\sigma)_{max}$	0.0010	0.0020	0.0000	0.0010	0.0000
$(\Delta\rho)_{max}$, e Å^{-3}	0.48	0.98	0.73	0.38	0.38
$(\Delta\rho)_{min}$, e Å^{-3}	−0.50	−0.88	−0.58	−0.39	−0.42
No. of params	399	389	246	435	435

Scheme 3. Preparation and Separation of the Isomers of (*i*-Pr(*p*-Tol)SiO)$_4$ **3**



eight-membered rings showed a wide range of values. For example, *cis-trans-cis*-(*i*-Pr(*p*-Tol)SiO)$_4$ (**3a**) adopted a planar structure; the dihedral angle was 0°. As a result, the Si−O−Si angles became wider in order to release the strain enforced by the eclipsed conformation of the adjacent substituents. On the other hand, large dihedral angles substantially decrease the repulsion of the vicinal substituents, resulting in smaller Si−O−Si angles, as seen in the case of all-*cis* **3d**. Only one crystallographic report for (RArSiO)$_4$ cyclotetrasiloxanes has appeared prior to our results, that is, *cis-trans-cis*-(MePhSiO)$_4$.[22] This compound adopts a nearly planar structure, and average Si−O bond lengths and O−Si−O and Si−O−Si bond angles were 1.622 Å, 109.6°, and 150.2°, respectively. Interesting to note is that these values are very close to those of isopropyl-substituted cyclotetrasiloxanes, indicating the steric congestion is not severe for this system. Similar to the isomers of laddersiloxanes,[4] the melting points vary, 80−199 °C for (*i*-PrPhSiO)$_4$ and 70−127 °C for (*i*-Pr(*p*-Tol)SiO)$_4$.

Dearylchlorination Reaction. Dephenylchlorination of oligosilanes has been known for years[11] and is widely adopted. However, this reaction has not been applied to siloxanes because HCl or HBr was known to cleave Si−O bonds.[17a] Quite recently, we have shown that this reactivity is observed only for methylsiloxanes, and we successfully transformed phenyl groups on isopropyl-substituted cyclic siloxanes to chlorine atoms in high yields by the action of HCl and $AlCl_3$.[4] Thus, we applied

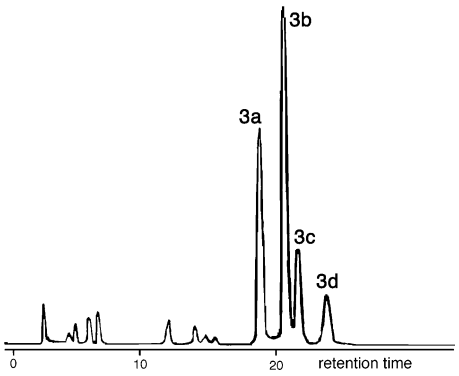


Figure 3. HPL chromatogram at the end of the reaction (ODS, MeOH).

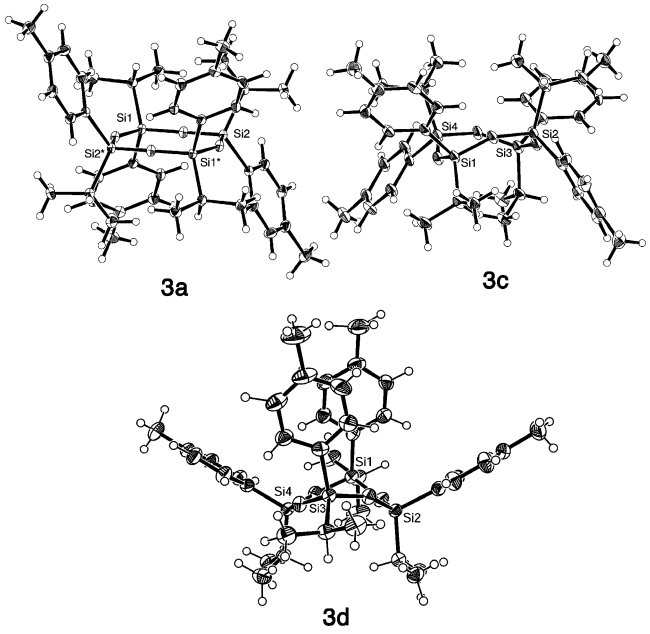
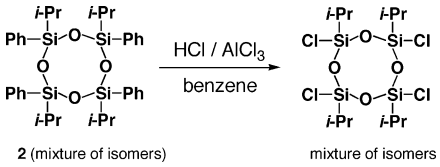


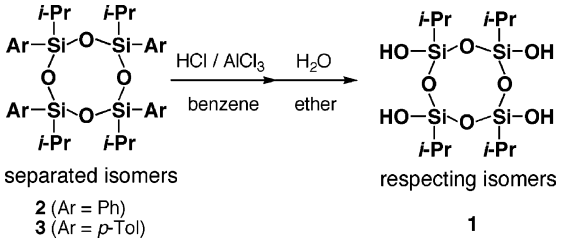
Figure 4. ORTEP representation of compounds **3a**, **3c**, and **3d**.

this reaction to **2** (mixture of isomers). In 30 min at 25 °C, the starting material completely disappeared, and workup followed by Kugelrohr distillation gave the target tetrachloride in 95% yield (Scheme 4). The spectroscopic analysis (NMR, MS, and IR) indicated the generation of the desired tetrachlorides. The obtained compound is stable in this procedure; however, it slowly decomposed with moisture in air. Since the yield is excellent and further purification seemed unnecessary, we decided not to separate the tetrachloride but to obtain the tetraol in a single procedure from tetraarylcyclotetrasiloxanes.

Scheme 4. Dearylchlorination of (*i*-PrPhSiO)$_4$ **2** (Mixture of Isomers)



Scheme 5. One-Step Synthesis of Cyclotetrasiloxanetetraols **1** from Four Isomers of **2** and **3**



Direct Synthesis of Cyclotetrasiloxanetetraol from (*i*-PrArSiO)$_4$. The separated isomers of **2a**−**d** and **3a**−**d** were subjected to dearylchlorination followed by hydrolysis. The reaction condition for the first step was the same as that described above; then the ethereal solution of tetrachlorides was treated with water. After usual workup, recrystallization of the crude product gave pure tetraols (Scheme 5). In every reaction, we were pleased to observe the formation of only single isomers. All of the spectroscopic analysis clearly indicated generation of the target tetraols. Regarding stereostructures, the assignment was accomplished as follows. First, *cis*-*cis*-*trans* isomer **1b** was determined by NMR spectra as in the case of **2b** and **3b**. Second, we have already reported the synthesis and structure of an all-*cis* isomer,[2,5] thus **1d** could be assigned by the comparison of its spectra and melting point. The structures of the remaining two isomers, all-*trans* and *cis*-*trans*-*cis*, are only unequivocally established by crystallographic analysis. Unfortunately, the single crystals of the all-*trans* isomer could not be obtained after repeated trials; however, the structure determination of *cis*-*trans*-*cis* isomer **1a** enabled us to assign all four isomers. The stereostructure around the silicon atom was maintained perfectly in these reactions, and thus we succeeded in obtaining all of the isomers in pure forms.

Structure of Cyclotetrasiloxanetetraols. The molecular structures are shown in Figure 5, and crystallographic data are summarized in Table 3. The structural parameters (Table 2) are all within the normal range for siloxanes. The most interesting point of cyclotetrasiloxanetetraols is their flexible framework and four hydroxyl groups that enable multiple connections by

Table 2. Comparison of Structural Parameters of (Si−O)$_4$ Rings

compounds	Si–O (Å)	Si–O–Si (deg)	O–Si–O (deg)	dihedral angles (deg)
cis-*trans*-*cis*-(*i*-PrPhSiO)$_4$, **2a**	1.629	153.2	110.9	41.7, 41.5
all-*cis*-(*i*-PrPhSiO)$_4$, **2d**	1.623	154.2	110.2	27.4, 26.2
cis-*trans*-*cis*-(*i*-Pr(*p*-Tol)SiO)$_4$, **3a**	1.624	159.6	110.2	0
all-*trans*-(*i*-Pr(*p*-Tol)SiO)$_4$, **3c**	1.632	148.0	110.3	34.6, 34.6
all-*cis*-(*i*-Pr(*p*-Tol)SiO)$_4$, **3d**	1.631	147.6	110.6	48.5, 49.7
cis-*trans*-*cis*-(MePhSiO)$_4$[a]	1.622	150.2	109.6	NA
all-*cis*-(Ph(OH)SiO)$_4$	1.612	147.5	109.6	NA
cis-*trans*-*cis*-(*i*-PrSi(OH)O)$_4$, **1a**	1.614	156.9	109.7	0
cis-*cis*-*trans*-(*i*-PrSi(OH)O)$_4$, **1b**	1.611	150.4	109.8	47.4. 46.2, 45.6, 43.7
all-*cis*-(*i*-Pr(OH)SiO)$_4$, **1d**[b]	1.593	152.7	110.4	42.2, 44.3
all-*cis*-(*i*-Pr(OH)SiO)$_4$, **1d**[c]	1.622	150.6	109.9	36.3−48.7 (avg. 41.7)

[a] From ref 22. [b] Cocrystallized with water. From ref 2. [c] Cocrystallized with *i*-Pr$_2$Si(OH)$_2$. From ref 5.

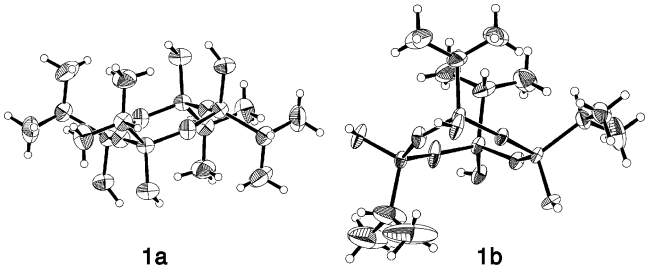


Figure 5. ORTEP structures of tetraols **1a** and **1b**.

Table 3. Crystallographic Data for **1a** and **1b**

	1a	1b
formula	$C_{12}H_{32}O_8Si_4$	$C_{12}H_{32}O_8Si_4$
formula weight	416.72	416.72
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/a$
a, Å	6.5367(2)	14.719(3)
b, Å	8.6085(1)	20.237(2)
c, Å	10.8444(5)	14.891(1)
α, deg	72.974(8)	
β, deg	82.221(9)	94.52(1)
γ, deg	72.695(8)	77.132(5)
V, Å^3	553.38(5)	4421(2)
Z	1	8
μ, mm^{-1}	0.299	0.300
2θ max, deg	64.1	55.0
independent reflns	2764	10481
observed reflns	2260	3242
solution	SIR92	SHELXS86
$R1$	0.060	0.077
$wR2$	0.172	0.084
S	1.533	0.831
$(\Delta/\sigma)_{max}$	0.0000	0.0020
$(\Delta\rho)_{max}$, e Å^{-3}	0.72	0.51
$(\Delta\rho)_{min}$, e Å^{-3}	−0.66	−0.46
No. of params	126	498

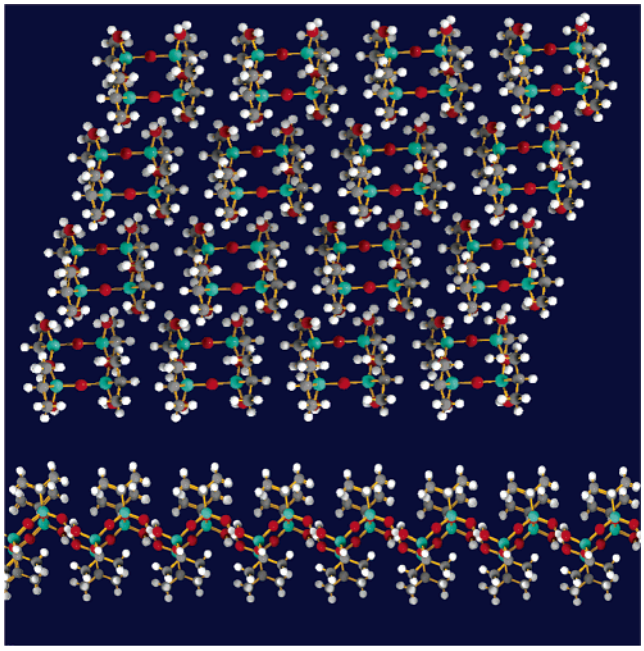


Figure 6. Top and side views of the hydrogen-bonded array found in the crystal structure of **1a** (Si: green, O: red, C: gray, H: white).

hydrogen bonding. As shown in Table 2, dihedral angles of **1a**, **1b**, and **1d** are different.

We have reported the structure of all-*cis* isomer **1d**, which composes sphere-type aggregates with water[2] and a nanosize

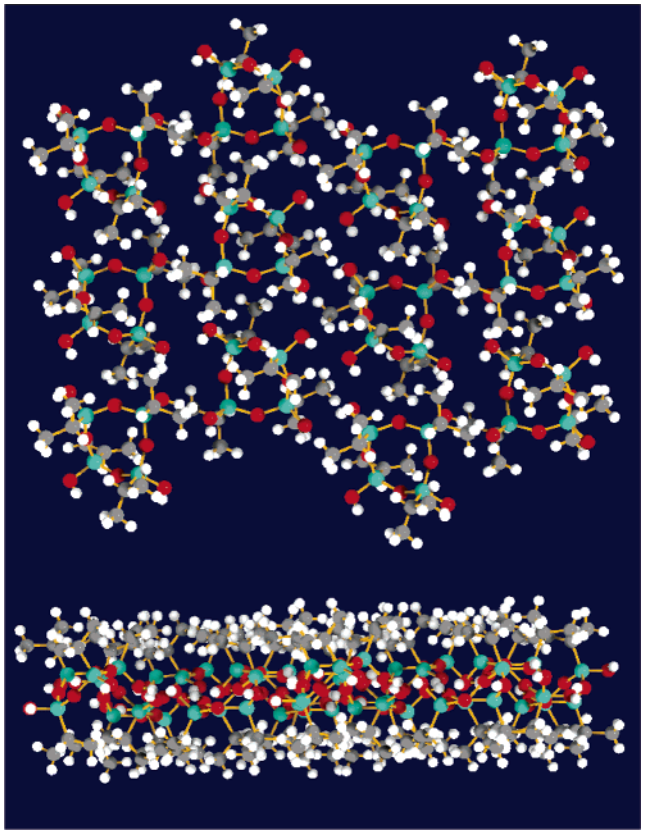


Figure 7. Top and side views of the hydrogen-bonded array found in the crystal structure of **1b** (Si: green, O: red, C: gray, H: white).

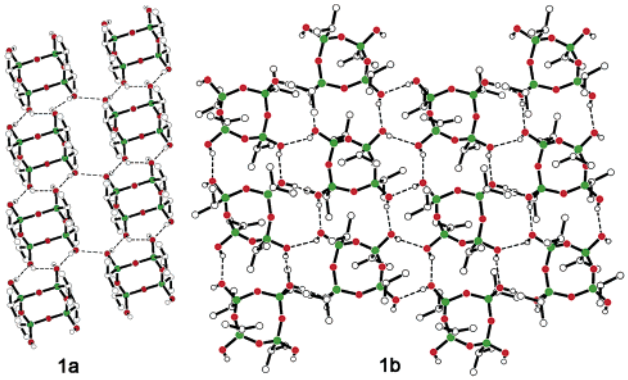


Figure 8. Detailed scheme of the hydrogen bonding of **1a** and **1b** (Si: green, O: red). Hydrogens on carbon atoms are omitted for clarity.

tubelike structure with *i*-$Pr_2Si(OH)_2$.[5] Similarly, **1a** and **1b** are proven to construct unique crystal structures. Notably, *cis-trans-cis* isomer **1a** possesses a planar $(Si-O)_4$ framework, and an infinite ladder structure was crafted in the crystal with two hydroxyl groups side-by-side. The packing diagram shown in Figure 6 represents its beautiful composition. Moreover, this structure indicates the possibility of access to the all-anti ladder polysiloxane. We are currently investigating its transformation, including solid-state reaction. For *cis-cis-trans*-(*i*-PrSi(OH)O)$_4$ isomer **1b**, four hydroxyl groups reside in nearly the same plane reflecting the large dihedral angles, and the molecular structures compose sheetlike aggregates. The packing scheme is shown in Figure 7. It is also fascinating if this could lead to the sheetlike polysiloxane. The details of the hydrogen bonding are depicted in Figure 8.

Conclusion

We have developed a simple procedure for the synthesis of cyclic silanols and prepared the formerly inaccessible three isomers of cyclotetrasiloxanetetraol (**1**). Four isomers of (*i*-PrArSiO)$_4$ (**2** and **3**) were obtained, and they were successfully transferred to (*i*-PrSiO(OH))$_4$ (**1**) while maintaining the stereostructure in excellent yields. The structures of *cis-trans-cis*- and *cis-cis-trans*-(*i*-PrSiO(OH))$_4$ were established unequivocally by X-ray crystallography, and their stimulating packing structures by hydrogen bonding were revealed.

Experimental Section

All reagents were obtained from commercial sources and used without additional purification. Ether and tetrahydrofuran were distilled from sodium benzophenone ketyl under argon. Analytical HPLC was performed in a JASCO 875UV/880PU with a Chemco 4.6 mm × 250 mm 5-ODS-H column. Preparative recycle-type HPLC was carried out using JAI LC-908 with a Chemco 20 mm × 250 mm 7-ODS-H column. Analytical GC was measured on a Shimadzu GC-8A with a column (KF-96 10% on Celite 545sk). Fourier transform nuclear magnetic resonance spectra were obtained by a JEOL Model AL-500 (^{1}H at 500.00 MHz, ^{13}C at 125.65 MHz, and ^{29}Si at 99.25 MHz). Chemical shifts were reported as δ units (parts per million) relative to SiMe$_4$, and residual solvents peaks were used for standard. Electron impact mass spectrometry was performed with a JEOL JMS-DX302. Infrared spectra were measured with a Shimadzu FTIR-8700.

Preparation of Dichloroisopropylphenylsilane. A THF solution of *i*-PrMgCl (1.8 mol/L, 350 mL) was added dropwise to a solution of PhSiCl$_3$ (133.3 g, 0.63 mol) in THF (450 mL) at 0 °C for 4 h. This solution was heated to reflux for 2 h. After filtration and removal of THF, distillation (113 °C/20 mmHg) gave target material (115.1 g, 83%). Spectral data: ^{1}H NMR ($CDCl_3$) δ 1.14 (d, 6H), 1.50 (sept, 1H), 7.48 (m, 3H), 7.72 (d, 1H), 7.74 (d, 1H); ^{13}C NMR ($CDCl_3$) δ 16.09, 19.13, 128.24, 131.47, 133.82; ^{29}Si NMR (99 MHz, $CDCl_3$) δ −21.49; IR NaCl) ν 3074, 3055, 2955, 2934, 2870, 1960, 1888, 1819, 1771, 1591, 1464, 1429, 1117, 1070, 997, 881, 741, 712, 696, 664, 621, 571, 534, 519.

Synthesis of 1,3,5,7-Tetraisopropyl-1,3,5,7-tetraphenylcyclotetrasiloxane (2). Aqueous KOH solution (6 mL, 4.2 mol/L) was added to a solution of *i*-PrPhSiCl$_2$ (2.02 g, 9.0 mmol) in THF (6 mL). The reaction mixture was heated to reflux until GC indicated complete consumption of the starting dichloride (24 h). After being cooled to ambient temperature, the reaction mixture was diluted with water and extracted three times with benzene. The combined organic extracts were dried over anhydrous magnesium sulfate and concentrated. The isomeric mixture of **2** was separated by recycle-type HPLC (ODS, MeOH) to afford **2a** (*cis-trans-cis*, 269 mg, 18%), **2b** (*cis-cis-trans*, 683 mg, 46%), **2c** (all-*trans*, 141 mg, 9%), and **2d** (all-*cis*, 125 mg, 8%). **2a**: Colorless plate, mp 122−124 °C; ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 28H), 7.44 (t, 12H, J = 6.7 Hz), 7.49 (d, 8H, J = 7.3 Hz), 7.73 (dd, 8H, J = 6.7, 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 14.95, 16.65, 127.55, 129.73, 134.20, 134.86; ^{29}Si NMR ($CDCl_3$) δ −32.21; MS (70 eV) *m*/*z* (%) 613 (M^+ − *i*-Pr, 100); IR (NaCl) ν 3071, 3051, 3003, 2943, 2893, 1591, 1464, 1429, 1382, 1364, 1246, 1161, 1123, 1082, 1061, 1028, 993, 918, 883, 854, 741, 721, 700, 644, 625, 615, 569. **2b**: Colorless plate, mp 79−80 °C; ^{1}H NMR ($CDCl_3$) δ 0.76 (d, 6H, J = 5.2 Hz), 0.79 (sept, 1H, J = 5.2 Hz), 1.08 (d, 6H, J = 7.7 Hz), 1.09 (d, 6H, J = 7.7 Hz), 1.11 (d, 6H, J = 7.7 Hz), 1.20 (sept, 3H, J = 7.7 Hz), 7.16 (t, 2H, J = 7.1 Hz), 7.19 (t, 4H, J = 6.8 Hz), 7.26 (t, 1H, J = 6.7 Hz), 7.29 (t, 2H, J = 7.1 Hz), 7.45 (m, 3H), 7.57 (d, 2H, J = 6.7 Hz), 7.59 (d, 4H, J = 6.8 Hz), 7.86 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.81, 15.03 (overlap), 16.48, 16.78, 16.89, 127.38, 127.46, 127.63, 129.61 (overlap), 129.82, 134.04, 134.13, 134.25, 134.54, 134.57, 135.12; ^{29}Si NMR ($CDCl_3$) δ −32.25, −32.11; MS (70 eV) *m*/*z* (%) 613 (M^+ − *i*-Pr, 100); IR (NaCl) ν 3071, 3051, 3024, 3015, 3003, 1591, 1464, 1429, 1385, 1364, 1246, 1161, 1123, 1084, 1061, 1028, 993, 918, 883, 854, 741, 700, 644, 623, 615, 569. **2c**: Colorless plate, mp 198−199 °C; ^{1}H NMR ($CDCl_3$) δ 0.85 (d, 24H, J = 7.0 Hz), 0.94 (sept, 4H, J = 7.0 Hz), 7.31 (t, 8H, J = 7.0 Hz), 7.38 (t, 4H, J = 7.0 Hz), 7.66 (d, 8H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 14.79, 16.67, 127.55, 129.70, 134.03, 134.99; ^{29}Si NMR ($CDCl_3$) δ −32.56; MS (70 eV) *m*/*z* (%) 613 (M^+ − *i*-Pr, 100); IR (NaCl) ν 3069, 3047, 2961, 2913, 2893, 1956, 1886, 1825, 1773, 1591, 1463, 1427, 1246, 1124, 1086, 1061, 1028, 993, 887, 743, 719, 700, 650. **2d**: Colorless plate, mp 150−151 °C; ^{1}H NMR ($CDCl_3$) δ 1.55 (d, 24H, J = 6.8 Hz), 1.62 (sept, 4H, J = 6.8 Hz), 7.40 (t, 8H, J = 7.0 Hz), 7.58 (t, 4H, J = 7.0 Hz), 7.67 (d, 8H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 14.91, 16.90, 127.15, 127.22, 129.30, 129.35, 134.02, 134.09, 134.20 (overlap); ^{29}Si NMR ($CDCl_3$) δ −32.59; MS (70 eV) *m*/*z* (%) 613 (M^+ − *i*-Pr, 100); IR (NaCl) ν 3071, 3049, 3009, 2947, 2893, 2864, 1464, 1427, 1385, 1362, 1248, 1121, 1088, 1065, 1028, 997, 918, 885, 739, 721, 698, 644, 596, 563.

Synthesis of 1,3,5,7-Tetraisopropyl-1,3,5,7-tetra(*p*-tolyl)cyclotetrasiloxane (3). A solution of *i*-Pr(*p*-Tol)SiCl$_2$ (1.2 g, 5.1 mmol) in THF (10 mL) was treated with aqueous NaOH solution (10 mL, 4.5 mol/L) in a similar manner (reflux, 36 h) as that described above. The isomeric mixture of **3** was separated by recycle-type HPLC (ODS, MeOH) to afford **3a** (*cis-trans-cis*, 201 mg, 22%), **3b** (*cis-cis-trans*, 290 mg, 32%), **3c** (all-*trans*, 99 mg, 11%), and **3d** (all-*cis*, 68 mg, 8%). **3a**: Colorless solid, mp 69−70 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (d, 24H, J = 1.2 Hz), 0.89 (br s, 4H), 2.37 (s, 4H), 7.16 (d, 8H, J = 7.7 Hz), 7.56 (d, 8H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 14.98, 16.71, 21.58, 128.29, 131.46, 134.28, 139.37; ^{29}Si NMR ($CDCl_3$) δ −32.17; MS (70 eV) *m*/*z* (%) 669 (M^+ − *i*-Pr, 100): IR (NaCl) ν 3069, 3034, 3013, 2943, 2924, 2893, 1607, 1464, 1383, 1246, 1161, 1117, 1084, 1063, 1022, 993, 883, 800, 721, 679, 658, 583, 540. **3b**: Colorless semisolid; ^{1}H NMR ($CDCl_3$) δ 0.80 (s, 7H), 1.10 (d, 12H, J = 7.2 Hz), 1.12 (d, 6H, J = 7.2 Hz), 1.18 (m, 3H), 2.36 (s, 1H), 2.38 (s, 2H), 2.45 (s, 1H), 7.08 (d, 6H, J = 7.7 Hz), 7.31 (d, 2H, J = 7.7 Hz), 7.48 (d, 6H, J = 7.7 Hz), 7.74 (d, 2H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 14.86, 15.09, 15.10, 16.55, 16.81, 16.91, 21.49, 128.15 (overlap), 128.36, 131.17 (overlap), 131.68, 134.11, 134.22, 134.32, 139.13, 139.19, 139.47; ^{29}Si NMR ($CDCl_3$) δ −32.25, −32.14, −32.09; MS (70 eV) *m*/*z* (%) 669 (M^+ − *i*-Pr, 100); IR (NaCl) ν 3069, 3013, 2945, 2924, 2866, 1607, 1464, 1385, 1246, 1117, 1084, 1063, 1022, 993, 883, 800, 719, 679, 658, 583. **3c**: Colorless solid, mp 125−127 °C; ^{1}H NMR ($CDCl_3$) δ 0.86 (d, 24H, J = 7.2 Hz), 0.93 (sept, 4H, J = 7.2 Hz), 2.36 (s, 4H), 7.13 (d, 8H, J = 7.6 Hz), 7.55 (d, 8H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 14.95, 16.77, 21.61, 128.29, 131.59, 134.09, 139.36; ^{29}Si NMR ($CDCl_3$) δ −32.37; MS (70 eV) *m*/*z* (%) 669 (M^+ − *i*-Pr, 100); IR (NaCl) ν 3036, 3015, 2943, 2891, 2864, 2847, 1651, 1502, 1464, 1392, 1364, 1346, 1309, 1248, 1215, 1188, 1119, 1057, 1022, 988, 918, 883, 847, 802, 758, 717, 679, 659, 608, 584, 542. **3d**: Colorless solid, mp 118−119 °C; ^{1}H NMR ($CDCl_3$) δ 1.10 (d, 24H, J = 6.5 Hz), 1.13 (sept, 4H, J = 6.5 Hz), 2.24 (s, 12H), 6.83 (d, 8H, J = 7.6 Hz), 7.15 (d, 8H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 15.07, 16.93, 21.49, 127.91, 130.82, 134.14, 138.85; ^{29}Si NMR ($CDCl_3$) δ −32.31; MS (70 eV) *m*/*z* (%) 669 (M^+ − *i*-Pr, 100); IR (NaCl) ν 3069, 3034, 3013, 2945, 2923, 2893, 2864, 1607, 1464, 1392, 1383, 1259, 1244, 1161, 1119, 1082, 1061, 1022, 989, 885, 800, 719, 692, 675, 656, 606, 586, 548, 505.

Synthesis of 1,3,5,7-Tetrachloro-1,3,5,7-tetraisopropylcyclotetrasiloxane (mixture of isomers). To a solution of (*i*-PrPhSiO)$_4$ (5.1 g, 7.8 mmol, mixture of isomers) and anhydrous AlCl$_3$ (2.1 g, 15.9 mmol) in benzene (90 mL) was passed HCl gas for 30 min. Acetone was added to the solution to quench aluminum chloride, and argon gas was bubbled. After filtration and removal of THF, Kugelrohr distillation gave 3.6 g (95%) of target tetrachloride. (*i*-PrClSiO)$_4$: Colorless liquid, bp 130 °C/2 mmHg; MS (70 eV) *m*/*z* (%) 443 (M^+ − *i*-Pr, 100); IR (NaCl) ν 2955, 2874, 1466, 1389, 1369, 1256, 1103, 1067, 1001, 924, 885, 681, 648, 509.

Synthesis of 1,3,5,7-Tetrahydroxy-1,3,5,7-tetraisopropylcyclotetrasiloxane from Tetrachloride (mixture of isomers). Water (0.5 g, 29.5 mmol) was added dropwise to (*i*-PrClSiO)$_4$ (mixture of isomers, 3.6 g, 7.4 mmol) and aniline (2.7 g, 29.5 mmol) in 50 mL of ethyl ether at 0 °C for 1 h. The solution was stirred at 0 °C for an additional 1 h. Water and ethyl ether were added to the solution, and the aqueous phase was extracted three times with ethyl ether. The combined organic phase was dried over anhydrous magnesium sulfate and evaporated. Recrystallized from ethyl ether gave (*i*-PrSi(OH)O)$_4$ (2.6 g, 84%).

General Procedure for the Synthesis of Tetraol 1a−d. To a solution of (*i*-PrPhSiO)$_4$ (**2**) or (*i*-Pr(*p*-Tol)SiO)$_4$ (**3**) and $AlCl_3$ (2.0 equiv) in benzene was passed HCl gas for 30 min. Acetone was added to the solution to quench $AlCl_3$, and argon gas was bubbled. After filtration, water (4.1 equiv) was added dropwise to the solution for 5 min at 0 °C, then the mixture was stirred for an additional 30 min. Water and ethyl ether were added to the solution, and the aqueous phase was extracted three times with ethyl ether. The combined organic phase was dried over anhydrous magnesium sulfate and concentrated. Recrystallization from ethyl ether gave pure tetraol **1**.

Synthesis of *cis*-*trans*-*cis*-1,3,5,7-Tetrahydroxy-1,3,5,7-tetraisopropylcyclotetrasiloxane (1a). Compound **1a** was prepared by following the general procedure employing *cis*-*trans*-*cis*-(*i*-PrPhSiO)$_4$ (**2a**, 101 mg, 0.15 mmol) and $AlCl_3$ (290 mg, 2.2 mmol) in 6 mL of benzene. Recrystallization from hexane gave **1a** (59.0 mg, 92%) as a colorless solid: mp 186−187 °C; ^{1}H NMR (DMSO-d_6) δ 0.72 (sep, 4H, J = 6.0 Hz), 0.95 (d, 24H, J = 6.0 Hz), 6.23 (s, 4H); ^{13}C NMR (DMSO-d_6) δ 12.50, 17.38; ^{29}Si NMR (DMSO-d_6) δ −58.97; MS (70 eV) *m*/*z* (%) 373 (M^+ − *i*-Pr, 6), 355 (100); IR (NaCl) ν 3275, 2949, 2870, 1628, 1466, 1387, 1367, 1258, 1109, 1067, 999, 872, 893, 731, 651, 619. Anal. Calcd for $C_{12}H_{32}O_8Si_4$: C, 34.59; H, 7.74. Found: C, 34.59; H, 7.76.

Synthesis of *cis*-*cis*-*trans*-1,3,5,7-Tetrahydroxy-1,3,5,7-tetraisopropylcyclotetrasiloxane (1b). Compound **1b** was prepared by following the general procedure employing *cis*-*cis*-*trans*-(*i*-Pr(*p*-Tol)SiO)$_4$ (**3b**, 434 mg, 0.61 mmol) and $AlCl_3$ (465 mg, 3.5 mmol) in 8 mL of benzene. Recrystallized from hexane gave **1b** (214 mg, 84%) as a colorless solid: mp 157−158 °C; ^{1}H NMR (DMSO-d_6) δ 0.72 (m, 4H), 0.95 (d, 12H, J = 7.0 Hz), 0.96 (d, 6H, J = 7.0 Hz), 0.97 (d, 6H, J = 7.0 Hz), 6.22 (s, 1H), 6.23 (s, 1H), 6.26 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 12.51 (overlap), 17.39, 17.41, 17.47; ^{29}Si NMR (DMSO-d_6) δ −59.69, −59.12, −59.00; MS (70 eV) *m*/*z* (%) 373 (M^+ − *i*-Pr, 2), 355 (43), 72 (100); IR (NaCl) ν 3261, 2947, 2870, 1466, 1387, 1259, 1165, 1103, 1067, 1001, 874, 802, 729, 652, 603. Anal. Calcd for $C_{12}H_{32}O_8Si_4$: C, 34.59; H, 7.74. Found: C, 34.69; H, 7.50.

Synthesis of All-*trans*-1,3,5,7-tetrahydroxy-1,3,5,7-tetraisopropylcyclotetrasiloxane (1c). Compound **1c** was prepared by following the general procedure employing all-*trans*-(*i*-PrPhSiO)$_4$ (**2c**, 3.73 g, 5.6 mmol) and $AlCl_3$ (1.5 g, 11.4 mmol) in 50 mL of benzene. Recrystallized from ethyl ether gave **1c** (2.41 g, 97%) as a colorless solid: mp 160−161 °C; ^{1}H NMR (DMSO-d_6) δ 0.70 (sept, 4H, J = 7.3 Hz), 0.94 (d, 24H, J = 7.3 Hz), 6.24 (s, 4H); ^{13}C NMR (DMSO-d_6) δ 12.24, 17.17; ^{29}Si NMR (DMSO-d_6) δ −58.46; MS (70 eV) *m*/*z* (%) 373 (M^+ − *i*-Pr, 10), 355 (100); IR (NaCl) ν 3288, 2949, 2870, 1468, 1389, 1367, 1259, 1067, 1001, 876, 727, 652, 604. Anal. Calcd for $C_{12}H_{32}O_8Si_4$: C, 34.59; H, 7.74. Found: C, 34.64; H, 7.80.

Synthesis of All-*cis*-1,3,5,7-tetrahydroxy-1,3,5,7-tetraisopropylcyclotetrasiloxane (1d). Compound **1d** was prepared by following the general procedure employing all-*cis*-(*i*-PrPhSiO)$_4$ (**2d**, 99 mg, 0.15 mmol) and $AlCl_3$ (40 mg, 0.30 mmol) in 5 mL of benzene. Recrystallized from ethyl ether gave all-*cis* tetraol, **1d** (58 mg, 93%). The reaction from all-*cis*-(*i*-Pr(*p*-Tol)SiO)$_4$ (**3d**, 68 mg, 0.10 mmol) with $AlCl_3$ (26 mg, 0.20 mmol) in 5 mL of benzene proceeded similarly to give **1d** (36 mg, 90%). This compound was identified by the comparison with the authentic sample.[2,5]

X-ray Structure Analysis (General Procedure). Single crystals were coated and mounted on a glass fiber using epoxy adhesive and were cooled by a Rigaku nitrogen-flow low-temperature apparatus. The measurement was performed on a Rigaku RAXIS-IV imaging plate diffractometer (**1b** was measured with Rigaku AFC-7S) using graphite monochromated Mo Kα radiation. Indexing was performed from four stills that were exposed for 60 s. A sweep of data was done using ϕ oscillations in 0.5° steps. The exposure rate was 180.0 s/deg. The detector swing angle was −0.15°. The crystal-to-detector distance was 99.89 mm. Readout was performed in the 0.100 mm pixel mode. The structure was solved by direct methods[24] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically. All calculations were performed using the CrystalStructure crystallographic software package, except for refinement, which was performed using SHELXL-97.[25]

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Supporting Information Available: Crystallographic information for **1a**, **1b**, **2a**, **2d**, **3a**, **3c**, and **3d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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