Syntheses and Structural Analyses of 1,3-Diphenyldisiloxanes as a Building Block of Silsesquioxanes

Isamu Seto, Takahiro Gunji,* Kaoru Kumagai, Koji Arimitsu, and Yoshimoto Abe

Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science,
2641 Yamazaki, Noda, Chiba 278-8510

Received April 1, 2003; E-mail: gunji@rs.noda.tus.ac.jp

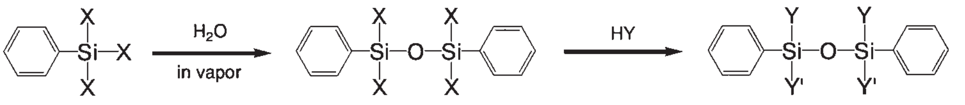
Syntheses of novel 1,3-diphenyldisiloxanes were investigated. 1,1,3,3-Tetrachloro-1,3-diphenyldisiloxane (**1**) and 1,1,3,3-tetraisocyanato-1,3-diphenyldisiloxane (**2**) were obtained by vapor-phase hydrolytic condensation of trichloro(phenyl)silane and triisocyanato(phenyl)silane, respectively. The reactions of **1** with 2-propanol, *t*-butyl alcohol, and diethylamine provided 1,1,3,3-tetraisopropoxy-1,3-diphenyldisiloxane (**3**), 1,3-di-*t*-butoxy-1,3-dichloro-1,3-diphenyldisiloxane (**5a**), and 1,1,3,3-tetrakis(diethylamino)-1,3-diphenyldisiloxane (**6**), respectively. 1,3-Diisocyanato-1,3-diisopropoxy-1,3-diphenyldisiloxane (**4**) and 1,3-di-*t*-butoxy-1,3-diisocyanato-1,3-diphenyldisiloxane (**5b**) were synthesized by the reactions of **2** with 2-propanol and with *t*-butyl alcohol, respectively. Hydrolysis of **5a** or **5b** afforded 1,3-di-*t*-butoxy-1,3-diphenyldisiloxane-1,3-diol (**7**). 1,3-Diphenyldisiloxane-1,1,3,3-tetrol (**8**) was isolated from the hydrolysis of **1**. A single crystal X-ray diffraction of **8** showed that four hydroxy groups are facing each other to form a ladder-type network by the intermolecular hydrogen bondings.

Ladder polysilsesquioxanes with a unique structure involving a $RSiO_{3/2}$ double-chain skeleton are expected to provide functional coatings, adhesive agents, and electronic materials because of their excellent thermal, chemical, and electrical properties. They have been synthesized, thus far, by hydrolytic condensation occurring by the following process:[1] the hydrolysis of tri-functional silanes, followed by alkali-equilibration of oligosilsesquioxanes formed by condensation of intermediate silanetriols.[2,3] Meanwhile, ladder oligosilsesquioxanes have been synthesized by the oxidation of ladder oligosilanes[4] and also by condensation of oligosiloxanes. In the latter method, the condensation between sila-functional siloxanes such as cyclotetrasiloxanes and disiloxanes or the self-condensation of disiloxanes with phenyl, isopropyl, or 1,1,2-trimethylpropyl groups afforded cyclic ladder oligosiloxanes of 1–5 ring systems.[5,6]

Disiloxanes can be a starting material for oligosilsesquioxanes.[2] There have been a few reports, however, of syntheses of sila-functional disiloxanes. Therefore, the developments of convenient synthetic methods are expected to result in syntheses of disiloxanes with functional groups. We have previously reported that 1,1,3,3-tetraisocyanatodisiloxanes having methyl, vinyl, and phenyl groups can be selectively synthesized by the vapor-phase hydrolysis of triisocyanatosilanes. Here, we wish to report the results of the syntheses of disiloxane derivatives, as shown in Scheme 1, and the crystal structure analysis of 1,3-diphenyldisiloxane-1,1,3,3-tetrol.

Results and Discussion

Syntheses and Properties of Tetrafunctional 1,3-Diphenyldisiloxanes. It is difficult to synthesize **1** by the hydrolysis of trichloro(phenyl)silane because it is highly reactive, quickly forming oligosiloxanes. Andrianov has reported that the vapor-phase hydrolytic condensation of alkyl- and phenyltrichlorosilanes affords disiloxanes in good yields, by passing a mixed gas of nitrogen and steam into a vapor of alkyl- or phenyltrichlorosilane at high temperature.[7] On the other hand, we found that the vapor-phase hydrolysis of triisocyanatosilanes with methyl, vinyl, or phenyl groups using stoichiometric amounts of water selectively provides the corresponding tetraisocyanatodisiloxanes.[8] In this method, a mixed gas of 1,4-dioxane and steam is introduced into a vapor of methyl-, vinyl-, or phenyltriisocyanatosilane under refluxing at ca. 2.7 kPa by using the apparatus shown in the literature.[8] Therefore, the syntheses of **1** and **2** from trichloro(phenyl)silane and triisocyanato(phenyl)silane, respectively, by vapor-phase hydrolysis in addition to their derivatives were investigated accord-



1 : (X = Cl)
2 : (X = NCO)

3 : (Y = Y' = OPr^i)
4 : (Y = OPr^i, Y' = NCO)
5a : (Y = OBu^t, Y' = Cl)
5b : (Y = OBu^t, Y' = NCO)
6 : (Y = Y' = NEt_2)
7 : (Y = OBu^t, Y' = OH)
8 : (Y = Y' = OH)

Scheme 1.

Published on the web October 15, 2003; DOI 10.1246/bcsj.76.1983

ing to Scheme 1.

Compound **1** was synthesized by using the device described in the literature.[8] A mixed vapor of water and 1,4-dioxane was blown into refluxing trichloro(phenyl)silane under reduced pressure and room temperature. In this device, trichloro(phenyl)silane is selectively hydrolyzed to produce **1**, as the boiling point of **1** is higher than that of trichloro(phenyl)silane, meaning that no hydrolysis of **1** followed by the formation of oligosiloxanes takes place. Gas chromatography of the crude product showed the peaks due to trichloro(phenyl)silane (1%), **1** (82%), and the other oligosiloxanes (17%). Thus the compound **1** was isolated in 73% yield by vacuum distillation.

1,3-Diphenyldisiloxane derivatives with isopropoxy and *t*-butoxy groups were synthesized from **1** and **2**, according to our previous work.[9] The reaction of **1** with 2-propanol was monitored by gas chromatography. The reaction of **1** with four equimolar amounts of 2-propanol proceeded gradually to provide **3** after stirring for 16 h. Compound **3** was isolated in 80% yield. When pyridine was used as a base, the reaction proceeded within 2 h with the production of pyridine hydrochloride in quantitative yield to give **3** in 81% yield.

When **1** was reacted with two equimolar amounts of 2-propanol, a mixture of $Ph_2Si_2O(OPr^i)_nCl_{4-n}$ ($n = 1$–4) was formed. The reaction of **2** with two equimolar amounts of 2-propanol afforded **4** in 78% yield. Figure 1 shows the ^{1}H NMR spectrum of **4** in the region ascribed to the methine group. More than three pairs of septet signals were observed. The spectrum suggests that the product **4** includes the conformational isomers of diastereomers and the *meso* form, as shown in Fig. 2.

The reaction of **1** with two equimolar amounts of *t*-butyl alcohol in the presence of pyridine gave **5a** in 75% yield. In this reaction, only **5a** was obtained without the formation of tri- and tetra-*t*-butoxydisiloxanes. The degree of substitution is regulated because the *t*-butoxy group is more hindered than the isopropoxy group. Compound **5b** was isolated in 35% yield by the reaction of **2** with *t*-butyl alcohol.

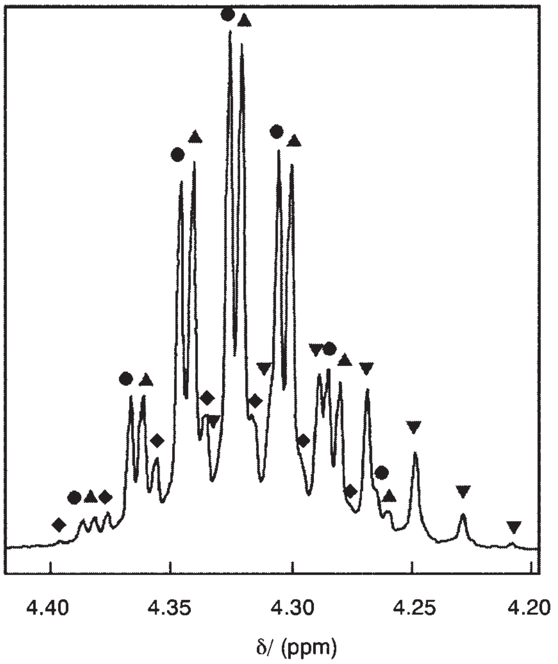


Fig. 1. ^{1}H NMR spectrum of **4**.

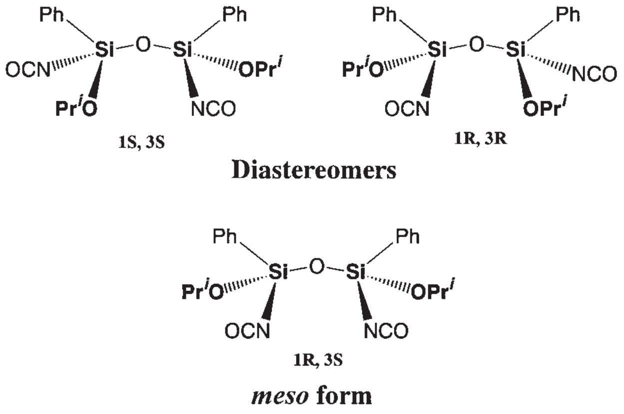


Fig. 2. Stereoisomers of **4**.

Disiloxane **6** was synthesized by the reaction of **1** with diethylamine. Because the reaction of isocyanatosilane with amine affords a mixture of silanamines and silylureas, **1** was subjected to a reaction with eight equimolar amounts of diethylamine. The reaction provided **6** in 55% yield as a colorless liquid, which then colored upon aging for several days. Therefore, the reaction of **1** with diethylaminomagnesium bromide was carried out to give **6** in 40% yield, which showed no color change on storage at room temperature.

The hydrolysis of **5a** or **5b** in THF in the presence of triethylamine at 0 °C gave **7** in 26% or 52% yield, respectively, when recrystallized from pentane. Compound **7** was highly soluble in methanol, acetone, THF, benzene, and diethyl ether, and was soluble in carbon tetrachloride, hexane, and pentane.

Synthesis and Structural Analysis of 1,3-Diphenyldisiloxane-1,1,3,3-tetrol (8). Generally, silanetriols and especially silanepolyols are unstable to self-condensation, easily forming oligo- or polysiloxanes. The condensation reaction is catalyzed in the presence of acid or base. However, silanols with bulky substituents are stable enough to be isolated as silanetriols. The same tendency is shown in disiloxanols $[(R_{3-n}Si(OH)_n)_2O]$. Even disiloxanetetrols can be isolated by the hydrolysis of *t*-butyltrichlorosilane and trichloro(1,1,2-trimethylpropyl)silane in potassium hydroxide aqueous solution[10,11] and the hydrolysis of $RSiCl_3$ (R = hexyl, octyl, decyl) in acetone with aniline.[12] Some of these have been analyzed by X-ray crystallography. Compound **8** was prepared by Brown by the hydrolysis of triacetoxy(phenyl)silane in 9% yield.[13] No structural analysis of **8**, not even an X-ray diffraction study, has been carried out. Here, we will report the results of a single crystal X-ray diffraction and the selective synthesis of **8**.

Synthesis of **8** was carried out under various reaction times using recrystallization solvents. Disiloxane **1** was hydrolyzed with stirring in diethyl ether in the presence of aniline at 0 °C and kept for 2 h at that temperature. The reaction mixture was filtered to remove the aniline hydrochloride. Slow evaporation of the solvent from the filtrate for 3 days gave **8** in 9% yield. When the hydrolysis of **1** was carried out by the same process mentioned above for 1 h, **8** was isolated in 50% yield because the condensation of **8** was minimized by decreasing the reaction time to increase the yield of **8**. Moreover, when hexane was added to the filtrate, crystallization took place within 1 day to give **8** in 76% yield. Disiloxanetetrol **8**, being unstable as a solution and comparatively stable as a solid, was isolated as crystals due to the hydrogen bonds of silanols in the crystal of **8**. Disiloxane **8** was found to be easily soluble in methanol, acetone, THF, and diethyl ether, and to be insoluble in chloroform, benzene, hexane, and carbon tetrachloride.

A single crystal of **8** was grown by slow evaporation of diethyl ether from a solution. The crystal was a colorless plate 0.5 mm × 0.4 mm × 0.1 mm in size. The single crystal was subjected to the X-ray analysis at 20 °C. Figure 3 shows the ORTEP drawing of **8**, and Tables 1 and 2 show the crystallographic data. This crystal belongs to the $C2/c$ space group. The average bond lengths were 1.6033 Å for Si–O in Si–O–Si, 1.6231 Å for Si–O in Si–OH, and 1.8443 Å for Si–C, all of which are close to the typical values for Si–O and Si–C bonds. The average bond angles were 168.49° for Si–O–Si, 108.44° for O–Si–O, and 110.50° for O–Si–C. The arrangement of atoms in Si–O–Si bond is almost straight, and silicon atoms have a typical value for sp^3 configuration.

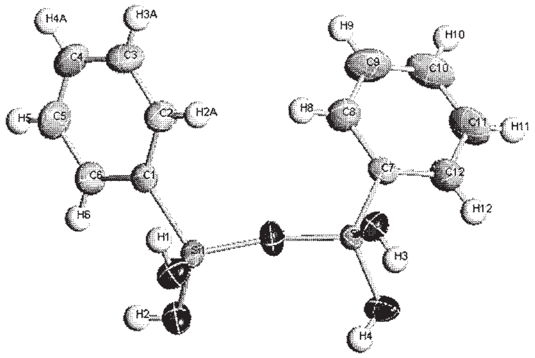


Fig. 3. ORTEP drawing of **8**.

Table 1. Crystallographic Data for **8**

Formula	$C_{12}H_{14}O_5Si_2$
Formula weight	294.41
Crystal descript	Colorless plate
Crystal size/mm	0.5 × 0.4 × 0.1
Cell setting	Monoclinic
Space group	$C2/c$
a/Å	30.6927(16)
b/Å	4.9784(3)
c/Å	19.7723(10)
β/degree	111.7520(10)
V/Å^3	2806.1(3)
Z	8
Density/g cm^{-3}	1.394
Radiation λ/Å	Mo Kα = 0.71073
Monochromator	Graphite
Temperature/K	293(2)
Absorpt coefficient μ/mm^{-1}	0.265
No. of reflections total	3493
No. of reflections gt	3175
No. of params	176
R	0.0421
R_w	0.1230

Table 2. Bond Lengths and Bond Angles of **8**

	Bond lengths/Å		
Si1–O5	1.6083(12)	C1–C6	1.384(3)
Si1–O2	1.6222(13)	C1–C2	1.394(3)
Si1–O1	1.6266(13)	C6–C5	1.385(3)
Si1–C1	1.8425(18)	C2–C3	1.377(3)
Si2–O5	1.5984(12)	C12–C11	1.393(3)
Si2–O4	1.6177(12)	C5–C4	1.365(4)
Si2–O3	1.6258(12)	C4–C3	1.383(3)
Si2–C7	1.8461(16)	C10–C9	1.366(4)
C7–C12	1.386(3)	C10–C11	1.367(4)
C7–C8	1.387(3)	C8–C9	1.392(3)
	Bond angles/°		
O5–Si1–O2	107.48(7)	C8–C7–Si2	121.50(15)
O5–Si1–O1	109.56(7)	C6–C1–C2	117.53(17)
O2–Si1–O1	108.60(7)	C6–C1–Si1	123.70(14)
O5–Si1–C1	109.54(8)	C2–C1–Si1	118.73(14)
O2–Si1–C1	113.49(8)	C1–C6–C5	121.2(2)
O1–Si1–C1	108.14(7)	C3–C2–C1	121.55(19)
O5–Si2–O4	110.81(8)	C7–C12–C11	121.2(2)
O5–Si2–O3	107.75(7)	C4–C5–C6	120.1(2)
O4–Si2–O3	106.46(7)	C5–C4–C3	120.1(2)
O5–Si2–C7	109.33(8)	C2–C3–C4	119.5(2)
O4–Si2–C7	108.85(7)	C9–C10–C11	119.8(2)
O3–Si2–C7	113.62(7)	C10–C11–C12	120.1(2)
Si2–O5–Si1	168.49(10)	C7–C8–C9	120.8(2)
C12–C7–C8	117.69(17)	C10–C9–C8	120.4(2)
C12–C7–Si2	120.80(14)		

According to the X-ray diffraction study of 1,3-di-*t*-butyldisiloxane-1,1,3,3-tetrol, *t*-butyl groups have a *trans* configuration.[10] In contrast, the phenyl groups have a *gauche* configuration in **8**. The four hydroxy groups are facing each other to form a ladder-type network by the intermolecular hydrogen bondings as shown in Figs. 4 and 5. The average bond lengths and bond angle of this hydrogen bonding were 1.9693 Å for OH···O, 2.7358 Å for O···O, and 156.99° for O–H···C. These values are typical for the intermolecular hydrogen bonding of two silanols.[14]

Experimental

Materials. Triisocyanato(phenyl)silane and 1,1,3,3-tetraisocyanato-1,3-diphenyldisiloxane (**2**) were synthesized according to the literature.[8]

Other chemicals such as 1,4-dioxane, tetrahydrofuran (THF), benzene, diethyl ether, hexane, 2-propanol, *t*-butyl alcohol, triethylamine, diethylamine, pyridine, and aniline were purified before use by a conventional method.

Synthesis of 1,1,3,3-Tetrachloro-1,3-diphenyldisiloxane (1). A mixed vapor of water and 1,4-dioxane was blown into refluxing trichloro(phenyl)silane at 3.3 kPa. The reaction mixture was distilled to give **1**.

1 Yield: 73%. Bp 136.0–136.5 °C/240 Pa. IR 543, 1100, 1430, 2973 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.32–7.69 (m, 10H); ^{13}C NMR (100.4 MHz) δ 128.4, 130.4, 132.6, 133.6; ^{29}Si NMR (79.3 MHz) δ −28.4; MS m/z 368 (M$^+$). Found: Si, 15.2%. Calcd for $C_{12}H_{10}Cl_4O_1Si_2$: Si, 15.2%.

Synthesis of 1,1,3,3-Tetraisopropoxy-1,3-diphenyldisiloxane (3). A solution of 2-propanol (4.80 g, 0.08 mol) and pyridine (6.33 g, 0.08 mol) in THF (50 mL) was added to a rapidly stirred cold (0 °C) solution of **1** (7.36 g, 0.02 mol) in THF (80 mL). The

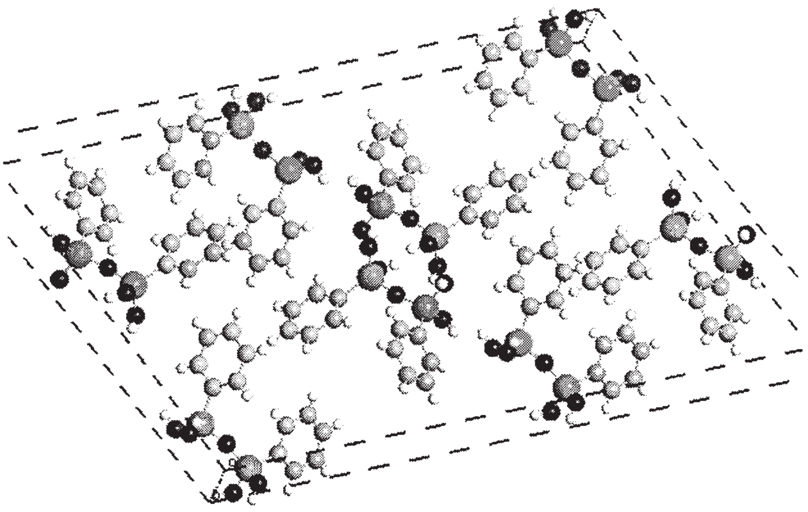


Fig. 4. Unit-cell structure of **8**.

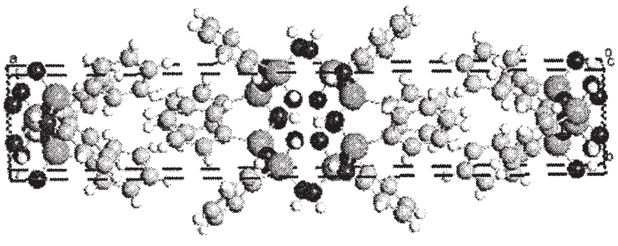


Fig. 5. Projection of the *c* axis of **8**.

reaction mixture was refluxed for 2 h, filtered, and distilled to give **3**.

3 Yield: 81%. Bp 167.1–168.2 °C/373 Pa. IR 1047, 1100, 1126, 1381, 1430, 2973 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.18 (d, 24H), 4.29 (m, 4H), 7.29–7.72 (m, 10H); ^{13}C NMR (100.4 MHz) δ 25.1, 64.8, 127.8, 130.3, 133.0, 134.7; ^{29}Si NMR (79.3 MHz) δ −68.1(s); MS *m*/*z* 403 (M^{+} − 59). Found: Si, 12.4%. Calcd for $C_{24}H_{38}O_5Si_2$: Si, 12.2%.

Synthesis of 1,3-Diisocyanato-1,3-diisopropoxy-1,3-diphenyldisiloxane (4). A solution of 2-propanol (2.40 g, 0.04 mol) in THF (50 mL) was added to a rapidly stirred cold (0 °C) solution of **2** (7.89 g, 0.02 mol) in THF (80 mL). The reaction mixture was refluxed for 2 h, filtered, and distilled to give **4**.

4 Yield: 72%. Bp 153–155 °C/267 Pa. IR 1029, 1383, 1174, 1593, 2291, 2895, 2975, 3074 cm^{-1}. ^{1}H NMR (300 MHz) δ 1.26–1.15 (m, 12H, $J = 6.3$ Hz), 4.39–4.20 (m, 2H, $J = 6.3$ Hz), 7.41–7.31 (m, 4H, *m*-C_6H_5, $J = 2.1$ Hz), 7.49–7.43 (m, 2H, *p*-C_6H_5, $J = 2.1$ Hz), 7.70–7.62 (m, 4H, *o*-C_6H_5, $J = 2.1$ Hz); ^{13}C NMR (75.5 MHz) δ 25.2, 25.3, 25.4, 65.9, 66.9, 67.2, 127.8, 128.0, 128.2, 130.3, 130.4, 131.0, 131.4, 133.9, 134.0, 134.6; ^{29}Si NMR (59.6 MHz) δ −70.6.

Synthesis of 1,3-Di-*t*-butoxy-1,3-dichloro-1,3-diphenyldisiloxane (5a). A solution of *t*-butyl alcohol (2.96 g, 0.04 mol) and pyridine (6.33 g, 0.04 mol) in THF (50 mL) was added to a rapidly stirred cold (0 °C) solution of **1** (7.36 g, 0.02 mol) in THF (80 mL). The reaction mixture was refluxed for 2 h, filtered, and distilled to give **5a**.

5a Yield: 82%. Bp 144.3–145.6 °C/200 Pa. IR 542, 1090, 1100, 1186, 1244, 1430, 2279 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.35 (s, 18H), 7.30 (m, 4H, *m*-C_6H_5), 7.32 (m, 2H, *p*-C_6H_5), 7.70 (m, 4H, *o*-C_6H_5); ^{13}C NMR (100.4 MHz) δ 31.4, 76.4, 127.6, 130.8, 133.0, 133.9; ^{29}Si NMR (79.3 MHz) δ −58.5; MS *m*/*z* 427 (M^{+} − 15). Found: Si, 12.5%. Calcd for $C_{20}H_{28}Cl_2O_3Si_2$: Si, 12.6%.

Synthesis of 1,3-Di-*t*-butoxy-1,3-diisocyanato-1,3-diphenyldisiloxane (5b). A solution of *t*-butyl alcohol (2.96 g, 0.04 mol) and triethylamine (0.40 g, 0.004 mol) in THF (50 mL) was added to a rapidly stirred cold (0 °C) solution of **2** (7.89 g, 0.02 mol) in THF (80 mL). The reaction mixture was refluxed for 2 h, filtered, and distilled to give **5b**.

5b Yield: 35%. Bp 161.0–162.0 °C/107 Pa. IR 1078, 1131, 1189, 1244, 1430, 2283, 2979, 3067 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.34 (s, 18H), 7.34 (m, 4H, *m*-C_6H_5), 7.39 (m, 2H, *p*-C_6H_5), 7.65 (m, 4H, *o*-C_6H_5); ^{13}C NMR (100.4 MHz) δ 31.5, 75.6, 123.2, 128.1, 131.0, 132.0, 133.8; ^{29}Si NMR (79.3 MHz) δ −76.2.

Synthesis of 1,1,3,3-Tetrakis(diethylamino)-1,3-diphenyldisiloxane (6). A solution of ethyl bromide (23.97 g, 0.22 mol) in diethyl ether was added to a rapidly stirred suspension of magnesium (5.35 g, 0.22 mol) in diethyl ether (100 mL) at 20 °C, and the mixture was refluxed for 2 h. A solution of diethylamine (16.06 g, 0.22 mol) was added to the mixture being stirred at 20 °C, and the mixture was refluxed for 2 h. A solution of **1** (20.24 g, 0.055 mol) in benzene (50 mL) was added to the mixture being stirred at 0 °C, refluxed, filtered, and distilled to give **6**.

6 Yield: 40%. Bp 182.6–183.5 °C/160 Pa. IR 1031, 1099, 1209, 1430, 2868, 2969 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.97 (t, 24H), 2.89 (q, 16H), 7.27–7.71 (m, 10H); ^{13}C NMR (100.4 MHz) δ 14.7, 38.8, 127.8, 130.7, 132.8, 134.6; ^{29}Si NMR (79.3 MHz) δ −37.6; MS *m*/*z* 514 (M^{+}). Found: Si, 11.0%. Calcd for $C_{28}H_{50}N_4O_1Si_2$: Si, 10.9%.

Synthesis of 1,3-Di-*t*-butoxy-1,3-diphenyldisiloxane-1,3-diol (7). A solution of water (0.72 g, 0.04 mol) and triethylamine (4.04 g, 0.04 mol) was added to a rapidly stirred cold (0 °C) solution of **5a** or **5b** (0.02 mol), and the mixture was refluxed for 2 h, filtered, and evaporated to give the crude **7**. Recrystallization from pentane (5 mL) afforded pure **7**.

7 Yield : 26% (from **5a**) and 52% (from **5b**). Mp 67.5–69.5 °C (decomp). IR 1043, 1105, 1370, 1430, 3345 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.22 (s, 18H), 4.38 (s, 2H), 7.20–7.60 (m, 10H); ^{13}C NMR (100.4 MHz) δ 31.7, 74.0, 127.6, 130.0, 134.0, 134.5; ^{29}Si NMR (79.3 MHz) δ −67.9; MS *m*/*z* 391 (M^{+} − 15). Found: Si, 13.7%. Calcd for $C_{20}H_{30}O_5Si_2$: Si, 13.8%.

Synthesis of 1,3-Diphenyldisiloxane-1,1,3,3-tetrol (8). A solution of **1** (7.36 g, 0.02 mol) in diethyl ether (40 mL) was added to a suspension of water (1.44 g, 0.08 mol) and aniline (7.44 g, 0.08 mol) under stirring at 0 °C and kept for 1 h. The reaction mixture was filtered to remove aniline hydrochloride. Recrystallization of filtrate from hexane (100 mL) afforded **8**.

8 Yield: 76%. Mp 114.0–115.6 °C (decomp). IR 911, 1110, 1429, 3200 cm^{-1}; ^{1}H NMR (400 MHz) δ 5.81 (br, 4H), 7.20–7.72 (m, 10H); ^{13}C NMR (100.4 MHz) δ 127.7, 129.7, 135.1, 136.9; ^{29}Si NMR (79.3 MHz) δ −62.1. Found: Si, 19.0%. Calcd for $C_{12}H_{14}O_5Si_2$: Si, 19.1%.

Crystal Structure Determination of 8. Suitable crystals for a single crystal X-ray diffraction study were grown by slow evaporation from a diethyl ether solution of **8**. A colorless crystalline plate 0.5 mm × 0.4 mm × 0.1 mm was attached to the tip of a glass fiber, and measured by a Bruker SMART APEX equipped CCD diffractometer (λ(Mo Kα) = 0.71073 Å, 25 ± 2 °C). The structure was solved by SHELXL-97 and refined by full-matrix least-squares techniques.

Measurements and Analyses. ^{1}H, ^{13}C, and ^{29}Si nuclear magnetic resonance (NMR) spectra were acquired using a JEOL JNM-EX-400 spectrometer or JEOL ECP-500 spectrometer in chloroform-*d* or tetrahydrofuran-d_8. Fourier-transform infrared (FT-IR) spectra were measured using a JEOL FT-IR-400 IR spectrophotometer by means of a carbon tetrachloride solution method or a KBr disk method. The mass (MS) spectra were obtained using a Shimadzu GCMS-QP2000A equipped with a direct insertion apparatus.

The silicon content was determined by following procedure. The sample (0.2 g) was weighed in a flask mixed with sulfuric acid (20 mL). Into this mixture, ammonium sulfate (1 g) was added and heated gently for 6 h. After cooling to room temperature, the content was poured into ice in a beaker. After filtration using ashless filter paper, the residue and filter paper were subjected to firing in a crucible, then weighed as silica, SiO_2.

Conclusion

The hydrolytic condensation of trichloro(phenyl)silane or triisocyanato(phenyl)silane in vapor phase afforded 1,1,3,3-tetrachloro-1,3-diphenyldisiloxane (**1**) or 1,1,3,3-tetraisocyanato-1,3-diphenyldisiloxane (**2**), respectively.

The reaction of **1** with 2-propanol, *t*-butyl alcohol, or diethylamine gave 1,1,3,3-tetraisopropoxy-1,3-diphenyldisiloxane (**3**), 1,3-di-*t*-butoxy-1,3-dichloro-1,3-diphenyl-disiloxane (**5a**), or 1,1,3,3-tetrakis(diethylamino)-1,3-diphenyldisiloxane (**6**), respectively.

The reaction of **2** with 2-propanol or *t*-butyl alcohol gave 1,3-diisocyanato-1,3-diisopropoxy-1,3-diphenyldisiloxane (**4**), or 1,3-di-*t*-butoxy-1,3-diisocyanato-1,3-diphenyldisiloxane (**5b**), respectively. ^{1}H NMR spectrum of **4** showed that **4** was a mixture of stereoisomers.

1,3-Di-*t*-butoxy-1,3-diphenyldisiloxane-1,3-diol (**7**) and 1,3-diphenyldisiloxane-1,1,3,3-tetrol (**8**) were obtained by the hydrolysis of **5a** (or **5b**) and **1**, respectively. A single crystal X-ray diffraction study of **8** found that **8** crystallized to form a cyclic structure in the crystal.

The authors would like to thank Mr. Yuji Sakamoto for his aid in the X-ray analysis.

References

1 J. F. Brown, Jr. and L. H. Vogt, Jr., *J. Am. Chem. Soc.*, **82**, 6194 (1960).

2 H. Nishida, H. Yamane, and Y. Kimura, *Kobunshi Ronbunshu*, **53**, 193 (1996).

3 T. Takiguchi and E. Fujikawa, *Nippon Kagaku Kaishi*, **1974**, 108.

4 H. Matsumoto, S. Kyushin, M. Unno, and R. Tanaka, *J. Organomet. Chem.*, **611**, 52 (2000).

5 T. C. Wu and P. J. Launer, *J. Chem. Eng. Data*, **18**, 350 (1973).

6 M. Unno, A. Suto, and H. Matsumoto, *J. Am. Chem. Soc.*, **124**, 1574 (2002).

7 K. A. Andrianov and V. N. Emel'yanov, *Dokl. Akad. Nauk SSSR*, **189**, 91 (1969).

8 Y. Abe, K. Abe, M. Watanabe, and T. Gunji, *Chem. Lett.*, **1999**, 259.

9 T. Gunji, K. Kubota, S. Kishiki, and Y. Abe, *Bull. Chem. Soc. Jpn.*, **75**, 537 (2002).

10 P. D. Lickiss and S. A. Lister, *J. Chem. Soc., Chem. Commun.*, **1991**, 173.

11 M. Unno, S. B. Alias, and H. Matsumoto, *Organometallics*, **15**, 2413 (1996).

12 K. A. Andrianov and B. A. Izmailov, *Zh. Obshch. Khim.*, **46**, 599 (1976).

13 J. F. Brown, Jr. and G. M. J. Slusarczuk, *J. Org. Chem.*, **29**, 2809 (1964).

14 P. D. Lickiss, "Advances in Inorganic Chemistry," Academic Press (1995), Vol. 42, pp. 147–251.