Cyclic Tetrasiloxanetetraols: Formation, Isolation, and Characterization

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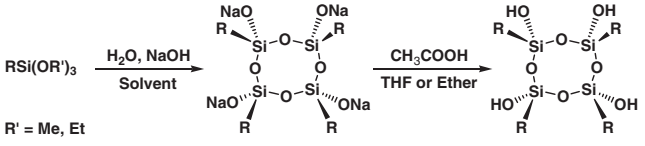
(Received January 21, 2009; CL-090074; E-mail: kawakami@jaist.ac.jp)

Hydrolysis of trialkoxysilanes having various substituents gave cyclic tetrasiloxanetetraols with all-cis isomer as the major fraction in the presence of equimolar amounts of water and sodium hydroxide. All stereoisomers of phenyl derivative were produced by isomerization of the all-cis isomer in the presence of hydrochloric acid, and isolated and identified.

Brown originally reported the formation of all-*cis* cyclic tetraphenyltetrasiloxanetetraol, all-*cis*-phenyl-T_4 from phenyltrichlorosilane in the formation of octahedral octaphenyloctasilsesquioxane, phenyl-T_8, and commented on the possibility of the compound as an intermediate.[1] We reported formation and isolation of all-*cis*-phenyl-T_4 in 2-propanol from phenyltrimethoxysilane in the presence of equimolar amounts of sodium hydroxide.[2] Russian scientists, Shchegolikhina et al.,[3] Klement'ev et al.,[4] and Makarova et al.[5] reported formation,[3] characterization,[3,5] isomerization,[4] and derivatization[5] of all-*cis*-phenyl-, or vinyl-T_4 derivatives. Meanwhile, Matsumoto et al. reported the formation of an isomeric mixture of phenyl(isopropyl)tetrasiloxane containing cis–cis–trans isomer as the major component, and commented on the unlike isomerization of all-*cis*-phenyl-T_4.[6b] Formation of completely or imcompletely condensed polyhedral oligosilsesquioxane is not a simple reaction, but includes many steps of equilibration depending on the reaction conditions.[7] Nevertheless, the all-cis T_4 might be a possible key intermediate for the formation of various T_8[8] and detailed study on the formation, isolation, and characterization of T_4 having various substituents was carried out. Synthetic scheme is shown in Scheme 1.



Scheme 1. Formation of all-cis cyclic tetrasiloxanetetraol.

As a typical example, phenyltrimethoxysilane (9.9 g, 50 mmol) was added to 2-propanol (50 mL), water (0.9 mL, 50 mmol), and sodium hydroxide (2.0 g, 50 mmol) at room temperature, and stirred for a few hours. Formed crystalline material was collected, dissolved in THF or ether and carefully neutralized with acetic acid. Selected results on the formation of all-cis cyclic tetrasiloxanetetraol are summarized in Table 1. Reasonable yields were obtained for all the substituents examined. Vinyl, vinylphenyl, and bromophenyl derivatives gave higher yield, but the products could be isolated only as sodium or potassium salt, or trimethylsilyl derivatives.

Aromatic derivatives showed only one ^{29}Si signal[10] at -69.7, -67.2, -68.4, and -68.8 ppm, respectively. The isobutyl derivative gave only one peak at -57.9 ppm, which is very close to the reported value (-59.7) for all-cis isopropyl derivative. The ^{29}Si signal at -69.7 ppm for phenyl-T_4 was thought to be due to all-cis isomer.[3b,5,11] Other aromatic derivatives are also considered to be all-cis. Methoxyphenyl, naphthyl, and methoxynaphthyl derivatives are good intermediates for further functionalization via electrophilic substitution reactions. By selecting suitable reaction conditions all-cis isomers could be obtained for substituents examined.

When phenyl-T_4 was obtained by the hydrolysis of phenyltrichlorosilane, stereoisomers other than all-cis seemed to be present in the product, evidenced by ^{29}Si NMR shown in Figure 1a. There are four stereoisomers in the tetramer, which should give 6 signals. Overlapping of the signal may have occurred. Since only limited information was available on the isomerization, and separation of the stereoisomers depending on the condition, isomerization of all-*cis*-phenyl-T_4 (0.68 g, 1.25 mmol) was carried out in acetone (10 mL) with 1 M hydrochloric acid (4 mL) at room temperature. After 10 min, the products remained as one peak in SEC, and showed $[M + Na]^+ = 575.50$ in MALDI-TOF MS,[10] consistent with the cyclic tetrasiloxanetetraol, but apparently four new peaks appeared in ^{29}Si at -70.5 (weak), -70.4, -70.2, and -70.1 with the consumption of the peak of all-cis at -69.7 ppm. Configuration of one silicon atom

Table 1. All-cis cyclic tetrasiloxanetetraols

Trialkoxysilane	Solvent	Product	Time/h	Yield/%	^{29}Si NMR/ppm
i-BuSi(OMe)$_3$	Hexane	[*i*-Bu(OH)SiO]$_4$	48	34	-57.9
		[*i*-Pr(OH)SiO]$_4$		93[6b]	-59.7[6a]
PhSi(OMe)$_3$	2-Propanol	[Ph(OH)SiO]$_4$	20	30–40	-69.7
4-MeOPhSi(OMe)$_3$	1-Butanol	[4-MeOPh(OH)SiO]$_4$	48	44	-67.2
4-BrPhSi(OEt)$_3$	EtOH	[4-BrPh(OH)SiO]$_4$	48	trace	—
		[4-BrPh(ONa)SiO]$_4$		41[9]	—
VinylSi(OEt)$_3$	Hexane–EtOH	[Vi(OK)SiO]$_4$	15	34	—
				74[3c]	—
4-VinylPhSi(OEt)$_3$	EtOH	[4-ViPh(ONa)SiO]$_4$		71[9]	—
NpSi(OMe)$_3$	1-Butanol	[Np(OH)SiO]$_4$	69	30	-68.4
4-MeONpSi(OMe)$_3$	1-Butanol	[4-MeONp(OH)SiO]$_4$	19	6	-68.8

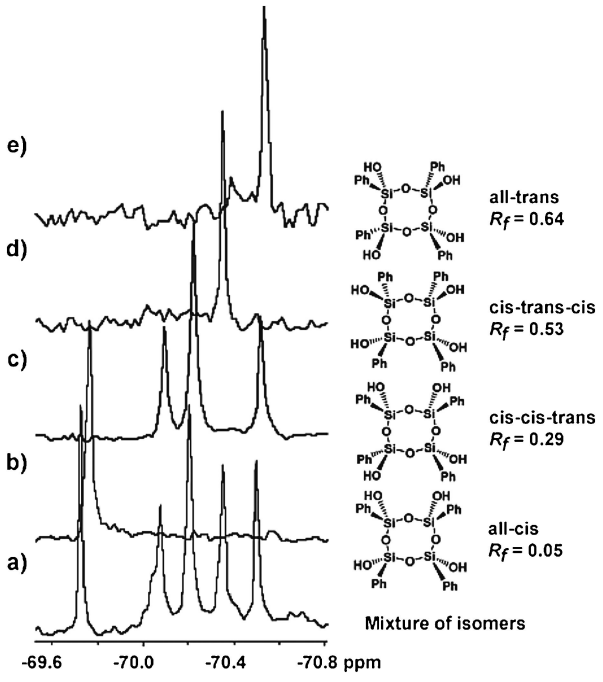


Figure 1. Identification of phenyl-T_4 by ^{29}Si NMR.

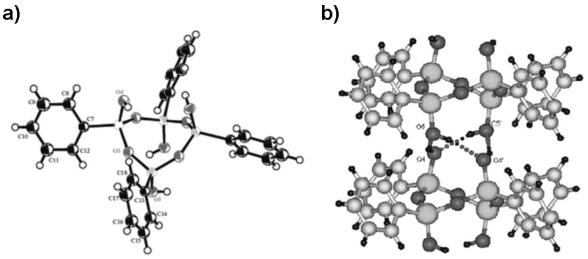


Figure 2. Structure of isomer with $R_f = 0.64$: a) ORTEP and b) hydrogen bonding.

in the ring might have been inverted as can be understood by the following assignment of the cis–cis–trans isomer.

A mixture of phenyl-T_4 (1.0 g, 1.81 mmol) shown in Figure 1a was used for separation. A major part of the all-cis isomer was removed by precipitation after dissolving in ether (5 mL) and pouring into hexane (20 mL) (≈25%, $R_f = 0.05$).

By two fold chromatography after removal of the all-cis isomer, three isomers with $R_f = 0.29$ (≈40%), 0.53 (≈15%), 0.64 (≈1%) (toluene–ether = 1:1) were separated, whose ^{29}Si are also shown in Figures 1b–1d. It was clearly shown that possibly 6 signals appeared as five overlapped signals in Figure 1a. To further confirm the structure, a single crystal of the isomer with $R_f = 0.64$; ^{29}Si at −70.5 (Figure 1e) was analyzed by XRD.[10] The ORTEP structure is shown in Figure 2.

It was definitely confirmed that this isomer is all-trans consistent with the NMR assignment. This compound actually forms hydrogen-bonded dimer in the unit cell as shown in Figure 2b. Other fractions with $R_f = 0.29$; ^{29}Si at −70.5, −70.2, −70.1, and $R_f = 0.53$; ^{29}Si at −70.4 were reasonably concluded as cis–cis–trans and cis–trans–cis isomer, respectively by considering symmetry of the molecule.

Matsumoto et al. reported the XRD of *cis*,*cis*,*trans*- and *cis*, *trans*,*cis*-tetrasiloxanetetraol with isopropyl substituents. They also reported one ^{29}Si at −58.97 for cis–trans–cis isomer and three signals at −59.69, −59.12, and −59.00 for cis–cis–trans isomer similar to our result.[6b]

In conclusion, all-cis cyclic tetrasiloxane tetraols with various substituents were synthesized, and four stereo isomers of cyclic phenyltetrasiloxanetetraol were identified with the aid of ^{29}Si NMR and XRD. By selecting suitable reaction condition all-cis isomer could be obtained for substituents examined.

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10 NMR (^{1}H at 500 MHz, ^{13}C at 125 MHz, and ^{29}Si at 99 MHz) spectra in ppm were obtained on a Varian model Unity INOVA. MALDI-TOF MS was performed with a Voyager DE RP. XRD was performed on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Cu Kα radiation. Indexing was performed from three oscillations exposed for 36 s. The crystal-to-detector distance was 127.4 mm. The exposure rate was 12.0 s/deg. Readout was performed in the 0.100 mm pixel mode. The structure was solved by direct methods and expanded using Fourier techniques. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using CrystalStructure crystallographic software except for refinement performed using SHELXL-97. Crystallographic data for all-trans isomer reported in here have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 683440.
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Published on the web (Advance View) March 21, 2009; doi:10.1246/cl.2009.364